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Mahdi Mubarok

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DOCTEUR DE L'UNIVERSITE DE LORRAINE

Sciences du Bois et de Fibres

Par

Mahdi MUBAROK

VALORIZATION OF BEECH WOOD THROUGH DEVELOPMENT OF INNOVATIVE AND ENVIRONMENTALLY FRIENDLY CHEMICAL MODIFICATION TREATMENTS

Sous la direction du Pr. Philippe GERARDIN et du Pr. Holger MILITZ

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A Ma Famille

«Maintenant ce n'est pas la fin. Ce n'est même pas le début de la fin. Mais c'est peut-être la fin du début »

Winston Churchill

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Contributions Scientifiques

Article scientifiques / Proceedings

1. Mahdi Mubarak, Stéphane Dumarçay, Holger Militz, Kévin Candelier, Marie France Thévenon, Philippe Gérardin. Comparison of different treatments based on glycerol or polyglycerol additives to improve properties of thermally modified wood. *Eur. J. Wood Prod.* DOI 10.1007/s00107-019-01429-4.
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Main Abbreviations

WPG	: Weight percent gain
ASE	: Anti-swelling efficiency
MOE	: Modulus of elasticity
MOR	: Modulus of rupture
ATR-FTIR	: Attenuated total reflectance-Fourier transform infrared
TGA	: Thermogravimetric analysis
PG	: Polyglycerol
Gly	: Glycerol
GM	: Glycidyl methacrylate
MA	: Maleic anhydride
PG-MA	: Polyglycerol maleate
Gly-MA	: Glycerol maleate
PG-GM	: Polyglycerol methacrylate
Gly-GM	: Glycerol methacrylate
PGM/MA	: Polyglycerol methacrylate maleate
GM/MA	: Glycerol methacrylate maleate
DTG	: Differential thermal gravimetry
WMLB	: Work to maximum load in bending
OHT	: Heat treated in an opened system
HPS	: Heat treated in a closed system (pressurized steam)
SorCA	: Sorbitol/citric acid treatment

VALORIZATION OF BEECH WOOD THROUGH DEVELOPMENT OF INNOVATIVE AND ENVIRONMENTALLY FRIENDLY CHEMICAL MODIFICATION TREATMENTS

Keywords: biological durability, citric acid, *Fagus sylvatica*, glycerol, maleic anhydride, mechanical properties, polyesterification, polyglycerol, sorbitol, termite, thermal modification, wood rotting

Summary

European beech (*Fagus sylvatica*) is one of the most important hardwood species in Europe. Besides its abundance which widely distributed in the western and central Europe, its good enough in mechanical properties and easy in workability has led to use it for many applications especially for interior destination. However, its low dimensional stability and poor biological durability are the main drawbacks of this species, limiting its utilization particularly for exterior purpose in hazard class 3 (exterior above ground) and hazard class 4 (exterior in the ground and/or contact with fresh water) (EN 335 2013). Even though wood is a renewable material, the term “renewable” can be qualified if the rate of its utilization or its harvesting is the same or lower than the rate of its growth. On the way to minimize the rate of its exploitation, some technologies are needed to expanse its serving time during utilization through improvement/development of wood properties corresponding to its destined applications.

Improvement of wood properties can be performed through various techniques, including the utilization of wood preservatives, such as creosote, oil-borne pentachlorophenol (penta), copper chrome arsenate (CCA), amine- or ammonium-complexed alkaline copper (II) and an organic co-biocide, triazoles, isothiazolon, quats (didecyldimethyl ammonium chloride/DDAC), imidacloprid, permethrin, etc. However, due to wider environmental issues since the last decade, some of these wood preservatives are limited or even restricted due to its negative effect on the environment or human health, intriguing treatment with totally free of biocide. As an alternative for this issue, wood modification techniques, such as wood thermal treatment and wood chemical modification are still getting much interest in the future.

Actually, wood thermal treatment has been inquired for decades. Under operating conditions which commonly performed above 150°C, hemicellulose, as the main susceptible wood component, is strongly degraded at the highest thermal condition. Meanwhile, lignin, as the main binder in wood matrix polymer, is modified. These changes in the wood components/its polymeric conformation generate a modified wood with better in dimensional stability and decay durability properties. However, as the effect of hemicellulose degradation and changes in the conformation of wood polymer matrix, the wood mechanical properties are degraded at an intensive thermal condition. In addition, a preferred improvement in biological durability of this thermally modified wood is not enough to protect the wood against termites.

On the other hand, wood chemical modification, including impregnation of a reactive chemical into the wood, is believed can improve almost all wood properties, particularly its physical and biological durability properties. A formation of new chemical bonds (covalent bonds) between the impregnated chemicals and wood components and/or the deposition of the impregnated chemical into the wood cell walls and/or in the lumen cell that cured/polymerized at certain temperature condition through bulk impregnation modification are the common mechanism in wood chemical modification. The changes in wood chemical configuration and/or reduction of the woods active sites (-OH groups)/active surface due to the impregnated chemicals generate new wood properties that can resist either against moisture/humidity or biological degrading agents, such as fungi, termites, and/or even marine borer. However, a meaningful change in wood properties sometimes needs a higher quantity of the chemicals or chemicals with high reactivity, promoting higher investment in chemicals and/or handling during modification.

As other alternatives for wood modification treatments, a combination of low concentration of the chemical followed with thermal treatment recently can improve the biological durability of thermally modified wood especially against termites (Salman et al. 2016, 2017), besides reducing the cost of the chemicals used. In this context, the “VALBEECH” project (Valorization of beech wood through development of innovative and environmentally friendly chemical modification treatments) organized between France (Université de Lorraine) and Germany (Göttingen University) with financially supported by Labex ARBRE was aimed to promote the use of European beech through different wood modification techniques. In general, the work was divided into three parts.

Part I

In this part, the work was based on the same principle as a previous wood modification method conducted by Salman et al. (2016, 2017) through the combination between low-concentration of chemical (polyglycerol maleate /PG-MA; polyglycerol methacrylate /PG-GM) impregnated into the wood followed with thermal treatment at certain conditions. Specifically, the work aimed to investigate other wood modification techniques through the development of other chemicals potentially as additives, including investigation whether glycerol could be used as a substitute polyol agent for polyglycerol. Hence, as a screening and comparison study, the chemicals used in this part was based on vinylic derivatives of polyglycerol (PG-MA; PG-GM; polyglycerol methacrylate maleate/PGM/MA_(3eq)) and glycerol (glycerol maleate/Gly-MA, glycerol methacrylate/Gly-GM; glycerol methacrylate maleate/GM/MA_(2eq)). In addition, maleic anhydride as a reactive agent in these systems was also applied as a single form.

The additives were synthesized under specific conditions which afterward each additive was diluted by the water until a concentration of 10% (w/w), impregnated into the beech wood with the vacuum pressure system. The impregnated woods were conditioned at room temperature, dried at 103°C, and thermally treated at different curing temperatures (150, 200, or 220°C) under inert condition. The additive-treated woods were then characterized for their physical (dimensional stability as anti-swelling efficiency/ASE, wettability, thermogravimetric analysis), chemical (FTIR analysis), mechanical (modulus of elasticity/MOE and modulus of rupture/MOR), and biological durability (decay resistance, termite resistance) properties.

The results revealed that this thermo-mild chemical modification permitted the modified woods had their own characteristics. Among the additives used, Gly-GM based additive had the lowest penetration capability, due to lower polarity than others. MA or Gly-GM-treated wood has lower thermal stability, presenting lower weight percent again after curing values than other additive-treated woods. Among the additive-treated woods, MA-treated wood had higher leaching values than others. PG-GM and Gly-GM-treated woods had higher leaching at lower curing temperature, but lower at higher curing condition. Glycidyl-methacrylate-based additive-treated woods (PG-GM, Gly-GM, PGM/MA_(3eq), GM/MA_(2eq)) had higher wettability than maleic anhydride-based additive-treated woods. Among the additive-treated woods, maleic anhydride-based additive-treated woods (PGM/MA_(3eq), GM/MA_(2eq), PG-MA, and Gly-MA) had higher ASE values than glycidyl methacrylate-based additive-treated woods (PG-GM and Gly-GM). However, the reverse

values were observed for the mechanical properties between both kinds of additives. Mechanical properties of all additive-treated woods were similar with thermally modified wood at the highest thermal treatment (220°C). FTIR analysis has shown that maleic anhydride-based additive-treated woods (MA, PGM/MA_(3eq), GM/MA_(2eq), PG-MA, and Gly-MA) presented higher wood modification than glycidyl methacrylate-based additive-treated woods (PG-GM and Gly-GM), indicating that the maleic anhydride-based additives had higher reactivity to the wood. Decay resistance after leaching against *Coriolus versicolor* revealed that maleic anhydride-based additive-treated woods (PGM/MA_(3eq), GM/MA_(2eq), PG-MA, and Gly-MA) had a higher resistance than glycidyl methacrylate-based additive-treated woods (PG-GM and Gly-GM), especially at lower thermal condition (150 or 200°C). Termite resistance after leaching against *Reticulitermes flavipes* presented that maleic anhydride-based additive-treated woods (PGM/MA_(3eq), GM/MA_(2eq), PG-MA, and Gly-MA) had a higher resistance than glycidyl methacrylate-based additive-treated woods (PG-GM and Gly-GM), especially at lower curing condition (103°C). Termite survival rates increased at higher curing temperature. In overall, based on the physical and biological durability properties, maleic anhydride-based additive-treated woods (PGM/MA_(3eq), GM/MA_(2eq), PG-MA, and Gly-MA) were considered as the better additive-based wood modification treatments in this comparison study. However, due to simplicity during formulation, treatment with PG-MA or Gly-MA-based additive was considered as treatments that possible to be implemented in a bigger scale. The temperature at 200 or 220°C was considered as the temperature at where the synergistic effect between mild chemical modification and thermal treatment occurred.

In addition, the advanced biological durability through field test (grave-yard test) was also performed in a tropical country, Indonesia, for almost one year period to confirm the previous screening test results. For this purpose, PG-MA and Gly-MA aqueous solution at 10% and 40% (w/w) concentration were used, followed with pursued thermal conditions at 180, 200, or 220°C under inert condition. Wood control as thermally modified wood at these thermal conditions was also made as well as untreated wood for comparison. The results have disclosed that PG-MA or Gly-MA-thermally modified wood particularly cured at 200 or 220°C had significantly far better durability (almost no mass loss observed) due to the field test than wood control (thermally modified wood) or untreated wood. In other words, the study has confirmed that the wood impregnated with a low concentration of additive (maleic anhydride-based additives) followed with

thermal modification at 200 or 220°C can generate the wood with highly durable against biological degrading agents and stable against humidity/wet conditions.

Part II

In this part, the work aimed to perform up-scaling trials of the best treatment chosen from the previous screening test in Part I. The additives used in this part were based on PG-MA, Gly-MA, and MA in consideration of their simplicity during synthesis, the chemical costs, and had better properties of the modified wood, especially their physical and biological durability properties. In addition, some new treatments as a screening test were also investigated aimed to lower temperature of thermal modification chosen from Part I without lowering the properties of its modified wood. Further, some series of up-scaling treatments were also conducted based on this screening test.

Screening treatments in this Part II were performed through impregnation of Gly-MA 10, 20, and 40% (w/w) or MA 10, 20, and 30% (w/w) using the vacuum pressure system. The impregnated woods were then conditioned at room temperature, followed with curing temperature under oven heating (OHT) in opened system (atmospheric pressure) at 120 or 180°C and under heat pressurized steam (HPS) in closed system at 150, 160, or 180°C with specific time, pressure, and humidity. Compared to the treatments in Part I, a principle of these screening treatments was based on the thought that a similar mass loss due to thermal modification would have a similar proportional relationship with the properties of thermally modified wood. Therefore, these trials, especially treatments under HPS, were directed to have a similar mass loss corresponding to the best treatments obtained in Part I. It is possible that a similar mass loss between thermal treatments in opened system/in the closed system would be achieved at a temperature lower than treatment under inert condition (Part I), minimizing heating energy and duration during modification.

From these screening treatments, results have disclosed that wood treated in opened systems (OHT) presented lower weight percent gain after curing, higher bulking after curing, lower weight loss due to leaching, and lower acidity values than wood treated in closed systems (HPS). Modulus of elasticity of wood treated under the pressurized system at 160 and 180°C was slightly higher than those of untreated wood, however, modulus of rupture decreased considerably. Decay durability of 10% (w/w) additive-treated wood under OHT at 180°C and HPS at 150, 160, or 180°C permitted to classify the corresponding treated wood as very durable.

Trials with a bigger sample size (up-scaling treatments) confirmed the results obtained on the smaller size samples. Comparable results in dimensional stability were obtained for additive-treated woods under both systems (OHT and HPS). Mechanical properties showed that wood control under HPS presented slightly higher in MOE values than that of untreated wood, however, the work to maximum load in bending (WMLB) decreased considerably. Under the same additive concentration, MOR and WMLB values of additive-treated wood were comparable between both systems, however, lower MOE values were observed under HPS. Durability against *Coniphora puteana* (CP) and *Coriolus versicolor* (CV) of wood control under HPS increased by 39% and 19%, respectively. At the same additive concentration and curing temperature, durability against CP and CV was comparable between both systems, meanwhile, durability against soft-rot fungi of additive-treated wood was higher under the OHT system. FTIR analysis evidenced the differences of the modified wood under both systems. Thermogravimetric analysis revealed that the additive-treated wood under both systems increased the initial degradation temperature, and certain treatments could decrease the end temperature point, promoting the possibility as self-fire-retardant. Additive-treated wood was dark pale brown in color under OHT, meanwhile, it was black under HPS.

Part III

With a similar wood modification technique through polyesterification-based bulk modification performed in the previous Part I & II, in this third part of the study, the wood modification was based on *in-situ* polyesterification of sorbitol and citric acid (SorCA), the well-known chemicals used as an ingredient in food and beverage industries. Since there are no studies inquired about an optimum condition for wood modification, therefore, this recent study investigated the optimum condition of SorCA-based modification for the application on beech wood.

The wood modification was conducted through impregnation of different concentrations of aqueous SorCA solutions (10, 20, 30, 55%) into the beech wood by means of the vacuum pressure system. The impregnated woods were then conditioned at room temperature, dried at 103°C, followed with curing at 140 or 160°C for 24 hours and conditioning at room temperature. Various parameter analysis during and after wood modification was demonstrated.

Based on the results, the study has uncovered that SorCA 30% was considered as the optimum condition for the modification, independently of the curing temperature. In comparison to untreated

wood, dimensional stability as ASE increased to approximately 55%, meanwhile, mechanical properties as MOE increased slightly (9%). Decay resistance against white rot (*Coriolus versicolor*), brown rot (*Coniphora puteana*), and soft rot fungi classified the SorCA-30%-impregnated wood as very durable wood. In addition, thermogravimetric study evidenced that SorCA 30%-impregnated wood has lower the end temperature of thermal decomposition in comparison to untreated wood/wood control by 20°C difference, indicating the SorCA-modified wood possibly has certain fire-retardant properties. However, due to acidic properties of SorCA solution, modulus of rupture and mainly work to maximum load in bending decreased considerably. Nevertheless, this environmentally friendly wood modification method is ready to be up-scaled and the modified could be used either for interior or estimated in exterior above the ground service area.

VALORISATION DU BOIS HÊTRE PAR LE DÉVELOPPEMENT DE TRAITEMENTS DE MODIFICATION CHIMIQUE INNOVANTS ET RESPECTUEUX DE L'ENVIRONNEMENT

Mots-clés: acide citrique, anhydride maléique, durabilité, *Fagus sylvatica*, glycérol, modification thermique, polyestérification, polyglycérol, propriétés mécaniques, pourriture, termites, sorbitol

Résumé

Le hêtre européen (*Fagus sylvatica*) est l'une des espèces du bois de feuillus les plus importantes d'Europe. Outre son abondance largement répandue en Europe occidentale et centrale, ses propriétés mécaniques suffisantes et sa maniabilité aisée, elle a été utilisée pour de nombreuses applications, en particulier pour les destinations intérieures. Cependant, sa faible stabilité dimensionnelle et sa faible durabilité biologique sont les principaux inconvénients de cette espèce, limitant son utilisation en particulier à des fins extérieures dans la classe de risque 3 (extérieur au dessus du sol) et la classe de risque 4 (à l'extérieur dans le sol et / ou au contact de l'eau douce) (EN 335 2013). Même si le bois est un matériau renouvelable, le terme «renouvelable» peut être qualifié si le taux d'utilisation ou de récolte est identique ou inférieur au taux de croissance. Afin de minimiser le taux d'exploitation, certaines technologies sont nécessaires pour augmenter la durée de service lors de l'utilisation, en améliorant / développant les propriétés du bois correspondant à ses applications.

L'amélioration des propriétés du bois peut être réalisée au moyen de diverses techniques, y compris l'utilisation de produits de préservation du bois, tels que la créosote, le pentachlorophénol en suspension dans l'huile (Penta), l'arséniat de cuivre-chrome (ACC), le cuivre alcalin complexé par des amines ou de l'ammonium (II) et co-biocide organique, triazoles, isothiazolon, quats (chlorure de didécylidiméthylammonium / DDAC), imidaclopride, perméthrine, etc. Cependant, en raison de problèmes environnementaux plus vastes depuis la dernière décennie, certains de ces agents de préservation du bois sont limités, même restreint, en raison de leurs effets négatifs sur l'environnement ou la santé humaine, ce qui en fait un traitement intrigant totalement exempt de

biocide. Au lieu de cela, les techniques de modification du bois, telles que le traitement thermique du bois et la modification chimique du bois, suscitent encore un vif intérêt.

En fait, le traitement thermique du bois a été étudié pendant des décennies. Dans des conditions d'exploitation généralement supérieures à 150°C, l'hémicellulose, principale composante sensible du bois, est fortement dégradée aux conditions thermiques les plus élevées. Pendant ce temps, la lignine, en tant que liant principal du polymère à matrice de bois, est modifiée. Ces modifications des composants du bois/de sa conformation polymérique génèrent un bois modifié doté de meilleures propriétés de stabilité dimensionnelle et de durabilité. Cependant, sous l'effet de la dégradation de l'hémicellulose et de la modification de la conformation d'une matrice polymère du bois, les propriétés mécaniques du bois sont dégradées dans des conditions thermiques intensives. En outre, une amélioration préférée de la durabilité biologique de ce bois modifié thermiquement ne suffit pas pour le protéger contre les termites.

D'autre part, on pense que la modification chimique du bois, y compris l'imprégnation d'un produit chimique réactif dans le bois, peut améliorer presque toutes les propriétés du bois, en particulier ses propriétés de durabilité physique et biologique. Formation de nouvelles liaisons chimiques (liaisons covalentes) entre les produits chimiques imprégnés et les composants du bois et/ou le dépôt du produit chimique imprégné dans les parois des cellules du bois et/ou dans la cellule de la lumière qui a durci/polymérisé à certaines conditions de température par modification de l'imprégnation en masse sont le mécanisme commun dans la modification chimique du bois. Les modifications de la configuration chimique du bois et/ou la réduction des sites actifs du bois (groupes -OH)/surface active due aux produits chimiques imprégnés génèrent de nouvelles propriétés du bois pouvant résister à l'humidité/aux agents de dégradation biologique, tels que champignons, termites et/ou même des térébrants marins. Cependant, un changement significatif des propriétés du bois nécessite parfois une plus grande quantité de produits chimiques ou de produits chimiques à réactivité élevée, ce qui favorise des investissements plus importants en produits chimiques et/ou une manipulation lors de la modification.

En tant qu'alternative aux traitements de modification du bois, une combinaison de la faible concentration du produit chimique suivie d'un traitement thermique peut améliorer la durabilité biologique du bois modifié thermiquement, en particulier contre les termites (Salman et al. 2016, 2017), tout en réduisant le coût des produits chimiques utilisés. Dans ce contexte, le projet «VALBEECH» (Valorisation du bois de hêtre par le développement de traitements de modification

chimique innovants et respectueux de l'environnement) organisé entre la France (Université de Lorraine) et l'Allemagne (Université de Göttingen) avec le soutien financier du Labex ARBRE visait à promouvoir l'utilisation du hêtre européen à travers différentes techniques de modification du bois. En général, le travail était divisé en trois parties.

Partie I

Dans cette partie, les travaux étaient basés sur le même principe qu'une méthode de modification du bois réalisé par Salman et al. (2016, 2017) grâce à la combinaison de produits chimiques à faible concentration (maléate de polyglycérol/PG-MA; méthacrylate de polyglycérol/PG-GM) imprégnés dans le bois, suivis d'un traitement thermique dans certaines conditions. Plus précisément, les travaux visaient à étudier d'autres techniques de modification du bois par la mise au point d'autres produits chimiques susceptibles d'être des additifs, notamment pour déterminer si le glycérol pouvait être utilisé comme agent de substitution du polyol au polyglycérol. Par conséquent, en tant qu'étude de dépistage et de comparaison, les produits chimiques utilisés dans cette partie étaient à base de dérivés vinyliques du polyglycérol (PG-MA; PG-GM; maléate de méthacrylate de polyglycérol/PGM/MA_(3eq)) et du glycérol (maléate de glycérol/Gly-MA, méthacrylate de glycérol/Gly-GM; maléate de méthacrylate de glycérol/GM/MA_(2eq)). De plus, l'anhydride maléique en tant qu'agent réactif dans ces systèmes était également appliqué sous une forme unique.

Les additifs ont été synthétisés dans des conditions spécifiques, puis chaque additif a été dilué par l'eau jusqu'à une concentration de 10% (p/p), imprégnée dans le bois de hêtre avec le système de vide sous pression. Les bois imprégnés ont été conditionnés à la température ambiante, séchés à 103°C et traités thermiquement à différentes températures de durcissement (150, 200 ou 220°C) dans des conditions inertes. Les bois traités aux additifs ont ensuite été caractérisés pour leur propriétés physique (stabilité dimensionnelle: efficacité anti-gonflement/ASE, mouillabilité, analyse thermogravimétrique), chimique (analyse FTIR), mécanique (module d'élasticité/MOE et module de rupture/MOR), et durabilité biologique (résistance à la pourriture, résistance aux termites).

Les résultats ont révélé que cette modification chimique thermo-douce permettait aux bois modifiés de posséder leurs propres caractéristiques. Parmi les additifs utilisés, l'additif à base de Gly-GM présentait la capacité de pénétration la plus faible, en raison de la polarité inférieure à celle des

autres. Les bois traités au MA ou au Gly-GM ont une stabilité thermique inférieure, présentant après le durcissement des valeurs en poids inférieures à celles des autres bois traités aux additifs. Parmi les bois traités aux additifs, les bois traités au MA ont eu des valeurs de lessivage plus élevées que les autres. Les bois traités au PG-GM et au Gly-GM ont eu un lessivage plus élevé à une température de durcissement plus basse, mais plus faible dans des conditions de durcissement plus élevées. Les bois traités avec un additif à base de glycidyle méthacrylate (PG-GM, Gly-GM, PGM/MA_(3éq), GM/MA_(2eq)) ont une mouillabilité supérieure à celle des bois traités avec un additif à base d'anhydride maléique. Parmi les bois traités avec additif, les bois traités avec un additif à base d'anhydride maléique (PGM/MA_(3éq), GM/MA_(2eq), PG-MA et Gly-MA) avaient des valeurs d'ASE plus élevées que les bois traités avec un additif à base de glycidyle méthacrylate (PG-GM et Gly-GM). Cependant, les valeurs inverses ont été observées pour les propriétés mécaniques entre les deux types d'additifs. Les propriétés mécaniques de tous les bois traités aux additifs étaient similaires à celles du bois modifié thermiquement au traitement thermique le plus élevé (220°C). L'analyse FTIR a montré que les bois traités avec des additifs à base d'anhydride maléique (MA, PGM/MA_(3éq), GM/MA_(2eq), PG-MA, et Gly-MA) présentaient une modification du bois supérieure à celles du bois traités à base de méthacrylate de glycidyle (PG-GM et Gly-GM), ce qui indique que les additifs à base d'anhydride maléique ont une réactivité supérieure au bois. La résistance à la décomposition après lessivage contre *Coriolus versicolor* a révélé que les bois traités avec additifs à base d'anhydride maléique (PGM/MA_(3éq), GM/MA_(2eq), PG-MA et Gly-MA) présentaient une résistance supérieure à celle des produits à base de méthacrylate de glycidyle (PG-GM et Gly-GM), en particulier dans des conditions thermiques inférieures (150 ou 200°C). La résistance aux termites après lixiviation contre *Reticulitermes flavipes* a montré que les bois traités avec un additif à base d'anhydride maléique (PGM/MA_(3éq), GM/MA_(2eq), PG-MA et Gly-MA) présentaient une résistance supérieure à celle des produits à base de méthacrylate de glycidyle (PG-GM et Gly-GM), en particulier dans des conditions de polymérisation plus faibles (103°C). Les taux de survie des termites ont augmenté à des températures de durcissement plus élevées. Globalement, à la base des propriétés de durabilité physique et biologique, les bois traités avec un additif à base d'anhydride maléique (PGM/MA_(3éq), GM/MA_(2eq), PG-MA et Gly-MA) ont été considérés comme le meilleur additif pour les traitements de modification du bois dans cette étude comparative. Cependant, en raison de la simplicité de la formulation, le traitement avec un additif à base de PG-MA ou de Gly-MA a été considéré comme un traitement pouvant être mis en œuvre à plus grande échelle. La température à 200 ou 220°C était considérée comme la température à

laquelle se produisait l'effet synergique entre une modification chimique légère et un traitement thermique.

En outre, la durabilité biologique avancée au moyen d'un essai sur le terrain a également été réalisée dans un pays tropical, l'Indonésie, pendant presque un an pour confirmer les résultats des tests de dépistage précédents. À cet effet, une solution aqueuse de PG-MA et de Gly-MA à une concentration de 10% et de 40% (p/p) a été utilisée, suivie de conditions thermiques déterminées à 180, 200, ou 220°C dans des conditions inertes. Un contrôle du bois sous forme de bois modifié thermiquement dans ces conditions thermiques a également été réalisé, ainsi que du bois non-traité à des fins de comparaison. Les résultats ont révélé que le bois modifié thermiquement au PG-MA ou au Gly-MA-particulièrement traité à 200 ou 220°C avait une durabilité bien meilleure (presque aucune perte de masse observée) due au test sur le terrain que le bois témoin (bois modifié thermiquement) ou bois non-traité. Autrement dit, l'étude a confirmé que le bois imprégné d'une faible concentration d'additif (additifs à base d'anhydride maléique) suivi d'une modification thermique à 200 ou 220°C peut générer du bois avec une résistance élevée aux agents de dégradation biologique et une résistance à l'humidité/conditions humides.

Partie II

Dans cette partie, les travaux visaient à effectuer des essais à grande échelle du meilleur traitement choisi parmi le test de dépistage précédent de la partie I. Les additifs utilisés dans cette partie étaient basés sur PG-MA, Gly-MA et MA en tenant compte de leur simplicité lors de la synthèse, les coûts chimiques, et avaient de meilleures propriétés du bois modifié, en particulier leurs propriétés de durabilité physique et biologique. En outre, certains nouveaux traitements utilisés en tant qu'essais de criblage ont également été étudiés dans le but d'abaisser la température de la modification thermique choisie dans la partie I sans réduire les propriétés de son bois modifié. De plus, certaines séries de traitements à grande échelle ont également été menées sur la base de ce test de dépistage.

Les traitements de criblage dans cette partie II ont été effectués par imprégnation de Gly-MA 10, 20, et 40% (p/p) ou de MA 10, 20, et 30% (p/p) en utilisant le système de vide sous pression. Les bois imprégnés ont ensuite été conditionnés à la température ambiante, puis à la température de polymérisation sous chauffage à l'étuve (OHT) dans un système ouvert (pression atmosphérique) à 120 ou 180°C et à la vapeur pressurisée à la chaleur (HPS) dans un système fermé à 150, 160 ou 180°C avec le temps, la pression, et l'humidité spécifiques. Par rapport aux traitements de la partie

I, un principe de ces traitements de criblage était basé sur la pensée qu'une perte de masse similaire due à une modification thermique aurait une relation proportionnelle similaire avec les propriétés du bois thermiquement modifié. Par conséquent, ces essais, en particulier les traitements sous HPS, visaient une perte de masse similaire, correspondant aux meilleurs traitements obtenus dans la partie I. Il est possible qu'une perte de masse similaire entre les traitements thermiques en système ouvert / en système fermé soit obtenue à une température inférieure à celle du traitement en condition inerte (Partie I), minimisant ainsi l'énergie et la durée de chauffage lors de la modification.

Les résultats de ces traitements de criblage ont révélé que le bois traité en systèmes ouverts (OHT) présentait un gain de masse après durcissement supérieur, un gonflement plus important après durcissement, une perte de masse inférieure à la lixiviation et des valeurs d'acidité inférieures à celles du bois traité en systèmes fermés (HPS). Le module d'élasticité (MOE) du bois traité sous le système pressurisé à 160 et 180°C était légèrement supérieur à celui du bois non-traité. Cependant, le module de rupture a considérablement diminué. La résistance à la décomposition du bois traité avec un additif à 10% (p/p) sous OHT à 180°C et HPS à 150, 160, ou 180°C est autorisée pour classer le bois traité correspondant comme très durable.

Les essais avec une plus grande taille d'échantillon ont confirmé les résultats obtenus sur des échantillons de petite taille. Des résultats comparables en termes de stabilité dimensionnelle ont été obtenus pour les bois traités aux additifs dans les deux systèmes (OHT et HPS). Les propriétés mécaniques ont montré que le contrôle du bois sous HPS présentait des valeurs de MOE légèrement supérieures à celles du bois non-traité. Cependant, le travail à la charge maximale en flexion (WMLB) a considérablement diminué. Sous la même concentration d'additif, les valeurs de MOR et WMLB du bois traité par additif étaient comparables entre les deux systèmes, cependant, des valeurs de MOE plus faibles ont été observées sous HPS. La durabilité vis-à-vis de *Coniphora puteana* (CP) et de *Coriolus versicolor* (CV) du contrôle du bois sous HPS a augmenté de 39% et 19%, respectivement. À la même concentration d'additif et à la même température de durcissement, la durabilité vis-à-vis du CP et du CV était comparable entre les deux systèmes, tandis que la durabilité vis-à-vis des champignons de la pourriture molle du bois traité avec additif était plus élevée avec le système OHT. L'analyse FTIR a mis en évidence les différences entre le bois modifié et les deux systèmes. Une analyse thermogravimétrique a révélé que le bois traité avec un additif dans les deux systèmes augmentait la température de dégradation initiale et que certains traitements

pouvaient diminuer le point de température finale, augmentant ainsi le risque d'auto-ignifugation. Le bois traité aux additifs était de couleur brun pâle sous OHT, alors qu'il était noir sous HPS.

Partie III

Avec une technique similaire de modification du bois par modification en masse basée sur la polyestérification effectuée dans les précédentes parties I et II, dans cette troisième partie de l'étude, la modification du bois reposait sur la polyestérification *in situ* du sorbitol et de l'acide citrique (SorCA), produits chimiques connus utilisés comme ingrédient dans les industries alimentaires et des boissons. A cause d'aucune étude n'a été examinée sur les conditions optimales pour la modification du bois, cette étude récente s'est donc penchée sur les conditions optimales de la modification à base de SorCA pour l'application sur du bois de hêtre.

La modification du bois a été effectuée par imprégnation de différentes concentrations de solutions aqueuses de SorCA (10, 20, 30, 55%) dans le bois de hêtre au moyen du système de vide sous pression. Les bois imprégnés ont ensuite été conditionnés à la température ambiante, séchés à 103°C, suivis d'un séchage à 140 ou 160°C pendant 24 heures et d'un conditionnement à la température ambiante. Divers paramètres d'analyse ont été démontrés pendant et après la modification du bois.

Les résultats ont révélé que SorCA 30% était considéré comme la condition optimale pour la modification, indépendamment de la température de durcissement. Par rapport au bois non-traité, la stabilité dimensionnelle (ASE) a augmenté environ 55%, tandis que les propriétés mécaniques (MOE) ont légèrement augmenté (9%). La résistance à la pourriture, vis-à-vis à la pourriture blanche (*Coriolus versicolor*), à la pourriture brune (*Coniphora puteana*), et à la pourriture molles, a classé le bois imprégné par SorCA à 30% dans la catégorie de bois très durable. En outre, une étude thermogravimétrique a montré que le bois imprégné par SorCA à 30% avait une température plus basse de décomposition thermique par rapport au bois non-traité / contrôle du bois par une différence de 20°C, indiquant que le bois modifié avec SorCA avait probablement certaines propriétés ignifuges. Cependant, en raison des propriétés acides de la solution de SorCA, le module de rupture (MOR) le travail à la charge maximale en flexion (WMLB) ont considérablement diminué. Néanmoins, cette méthode de modification du bois respectueuse de l'environnement est prête à être étendue et l'application du bois modifiée pourrait être utilisée pour l'intérieur ou estimée en extérieur au-dessus de la zone de service au sol.

Introduction

According to Global Forest Resources Assessment, the total forest area in Europe reached 1,015 million ha in 2015, with an increasing annual rate reached 0.08 million ha per year since 1990 (FAO 2016). Even though the annual increase in forest decreased since the last five years from the latest reporting year (2015), the annual growth rate in total remain high, promising high availability of wood as the main forest product to support increasing demand in various human applications. Among this huge abundance, one of the most important commercial hardwood species in Europe is European beech (*Fagus sylvatica* L.). This species covered 12 million ha of territory in the West and Central Europe (CapDecision 2010), and particularly it dominated > 300,000 km² in Central Europe and was called the most successful Central European species (Leuschner et al. 2006), which can be seen in the Figure 1. In France, it accounts for more than 1.4 million ha of principal beech area (IGN 2017). Meanwhile, in Germany, it covers more than 1.5 million ha (Wuhlisch and Muhs 2011). This species, known for its good enough in mechanical properties and workability, has been widely used in various applications such as furniture, interior joinery, flooring, decorating material, LVL, plywood, fuel, siding, and other things which generally destined for interior applications. Unfortunately, beside its huge abundance which some of them still underexploited in the nature, the low dimensional stability and poor biological durability of this species (EN 350 2016) limits its utilization particularly for exterior application in hazard class 3 (exterior above ground) and class 4 (exterior in ground and/or contact with fresh water) (EN 335 2013). Based on these drawbacks, research on beech wood is still challenging to investigate for its properties improvement.

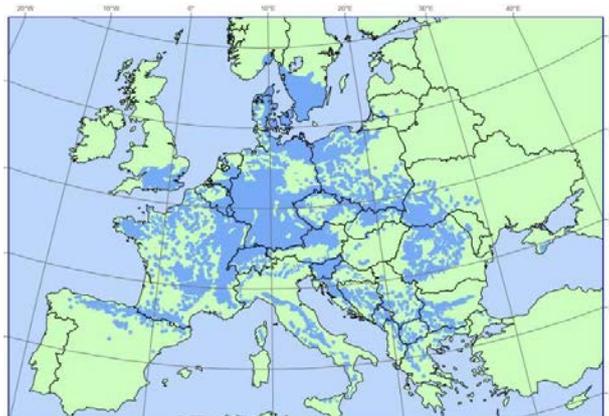


Figure 1: Natural distribution of *Fagus sylvatica* in central Europe (EUFORGEN 2009)

Generally, improvement of wood properties has been studied for decades. Particularly in terms of decay durability properties against fungi and termites, development of wood properties in order to meet their service of the application for exterior uses (use class 3 and 4) has been examined and some of them have been applied at industrial scale. The first common applied techniques in the ancient method were the utilization of creosote and oil-borne pentachlorophenol (penta) as the first-generation organic wood preservatives, and waterborne arsenical, copper chrome arsenate (CCA) as the first-generation metallic wood preservative. These techniques served the best performance on treated wood particularly through its fungal and termites resistances properties for long term protection. Along with scientific development and pressure for a security of human health and environment, these techniques were gradually prohibited in consideration of its toxicity properties either during in their preparation or in their service area, especially for residential application (Schultz et al. 2008).

Other techniques, as the second-generation biocide system, were the utilization of waterborne copper-rich system that contain amine- or ammonium-complexed alkaline copper (II) and an organic co-biocide to control copper-tolerant fungi. Limitation for its application was also occurred when copper could disrupt the ecosystem and fasten of metal corrosion, and a high cost organic amine used during production (Schultz et al. 2008). Even though micron-sized dispersed copper (II) (as copper carbonate) could resolve some problem above, more or less this technique could give the same impact to the environment.

As the increasing environmental pressure since then, European countries eventually obliged to use a totally organic system for wood preservative or suggested for the use a totally non-biocide system. Some methods have been applied based on totally organic material derived from agrochemicals as third-generation biocide. Some of them have a function as fungicidal biocides such as triazoles (propiconazole, tebuconazole, and cyproconazole), isothiazolon (kathon 930TM), quarternary ammonium compounds or quats (didecyldimethyl ammonium chloride/DDAC), and a function as termiticidal and insecticidal such as imidacloprid and permethrin (Schultz et al. 2008).

Other biocides which generally applied for decades as the wood preservative because of its economical and benign properties is derived from boron-based element, such as borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), boric acid (H_3BO_3), or Tim-Bor[®] (disodium octaborat tetrahydrate, $\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$). Although boron-based compounds are more effective as a fungicidal and termiticidal activity than copper and zinc system, their easily leaching properties in water make

them not suitable for wood destined for ground contact area or exterior application which frequently contact with water (Obanda et al. 2008). Many studies have investigated for minimizing its leaching properties, as reviewed by Obanda et al. (2008), including the utilization of non-biocide additives for making better fixation of borat (as borax) in wood (Salman et al. 2014, 2016). Even though these efforts could successfully solve the problem, the utilization of biocide tends to be minimized and even be restricted in the future in consideration of its effect to the human being and environment according to the Biocide Products Directory adopted by European countries in 2016 (Ministre de l'Environnement 2016). Considering this issue, a system with totally free biocide will be the most favorable in the future.

Actually, a totally free biocide wood preservation system has also been inquired for decades. In general, this system can be derived by two methods, thermal treatment and chemical modification which some of them have been reviewed in the literature (Rowell 1983; Hill 2006; Gérardin 2016). Thermal treatment of wood is one of the alternative processes that have widely been studied to overcome the problem of wood dimensional stability and decay durability (Militz 2002a; Weiland and Guyonnet 2003; Esteves and Pereira 2009). This technique has also been applied on an industrial scale in many countries (Militz 2002b; Homan and Jorissen 2004). It was reported that temperature over 150°C could alter the physical and chemical properties of wood permanently (Kotilainen et al. 2000; Boonstra 2008). During thermal treatment, hemicellulose is strongly degraded (Nuopponen et al. 2004; Inari et al. 2007), crystallinity of cellulose modified (Sivonen et al. 2002; Hakkou et al. 2005b), and lignin depolymerized partially and subjected to thermo-induced cross-linking reaction (Tjeerdsma et al. 1998; Wikberg and Maunu 2004; Tjeerdsma and Militz 2005; Brosse et al. 2010), leading to an increase of apparent lignin content in the thermally modified wood (Yildiz et al. 2006). All of these chemical changes generated the new wood properties, especially its dimensional stability and decay durability. However, the decrease in hemicelluloses content, as an interpenetrating agent among the cellulose and lignin in the wood cell wall, weakens the wood structure. Consequently, mechanical properties such as impact bending and tensile strength are decreased (Boonstra et al. 2007a; Korkut et al. 2008; Mburu et al. 2008). Furthermore, the durability towards insect attacks (Unsal et al. 2009; Surini et al. 2012; Sivrikaya et al. 2015) or in ground contact area (Welzbacher and Rapp 2007; Ringman et al. 2016) is still insufficient.

Chemical modifications involving impregnation of active chemical into the wood can also be an alternative to overcome the problems of biodegradability and dimensional stability of wood. Moreover, it can be applied at lower temperature process minimizing degradation of wood comparatively to thermal modification exposed previously. These chemical modifications have retained a great attention since the middle of 20th century. Although many research have been conducted since then (Rowell 1983; Hill 2006), the low reactivity of wood polymers which require the use of highly reactive chemical and catalyst, the accessibility of the reactants into the wood structure which depend on the anatomy and impregnability of each wood species, the difficulty of handling of hazardous materials, the limited technology transformation, and the high cost of processes are as many reasons that hinder the utilization of these research results on the commercial scale. Up to now, only few of them could be implemented in industrial scale, such as acetylation (Rowell et al. 1997; Ibach et al. 2000; Bongers et al. 2015), furfurylation (Lande et al. 2004; Hadi et al. 2005), and DMDHEU (1,3-dimethylol-4,5-dihydroxyethyleneurea) treatments (Militz et al. 2011), although the higher concentration of the chemical is still needed in order to get the modified wood with better characteristic (Gérardin 2016).

As an effort to find other non-biocide treatments that economically viable for wood protection, in very recent year, it was reported that combination low concentration of chemical as additive impregnated into the wood followed with thermal modification at certain temperatures could improve durability against decay and termite attacks (Salman et al. 2016, 2017). These improvements have given a novel insight that combination of thermal and mild-chemical modification allowed a synergic effect of both systems, generating a thermo-modified wood with better in durability properties either against decay or termite attacks. Regarding to the chemical used, they impregnated low concentration of vinylic-based polyglycerol as polyglycerol maleate or polyglycerol methacrylate into the wood. The use of polyglycerol was not only based on its renewable properties (Martin and Richter 2011), but also its biocompatibility polyols with high thermal and chemical stability (Ciriminna et al. 2015). On the other hand, maleic anhydride and glycidyl methacrylate, as the reactive in these systems, are versatile chemicals that are widely used in polymer industry, besides their low hazard and biodegradable chemical (United State Environmental Protection Agency, US EPA; Felthouse et al. 1933; Hernandez 1999). Moreover, especially for polyglycerol maleate, a water-soluble polyester, a good penetration into the wood during impregnation, and a reusable impregnating solution could become other benefits for this

system. Based on these prospective treatments, a profound investigation on the synergistic effect of thermal and mild-chemical modification would be interesting to study, as well as performing analysis of certain physical and mechanical properties of the modified wood. Further, since the polyglycerol that available commonly in the market has low degree of polymerization, it came to mind to use glycerol as monomer form of polyglycerol, a versatile renewable polyol. Availability on the market as by-product of certain industrial processes (Israel et al. 2008; Leoneti et al. 2012) is another beneficial aspect for the use of glycerol.

In this context, the “VALBEECH” project (Valorization of beech wood through development of innovative and environmentally friendly chemical modification treatments) carried out between France (Université de Lorraine) and Germany (Göttingen University) with a financial support of Labex ARBRE is aimed to promote the utilization of European beech through different techniques of wood modification. The work has been divided in 3 parts, as follows:

Part I (Chapter II)

Wood modification based on impregnation of low concentration of vinylic derivatives of glycerol and polyglycerol combined with thermal modification at different temperatures. This section was the continuation of previous studies (Salman et al. 2016, 2017), analyzing the utilization of glycerol instead of polyglycerol in vinylic derivatives for chemical wood modification. Investigation for studying the synergistic effect of combination between thermal and mild-chemical modification and analyzing the properties of the modified wood (physical, chemical, mechanical, and biological durability properties against decay, and termite in the lab and in-ground contact area) was also undertaken.

Part II (Chapter III)

In this section, implementation and up-scaling of the selected wood modification methods from the part I was examined through collaboration with Laboratory of Wood Biology and Wood Technology, Faculty of Forestry, Göttingen University, in Germany. Other curing procedures based on the same chemicals were investigated for wood modification, such as thermo-chemical wood modification in opened and in closed system with varying in the chemical concentrations. Certain physical, chemical, mechanical, and biological durability (decay white rot, brown rot, soft rot, and field test) properties of the modified wood, as well as analyzing the modification process were evaluated.

Part III (Chapter IV)

In this last section, similarly as the research Part I and Part II where wood modification was based on polyesterification based-bulk impregnation, research Part III concerned to wood modification based on *in-situ* polymerization of sorbitol and citric acid (SorCA), two well-known renewable chemicals commonly used as ingredients in foods and beverages industries. The modification was carried out under different SorCA concentrations and curing temperatures. Further, investigations of the modified wood for their physical, chemical, mechanical properties, and biological durability against decay (white rot, brown rot, and soft rot) were also evaluated.

Introduction

Selon FAO (Food and Agriculture Organization), la superficie forestière totale en Europe a atteint 1 015 millions d'hectares en 2015, avec un taux annuel de croissance atteignant 0.08 millions d'hectares par an depuis 1990 (FAO 2016). Même si l'accroissement annuel de la forêt a diminué légèrement au cours des cinq dernières années depuis la dernière évaluation (2015), le taux de croissance annuel total reste élevé, conduisant à une disponibilité élevée la ressource permettant de répondre à la demande de croissante de bois pour diverses applications humaines. Parmi les différentes essences forestières disponibles, le hêtre (*Fagus sylvatica* L.) constitue une des essences de feuillus disponibles en forêt la plus importante en Europe. Cette essence représente plus de 12 millions d'ha du territoire en Europe occidentale et centrale (CapDecision 2010), et plus de 300 000 km² en Europe centrale qualifiée de ce fait comme l'essence la plus prometteuse d'Europe centrale, comme représenté dans la figure 1 (Leuschner et al. 2006). En France, le hêtre représente plus de 1.4 millions d'hectares (IGN 2017). En Allemagne, l'essence couvre plus de 1.5 millions d'hectares (Wuhlisch et Muhs 2011). Cette essence, connue pour ses propriétés mécaniques et sa facilité d'usinage, a été largement utilisée dans de diverses applications telles que le mobilier, la menuiserie d'intérieur, les revêtements de sol, les matériaux de décoration et autres objets généralement destinés à des applications intérieures, la fabrication de LVL et de contreplaqué, ou encore comme combustible. Malheureusement, malgré sa grande abondance et une sous exploitation récurrente de cette essence, la faible stabilité dimensionnelle et la faible durabilité biologique du hêtre (EN 350 2016) limitent fortement l'utilisation de cette essence, notamment pour les applications extérieures dans les classes d'emploi 3 (extérieur au-dessus du sol) et 4 (extérieur dans le sol et / ou en contact avec de l'eau douce) (EN 335 2013). Du fait de ces inconvénients, la recherche sur le bois de hêtre reste en défi à étudier pour améliorer ses propriétés.

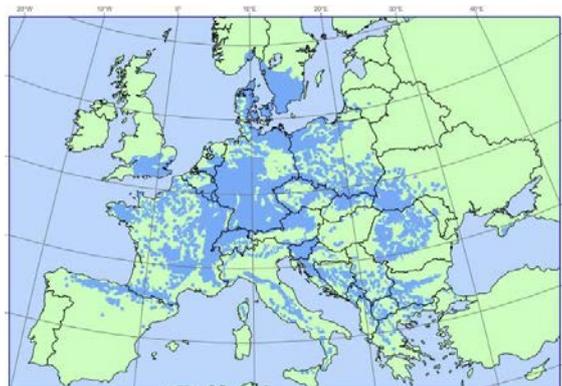


Figure 1. Répartition naturelle de *Fagus sylvatica* en Europe (UFORGEN 2009)

L'amélioration des propriétés du bois fait l'objet d'importantes recherches depuis de nombreuses années. Le développement de traitements de préservation permettant de répondre aux besoins pour des utilisations du bois en conditions extérieures (classes d'utilisation 3 et 4) a fait l'objet de nombreux travaux, certains d'entre eux ayant conduit à des applications industrielles et commerciales. Les premiers traitements de préservation de première génération développées ont impliqué l'utilisation de différents biocides tels que la créosote, le pentachlorophénol (penta) en solution dans des solvants organiques, ou les mélanges Cuivre Chrome Arsenic (CCA) en solution aqueuse comme agent de préservation du bois. Ces techniques ont permis d'améliorer considérablement les performances des bois traités, notamment vis-à-vis des champignons et des termites permettant une protection à long terme. Parallèlement, la prise de conscience collective pour une gestion durable de notre environnement apparu au cours de la dernière décennie et la mise en place de différentes lois pour protéger l'environnement a conduit à un abandon progressif de ces techniques, voir des interdictions pures et simples, compte tenu de la toxicité des différents biocides utilisés lors du traitement, de l'utilisation ou du recyclage en fin de vie des bois traités (Schultz et al. 2008).

Devant ces interdictions, différents biocides dits de deuxième génération ont été proposés. Parmi ceux-ci, on peut citer l'utilisation de cuivre en milieu alcalin en présence d'ammoniaque ou d'éthanol amine, complexé par différents agents chélateurs ou non, en présence de co-biocide organiques tels que des ammoniums quaternaires ou des triazoles. Cependant, ces produits rencontrent également des limitations dues à la quantité importante de cuivre utilisé pouvant perturber les écosystèmes, la corrosion du métal, et le coût élevé des amines et co-biocides organiques utilisés (Schultz et al. 2008). Même si le cuivre (sous forme de carbonate de cuivre) micronisé peut résoudre certains problèmes ci-dessus, son impact sur l'environnement reste cependant un frein à son utilisation.

Face aux pressions environnementales croissantes, on assiste actuellement en Europe à un développement de plus en plus important de systèmes biocides à base de produits organiques n'impliquant pas l'utilisation de métaux lourds, ainsi qu'au développement de méthodes n'impliquant pas l'utilisation de substances biocides. L'utilisation de produits organiques, initialement destinés à l'agrochimie, constitue aujourd'hui les biocides de troisième génération les plus utilisés dans le domaine de la préservation du bois. Certains d'entre eux jouent le rôle de fongicides tels que les triazoles (propiconazole, tébuconazole et cyproconazole), l'isothialozone

(kathon 930TM), les ammoniums quaternaires ou quats (chlorure de didécyltriméthylammonium / DDAC), ou fonctionnent comme termiticides et insecticides comme l'imidachloprid et la perméthrine (Schultz et al. 2008).

D'autres biocides, généralement utilisés depuis des décennies comme agents de protection du bois en raison de leur efficacité et de leur faible coût, appartiennent à la famille des dérivés du bore, tels que le borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), l'acide borique (H_3BO_3) ou le Tim-Bor® (disodium octaborat tétrahydrate, $\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$). Bien que les composés à base de bore soient plus efficaces que les systèmes à base de cuivre et de zinc en tant que fongicide et termiticide, leur forte solubilité dans l'eau les rend inadaptés au bois destiné à une application extérieure fréquemment (Obanda et al. 2008). De nombreuses études ont cherché à minimiser leur lessivage (Obanda et al. (2008), comme récemment l'utilisation d'additifs non biocides pour améliorer la fixation du borax dans le bois (Salman et al. 2014, 2016). Bien que ces dernières études puissent résoudre le problème du lessivage du bore avec succès, le recours à l'utilisation de substances biocides reste incertain à l'avenir, compte tenu de leurs effets sur l'homme et l'environnement et à la révision de la Directive Biocide de 2016 par le parlement Européen (Ministre de l'Environnement 2016). Compte tenu de ce contexte, le développement de méthodes de protection du bois non biocide constitue l'alternative la plus prometteuse pour l'avenir.

Les méthodes de préservation du bois sans biocide font l'objet de recherches importantes depuis une vingtaine d'années. Deux grandes catégories de traitements sont rapportées dans la littérature : les méthodes basées sur la modification thermique du bois et celles basées sur sa modification chimique (Rowell 1983; Hill 2006; Gérardin 2016). Le traitement thermique du bois est l'une des alternatives la plus étudiée pour résoudre le problème de la stabilité dimensionnelle du bois et de sa durabilité face aux attaques fongiques (Militz 2002a; Weiland et Guyonnet 2003; Esteves et Pereira 2009). Cette technique a également été développée à l'échelle industrielle dans différents pays (Militz 2002b; Homan et Jorissen 2004). Il a été rapporté qu'une température supérieure à 150°C modifiait de manière permanente les propriétés physiques et chimiques du bois (Kotilainen et al. 2000; Boonstra 2008). Au cours du traitement thermique, les hémicelluloses sont fortement dégradées (Nuopponen et al. 2004; Inari et al. 2007), la cristallinité de la cellulose modifiée (Sivonen et al. 2002; Hakkou et al. 2005b) et la lignine partiellement dépolymérisée soumise à des réactions de thermo-réticulation (Tjeerdsma et al. 1998; Wikberg et Maunu 2004; Tjeerdsma et Militz 2005; Brosse et al. 2010), conduisant à une augmentation de sa teneur apparente dans le bois

modifié thermiquement (Yildiz et al. 2006). Toutes ces modifications chimiques confèrent au matériau de nouvelles propriétés, en particulier une meilleure stabilité dimensionnelle et amélioration de la résistance aux champignons basidiomycètes. Cependant, la diminution de la teneur en hémicelluloses, en tant qu'agent interpénétrant parmi la cellulose et la lignine dans la paroi cellulaire du bois, affaiblit la structure du bois. En conséquence, les propriétés mécaniques telles que la résistance aux chocs, à la flexion et à la traction sont diminuées (Boonstra et al. 2007a; Korkut et al. 2008; Mburu et al. 2008). En outre, la durabilité face aux attaques d'insectes (Unsal et al. 2009; Surini et al. 2012; Sivrikaya et al. 2015) ou pour des applications au contact du sol en classe d'emploi 4 (Welzbacher et Rapp 2007; Ringman et al. 2016) reste insuffisante.

Des modifications chimiques impliquant l'imprégnation de substances chimiques réactives dans le bois peuvent également constituer une autre alternative pour résoudre les problèmes de biodégradabilité et de stabilité dimensionnelle du bois. De plus, ces modifications peuvent être menées à plus basse température minimisant les réactions de dégradation du bois comparativement aux traitements de modification thermique exposés précédemment. De telles modifications chimiques ont été décrites dès le milieu du XX^{ème} siècle. Bien que de nombreuses recherches aient été menées sur ce type de traitements (Rowell, 1983; Hill, 2006), la faible réactivité des polymères du bois nécessitant l'utilisation de produits chimiques et de catalyseurs hautement réactifs, l'accessibilité des réactifs à la structure du bois, fonction de l'anatomie et de l'imprégnabilité de l'essence, la difficulté à manipuler et à recycler des matières premières réactives, ainsi que la mise en place de processus onéreux sont autant de raisons qui expliquent les difficultés de transfert de ces recherches à l'échelle industrielle. Jusqu'à présent, seules quelques traitements ont donné lieu à au développement d'applications à l'échelle industrielle, telles que l'acétylation (Rowell et al. 1997; Ibach et al. 2000; Bongers et al. 2015), la furfurylation (Lande et al. 2004; Hadi et al. 2005), et traitements au DMDHEU (1,3-diméthylol-4,5-dihydroxyéthylène) (Militz et al. 2011), bien qu'une concentration plus élevée en réactifs soit encore nécessaire pour obtenir des bois modifiés avec des caractéristiques intéressantes (Gérardin 2016).

Dans le but de trouver d'autres traitements non biocides économiquement plus viables pour la protection du bois, il a été rapporté récemment, qu'une imprégnation mettant en jeu de faibles concentrations de différents dérivés du polyglycerol, utilisés initialement comme additifs pour fixer du bore, suivie d'une seconde étape de modification thermique améliorerait la durabilité du bois contre les agents de pourriture et les attaques des termites (Salman et al. 2016, 2017). Ces travaux

ont montré que la combinaison d'un traitement de modification chimique impliquant de faibles concentrations de réactifs à un traitement de modification thermique permettait un effet synergique des deux systèmes générant un bois thermo-modifié offrant de meilleures propriétés de durabilité, notamment vis-à-vis des termites. Concernant les réactifs utilisés, deux dérivés vinyliques de polyglycérol ont été étudiés : le maléate de polyglycérol et le méthacrylate de polyglycérol. L'utilisation du polyglycérol reposait non seulement sur le caractère renouvelable de ce polyol capable de complexer le bore (Martin et Richter 2011), mais également sur sa stabilité thermique et chimique élevée (Ciriminna et al. 2015). Par ailleurs, l'anhydride maléique et le méthacrylate de glycidyle sont des produits chimiques largement utilisés dans l'industrie des polymères peu dangereux et biodégradables (United States Environmental Protection Agency, US EPA; Felthouse et al. 1933; Hernandez 1999). De plus, le maléate de polyglycérol, est soluble dans l'eau permettant une bonne pénétration dans le bois lors de l'imprégnation.

Sur la base de ces essais préliminaires, il a semblé intéressant d'étudier de manière plus approfondie l'effet synergique du couplage entre un traitement de modification thermique et un traitement de modification chimique modérée, ainsi que d'analyser certaines propriétés physiques et mécaniques des bois modifiés. En outre, comme le polyglycérol utilisé présente un faible degré de polymérisation, il a été envisagé d'utiliser directement le glycérol comme source de polyol renouvelable. Sa bonne disponibilité sur le marché en tant que sous-produit de certains processus industriels (Israel et al. 2008 ; Leoneti et al. 2012) est un autre paramètre important pour l'utilisation du glycérol.

Dans ce contexte, le projet «VALBEECH» (Valorisation du bois de hêtre par le développement de traitements de modification chimique innovants et respectueux de l'environnement) réalisé en partenariat entre la France (Université de Lorraine) et l'Allemagne (Université de Göttingen) dans le cadre d'un financement du laboratoire d'excellence ARBRE, a pour objectif de promouvoir la valorisation et l'utilisation du bois de hêtre suite à sa modification par différentes techniques de modifications chimiques. Le travail se compose de trois parties.

Partie I (Chapitre II)

Modification du bois basée sur l'imprégnation de solutions aqueuses de dérivés vinyliques du glycérol et du polyglycérol utilisés en faibles concentrations, suivi d'une étape de modification thermique réalisée à différentes températures. Cette partie s'inscrit dans la continuité d'études

précédentes (Salman et al. 2016, 2017), en évaluant l'effet de l'utilisation du glycérol au lieu du polyglycérol pour la préparation des dérivés vinyliques nécessaires à la modification chimique. L'étude vise également à étudier les effets synergiques obtenus suite à la combinaison de traitements de modification chimique et thermiques. Les différentes propriétés des bois modifiés (propriétés physiques, mécaniques et durabilité face à la pourriture et aux termites) seront également étudiées.

Partie II (Chapitre III)

Dans cette partie, des méthodes de modification sélectionnées dans la partie I seront mises en œuvre en collaboration avec le Laboratoire de Biologie et de Technologie du Bois de la Faculté de Foresterie de l'Université de Göttingen en Allemagne pour compléter la caractérisation des propriétés des matériaux obtenus. D'autres conditions de cuisson seront évaluées sur des éprouvettes de plus grande dimension à partir des traitements de modification chimique retenus en effectuant le traitement thermochimique dans des conditions de système ouvert ou fermé avec des concentrations variables de produits chimiques. Certaines propriétés physiques, chimiques, mécaniques et biologiques (résistance aux pourritures blanches, brunes, molles, et essais de durabilité vis-à-vis des termites en laboratoire et en champs) des bois modifiés seront évaluées.

Partie III (Chapitre IV)

La dernière partie, de la même manière que les parties I et II de la recherche, où la modification du bois reposait sur une imprégnation en masse à base de polyesterification, la partie III de la recherche concernait la modification du bois basée sur la polymérisation in situ du sorbitol et de l'acide citrique (SorCA), deux produits chimiques renouvelables connus utilisés couramment comme ingrédients dans les industries des produits alimentaires et des boissons. La modification a été effectuée à différentes concentrations et températures de durcissement du SorCA. En outre, des études sur le bois modifié pour ses propriétés physiques, chimiques, mécaniques et sa résistance biologique à la pourriture (pourriture blanche, pourriture brune et pourriture douce) ont également été évaluées.

CHAPTER I

LITERATURE REVIEW

I.1. Wood as renewable resource

Wood has been used for thousands of years, serving for many kinds of human activities. As the main component and act as construction material in trees, wood serves as transporting material between root and leaves. Through vascular cambium, wood is formed. Constructed by interconnected complex biopolymer composites of cellular structure inside, it has high mechanical strength at low weight level. Wood is known as a biodegradable, unique, recyclable, and versatile material. As a biodegradable material, wood can be decomposed by certain organisms such as fungi, termites, and bacteria. As the unique and versatile material, wood has unique physical properties that can be useful for many applications such as a thermal isolator, shock absorber, air pollution absorber, aesthetic, natural, etc. Through its chemical properties, wood can be used for many applications such as for producing many kinds of organic chemicals (cellulose, furfural, acetic acid, benzene-based chemicals, etc.), paper, bioenergy, and nanotechnology applications (nanocellulose and its derivatives). Some wood products and its derivatives can be recyclable, wood particles or flakes from sawmill wood industry or wood-based furniture can be used for making particleboard, fiberboard, paper, paper boards, etc.

Unlike fossil fuels, wood is also known as a renewable material. The renewable sources become one of the most efficient and effective solutions for environmental and resource crisis recently and in the future. The so-called “renewable” for wood as a product from the forest can be qualified if the rate of its utilization/harvesting is the same or lower than the rate of its growth. A good implementation of this role would have sustainable results that can serve for many years to come. On the way to minimize the rate of its exploitation/harvesting, some technologies are needed to recycle well the used wood-based products to become the newest products or for other certain applications. Other techniques, including an expansion of its serving time during utilization, are needed through some improvements of its properties corresponding to its destined applications.

I.2. Anatomical structure of wood

I.2.1 Cross section of wood

The cross section of wood (the transverse plane section) figures out the information about the features from the pit-to-bark (radial direction) and from the circumferential direction (tangential direction). The radial plane provides information about longitudinal changes in the stem from the pit to the bark along the radial system. Whereas, the tangential plane provides information about the tangential dimension of features (Rowell 2012).

The cross section of wood comprises some subdivisions part of wood, from the center to the outside, which consists of pith, heartwood, sapwood, vascular cambium, and bark (Figure 2)

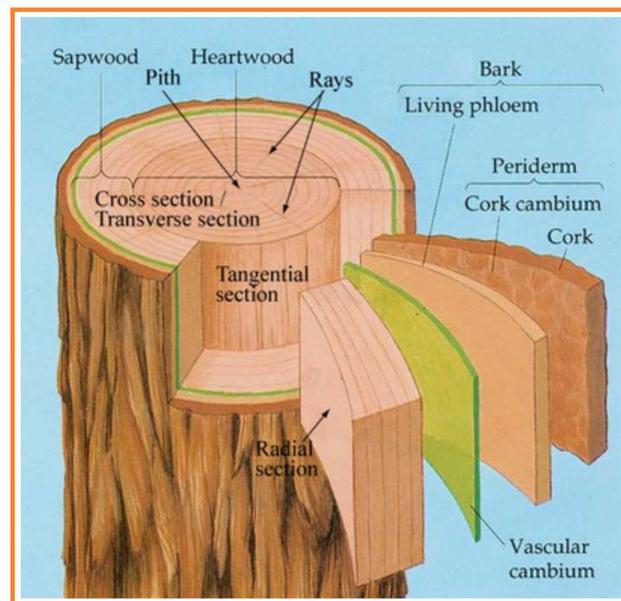


Figure 2: Scheme of tree-trunk transverse cut. Copyright University of Cambridge, DoITPoMS 2019.

Bark consists of two main parts, an inner bark and an outer bark. The inner bark comprises a secondary phloem/living phloem (transfers nutrients from the leaves to the rest of the tree) and cork cambium. Cork cambium and outer bark layers are also dubbed together as periderm. The outer bark functions as the protector for the inner bark (phloem) from outside attacks, disease, and drought (Rowell 2012).

Vascular cambium is a thin layer lies between the inner bark and the wood (secondary xylem). It is responsible for producing wood to the inside, and the bark (secondary phloem) to the outside of the tree (Larson 1994). Vascular cambium creates the axial and radial systems in the tree by means of two types of cells: the ray initial and the fusiform initial. Fusiform initial gives rise in the axial system, whereas ray initial gives rise in the radial system. Thus, there is a direct and continuous

connection between the vascular cambium, the inner bark, and the most recently formed wood (Rowell 2012).

The sapwood is part of the tree where parenchyma cells (the living cell at maturity and metabolically active) is located, found both in softwood and hardwood. Sapwood is usually a lighter-colored wood adjacent to the bark. Heartwood is an older xylem that has been penetrated by gums and resins. Heartwood is usually the darker-colored wood located in the interior of sapwood, denser and more resistant than sapwood. Pith is the remaining of the initial growth trunk before the formation of wood (Rowell 2012).

Vascular cambium produces the wood at a time through its one layer of cell divisions, but in general many woods are formed approximately together in time, as known that woods comprise a large group of cells. The compilation of those produced cells over a period of time interval is called growth ring. Earlywood (springwood) cells are formed at the beginning of the growth ring. Whereas, latewood (summerwood) is the cell in the latter portion of the wood increment.

I.2.2 Structural difference between softwoods and hardwoods

Softwood structure is relatively simple. Axial tracheid is mostly constructed in the axial/vertical system. They serve for both conductive and mechanical functions in wood. Axial parenchyma is another cell type that sometime exist. In some softwood species, there is structure called resin canals. Compared to hardwoods, it is structurally more complicated than softwood. Constructed by various kinds of fibrous elements, vessel elements in various size and arrangements, and parenchyma cells in various patterns and abundance are composed in the axial system of the hardwoods (Table 1).

Table 1: The main difference between softwood and hardwoods (Rowell 2012)

	Softwoods	Hardwoods
Botanically	gymnosperms	angiosperms
Leaves feature	commonly as needle-leaved	broadleaf
Transport system	no pores (tracheid)	vessel (pores)
Density	mostly lower than hardwood	mostly higher than softwood
Microscopic structure	tracheid, axial parenchyma and resin canal complexes, rays	vessels, fibers, axial parenchyma, rays

I.2.3 The wood cell wall

The tree species, the location at where the trees growth, and the location at where wood samples are taken in the tree would influence the content of the wood cell wall components. Hardwoods are different from softwoods, sapwood from heartwood, and earlywood from latewood. In the latewood, glucomannans contents is higher than in the earlywood, but glucoronarabinoxylans contents are higher in the earlywood. On the other hand, extractives are higher in the heartwood than in the sapwood. There are three main regions in the cell wall, the middle lamella, the primary wall, and the secondary wall (Figure 3). The cell wall has the main constituents: cellulose microfibrils (specify the organization and distribution), hemicellulose, and a matrix (pectin in the primary walls and lignin in the secondary walls) (Rowell 2012).

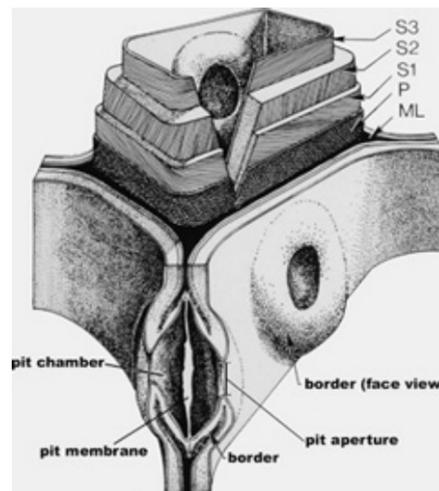


Figure 3: Layered structure of wood cell wall including the structural details of a bordered pit.

ML: middle lamella, P: primary wall, and {S1, S2, S3}: the secondary layer. The microfibril angle of each layer is also illustrated, as well as the relative thickness of the layers. At the lower position, the bordered pit is illustrated the pit aperture, the pit chamber, the pit membrane, and the border (Rowell 2012)

The primary cell wall (P) is composed of microfibrils with largely random orientation (microfibril angle is between 0 – 90 degrees) and enables for the expansion of the cell to take place as cell growth. It is the first layer to be laid down when the cell is formed. Afterwards, the secondary cell wall is formed and organized by its sub-layers (S1, S2, and S3), displaying different pattern and specific orientation corresponding to their microfibrils (Figure 3). The secondary wall occupies the greatest portion of the cell wall and plays the greatest effect on the cell properties and consequently

to the wood macroscopic properties. It is composed of many lamellae of associated microfibrils exhibiting a helical twisted pattern (Hill 2006).

The middle lamella and primary wall are composed mainly by lignin and a small amount of cellulose and hemicellulose. In secondary walls, from the first layer (S1) to the second layer (S2) and third layer (S3), the lignin content decreases towards the lumen. The total amounts of lignin is located in S2, even though the highest lignin concentration is located in middle lamella and primary wall (Rowell 2012). Since the S2 layer is the thickest layer of the cell wall, it has about 80% of the cell wall by weight. Therefore, it dominates the wood properties integrally, such as mechanical performance and swelling (Salmén and Burgert 2009).

The arrangement of the polymers in each layer of the secondary cell wall shows different orientation in some degree of order. Imbedded in the matrix of lignin and hemicellulose, the cellulose microfibrils have different inclination in relation with the fiber axis (microfibril angle, MFA) in the different layers. MFA of S2 layer is lower than MFA of S1 (50 – 70 degrees) and S3 (70 – 90 degrees) layers. In the normal wood, MFA of S2 layer is 5 – 30 degrees (Rowell 2012). In the secondary cell wall, cellulose microfibrils are arranged in an undulating aggregate structure with diameter reaching up to 30 nm. The amorphous cell wall polymers (hemicellulose and lignin) fill the spacing between those aggregates (Salmén and Burgert 2009). Hemicelluloses present much lower degree of orientation than cellulose (Salmén et al. 2012). They do not bond covalently with the cellulose fibril surface, but mostly by hydrogen bonds, which then some physical entanglements from non-crystalline regions might support and tighten all of the components (Salmén and Burgert 2009). On the other hand, lignin does not bond to the cellulose directly, but they make some covalent bonds with hemicelluloses to form lignin-carbohydrate complex. Thus, hemicelluloses play the main role in conserving the cell wall assembly (Salmén and Burgert 2009). The illustration of the cell wall assembly can be seen in Figure 4.

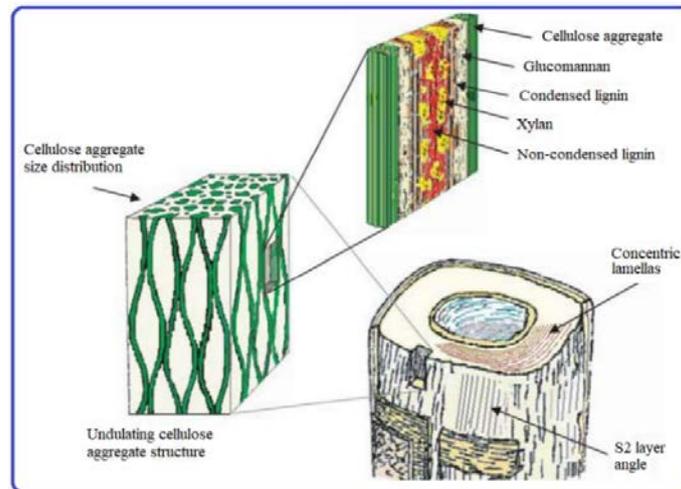


Figure 4: An illustration image of the cell wall of softwood fiber, showing the cellulose microfibril (MFA) of the secondary wall (S2), the concentric lamellar arrangement of cellulose aggregates interspaced by lamella matrix, the undulating cellulose aggregate structure and the variability of cellulose aggregate sizes, and also the arrangement of the matrix component from glucomannan closest to the cellulose microfibrils and to condensed lignin followed by the xylan (more highly substituted xylan in hardwoods) associated to a more non-condensed lignin (Salmén and Burgert 2009)

I.3. The chemical compositions of wood

In regards to an ultra-structural level, wood is considered as a three-dimensional biopolymeric composite, built up of interconnected networks of cellulose, hemicelluloses, and lignin with small quantities of extractives and minerals. Based on its dry weight, wood is composed mainly of polysaccharides (65 – 75%) and combined with lignin (18 – 35%). In total, an elemental composition of wood consists approximately of carbon (50%), hydrogen (6%), oxygen (44%), and trace amounts of minerals. The polysaccharides are mainly composed of cellulose (40 – 45%) and hemicellulose (15 – 25%), also a small amount of starch and pectin. The chemical composition is different between the wood species. In general, softwoods have higher cellulose content (40 – 45%), higher lignin (26 – 34%), and lower pentosan (7 – 14%) content compared to hardwoods (cellulose 38 – 49%, lignin 23 – 30%, and pentosans 19 – 26%) (Rowell 2012). The three major polymers of wood cell walls are represented briefly below.

I.3.1 Cellulose

Cellulose is a linear-chain high-molecular weight homopolymer of D-glucopyranose units that linking together by β -(1 \rightarrow 4)-glycosidic bonds. Cellobiose unit is a repeating unit of the cellulose (Figure 5a). The size of the chain is commonly characterized as degree of polymerization (DP),

which is the molecular weight of the cellulose chain divided by the molecular weight of one glucose unit. Cellulose in wood has an average DP number for about 10,000 (Hill 2006).

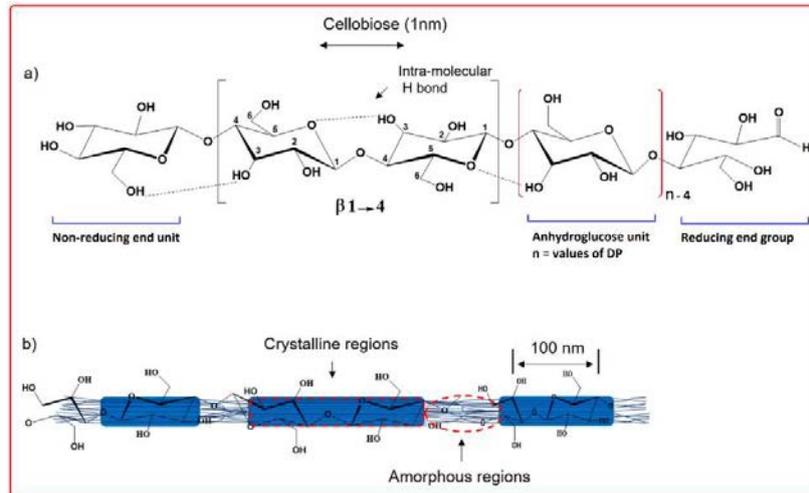


Figure 5: Chemical structure of cellulose (a) and hypothetical configuration of crystalline and amorphous regions in cellulose nanofibrils (b). Image is taken from Tayeb et al. (2018), corrected and modified

Beside their randomly oriented, cellulose molecules tend to form intra- and intermolecular hydrogen bonds and aggregate to microfibrils. With a high packing density, these microfibrils contain highly ordered crystalline region (Figure 5b), which can reach up to 65%. The lower packing density, which lies as the remaining portion of the cellulose, refers to amorphous cellulose.

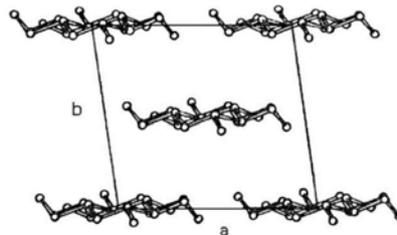


Figure 6: The crystal structure of cellulose I with axial projection

According to the X-ray diffraction test, crystalline cellulose has space group symmetry where $a = 16,34 \text{ \AA}$ and $b = 15,72 \text{ \AA}$ (Figure 6). One repeating unit (i.e., one cellobiose unit) has a distance of $c = 10,38 \text{ \AA}$ (Figure 7). The unit cell consists of eight cellobiose moieties. A weak Van der Waals forces is interacted between the layers of molecular chains. A number of parallel chains of anhydroglucopyranose units of the layers are held together by intermolecular hydrogen bonds. A

number of intramolecular hydrogen bonds between the atoms of adjacent glucose residues are also connected (Figure 7) (Rowell 2012).

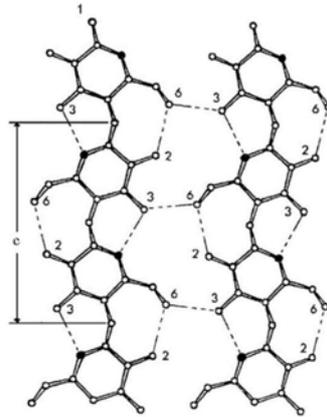


Figure 7: The crystal structure of cellulose I with hydrogen bond between cellulose chains in planar projection

Beside crystalline and amorphous celluloses, wood celluloses have differences in accessibility towards the water, microorganism, etc. The surfaces of the crystalline cellulose are accessible, whereas the rest of the crystalline cellulose is non-accessible. Most of the non-crystalline celluloses is accessible but the existence of both lignin and hemicellulose by which it is covered make non-crystalline celluloses to become non-accessible. In application, the accessible or non-accessible cellulose are very necessary properties in relation with chemical modification, moisture sorption, extraction, finishing, interaction with microorganism, etc (Rowell 2012).

I.3.2 Hemicellulose

Hemicelluloses are heteropolysaccharides like cellulose, but they consist of a number of different sugar units. The average DP number of hemicellulose is about 100 – 200 (Hill 2006). The main monosaccharides that exist in the hemicellulose are shown in Figure 8, which consist of hexoses (β -D-mannose, β -D-glucose, α -D-galactose), pentose (β -D-xylose, α -L-arabinose), uronic acids (β -D-glucuronic acid, α -D-4-O-methylglucuronic acid and α -D-galacturonic acid). With a smaller level that may emerge are α -L-rhamnose and α -L-fucose (Pereira 2007).

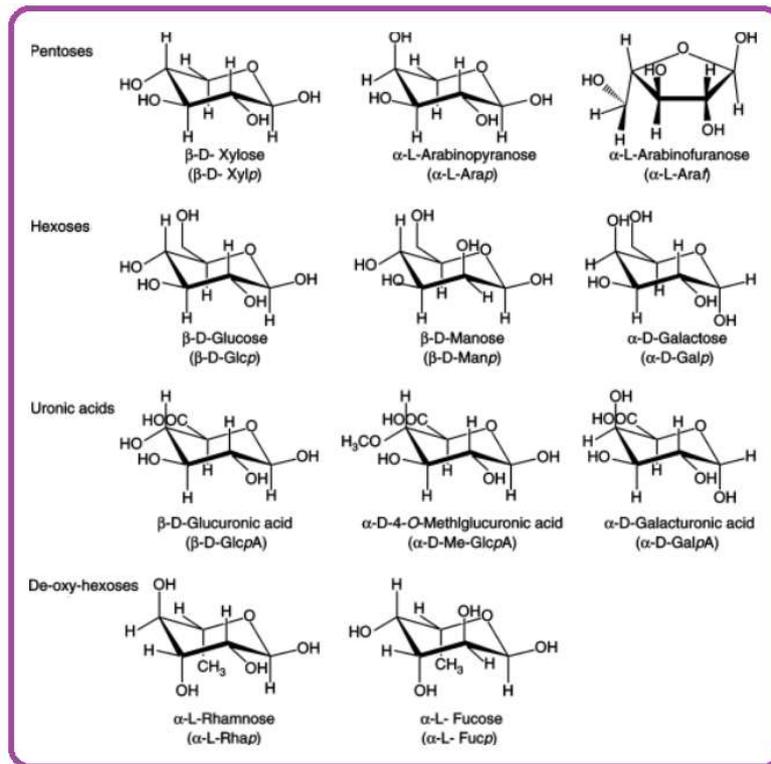


Figure 8: Structural units of hemicellulose (Pereira 2007)

Compared to cellulose, some OH groups of hemicellulose are naturally acetylated, methylated, and there are also carboxylate groups in the structure. The main backbone of hemicellulose structure is also attached by some short branches of sugar units (Figure 9 & 10).

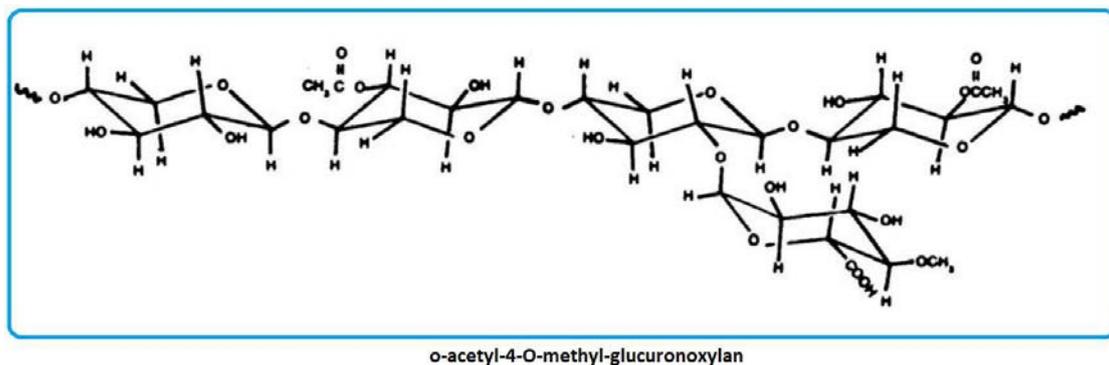


Figure 9: Structure of the main component in hemicellulose of hardwood (Rowell and Banks 1985)

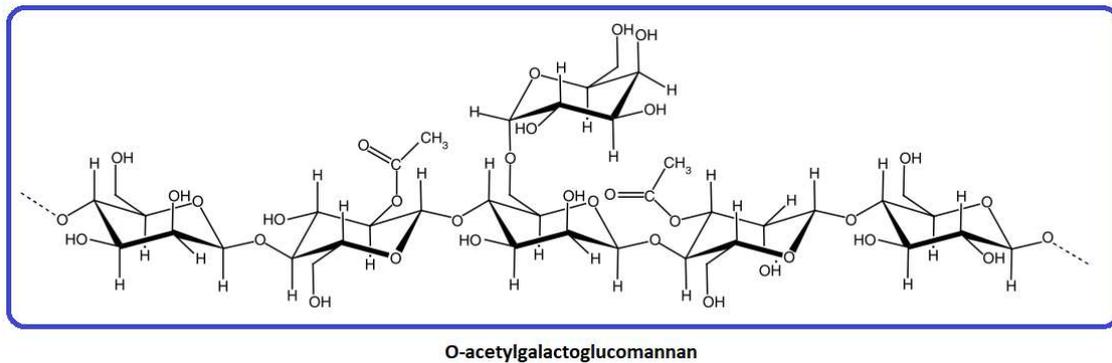


Figure 10: Structure of the main component in hemicellulose of softwood (Hill 2006)

Hemicelluloses are closely associated with cellulose. They act as interfacial coupling agents between the highly polar surface of the microfibrils and the much less polar lignin matrix. Degradation of the hemicelluloses in wood affects the wood becoming brittle rigid, explaining that they have main role in wood viscoelastic properties. They form covalent linkages with the lignin matrix and hydrogen bonds with microfibrils. Generally, hardwoods have higher proportion of hemicelluloses than softwoods, with a higher degree of acetylation and higher proportion of pentosans (Hill 2006). Principally, glucuronoxylan (15 – 30%) and glucomannan (2 – 5%) are the main hemicelluloses in hardwoods, while galactoglucomannans (about 20%) and arabinoglucuronoxylan (5 – 10%) are the main hemicelluloses in softwoods (Sjöström 1993).

I.3.3 Other Minor Polysaccharides

Both hardwoods and softwoods compose small amount of starch, pectin, and proteins. Pectin, as polysaccharide polymer, made from a number of repeating units of D-galacturonic acid linked α -(1 \rightarrow 4). Pectin can be found in the middle lamella and in the membrane in the bordered pits between wood cells. Wood permeability will increase if degradation happened in this membrane, allowing a prone water-based chemical treatment such as wood preservatives or fire retardant (Rowell 2005).

Starch is the main reserve in plants. This type of polysaccharide can be found in a small amount in wood cell wall. It forms as a granule composing D-glucopyranose unit linked α -(1 \rightarrow 4) as amylose or α -(1 \rightarrow 4) with branches about every 25 glucopyranosyl units at α -(1 \rightarrow 6) as amylopectin (Rowell 2005).

I.3.4 Lignin

Lignin is an amorphous complex phenolic polymer mainly based on phenylpropane units. Through C-O-C and C-C linkages, a random three-dimensional polymer is formed, via a free radical mechanism in nature (Hill 2006). *p*-coumaryl alcohol (Figure 11, structure H), coniferyl alcohol (Figure 11, structure G), and sinapyl alcohol (Figure 11, structure S) are the precursors of lignin. Different wood species make a wide variation of lignin structures (Figure 12) as the results of the substitution of phenylpropane at the α , β , or γ positions. Hardwoods lignin content can reach of about 18 – 25%, whereas softwoods lignin varies in the range of 25 – 35%. In softwoods, lignin contains of about 15 – 16 % of methoxyl group, whereas in hardwood, it can reach for about 21% of methoxyl group (Rowell 2005).

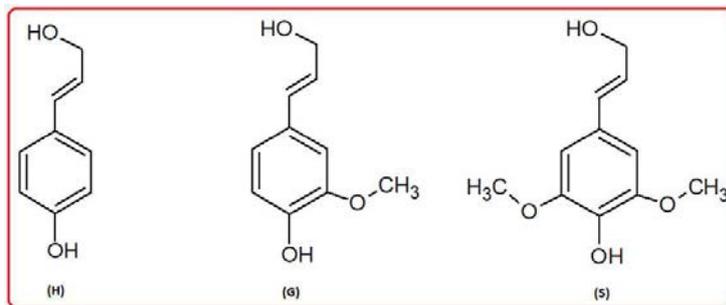


Figure 11: Lignin precursors: (H) *p*-coumaryl alcohol, (G), coniferyl alcohol, (S) sinapyl alcohol

The function of lignin in wood cell wall is to provide stiffness to the cell wall and bond together the individual cells in the middle lamella. Lignin is highly resistant to chemical and biochemical degradation (Le Floch et al. 2015). At room temperature, lignin is rigid but it goes to a glass transition at about 140°C. As an addition, the presence of moisture in cell wall can act as plasticizer by opening up the lignin network structure.

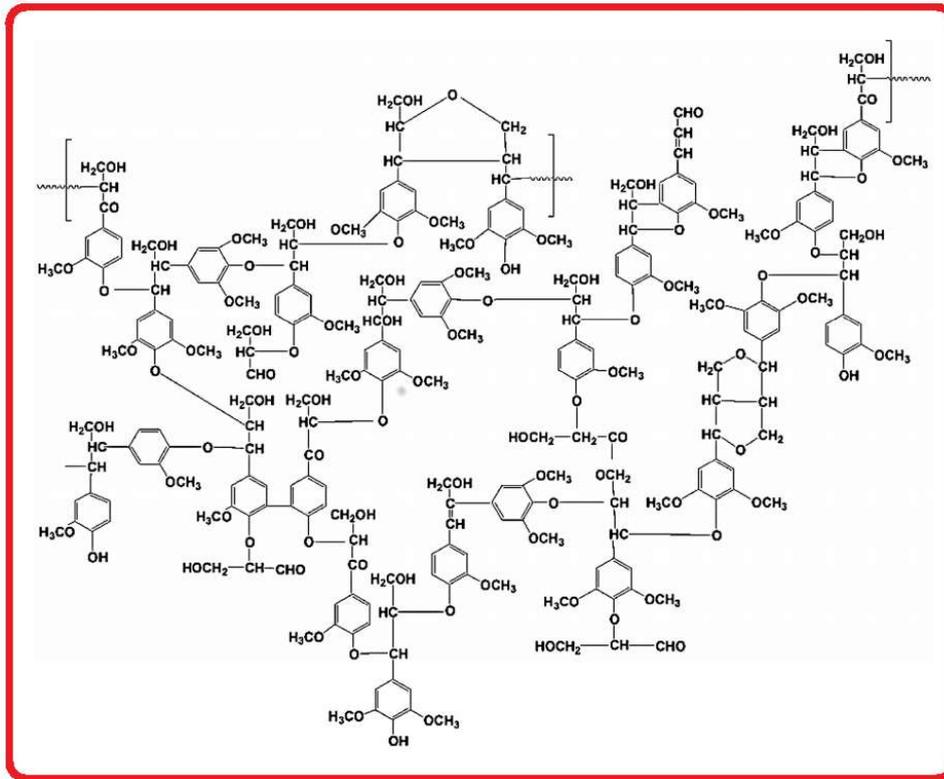


Figure 12: A representative chemical structure of lignin in European beech (*Fagus sylvatica*) (Le Floch et al. 2015)

I.3.5 Extractives

Extractives contents depend on the species, ranging from about 0.5 – 20% by weight. These extractives can be in the form of fats, rosin, fatty acids, phenolic, steroids, fatty alcohols, rosin, waxes, terpenes, any other minor organic acids. Those chemicals present as monomers, dimers, or polymers. Deposited in the cell cavities or penetrated into the cell wall, however, they are located mostly in the heartwood. Some of them are responsible for durability of wood, smell and color. Generally, terpenoid, phenolic, and resin acid-based extractives are responsible for protecting wood from insect or microorganism attacks, whereas, fats become the energy source of wood cell (Sjöström 1993).

Tannins are aromatic based-extractives, which most of them are phenolic-based compounds derived mainly from phenylpropanoid structure. They are located in the heartwood and bark. Among many kinds of phenolic compound-based extractives in wood, the most important group are flavonoids (structure based on $C_6C_3C_6$ carbon skeleton), condensed tannins (polymer of

flavonoids), hydrolysable tannins, lignans (oxidative coupling of two phenylpropane units), and stilbenes (derivatives of 1,2-diphenylethylene) (Sjöström 1993).

In European beech, the wood contains an average of 1.04% of lipophilic (solvent: cyclohexane at 90°C and 110 bars) and 3.71% hydrophilic (solvent: methanol : water mixture = 95 : 5 v/v at 100°C and 110 bars) extractives. Fatty acids, fatty alcohols, and free sterols are dominant in the red heart part of the wood. A larger amount of total hydrophilic extractives was contained in the sapwood. Mono- and oligosaccharides, sugar acids and alcohols, simple phenols, carboxylic acids, and flavonoid were the main hydrophilic soluble constituents in sapwood, whereas the concentration of sugar alcohols was higher in the red heart (Vek et al. 2015). Details of the components in lipophilic and hydrophilic extractives in sapwood and red heart wood are shown in Figure 13 and 14.

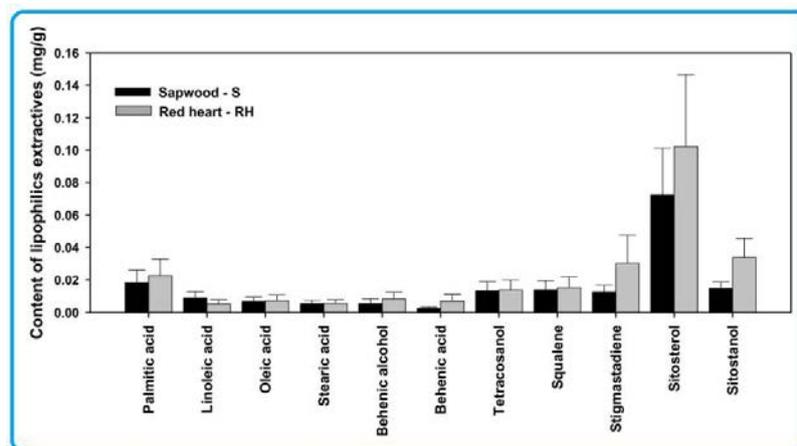


Figure 13: Identified contents of lipophilic extractives in the cyclohexane extracts of sapwood and red heart of European beech (*Fagus sylvatica*) (Vek et al. 2015)

The existence of extractives could be a problem in chemical modification, especially when the wood have to pass the impregnation process, where some amount of extractives would be leached out from the wood, and can contaminate the impregnating solution by which inaccurate weight percent gain calculation for the modified wood and the stability of the impregnating solution to be used for the next impregnation batch would be inaccurate/less reactive (Hill 2006). During thermal treatment, some of those extractives can evaporate out of wood as the result of the high temperature process that surpass their boiling point.

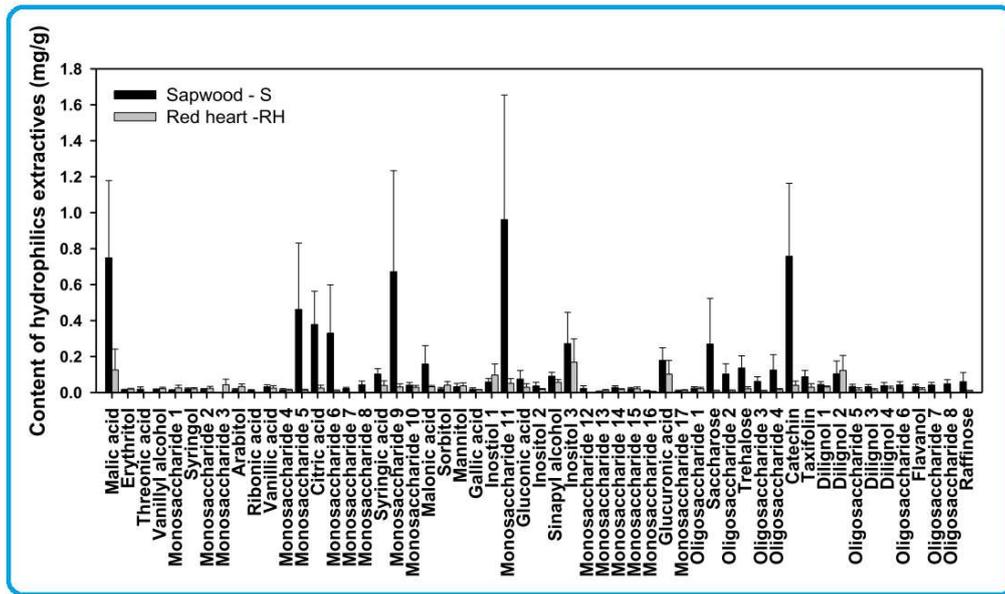


Figure 14: Identified contents of hydrophilic extractives in the methanol extracts of sapwood and red heart of European beech (*Fagus sylvatica*) (Vek et al. 2015)

I.4. Natural properties of wood

The uneven chemicals/components compositions, distribution, and their constructed cells structures with different orientation make wood known as heterogenous mixture and anisotropic material. The anisotropic properties of wood make different mechanical properties in different directions and different swelling and shrinkage properties. The specific and different distribution of chemical compositions in many parts of wood make different durability properties against varied degradation in nature.

I.4.1 The interactions of wood-water

I.4.1.1 Fiber saturation point

Moisture can be found in wood as free water (held as liquid water or water vapor in cell lumina and cavities) or as bound water (held in the cell wall by intermolecular interaction). Variation in temperature and moisture of the environment can change moisture content of wood. Wood can reach fiber saturation point (FSP) at the condition when only the cell walls that completely saturated by the moisture (all bound water), but no water exists in lumen cell (Ross and USDA Forest Service. 2010). The main sorption sites for those bound water is certainly as the results of the existence of hydroxyl (OH) groups of wood polymers. Hemicellulose is one of the main constituents in serving these water-accessible OH groups. However, the less hydroxyl groups

contents in lignin make this polymer are less hygroscopic than polysaccharide, even though only certain parts of cellulose that can perform this action particularly on the surface of the microfibrils Runkel (1954) and Runkel Luthgens (1956) in Wentzel et al. (2018). In operational condition above FSP, the physical and mechanical properties of wood do not change as a function of moisture content. Depending on wood species and part in wood, FSP averages of about 30% moisture content. Principally, FSP differs between bound water and free water in wood at which a more gradual transition happens between them (Ross and USDA Forest Service. 2010). In case of modified wood, for acetylated wood, the FSP is negatively correlated with the increase of weight percent gain (WPG) since the acetic anhydride has the potential to reduce the capacity of the cell wall to accommodate water because the acetyl groups occupy space within the cell wall which is thereby denied to water molecules (Hill 2009).

1.4.1.2 Equilibrium moisture content

Equilibrium moisture content (EMC) is a moisture content at which the wood is not gaining or losing the moisture. The EMC depends on humidity and temperature. Figure 15 shows the relationship between EMC, relative humidity, and temperature.

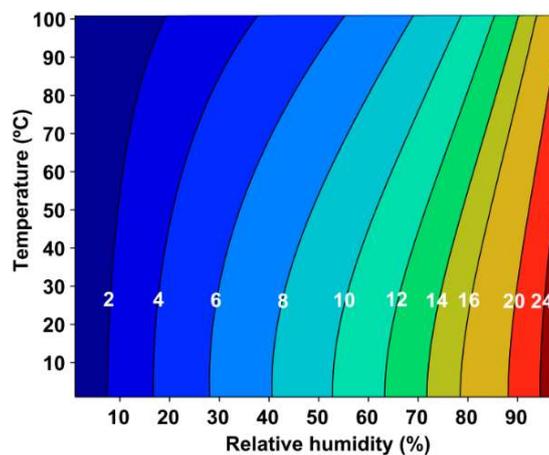


Figure 15: EMC of wood (contours) as a function of relative humidity and temperature (Ross and USDA Forest Service. 2010)

In case of a modified wood. The reduction in EMC of the modified wood, e.g. acetylated wood, is occurred as a combination effect of the cell wall bulking and OH substitution. An increase in time taken to achieve equilibrium is also influenced by the increase of WPG in particular (Hill 2006).

1.4.1.3 Sorption isotherm

Wood in service area is constantly subjected to cyclic humidity changes in surrounding environment. As hygroscopic material, under fluctuating atmospheric humidity, it gains or loses moisture. At constant temperature (<75°C), the relation between EMC and relative humidity can be drawn as a sigmoidal curve in Figure 15 as the results of sorption isotherm with a hysteresis between adsorption and desorption (Time 1998). At certain temperature, there are three main sorption isotherms for wood, these are the initial desorption isotherm, the absorption isotherm, the secondary desorption isotherm.

In case of the modified wood, e.g. thermo-chemically modified wood, a higher applied temperature during modification (highly modified wood) results lower EMC values than at lower temperature. As an example, wood modification with glycerol succinic anhydride (GSA) at different curing temperatures resulted different EMC values at a given RH (L'Hostis 2017). Figure 16 shows that sorption isotherm of beech wood modified with the same concentration of GSA at higher curing temperature results lower EMC at a given RH compared to lower curing temperature and untreated beech. In this case, reduction in EMC occurred as the results of degradation of macromolecule (hemicellulose in particular), a combination of the cell wall bulking, and a possibility reduction of OH-group in wood by ester bonds formation.

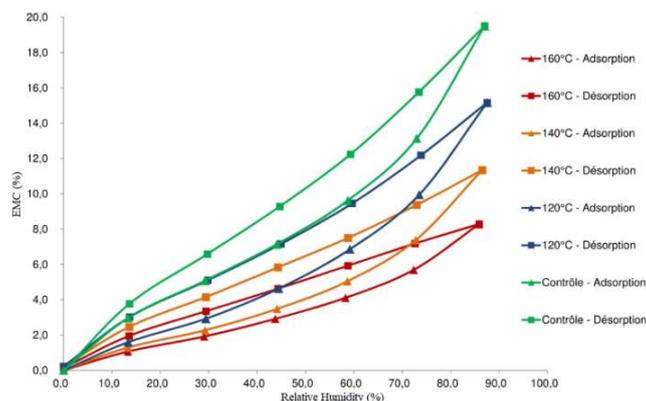


Figure 16: Sorption isotherm of beech wood modified with glycerol succinic anhydride at different curing temperatures (L'hostis 2017)

1.4.1.4 Dimensional instability

Under fiber saturation point, the changes in wood moisture content could be responsible for its dimensional changes. Wood will swell if it absorbs the water, in reverse, wood will shrink if it

releases the water/moisture. A more significant swelling occurs in the radial/tangential plane than in the longitudinal direction as the effect of the winding angle of the microfibril in S2 layer (Hill 2006). The swelling process of wood continues until it reaches the FSP, additional water as free water beyond FSP does not contribute to further swelling (Rowell 2005). This wood dimensional instability limits its utilization especially for exterior condition.

It has been known that the amount of swelling is depend on the density of the wood (Stamm 1964) in Rowell (2012). The formula suggested for this volumetric swelling is as follow:

$$V = K_{fsp} \times d$$

where V is the volumetric swelling, K_{fsp} is the constant showing how much water (ml) needed to reach fiber saturation point per weight of wood (g), d is the wood density (g/ml).

By referring to the volumetric swelling above, this swelling characteristic would depend on the wood species, location that they were harvested, and in which location that they were taken in the tree. In case of modified wood, either as chemically modified wood or thermally modified wood, or combination of both of them, the volumetric swelling would have the same formula as suggested above with additional influential factors such as how much level of modification had been taken place (reactive used, WPG, curing temperature). As a note, this volumetric swelling would strongly depend on the type of medium where they are tested. Swelling in water would have different result compare to swelling in other solution/solvent.

Practically, determination of wood swelling in laboratory scale is commonly done by measuring its external dimension (longitudinal \times radial \times tangential) of small wood (avoiding inaccuracy by the distortion of the wood). Dimensional changes are measured in dry and wet (swollen) conditions. As an example, Rowell and Ellis (1978) measured an oven-dry dimension of wood which then vacuum impregnated into the water and laid submerged in there for several days until it reached the maximum swelling (no other increase in dimension) which afterwards the dimension is measured. Dimensional stability is then calculated as swelling coefficient (S) by following formula (Hill 2006):

$$S = 100 \times (V_1 - V_0)/V_0$$

where, S is the volumetric swelling of wood, V_1 is the volume of water-swollen wood, V_0 is the volume of oven-dry wood.

According to the formula of dimensional stability above, wood has good dimensional stability if it has low swelling value (low S value). In the case of modified wood, if the modification makes dimensional stability to the wood, reduction on the difference between oven-dry and water-saturated volume of the wood is occurred, creating in lower value for S of the modified wood. Eventually, the increase of dimensional stability of the modified wood can be presented as anti-swelling efficiency (ASE) (Hill 2006):

$$\text{ASE (\%)} = 100 \times (S_0 - S_1) / S_0$$

where, S_0 is the swelling coefficient of untreated wood and S_1 is the swelling coefficient of modified wood.

Again, it is important to consider during sample preparation for this ASE measurement. Sample geometry is a critical factor that influence the results. Selecting the same well oriented geometry of the wood samples in term of growth ring orientation and its number, and also parallel to the tangential and longitudinal direction must be conducted to minimize the variability of the obtained results. Samples containing defects also have to be avoided in order to have comparable results (Hill 2006).

1.4.1.5 Water repellency

Water repellency is defined as the ability of a treatment to prevent or control the rate of the liquid water uptake (Rowell and Banks 1985). This water repellency is relied with contact angle formed between water drop and wood at certain time under atmospheric pressure. Between the solid and liquid, there is a force, which its net value is governed by the relative magnitude of the cohesive forces within the liquid and the adhesive force formed between the liquid and solid. When the adhesion force of the liquid to solid is stronger than the cohesion within the liquid, the liquid will spread spontaneously on the solid surface and the contact angle would be zero. In reverse, if the cohesion force within the liquid is stronger than adhesion force between the liquid and the solid, the liquid does not spread but keeps stand on the surface making a finite contact angle with it (Rowell 2012).

Contact angle of wood is influenced by many factors such as wood porosity (due to capillary penetration into the wood structure), surface roughness (affecting the liquid spreading orientation) and chemical heterogeneity of the wood surface (cellulose, 40 – 50%; hemicellulose, 15 – 25%; lignin, 20 – 35%; and extractives, 5 – 15%), which have different chemical properties when they

contact with the liquid during measurement (De Meijer et al. 2000). In term of modified woods, their contact angle results would be depended on the type of modification applied. For thermally and chemically modified wood, all of the influential factors above would be affected and make different results on contact angle values as well as their water repellency properties. Chemical changes on the wood surface as the result of the surface modification or deep modifications (e.g. chemical and thermally wood modifications) would have two properties, a polar (hydrophilic) and a non-polar (lipophilic) surface. The polar surface presenting polar functional groups is capable to form hydrogen bonds with the water, whereas the non-polar surface consisting of non-polar moieties would refuse water (Rowell 2012).

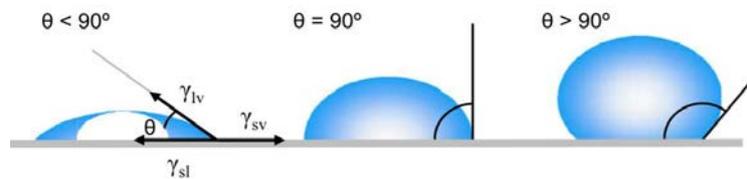


Figure 17: illustration of sessile drop contact angle on the smooth homogenous solid surface

Theoretically, contact angle can be illustrated in the Figure 17, which shows that contact angle on ideal solid surface is formed by the mechanical equilibrium of the drop under the action of three interfacial tension, which is known as Young equation.

$$\gamma_{lv} \cos \theta_y = \gamma_{sv} - \gamma_{sl}$$

where γ_{sl} , γ_{sv} , and γ_{lv} indicate the solid-liquid, solid-vapor, and liquid-vapor interfacial tensions, respectively. Whereas, θ_y is the contact angle or known as Young's contact angle [Yuan and Lee (2013) in Bracco and Holst (2013)].

Contact angle can be measured by three methods that commonly used. The first one is based on the direct measurement of the contact angle of a spreading droplet (sessile drop) or known as static contact angle method. The spreading of the droplet is recorded by videotape and contact angle is measured according to the certain elapsed time. The second is based on the measurement of the largest contact angle from the advancing and receding angle during a dynamically liquid immersion on the wood surface, which is known as dynamic contact angles method (according to the Wilhelmy-plate principal). The third is based on the measurement liquid capillary rise in wood powder column (based on the Washburn equation) (De Meijer et al. 2000).

I.4.2 Mechanical Properties of Wood

Wood as tubular fibers or cells that cemented together is the source of strength in solid wood. As has been explained previously that wood is constructed of three main polymer, cellulose, hemicellulose, and lignin, these main components have a great influence to the wood mechanical properties integrally. Cellulose, known for its high degree of polymerization and linear orientation is responsible as the strongest polymer in wood. It performs very high modulus of elasticity (MOE) under tension, hence contribute to the wood stiffness (Eichhorn and Young 2001). However, under compression along the fiber axis, cellulose microfibrils are likely to buckle, hence, not contribute to the stiffness as much as in tension (Gindl et al. 2004). The hemicelluloses, known as the matrix for the cellulose, increase the packing density of the cell wall, and make very close relation with the lignin, have been indicated as the critical point in overall engineering performance. It is capable to associate the more random area of hydrophilic amorphous cellulose and hydrophobic area of lignin, enabling the transfer of stress between the individual cell wall polymer (Sweet and Winandy 1999; Winandy and Rowell 2005). Meanwhile, the lignin act not only as a binder amongst fibers but also as a binder of carbohydrate molecules within the cell wall of the wood fiber, compensating the low resistance of cellulose microfibril against compressive loads. Moreover, the low affinity of lignin against water, retaining the wood strength and stiffness when exposed to the moisture (Kluppel and Mai 2012). Besides its inherent influential factors, there are some other influential factors from exterior/environment that can change the mechanical properties of wood. Chemical adsorption from the environment, temperature, humidity, UV radiation, fire, pH, pressure or biological degradation are amongst those factors. The severity level of these factors would directly correlate with the wood's susceptibility to strength loss and its degradation effects (Rowell 2012).

In general, mechanical properties of wood consist of three main parts: elastic properties, strength properties, and vibration properties. The elastic properties of wood can be explained by three parameters, modulus of elasticity E (a complete recoverable deformation of material after imposing and removing loads), modulus of rigidity G (the resistance to deflection of material caused by shear stress), and Poisson's ratio μ (the ratio of the transverse to axial strain). The strength properties which are generally measured in mechanical properties can be explained by modulus of rupture (the load-carrying capacity of material in bending and is proportional to maximum moment borne by the specimen), work to maximum load in bending (the ability to absorb shock with some permanent deformation to a specimen), compressive strength parallel to grain (the maximum stress

sustained by a specimen against compression parallel to grain), compression stress perpendicular to grain (the stress at proportional limit), shear strength parallel to grain (the ability to resist internal slipping of one part upon another along the grain), impact bending (the ability of wood to absorb shocks that cause stress beyond the proportional limit), tensile strength perpendicular to grain (the resistance of wood to forces across the grain that tend to split a member), and hardness (the resistance to indentation), tensile strength parallel to grain (the maximum tensile stress sustained in parallel to grain). Meanwhile, the vibrational properties of wood can be explained a speed of sound (the speed of sound is a function of density and modulus of elasticity in structural material), and internal friction (the energy dissipated as a heat when the solid material is strained) (Ross and USDA Forest Service. 2010).

I.4.3 Wood degradation by biological agents

Wood is susceptible to degradation against biological organism, such as fungi (microbiological organism), bacteria, insect, and marine borer (macro-biological organism). In terms of wood-decaying fungi, there are some components that required for fungal attack to occur, as follows: the existence of the free water, the presence of oxygen in wood, a favorable temperature and pH range, a digestible substrate that provides energy and metabolites, chemical growth factors (e.g. nitrogen compounds, vitamins, and essential elements), and the absence of toxic extractives (Zabel and Morrell 1992). Prevention the wood and condition from these favorable fungal attack requirements is usually taken to minimize or to preserve completely the wood during its application. Particularly for basidiomycetes fungi, they represent the highest risk on wood because they degrade the structural polymers of wood for their food, which results in a decrease in mechanical properties and a change in the smell and color of the wood. These fungi secrete enzymes depolymerizing the lignocellulosic constituents of wood into simple molecules so that they can be absorbed by the membrane of their hyphae. Basidiomycetes include brown rot (cubic rot) and white rot (fibrous rot) that are distinguished by their patterns of wood degradation and their preferred substrates. In general, there are three classes of fungal attack that may result considerable degradation on wood: white rot, brown rot, and soft rot (Hill 2006).

I.4.3.1 White rot (belonging to Basidiomycetes)

Due to production of ligninolytic extracellular oxidative enzymes, white rot fungi decay selectively the lignin component of the cell wall and use it as an energy source, effecting a bleaching of the

wood which can be patchy. Hardwoods are more susceptible to white rot than softwoods. Based on its subdivision, simultaneous white rot degrades the lignin and polysaccharide at similar rate, while preferential white rot degrades the lignin prior to the polysaccharide. The attacking wood becomes softened, accompanied with shrinkage at advanced extent of decay. Species that include in this white rot fungi are *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, *Coriolus versicolor* (*Trametes versicolor*), *Cyathus stercoreus*, *Ceriporiopsis subvermispora*, *C. subvermispora*, *Phellinus pini*, *Phlebia spp.*, *Pleurotus spp.*, *Heterobasidion annosum*, and *Irpex lacteus* (Abdel-Hamid et al. 2013).

1.4.3.2 Brown rot (belonging to Basidiomycetes)

Even using microscope, an early stage of attacks by brown rot is difficult to detect. Brown rot decays the wood by removing its polysaccharide components (Figure 18), resulting wood with reddish-brown in color and exhibiting a deep cross-cracking at the advanced attack when wood is dried. Whereas, lignin is partially degraded through de-methoxylation of the aromatic sections. Due to this polysaccharide degradation, mechanical properties of wood decreased considerably (Hill 2006). Species that include in this brown rot fungi are *Gloeophyllum trabeum*, *Poria placenta* (*Rhodonina placenta*), *Laetiporus portentosus*, *Fomitopsis lilacinogilva*, *Coniophora puteana*, *Postia placenta*, and *F. pinicola* (Goodell et al. 2002; Abdel-Hamid et al. 2013)

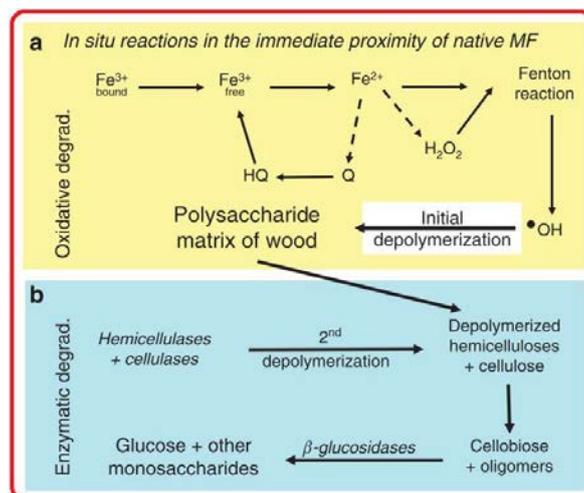


Figure 18: Mechanism of polysaccharide degradation in untreated wood, reviewed by Ringman et al. (2014). HQ, hydroquinone; MF, microfibrils; Q, quinone

In France, it accounts for approximately €30 million estimated for the cost due to fungal damages in 2011. The fungal species dominantly responsible for these damages were from the species of *Serpula lacrymans*, *Donkioporia expansa*, and *Coniphora Puteana* as the brown rot fungi, and *Trametes versicolor* (*Coriolus versicolor*) and *Hypodontia sp* as the white rot fungi (Maurice et al. 2011).

1.4.3.3 Soft rot (belonging to Ascomycetes and Fungi Imperfecti)

Attacking by different manner, a favorable attack by the soft rot on wood occurs in condition where the basidiomycete fungi is retarded. A cheesy soft and darkened on the wood surface are some characteristic of its effects apparently, however, degradation under the surface is sound/intense. Generally, soft rot attacks on wood is in dominant form at where the level of moisture is high. Therefore, during soft rot test, the moisture content of the soil medium is kept at wet condition under certain level (CEN/TS 15083-2:2004).

Table 2: Classification of morphological effects of fungal attack of wood cell walls (Daniel 2005)

Decay type	Morphological changes of wood cell walls	Cell wall components attacked	Taxonomic grouping	Typical examples
White rot (simultaneous)	Hyphal bore holes enlarge Cell wall thinning from lumen Middle lamellae degraded Development of cavities in some species	Cellulose, lignin, hemicelluloses Extractives	Basidiomycetes Higher ascomycetes	<i>T. versicolor*</i> <i>Heterobasidium annosus</i> <i>Xylaria polymorpha**</i> <i>Daldinia concentrica**</i>
White rot (preferential)	Hyphal bore holes enlarge Cell wall attack from lumen Middle lamellae degraded Fiber defibrillation and separation	Hemicelluloses, lignin Extractives	Basidiomycetes	<i>Cerioporiopsis subvermispora</i> <i>Heterobasidium annosum</i> <i>Phl. radiata</i> Cel 26
Brown rot	Rapid attack of cell walls Cell wall attack from lumen	Depolymerization of cellulose, hemicelluloses; lignin modified	Basidiomycetes	<i>C. puteana*</i> <i>Ol. (Postia) placenta*</i>
Soft rot Type I	Hyphal bore holes remain small Longitudinal cavities Middle lamellae remain	Cellulose, hemicelluloses lignin modified/degraded	Ascomycetes Fungi imperfecti	<i>Chaetomium globosum*</i> <i>Phialophora mutabilis</i>
Soft rot Type I "Diffuse type"	Hyphal bore holes remain small Coalescence of longitudinal cavities Middle lamellae remain	Cellulose, hemicelluloses lignin modified/degraded	Ascomycetes	<i>Phi. dimorphospora</i> <i>Ch. globosum</i>
			Fungi imperfecti	<i>Bispora betulina</i>
Soft rot Type II	Hyphal bore holes remain small Cell wall thinning from lumen Middle lamella remains	Cellulose, hemicelluloses lignin modified/degraded	Ascomycetes Fungi imperfecti	<i>Ch. globosum</i> <i>Phialop. mutabilis</i>
Blue stain fungi	Fine bore holes Small cavities/erosion troughs	Primarily nonlignified cells (ray parenchyma), extractives	Ascomycetes Fungi imperfecti	<i>Ophiostoma piceae</i> <i>L. theobromae</i>
Mold fungi	Growth in surface regions	Soluble sugars, extractives	Ascomycetes Fungi imperfecti Zygomycetes	<i>Ch. globosum</i> <i>Penicillium brevicompactum</i> <i>Aspergillus versicolor</i> <i>Rhizopus spp.</i>

*Frequently used as test fungi for assessing new types of wood protection – for example, preservatives, wood modification.
**Higher Ascomycete cause white rot but are not known to degrade middle lamella regions.

There are two types of attack by soft rot fungi. Type 1 is characterized by the formation of cavity in the wood cell walls, while type 2 by erosion of the wood cell walls, effecting in thinner walls.

Type 1 (cavity formation) is only important in softwood, while type 2 is only significant in hardwood (e.g. beech and birch). During this soft rot test, other microorganisms, such as tunneling bacteria and some fungi, also attack the cell walls of wood, resulting the formation of small-bore holes that can be visible in transverse sections.

Even though only few wood-decaying fungi are explained here, in overall, the classification and morphological effects of fungal attack on wood cell wall are summarized in the Table 2.

1.4.3.4 Tunneling bacteria

Altogether during the soft rot test, these bacteria are very common in fertile soil, and known for its capability to attack wood which resistant against the most fungal decay. A granular structure of the outermost layer of wood is the characteristic of the advanced attack by these bacteria. Through these bacteria, even the green color of samples containing copper is bleached to a light yellow/brown color. Some types of attack are characterized by long tunnels spreading through the wood cell walls, while other forms are observed as colonies with compact formation, resulting in a structure like a honeycomb. Advanced attacks are shown as granular appearance of the fibers, observably in longitudinal sections. Sometimes, tunnels perpendicular to the longitudinal axis are also observed (CEN/TS 15083-2:2004).

1.4.3.5 Insects

Some lumber insects such as carpenter ants make cavities in the wood used for their reproduction without feeding on them. Others such as beetles and termites are xylophagous. Beetles degrade wood only during their larval stage. Their feed is only starch of the parenchyma in the sapwood which is also their home. Termites are also xylophagous insects that degrade timber, and because of its important impacts on wood, discussion about termite would be given more detail in this paper.

Termites are known as a serious menace for both structures and crops. They effect a huge problem on agriculture and urban environment, causing significant losses to annual and perennial crops and damage the wooden components in buildings, particularly in the semi-arid and sub-humid tropics (Verma et al. 2009).

As classified at the taxonomic rank of order Blattidae, termites are organized in colonies composed of several castes: workers, soldiers, nymphs, breeders, king, queen, and larvae that live side by side through complex communication systems. Each member of this colony has a role to play in order to survive the colony. The workers, who make up the majority of the colony (about 90 to 95% of

the individuals), are responsible for meeting the colony's food needs, caring for the larvae and building the termite mound. Soldiers represent just under 10% of the population and are responsible for protecting the colony. The reproductives are the least represented in the colony and their sole function is reproduction [Fouquet et al. (2009) in Salman (2017)].

Termites feed on plant matter and more particularly dead wood. There are two main types of termites according to the nutritive modes: higher termites (fungal-growing termites) and lower termites. Cellulose is a complex polymer that is difficult to digest and is completely degraded only by microorganisms and fungi. So that termites can digest cellulose, they have in their tube digestive system of unicellular microorganisms: flagellated protozoa and bacteria (lower termites). The degradation of cellulose results in glucose molecules that are simple and assimilable by the body. In addition to cellulose, termites can feed on other complex sugars such as hemicelluloses and starch. In contrast, the lignin found in their excrement is only partially digested. These excrements are used for the construction of termite mounds, cords, and galleries. The relationships between fungi and termites can be simple or complex. Some species of basidiomycetes (fibrous rot/white rot fungi) contribute to the decomposition of wood by attacking mainly lignin. The released cellulose becomes accessible to termites that recognize the odor of the components of the mycelia that serve attractive (Zaremski et al. 2009; Peterson and Scharf 2016; Hu et al. 2018)

Termite is superficially similar with ants in size, habit of living in colonies, and general appearance. In term of their methods of attacks on wood, termite is grouped into two main classes: (a) ground-inhabiting or subterranean termites, and (b) wood-inhabiting or non-subterranean termites (Clausen 2010).

The colonies of the subterranean termites are developed and maintained in the nest in the ground. To reach the wood, they build the tunnels through earth and around obstructions. However, a constant source of moisture must exist for their life. The worker members of the colony make destruction on wood. Therefore, preventing the termites from gaining the access to a building is the best way to protect the wood or wood-based material, such as making the foundation made from concrete (with cement mortar), treated wood, or material that cannot be penetrated by termites. On the other hand, non-subterranean termites, particularly dry-wood type, grow not multiply as rapidly as the subterranean termites, and somewhat different colony life and habits. Even though the destruction is not rapid, they can thoroughly riddle timbers with their tunneling (Clausen 2010).

From over 2951 termite species present in the world (Constantino 2018), only six are listed in France (five species of subterranean termites and one species of dry wood termites). All species of subterranean termites belong to the genus *Reticulitermes* of the family Rhinotermitidae. They are responsible for the majority of claims and the economic impact. These species are as follows: *Reticulitermes flavipes* (ex *Reticulitermes santonensis*) (in the region of Grand-Ouest until Paris), *Reticulitermes grassei* (in the southwestern France), *Reticulitermes banyulensis* (in Roussillon in the region of Banyuls), *Reticulitermes lucifugus* (in Corsica), *Reticulitermes urbis* (in Marseille and Grenoble) (Salman 2017).

Because termites are not only prominent decomposers of dead wood and other sources of cellulose but also become a serious problem when they attack dwellings and crops, some effective methods have to be found to control them. Different control methods have been applied so far (Figure 19), however, only few methods would be presented further in this paper.

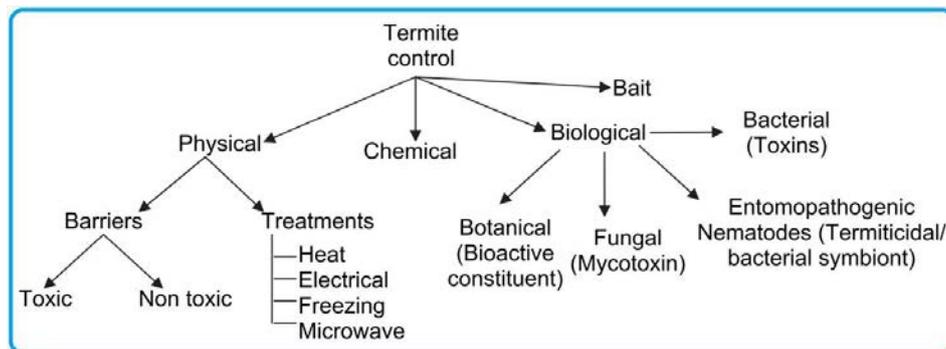


Figure 19: Representative of different control methods of termites (Verma et al. 2009)

1.4.3.6 Marine Organisms

In case of wood exposed/submerged in the marine environment, attacks by marine organisms, such as bacteria, fungi, and marine boring animals (molluscs and crustaceans), can take place. In this harsh condition, where the leaching process of wood occurs at all time, degradation of wood can be more severe compared to the other wood degrading organism.

1.5 The need for wood modification

1.5.1 Biocide-based wood treatments

Since most of the European timbers possess low biological durability and low dimensional stability, improvement in these critical properties is really demanded, especially when the timbers are

exposed to exterior conditions. As previously presented in the introduction, various techniques have been adopted aiming to have longer service-life of wood, reducing the rate of wood harvesting of the forest. These techniques include the utilization of wood preservatives to control the wood-degrading microorganism and insects, such as the utilization of the first-generation biocides (creosote, oil-borne pentachlorophenol, copper chrome arsenate), the second-generation biocides (waterborne copper-rich system that contain amine- or ammonium-complexed alkaline copper (II) and an organic co-biocide, also micron-sized dispersed copper (II) as copper carbonate), the third-generation biocides (totally organic material derived from agrochemicals, e.g. triazoles, quaternary ammonium compounds or quats, imidacloprid and permethrin), and boron-based compounds. Although most of those compounds are effective to preserve the wood, however, only certain of these products are authorized to be used according to Biocide Product Directory adopted by European countries in 2016 (Ministre de l'Environnement 2016). Moreover, the increasing environmental pressure since the last decade insists a tendency to use techniques with totally free biocides, abandoning the use of toxic chemical that can harm to human and environment. Responding to this issue, wood modification including thermal treatment and chemical modification have become alternatives for non-biocide wood preservation treatment (Schultz et al. 2008).

Relating to the risk of biological degradation of wood and the objective of the wood preservation/wood modification above, the uses classes based on EN 335 (2013) (hazard class, in the former term) define different implementation situations for wood/wood-based products corresponding to a greater or lesser exposure to biological degradation agents. Further, it can also be used as a characteristic of the preserved wood/modified wood products corresponding to its applied treatment/modification level to the wood. Summary of the use classes and relevant attacking biological agents is presented in the Table 3.

Table 3: Summary of use classes and relevant attacking biological agents for wood and wood-based products (EN 335 2013)

Use class	General use situation ^a	Occurrence of biological agents ^b				
		Disfiguring fungi	Wood-destroying fungi	Beetles	Termites	Marine borers
1	Interior, dry	-	-	U	L	-
2	Interior, or under cover, not exposed to the weather. Possibility of water condensation	U	U	U	L	-
3	Exterior, above ground, exposed to the weather. When sub-divided: 3.1 limited wetting conditions 3.2 prolonged wetting conditions	U	U	U	L	-
4	Exterior in ground contact and/or fresh water	U	U	U	L	-
5	Permanently or regularly submerged in salt water	U ^c	U ^c	U ^c	L ^c	U
U = ubiquitous in Europe and EU territories L = locally present in Europe and EU territories						
^a Border line and extreme cases of use of wood and wood-based products exist. This can cause the assignment of a use class that differs from that defined in this standard (see Annex B). ^b It may not be necessary to protect against all biological agents listed as they may not be present or economically significant in all service conditions in all geographic regions, or may not be able to attack some wood-based products due to the specific constitution of the product. ^c The above water portion of certain components can be exposed to all of the above biological agents.						

I.5.2 Wood Modification

Wood modification can be defined as an action chemically, biologically, or physically upon a wood material, resulting in a desired improved property during the service life of the modified wood. Further, the modified wood should be nontoxic and no release any toxic substance during service or at end-life following disposal or recycling process. Non-biocidal action should applied if modification is intended to improve resistance to biological attacks (Hill 2006).

Wood modification can involve active or passive modification, depending on whether there are some changes at chemical nature of material level or not. With the active modification, the basic chemical structure of the material would be changed, while with the passive modification, it would not happen (Hill 2006). The passive modification is generally occurred through entailing lumen and/or cell wall filling. Since wood properties are depend on the chemical components and structures in wood itself, therefore, most of wood modification are based on the active modification through which modification of the nature of chemical components or structure is changed. In addition, it should be noted that all of these modifications do not necessary to exclude the use of

the hazardous chemical in the preparation/during the modification process, however, it should no hazardous residue remained once the wood modification process is complete (Sandberg et al. 2017).

Wood modification can be divided into four subdivisions as follows: thermal modification (the application of heat to wood which generating chemical changes in wood), chemical modification (the formation of the covalent bond between a chemical reagent and the wood substrate), impregnation modification (including the chemical reaction/polymerization among the impregnated chemicals in the wood cell walls and/or in the lumen), and surface modification (including chemical or biological modification, modification by plasma on the wood surface) (Hill 2006). However, only the first three modifications, thermal treatment, chemical modification, and impregnation modification, would be presented in this paper. Figure 20 shows a simple illustration of wood modification mechanism in the wood cell wall level.

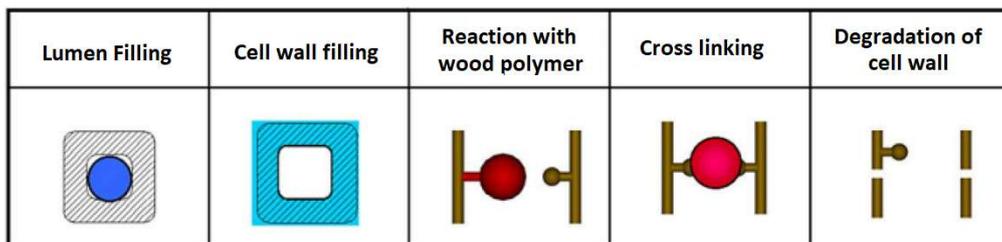


Figure 20: Schematic diagram illustrating the effect of the chemical modification and thermal treatment in the wood cell wall level (courtesy: Emil IT, University of Copenhagen, Denmark, extracted from Sandberg et al. (2017))

1.5.2.1 Thermal Wood Modification

Wood properties can be altered by heating wood to elevated temperature, higher than those generally used for drying timber ($> 120^{\circ}\text{C}$) (Borrega and Kärenlampi 2008a), but lower than those where an excessive fast degradation and decomposition of wood occurred (280°C) (Boonstra et al. 2007a; Boonstra 2008; Kučerová et al. 2017).

It has been known for decades that by this thermal modification, wood becomes less hygroscopic and changes in color (Mitani and Barboutis 2014), increased resistance of wood to natural weathering (Nuopponen et al. 2003b), improvement in color stability (Ayadi et al. 2003), dimensional stability is improved (Stamm and Hansen 1935), and has more resistance against wood-destroying fungi at the expense in mechanical strength loss (Stamm et al. 1946b).

Regardless of the principal foundation of the thermal modification, numerous different implemented process conditions and process steps exist among the various technologies that are applied in Europe (Militz 2002). Beside peak temperature and duration, the pressure regime and heat transferring medium are some of the key factors to distinguish the existing thermal modification technologies (Altgen et al. 2016b). The existence of air (containing oxygen) in the thermal reactor could accelerate the excessive strength losses and strong exothermal reaction (Stamm et al. 1946b).

Depending to the pressure level, some research worked at sub-atmospheric (Allegretti et al. 2012; Hofmann et al. 2013) to atmospheric (Esteves et al. 2008b) and even at higher pressure environments (Willems 2015). On the other hand, medium in which the thermal modification is taken place could be useful not only to ensure the transfer of heat to the wood, but also to minimize/remove the oxygen content in the treatment reactor. Based on the medium used during process, some technologies are applying hot oil (Wang and Cooper 2005; Dubey et al. 2012) or inert gas such as nitrogen (Nguila Inari et al. 2007; Inari et al. 2009) or with steam which is mostly applied in Europe (Militz 2002).

The ThermoWood process, as an example, uses superheated steam. During process, the relative humidity decreases severely when the elevated temperature is applied. In order to reduce the humidity, pre-drying process (100 – 130°C) must be performed before the actual peak temperature. At higher temperature, steam flows continuously through the treatment chamber to remove the volatile organic compound (VOCs) that are emitted from the wood. Sub-atmospheric pressure even needed for the removal of the VOCs. However, the transfer of heat to the wood is hampered at this condition, but with the aid of convective heating system by means of highly efficient fans (Allegretti et al. 2012) or by conductive heating plates between the wood layers (Candelier et al. 2013), this problem could be minimized.

In steam wood modification process with closed system, the pressure is depended on the level of humidity set before process begin. The pressurized steam atmosphere improves the heat transfer into the wood (Altgen et al. 2016b). A rapid drying of wood can also be prevented by a sufficiently high pressure, and if water vapor is the source for generating the pressure, an equilibrium moisture content as a function of the relative water vapor can also be occurred (Lenth and Kamke 2001; Kubojima et al. 2003; Ishikawa et al. 2004). In this close system, the VOCs are accumulated and even accelerate thermal degradation reaction (Stamm 1956). Compared to the sub-atmospheric

system at the same peak temperature and duration, the pressurized system can accelerate wood degradation in the process. In Europe, the pressurized system is applied by the WTT process with a maximum gauge pressure regulation, or the FirmoLin process which combine a process at saturated water vapor pressure (hydrothermolysis) from external source with a drying step and subsequent process step with superheated steam at atmospheric pressure (Willems 2015).

a. Structural defects (micro and macro)

The existence of crack and other wood defects during process or service application are problems that could decrease the mechanical strength and increase the optimal moisture condition for fungal decay. Therefore, crack problem during process must be maximally avoided. Crack are a result of stresses. Wood responds it by creeping that loosens some of the stress. Crack or other defects in thermally modified wood can be generated from the selected raw material or thermal condition itself. Generally, crack or other defects issued from the wrong selected raw material could not be avoided by the optimized thermal process. In other case, cracks issued from the early stage of drying can be very small and not visible to the naked eye, but may grow into visible and even more cracks at a later stage (Hanhijärvi et al. 2003). Therefore, cracks or defects of wood after thermal modification are difficult to differ between defects as the result of the modification or as already present in the wood before modification.

As the respond to the increasing temperature during thermal modification, stresses of wood can arise. As the result of its anisotropic and hygroscopic properties, wood dimension is changed and some deformations are emerged. Wood stresses can reach maximum at oven dry-state condition where it is often happened in open reactor systems. Boonstra et al. (2007b) quoted that stresses can also occur due to the decomposition and modification of wood cell wall components at high temperatures in humid condition. Thus, process optimization is needed in the way to avoid such of defects that can downgrade the visual state of wood. Boonstra et al. (2006) reported that the visual state in the level of microscopic scale of the modified wood can be improved by optimizing the process condition, such as by reducing the difference in temperature between the wood surface and its core side. Microscopic defects that commonly occurred in thermally modified wood are caused by the damages of parenchyma and epithelial cells in rays and resin canals, damages of the pits, cracks running near the compound of middle lamella between tracheid and even damages axial tracheid walls (Boonstra et al. 2006a; Awoyemi and Jones 2011; Biziks et al. 2013).

Microscopic defects can vary in quantity depending on the wood raw material modified. Broad rays in European beech (*Fagus sylvatica* L.) has high sensitivity against the formation of radial cracks (Altgen et al. 2016b). Boonstra et al. (2006b) reported that thermal modification of some softwood species such as Norway spruce (*Picea abies* L.) and Scots pine (*Pinus sylvestris* L.) often results in delamination (grain raising) between early- and latewood on the growth ring boundary. Even though evaluation of the impact of micro-structural defects on thermally modified wood is difficult to know, but some indications that may lead on it can be observed. The damage to the pits membranes in the fenestriform Crossfield pits that connect radial ray parenchyma cell with axial tracheid in the Scots pine sapwood after mild thermal modification can increase its capillary water up-take (Johansson and Morén 2006; Metsä-Kortelainen et al. 2006). In other case, the occurrence of some broken tracheid cell walls perpendicular to the fiber direction is connected to abrupt fractures of thermally modified spruce and poplar during bending test. Even though micro-structural properties must be taken into accounts, but the majority properties of thermally modified wood are greatly generated from the chemical changes occurred in wood during process (Awoyemi and Jones 2011).

b. Changes in chemical composition and ultra-structure

Since there are many factors influencing the modification process, it is not easy to define at which temperature precisely the wood chemical changes start. Those factors include such as moisture content, oxygen content, duration of heat exposure, and other factors that affect the chemical reaction and shift the temperature limit are required to induce depolymerization of the cell wall components (Stamm 1956; Mitchell 1988; Borrega and Kärenlampi 2008a). Sandermann and Augustin (1963) in Altgen (2016) quoted that if the duration of the process is long, chemical changes of wood components and loss in substance by thermal degradation can be detected even below 100°C. Furthermore, Obataya (2007) in Altgen (2016) reported that some chemical changes of wood heated at elevated temperature for several hours are very similar to those of natural ageing wood in the duration for several decades. However, temperature as low as 150°C is required to obtain a significant changes in wood constituents and measurable loss in wood substance during which the duration of the peak temperature is limited to several hours (Borrega and Kärenlampi 2008a).

Because of the variety of individual chemical reaction occurred simultaneously within the different wood constituents, the qualitative analysis of the chemical changes is complicated to understand.

However, the determination of the chemical reactions in wood are not only by measuring the percentage of individual constituents, but also by their configuration in the cell wall, their chemical bonds or the presence of intermediates derived from other reaction (Fengel and Wegner 1989). The current understanding of the chemical changes during thermal modification processes is mainly based on *ex situ* rather than on *in-situ* measurement (Altgen 2016). Nevertheless, some knowledges on wood chemical changes during thermal modification has been studied extensively within decades ago and some of them are presented below.

1) Hemicellulose

The first wood component that would be attacked as the results of the increasing temperature during thermal modification is hemicellulose. The hydrolytic cleavage of the acetyl group from the side chain of the hemicellulose polymer is the first step of its degradation which leads to the formation of acetic acid (Carrasco and Roy 1992; Garrote et al. 2001). Acetic acid is the most common acid formed during thermal modification, followed by formic acid and other organic acids (Sundqvist et al. 2006). Those organic acids catalyze further degradation of the cell wall polysaccharides (Garrot et al. 1999). The amorphous molecular structure of the hemicellulose leads to the less thermal stable of the polymer compared to cellulose (Emsley and Stevens 1994; Alén et al. 2002; Rowell 2012). Hydrolysis of the polymer chain into oligomers and monomers is involved in the degradation (Tjeerdsma et al. 1998; Garrot et al. 1999). Some corresponding sugar can further dehydrated to become aldehydes, such as furfural and hydroxymethylfurfural which are formed from the pentose and hexose, respectively (Peters et al. 2009; Karlsson et al. 2012). The heterogenous structure of hemicellulose is built from the different kinds of monosaccharide such as pentose and hexose which results in different thermal behaviour one and each other. Xylan as an example of pentose-based monosaccharide is less thermal stable than galactoglucomannan as an example of hexose-based monosaccharide (Alén et al. 2002).

2) Cellulose

Different in structural arrangement and composition than hemicellulose, cellulose is more thermal stabile even though some degradation reactions are similar with hemicellulose (Alén et al. 2002; Rowell 2012). Based on its structural arrangement, the crystalline parts (the highly ordered structure) of the cellulose microfibrils are more thermal stable and resistant against hydrolysis (Emsley and Stevens 1994; Rowell 2012). The amorphous parts (the less ordered) of cellulose

microfibrils are susceptible against hydrolytic cleavage and become the first part of cellulose where degradation is initiated. The reduction of the amorphous parts of the cellulose microfibril results an increase in the relative crystallinity of the cellulose integrally (Sivonen et al. 2002; Wikberg and Maunu 2004; Andersson et al. 2005) and a decrease in DP (Degree of Polymerization). Andersson et al. (2005) reported that the MFA of the cellulose microfibrils remains unchanged even though the aggregation of the cellulose as the results of the removal of amorphous cell wall polymer is increased.

3) Lignin

Lignin is the most thermal stable wood cell wall component which gravimetrically after thermal modification can lead to the increase of relative percentage of lignin in the wood (Alén et al. 2002; Brosse et al. 2010; Miklečić and Jirous-Rajković 2016). However, chemical changes are also occurred in lignin. It was reported that lignin undergoes depolymerization due mainly to cleavage of β -aryl-ether linkages and re-condensation reaction (Brosse et al. 2010). A cleavage of methoxyl groups and a depolymerization of lignin to low molecular weight compounds are also occurred during thermal degradation (Tjeerdsma et al. 1998; Sivonen et al. 2002; Nuopponen 2005). Further, Li et al. (2007) quoted that competition between depolymerization and repolymerization reaction of lignin can be involved during thermal degradation of lignin in the presence of heat and moisture. Condensation reaction of lignin and other wood degradation products (e.g. furfural, HMF, etc.) can be taken place simultaneously during process (Tjeerdsma et al. 1998; Garrot et al. 1999). Moreover, Sivonen et al. (2002) and Willems et al. (2010) reported that a semi quinoic structure as a stable free radical molecule is believed to be formed during the process.

4) Extractives

At elevated temperatures, most extractives in unmodified wood is degraded or evaporated. Even though many native extractives evaporated/degraded during thermal process, but some thermal degradation products may partly remain in the wood as a new extractives (Esteves et al. 2008a, 2011; Poncsák et al. 2009).

c. Mass loss by thermal modification

Chaouch et al. (2013) defined mass loss as a marker for the impact of process condition on thermal degradation and is related to the changes in properties of wood during thermal modification process. Depolymerization of cell wall components such as hemicellulose which then turns into

varied degradation products (furfural, HMF, organic acid, or carbon dioxide) and degradation of extractives at elevated temperatures become basic indications of the total loss in wood substances for the quantification of the thermal degradation (Alén et al. 2002). Inaccuracy of this quantification can be happened when the extractives evaporated during drying process where the temperature set less than the temperature of thermal modification (Nuopponen et al. 2003a; Poncsak et al. 2009), particularly at the (sub-)atmospheric process. Moreover, the thermal degradation products that remain in wood or other chemical reaction such as condensation or esterification reaction that do not result in a strong loss in mass but make a fixation with other degradation products are not fully countable based on the mass loss (Garrot et al. 1999; Tjeerdsma and Militz 2005).

d. Water related properties.

Thermal modification influence greatly to a relation between wood and water. Investigation on the reduction in hygroscopicity of wood after thermal treatment has been reported by many studies (Jalaludin et al. 2010; Hill et al. 2012; Olek et al. 2013). Parameter that usually used for measuring the hygroscopicity of wood is the equilibrium moisture content (EMC) analysis. EMC is defined as the ratio of the amount of moisture within the sample that conditioned in the specific climate area to the dry mass of the samples. EMC of thermally modified wood is correlated with the mass loss resulted from the process. EMC decrease almost linearly at lower mass loss range when process works at atmospheric pressure in superheated water vapor (Esteves et al. 2007; Altgen et al. 2016a).

The reduction of hygroscopicity of thermally modified wood is caused by the reduction of the water accessible OH groups as a result of the chemical changes during process (Engelund et al. 2013). These OH-groups are shared largely by the amounts of polysaccharides of the wood cell wall. Therefore, the degradation of polysaccharides during thermal degradation presumably affect to the reduction of OH-groups in general which then results to the difficulties of wood to absorb moisture/water vapors of the environment. Moreover, the increasing cross-linking of lignin-carbohydrate-complex also limits the remaining water accessible OH group of polysaccharide and the expansion of the cellulose microfibrils which eventually reduce the capacity to absorb water between the cellulose chains (Tjeerdsma et al. 1998).

Correlation between the water accessible OH groups content and EMC has also studied by Rautkari et al. (2013), using hydrogen-deuterium-exchange method. The result revealed that there was a

poor relation between the amount of water accessible OH groups versus EMC. On the other hand, an additional mechanism was also proposed by Borrega and Kärenlampi (2010) quoted that the formation of irreversible hydrogen bond and a more tightly bonded structure as the results of wetting and re-drying process at elevated temperature might become the reason for the reduction of EMC. Hill et al. (2012) suggested an alternative mechanism by postulating that cell wall modulus can be used to determine the EMC of wood. The limited void volume and the stiffness of the cell wall matrix caused by thermal modification could limit/resist the expansion of the cell wall nanopores caused by the swelling as the effect of the water absorption. The restriction of the cell wall nanopores to expand would consequently reduce the EMC of wood integrally. Other study reported that Scots pine sapwood with the high initial wood moisture contents had higher mass loss during thermal treatment in saturated water vapor but resulted low reduction in EMC (Rautkari and Hill 2014).

Wettability measurement by water droplet test can also explain the relation between wood-water for thermally modified wood. The wettability of thermally modified wood, which measured by contact angle, decreased compared to untreated wood (Pétrissans et al. 2003; Hakkou et al. 2005; Gérardin et al. 2007). During the wetting wood by water, interaction in the form of hydrogen bond between free OH-group on wood and water droplet may be strongly involved. Reduction in hemicellulose content (reduction of reactive OH-group) of thermally modified wood as the effect of the thermal degradation is most likely a cause of the reduction in wettability (Gérardin et al. 2007). Another mechanism that could support in this case is that wettability of wood heated in the range between 100 and 160°C decreased even though there were no significant mass loss detected (Hakkou et al. 2005). In other words, wettability could also be affected by other mechanism, such as plasticization and re-organization of wood polymer during modification process.

Wettability has a direct relation with the ability of liquid water uptake into the wood. Reduction in wettability will also reduce the capillary force during liquid water uptake. Therefore, the increasing peak temperature during thermal treatment would decrease the ability of wood to take up some water (Metsä-Kortelainen et al. 2006), besides decreasing its wettability properties. Other factor that can also influence the water uptake ability is the existence of microstructural defects as the effect of the modification (Andersson et al. 2005). The increasing numbers of microstructural defects in wood cell wall could increase its capillary force for the water uptake from cell by cell.

e. Dimensional changes

Zauer et al. (2013) reported that even though thermal modification can affect degradation of the wood cell wall constituents, wood porosity is not significantly increased, but may even decrease after the modification process. Porosities or voids can be created during thermal modification as the effect of the removal of some wood constituents, but then it is closed resulting in the reduction in dry dimension at the end (González-Peña et al. 2009).

The closure of the voids might be caused by the rearrangement and annealing of the amorphous cell wall polymer at high temperature (Obataya and Tomita 2002). Hemicellulose is preferentially removed from the sugar chains, leaving less space within the cell wall than the residue occupies; the more condensed lignin and crystalline cellulose are also achieved (González-Peña et al. 2009). Higher reduction takes place in the tangential direction than in the radial one. The higher content of lignin in the radial cell walls than in the tangential one was their hypothesis regarding this phenomenon. On the contrary, longitudinal dimension does not decrease, but even slightly increases for mass loss under 10% (in case of pine and spruce, but not for beech). The dimensional change in the transverse direction is assumed to be the reason for this case (González-Peña et al. 2009).

Compared to untreated wood, the swelling of thermally modified wood is reduced as the result of a higher reduction in wet dimension than the reduction in dry dimension. Dimensional stability correlates with the mass loss of the thermal modification process. In thermal treatment at dry state, anti-swelling efficiency (ASE) increases sharply at a big mass loss of the sample (Stamm et al. 1946a), which is also comparable with the EMC. During thermal modification under saturated steam, mass loss increases with the increase of moisture content, but dimensional stability is not improved at this condition (Rautkari and Hill 2014). Other potential mechanisms that possibly support the improvement in dimensional stability of thermally modified wood are an ultra-structural change and modification in the lignin-carbohydrate complex (Repellin and Guyonnet 2005). Moreover, the occupation of cell wall micropores by thermal degradation products resting within the cell wall, which might be making a bulking effect, could be another reason for the improvement in dimensional stability (Biziks et al. 2015; Čermák et al. 2015).

f. Mechanical Properties

Mechanical properties of wood are influenced by some inherent factors, such as anatomy (growth characteristic), density, moisture content, etc. In thermally modified wood, mechanical properties

of the initial wood are commonly decreased with different extent of severity depending on the applied thermal modification condition. Affected to the three primary stresses, thermal modification undermine much on the tensile strength, followed with shear and compressive strength (Boonstra et al. 2007a; Korkut et al. 2008). On the other hand, the compressive strength may even increase in the longitudinal direction (Boonstra et al. 2007a). The bending stress is also decreased in combination with the three primary stresses. For the mass loss less than 20%, bending strength can decrease 50 - 60% from the original value (Esteves et al. 2007; Borrega and Kärenlampi 2008b). Surprisingly, bending strength can increase when the mass loss has the minor value especially happened in the mild thermal modification (Kubojima et al. 2000; Rautkari et al. 2014).

Even though all samples before mechanical test have been climatized in certain condition, the reduction in hygroscopicity of thermally modified wood might offset for its decrease in strength to some level (Borrega and Kärenlampi 2008b; Arnold 2010). During a bending test for mild-thermo modified wood, the increase in compressive strength is more important than the effect of the reduction in tensile strength (Boonstra et al. 2007a).

On the contrary to the wood strength, the limited impact on modulus of elasticity (MOE) is occurred as the result of this thermal modification although the process works at comparable higher temperature condition (Kubojima et al. 2000; Boonstra et al. 2007a). Surprisingly, the MOE of thermally modified wood sometime has higher value than the original value, as the result of the increasing wood stiffness (Kubojima et al. 2000; Borrega and Kärenlampi 2008b; Rautkari et al. 2014).

A maximum load to bending is drastically decreased as the exposure to higher temperature (LeVan et al. 1990; Kubojima et al. 2000; Borrega and Kärenlampi 2008b). As a function of stress and strain, the work to maximum load is commonly affected long before significantly affected strength properties or properties related to the proportional limit (e.g. MOE) (Winandy and Rowell 2005). Impact bending strength as an example to measure the toughness of wood is also fiercely affected by thermal modification (Kubojima et al. 2000; Boonstra et al. 2007a). Moreover, a higher reduction of toughness is happened in the inelastic region compared to elastic region of the load-deflection curve (Kubojima et al. 2000; Phuong et al. 2007; Borrega and Kärenlampi 2008b). This explains that thermal modification can change wood properties from ductile and viscoelastic to glassy and more brittle (Kubojima et al. 2000; Phuong et al. 2007).

Boonstra et al. (2007a) suggested that the reduction in toughness and strength of thermally modified wood is resulted from the loss of substances (wood components) during thermal modification. Therefore, since the external load is applied on the thermally modified wood, the resulted stresses are distributed over the less wood cell wall material. Nevertheless, the reduction of the toughness and strength is somehow considerably higher than the corresponding reduction of the wood components (mass losses) (Esteves et al. 2007; Borrega and Kärenlampi 2008b). Thus, a considerable reduction on mechanical properties of the thermally modified wood is more probably caused by the changes in chemical and ultra-structural composition of the wood cell wall (Boonstra et al. 2007a; Arnold 2010; Hughes et al. 2015). Degradation of hemicellulose during thermal modification plays dominant role on the reduction of the initial loss of mechanical properties (approximately 30 – 40% loss in bending strength) than the degradation of cellulose or its reduction in degree of polymerization (DP). Some studies suggested that degradation of the side chain hemicellulose constituents (e.g. galactose and arabinose) and furthermore degradation of the main chain hemicellulose constituents (e.g. xylose and mannose) are responsible for the initial reduction of the mechanical properties above (LeVan et al. 1990; Sweet and Winandy 1999). Other factors that contribute to the changes on the mechanical properties are the rearrangement and the reorientation of cellulose and lignin molecular structures even though their prominent degradation take place at a later stage of wood strength loss. An increase on MOE is possibly happened by an increase in cross-linking of the lignin network, which then enhance the cell wall matrix stiffness. Moreover, as the results of the favored depolymerization of amorphous polysaccharide, the percentage of the crystalline cellulose seems rise. Therefore, the rigidity of the cell wall increases, the wood becomes easily to break by tension, however the compressive strength increases in longitudinal direction (Boonstra et al. 2007a).

g. Biological durability

Wood resistant against fungal decay increases as the effect of the thermal modification process. The resistance value is usually represented by a reduction of mass loss after incubation periods against basidiomycetes fungi decay. The peak temperature, the duration, and the high mass loss during thermal modification process are factors that influence the decay resistance of the thermal modified wood (Hakkou et al. 2006; Boonstra et al. 2007c; Šušteršič et al. 2010; Mohareb et al. 2012). A big improvement in decay durability for non-durable wood (durability class 5, EN 350-1: 1994) to become very durable wood (durability class 1) can be accomplished, however, some of

the mechanical properties would decrease even severely (Candelier et al. 2016). Moreover, decay resistance of thermally modified wood is still depended on kinds of raw material used for the modification. For example, thermally modified Scots pine sapwood has lower decay resistance than thermally modified Scots pine heartwood with the same process condition (Boonstra et al. 2007c).

In laboratory tests, some research reported that the most aggressive decay fungi for thermally modified wood on agar-malt medium was *Rhodonia placenta* (*Poria placenta*) (Boonstra et al. 2007c; Welzbacher and Rapp 2007). On the contrary to the test on agar-malt medium, insufficient durability result was occurred for thermally modified wood when it is testified in soil contact test in laboratory (Kamdem et al. 2002). According to the field test aimed for hazard class 3 (EN-335-1: 2006), it was proven that decay durability against fungi above ground contact was increased for thermally modified wood (Welzbacher and Rapp 2007; Metsa-Kotelaianen et al. 2011). Whereas, field test in ground contact area (EN 252 : 2014) aimed for European hazard class (EHC) 4 seemed not sufficient in decay durability of thermally modified wood (Welzbacher and Rapp 2007).

Compared to unmodified wood, thermally modified wood was degraded slowly by *Poria placenta*, even though the same mechanism was used by the fungus to degrade wood (Ringman et al. 2016). Nevertheless, no sign confirmed for an existence of toxic compounds during thermal modification that could increase decay resistance of the modified wood (Kamdem et al. 2000, 2002; Hakkou et al. 2006; Mohareb et al. 2012). The changes in chemical composition of thermally modified wood is believed to be the influential factor for its improvement in decay resistance. The most possible factors suggested for this improvement are the degradation of hemicellulose as the nutrition for the decaying fungi (Hakkou et al. 2006), the wood polymer modification that makes the modified wood is not recognized by the enzyme of the fungi (Weiland and Guyonnet 2003; Hakkou et al. 2006), the penetration hindrance of wood cell wall caused by the previous factors that makes difficulties for fungi to penetrate into the modified wood (Boonstra et al. 2007c; Thybring 2013; Hosseinpourpia and Mai 2016), and the stable free radical that formed during thermal modification and behaves as antioxidant for oxidative substance come from fungi at the first step of degradation (Willems et al. 2010).

1.5.2.2 Chemical Wood Modification

Chemical modification aiming to improve wood resistance against termite, decay, marine organism, and increasing dimensional stability would depend on the adequate distribution of reacted chemical in water-accessible regions of the cell wall. It is critical that the chemical used for wood modification be able to swell the wood, facilitating penetration and reaction with the hydroxyl groups of the wood cell wall polymer at temperature equal or below 120°C. Numerous studies have been investigated on this chemical wood modification which some of them have been reviewed in certain reliable literatures (Rowell 1983; Hill 2006), including the esterification (acetylation, phthalylation, propionic and butyric anhydride-based esterification, acetyl chloride-based esterification, carboxylic acid-based esterification, isocyanates-based esterification), acetal formation (formaldehyde, acetaldehyde, benzaldehyde, glyoxal, glutaraldehyde, trichloroacetaldehyde, phthaldehydic acid, N,N'-dimethylolethylene urea, glycol acetate, acrolein, chloroacetaldehyde, heptaldehyde, o- and p-chlorobenzaldehyde, furfural, p-hydroxybenzaldehyde, and m-nitrobenzaldehyde), etherification (methylation, alkyl chlorides, β-propiolactone), acrylonitrile, and epoxides (ethylene oxide, propylene, butylene oxides) reaction. Improvement in biological resistance and dimensional stability of the modified wood are commonly obtained through this chemical modification.

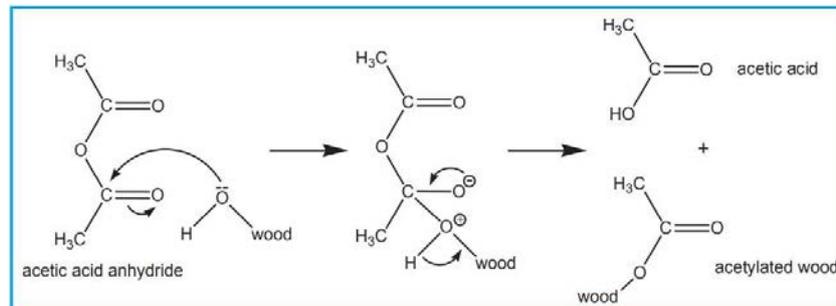


Figure 21: General scheme for wood acetylation by reaction with anhydride acetic acid (Schwanninger et al. 2011)

The increase in wood volume in proportion to the volume of the added chemical, the leach resistance of the added chemical, and the new absorption in infrared data are some characteristic evidenced in chemically modified wood. However, due to high cost of the chemical/process and/or handling of the reactive chemical used during process, only certain chemical wood modification techniques that can be implemented in industrial scale. Wood acetylation (Figure 21) (Ibach et al.

2000; Hill 2006; Rowell 2006; Bongers et al. 2015) is the well-known chemical wood modification technique that has been commercialized recently, under the trade name ACCOYA®.

Technically and principally in chemical wood modification, it is important to know how much the added chemical in the wood, whether they remain in the lumen or penetrate into the cell wall. Weighing and measuring the weight of wood and its dimension before and after modification are the common technique to know the existence of the added chemical and its distribution in wood. The weight gain (the increase in mass) and the bulking values (the increase in wood volume) of wood due to the modification can be calculated as follows:

$$\text{WPG (\%)} = 100 \times (m_m - m_u) / m_u$$

$$\text{B (\%)} = 100 \times (V_m - V_u) / V_u$$

where WPG is the weight percent gain of wood after modification, m_u the dry mass of wood before modification, m_m the dry mass of wood after modification. On the other hand, B is the bulking value of wood due to modification, V_u the dry volume of wood before modification, and V_m the dry volume of wood after modification.

Based on the formula above, when the WPG value is detected due to the modification while the B value is not detected, it is presumably that the added chemical lies in lumen cell. Meanwhile, when the B value is detected due to this modification, it means that the added chemical penetrates into the cell wall, increasing the initial volume of wood.

If we look more detail into the process, the detected WPG due to the modification above is not fully due to the added chemical, because sometime and commonly happened during impregnation, some of wood components (e.g. extractive) could be released out of the wood, tending to decrease slightly the real WPG value that should be obtained of the modification. Moreover, when the modified wood is subjected to the rigorous solvent extraction (leaching process), then the WPG and B values are still observed after leaching process, it means that the wood has truly been modified, however the existence of the new chemical bond between the added chemical and wood is still need to be proved. Observation by means of infrared of the leached modified wood powder could be an alternative that commonly used to prove the existence of this new chemical bonds.

Related to the properties of the modified wood, bulking and cross-linking modifications have direct effect on wood dimensional stability. Swelling properties of the modified wood is limited. Between both bulking and cross-linking modification, the bulking modification principally works by

enduringly bulk the wood cell walls with persistent entities, so water-induced swelling is decreased. However, the final dimension of the fully swollen modified wood ($V_{m1,w}$) is similar with the unmodified wood ($V_{u,w}$). On the other hand, cross-linking modification reduce the cellulose microfibril to be forced to close, as they are linked through covalent bonds. Therefore, the cell walls are permanently bulked after curing process, limiting the water-induced swelling, and reducing the fully swollen volume of the modified wood in the end (Figure 22).

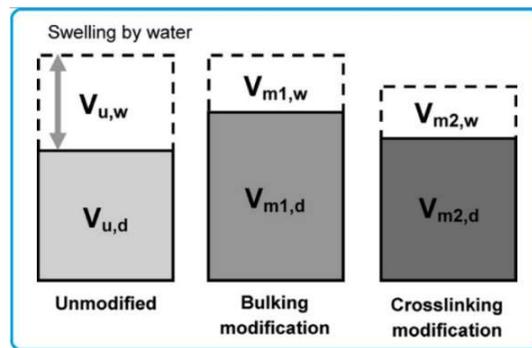


Figure 22: Illustration of dry (index d) and water-swollen (index w) volumes of unmodified (u) and modified (m) wood (Thybring 2013)

Based on this basic theory of wood chemical modification, this paper will bring us to the systematic experiments dealing with wood chemical modification, including certain analytical parameters that considered as important parameters for the properties of the chemically modified wood. The important parameter analysis observed consists of weight percent gain (WPG), retention values, bulking values, density, anti-swelling efficiency (ASE), leaching, wettability, mechanical analysis (modulus of elasticity/modulus of rupture, work to maximum load in bending), thermogravimetry analysis (TGA), and biological durability (white rot, brown rot, soft rot, laboratory termite test, graveyard test/field test).

1.5.2.3 Impregnation modification

Impregnation of the wood cell walls with chemical or combination of chemicals which then react to form a material that is locked into the wood cell wall is the principle of wood impregnation modification (Hill 2006). This technique is generally applied by impregnation of monomers that can polymerize *in-situ* in the lumen or in the wood cell walls, with or without chemical grafting. Limiting penetration of water and reducing the possible development of decay are the main objective of this treatment. Numerous research have been investigated dealing with this technique for decades, including the use of phenol-formaldehyde, urea-formaldehyde, melamine-

formaldehyde resin (Hill 2006), maleic anhydride and polyglycerol (Roussel et al. 2001; Salman et al. 2014, 2016, 2017; Salman 2017), glycidyl methacrylate and polyglycerol (Soulounganga et al. 2004; Salman et al. 2014, 2016, 2017; Salman 2017), maleic anhydride - glycidyl methacrylate - methyl methacrylate (Li et al. 2011; Liu et al. 2012), furfurylation (Lande et al. 2004; Hadi et al. 2005; Sejati et al. 2017), DMDHEU (1,3-dimethylol-4,5-dihydroxy- ethyleneurea) (Schaffert et al. 2006; Xie et al. 2007; Miltz et al. 2011; Emmerich et al. 2019), tannin-caprolactam (Tondi et al. 2017), glycerol-citric acid/tartaric acid/succinic acid (L'Hostis 2017; L'hostis et al. 2017), industrial polyurethane treatments (Mubarok et al. 2016), etc. However, up to now, only a few treatments that can be feasibly implemented in industrial scales, such as furfurylation (Figure 23) and DMDHEU (Figure 24) treatments (Gérardin 2016; Sandberg et al. 2017).

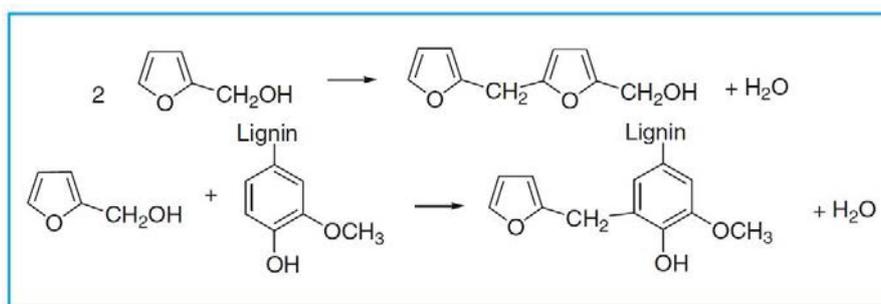


Figure 23: The main reaction involved in polymerization of furfuryl alcohol in wood modification (Gérardin 2016)

Based on the furfuryl alcohol, a renewable chemical derived from hydrolyzed biomass, furfurylation of wood has led in the development for commercial purpose. In principle, the main properties of the furfurylated wood depend on the retention and the polymerization of furfuryl alcohol in the wood. Regarding to the modification levels, it was reported that dimensional stability, hardness, MOE, MOR, and resistance to insect attacks were improved (Epmeier et al. 2004; Lande et al. 2004; Hadi et al. 2005; Pfriem et al. 2012; Gascón-Garrido et al. 2013; Gérardin 2016; Sejati et al. 2017). Through this modification, certain products that have been commercialized are as follows, VisorWood for softwood modification (20 – 40% WPG), and Kebony™ for hardwood modification including Kebony 30 (10 – 50% WPG) and Kebony 100 (70 – 100% WPG) (Hill 2006; Gérardin 2016). The use of these furfurylated woods includes for marine applications, window joinery, poles, decking, garden furniture, roofs, and building material (Hill 2006).

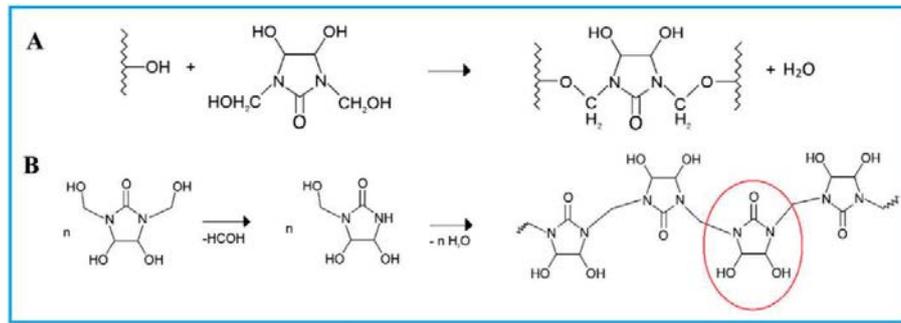


Figure 24: The main reaction of wood with DMDHEU (Emmerich et al. 2019)

On the other hand, 1,3-dimethylol-4,5-dihydroxyethylurea (DMDHEU) treatment has also been applied in industrial scales, such as HartHolz (Dunningham and Sargent 2015) or the Belmadur process, marketed by BASF. The monomer-impregnating solution in this technique consists of the reagent (DMDHEU), catalyst (acid-based catalyst, Lewis acid catalyst), and water. The modification is performed in two-stage processes, vacuum-pressure-impregnation of wood and curing process at temperature $> 120^{\circ}\text{C}$ (usually at 130°C). Through this technique, in principle, it was reported that at certain concentration of DMDHEU (approx. 30 %) and certain catalyst, the modified wood have good resistance against brown rot (*Poria placenta*, *Gloeophyllum trabeum*, *Coniophora putena*), white rot (*Trametes versicolor*), and soft rot fungi (in soil substrate) compared to untreated wood (Emmerich et al. 2019). It was also reported that the modified wood was specified as durable to moderately durable against Mediterranean subterranean termite (Gascón-Garrido et al. 2013). Moreover, some field studies also revealed that the modified wood indicated ‘no to slight attack’ compared to untreated pine (in Germany, for 36 months) and spruce (in Portugal, for 30 months) (Schaffert et al. 2006; Emmerich et al. 2019). Another field test study also reported for the location in the south-east and northern Queensland, disclosing that the modified wood has good resistance against *Coptotermes acinaciformis* in south-east Queensland, Australia (Militz et al. 2011). In addition, mechanical properties of the modified wood showed that hardness and compressive strength increased, MOE and MOR were more or less similar, while, tensile strength, shear strength, and work to maximum load in bending (WMLB) decreased (Emmerich et al. 2019).

a. Wood modification with polyglycerol-maleic anhydride

Impregnation wood modification based on an esterified product of polyglycerol and maleic anhydride (PG-MA) (Figure 25) was initially demonstrated by Roussel et al. (2001).

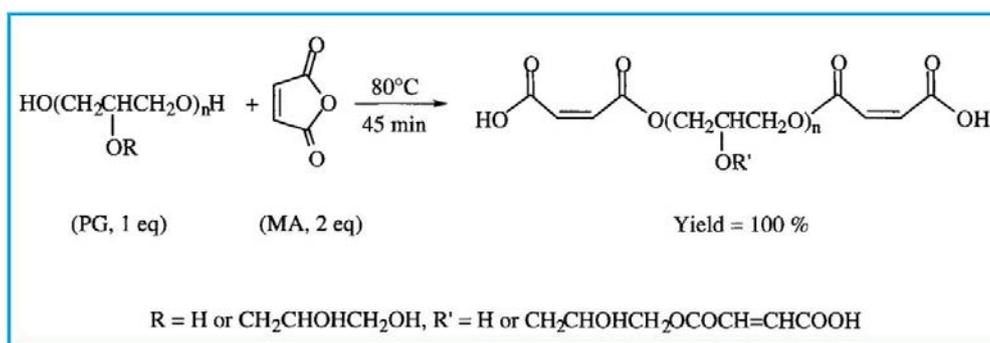


Figure 25: Reaction of polyglycerol and maleic anhydride

According to this study, the polymerization of pure PG-MA was observed at the temperature of 150°C, or at the low curing temperature of 120°C with the existence of catalysts, methyl ethyl ketone peroxide (MEKP 2%) and cobalt naphthenate (2%). Impregnation of pine wood blocks in 10% or 30% w/w of aqueous solution of PG-MA adduct with catalyst followed by thermal treatment at 150°C and leaching process revealed that WPG after leaching remained high for treatment using PG-MA 30% solution, indicating that polymerization occurred intensively at high concentration, allowing the modified wood to limit contact with solvent (solvent) during leaching process. Dimensional stability (ASE) ranged between 38 – 54% and MOE values increase more than two times compared to untreated wood based on the 30% PG-MA solution and catalysts at 150°C. Concentration of 10% PG-MA in the presence of catalysts at 150°C improved considerably decay resistance properties against *Poria placenta* and *Coriolus versicolor*.

b. Wood modification with polyglycerol-glycidyl methacrylate

This impregnation wood modification was initially conducted by Soulounganga et al. (2004) through impregnation of pine and beech wood using aqueous mixture of polyglycerol-glycidyl methacrylate ester adduct (PG-GM) (Figure 26) at different concentrations, 10, 20, 30, and 50% w/w with the presence of catalyst MEKP 2%, followed with different curing temperatures at 20, 40, 80, or 120°C for three days.

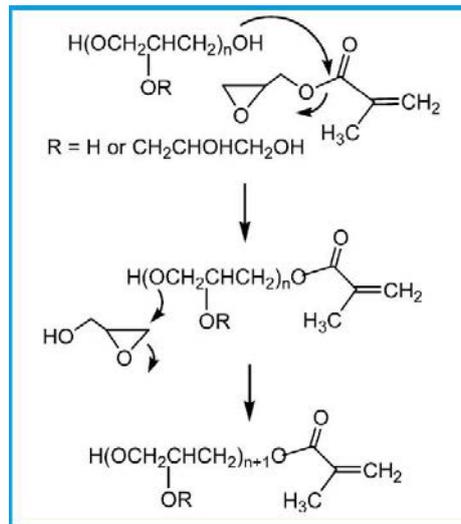


Figure 26: Reaction of polyglycerol and glycidyl methacrylate

Results of this study revealed that the increase in concentration of the aqueous mixture of PG-GM for more than 10% w/w did not give proportional increase to its WPG, gave higher leaching value and inferior ASE value at lower applied concentration of PG-GM, and WPG after leaching process increased with the increase of curing temperature. The addition of methyl methacrylate (MMA) into the formulation could improve WPG, reduced leaching, increased ASE, and imparted lower mass loss due to decay against *Coriolus versicolor*.

c. Wood modification based on combination of chemical polymer and thermal modification

With the similar products as Roussel et al. (2001) and Soulounganga et al. (2004) created previously, Salman et al. (2014) have investigated to use these products (were called “additives”) to minimize the leaching properties of boron (in the form of borax)-treated wood. The study demonstrated to combine the additives with thermal treatment at 150, 180, 200, or 220°C. The results revealed that the combination effect between additives and thermal modifications could reduce the leaching of boron-treated wood.

Further study dealing with effectivity of the combined treatments against decay and termites attacks has also inquired. Salman et al. (2016) used polyglycerol-methacrylate (PG-GM) (Soulounganga et al. 2004) in the concentration of 10% w/w combined with thermal treatment at 220°C to minimize the leaching characteristic of boron-treated wood and its durability properties against decay (white rot and brown rot fungi) and termites. The results of this study revealed that besides limiting the

leaching properties of boron impregnated wood, the boron-additive-thermal modified wood presented highly resistance against decay and termites. Surprisingly, the only additive-thermal modified wood also gave comparable results with the boron-additive-thermal modified wood, allowing it to be use as non-biocide wood preservation treatment.

More intense studies and also as confirmed studies from the previous research, Salman et al. (2017) investigated the use of two kinds of additives, polyglycerol-maleic anhydride (PG-MA) and polyglycerol-methacrylate (PG-GM) with the concentration of 5 and 10% w/w combined with thermal treatment at 150, 180, 200, or 220°C to see their decay and termites resistance properties. The study revealed that treatment at 220°C presented good decay (white rot and brown rot fungi) and termite resistance properties than others and untreated wood, while at 200°C thermal condition, the modified wood presented moderately good properties. Between the wood species used (pine and beech), beech wood showed more susceptible against those biological degrading organisms. In addition, it was noted that decay test against *Trametes versicolor* (white rot fungus) presented heavily attacks on the additive-modified woods than that against *Coniophora puteana* (brown rot fungus).

d. Wood modification based on *in-situ* esterification of citric acid and sorbitol

Study on esterification of sorbitol and citric acid was initially demonstrated by Doll et al. (2006) by using solvent free method for investigating the optimum condition for the esterification (Figure 27). Experimentally, they used different ratios of citric acid to sorbitol ranging from 1/1 to 6/1 at different curing temperatures, at 110 and 150°C.

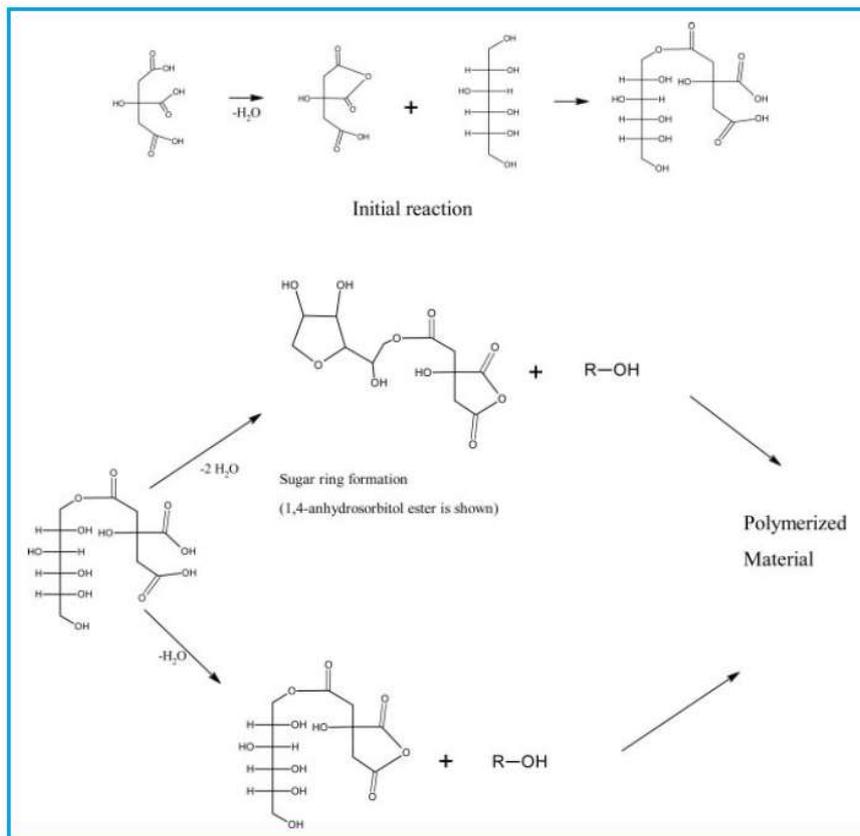


Figure 27: Reaction of the polymerization of citric acid and sorbitol through an anhydride intermediate. Further condensation of citric acid can then undergo, and the resulting cross-linking can generate an insoluble material under certain conditions (Doll et al. 2006)

The main results of study revealed that polymerization of citric acid and sorbitol with the ratio of 3/1 presented good polymerization, which was indicated by the lower quantity of water solubility (WSI) product.

Using the same formulation of citric acid and sorbitol with the ratio of 3/1 as Doll et al. (2006) created above, Larnøy et al. (2018) has initiated to use it to modify wood (pine wood). Experimentally, the pine wood was impregnated in the aqueous solution of sorbitol and citric acid under high concentration (approx. 55% w/w) and followed with curing process at 103 or 140°C. The study reported that curing at 140°C gave significant increase of WPG after leaching, almost undetected leaching components (sorbitol or citric acid), better in dimensional stability, very good in decay resistance (*Postia placenta* and *Trametes versicolor*), and better resistance against blue stain fungi than samples cured at 103°C and untreated wood.

CHAPTER II (Part I)

WOOD MODIFICATION BASED ON COMBINATION OF CHEMICAL TREATMENT USING GLYCEROL AND POLYGLYCEROL DERIVATIVES AND THERMAL MODIFICATION IN OPENED SYSTEM

II.1. Introduction

In this section, wood modifications were mainly based on the research of Salman et al. (2016, 2017), who studied the combination between chemicals at certain concentrations and thermal modification at different curing temperatures to improve biological durability of beech and pine wood. The chemicals used were based on the chemical developed by Roussel et al. (2001) (polyglycerol maleate) and by Soulounganga et al. (2004) (polyglycerol methacrylate), under two different aqueous solution concentrations (5 and 10% w/w). Meanwhile, the curing temperature was varied at 150, 180, 200, or 220°C under inert atmosphere (N₂) for 20 h. From these studies, they found that curing temperature at 220°C was considered as temperature at which decay and termite durability of the modified wood were much better properties than untreated wood or thermally modified wood at the same temperature.

As continuation study, the research addressed in this part is to develop other possible alternative wood modification methods based on utilization of glycerol instead of polyglycerol. Modifications were based on the development of new chemicals as additives and the variation in curing temperatures. The new chemical formulations developed consist of glycerol maleate (Gly-MA), glycerol methacrylate (Gly-GM), glycerol methacrylate maleate (GM/MA_(2eq)), and polyglycerol methacrylate maleate (PGM/MA_(3eq)). As comparison, this study used also the former chemicals used from the previous works, polyglycerol maleate (PG-MA) and polyglycerol methacrylate (PG-GM). In addition, maleic anhydride (MA), as reactive in the system of the previous maleic anhydride-based additives, was also used as single additive for comparison. Curing temperatures were varied at 150, 200, or 220°C. As a substrate, this study used only European beech (*Fagus sylvatica*), known for its low dimensional stability and biological durability (EN 350 2016). Wood modification scheme in this screening work is presented in Figure 28. Meanwhile, equipment used for impregnation and thermal treatment in this Part I is shown in the Figure 29.

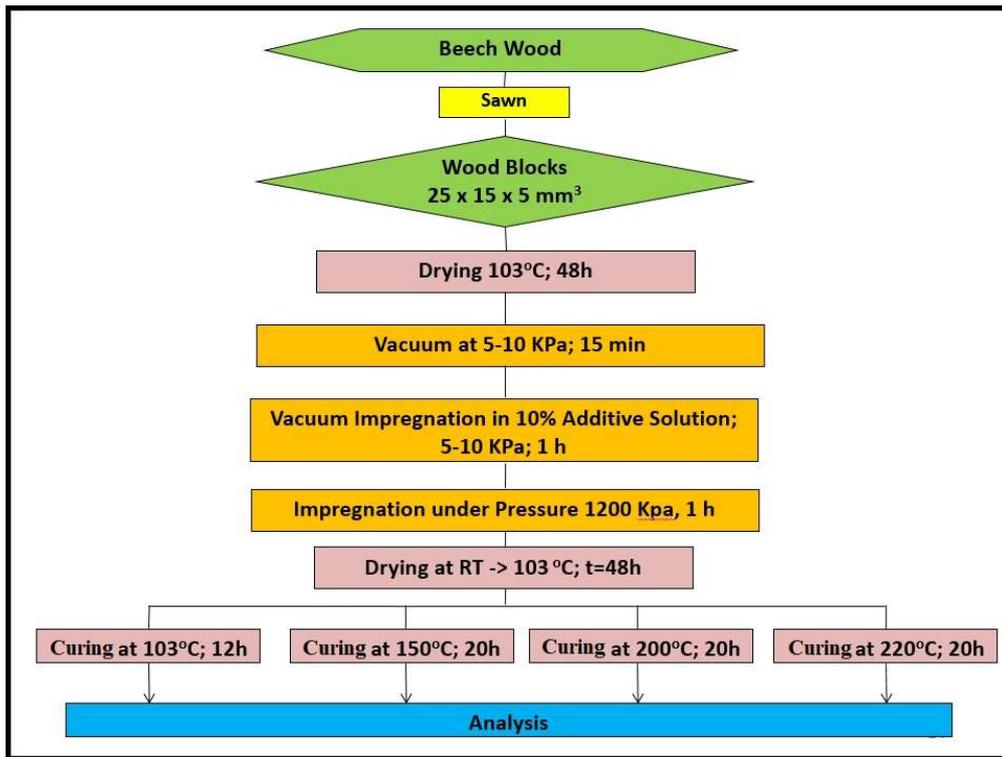


Figure 28: Wood modification scheme in the first screening test



Figure 29: Vacuum-pressure & thermal treatment machine, LERMAB 2018

Chapter II (Part I)

In general, research in this Part I is divided into 6 papers, as follows:

Paper 1. Comparison of different treatments based on glycerol or polyglycerol additives to improve properties of thermally modified wood. *Eur. J. Wood Prod.* DOI 10.1007/s00107-019-01429-4.

The Paper 1 investigated the use of glycerol instead of polyglycerol in the vinylic-based additive formulations for wood modification. As comparison, vinylic derivatives of polyglycerol that previously studied by Salman et al. (2017) were also made and applied into the wood followed with different curing temperatures. Various parameter analysis including physical, mechanical, and biological durability properties of the modified woods were evaluated. The paper is already published in the *European Journal of Wood and Wood Product*.

Paper 2. Non-biocide antifungal and anti-termite treatments based on combinations of thermal modification with different chemical additives. Under review in *Eur. J. Wood Prod.*

The Paper 2 investigated wood modification based on the new additive formulations made from three compositions (glycerol methacrylate maleate or polyglycerol methacrylate maleate) to improve leaching resistance and biological durability properties of the modified wood made from glycerol methacrylate or polyglycerol methacrylate that previously studied in the Paper 1. Maleic anhydride as a reactive in the system was also applied in a single form for comparison. Various characteristics of the modified wood including physical, chemical, mechanical, and biological properties were evaluated. A synergistic effect between additives and curing temperatures was also examined. The paper is under review with minor correction in the *European Journal of Wood and Wood Product*.

Paper 3. Combination of Thermal Modification with Chemical Treatments using Glycerol / Maleic Anhydride derivatives to Improve Termite Resistance of Thermally Modified Beech. Under review in *Holzforschung*.

The Paper 3 studied the comparison between wood modified by the additives made from glycerol maleate or polyglycerol maleate that previously investigated in the Paper 1 with the wood modified by the additive made from maleic anhydride in the single form that previously investigated in the Paper 2. With the similar curing temperature as applied in the Paper 1 and 2 (103, 150, 200, 220°C), the modified woods were compared for their physical, mechanical, and biological durability properties. The paper is under review in the *Holzforschung* journal.

Chapter II (Part I)

Paper 4. Valorization of Beech Wood through Development of Innovative Friendly Environmentally Chemical Modification Treatments. Proceeding in ECWM9, Arnhem, Netherland, 2018.

With the same principle and additives used in the Paper 3, the Paper 4 presented part of the contents in the Paper 3 in the form of proceeding published in the 9th European Conference of Wood and Wood Product (ECWM9), on 17 – 18 September 2018, Arnhem, Netherland.

Paper 5. Development of beech wood thermo-chemical modification treatments based on different vinylic derivatives of glycerol and polyglycerol. IRG/WP 19-40855, Canada, 2019.

The Paper 5 presented all wood modifications performed from the Paper 1 to 4, including their characterization. Selection for the better characteristics of the modified woods was evaluated in this paper. The paper is already published in the form of proceeding of the International Research Group for Wood Protection (IRG/WP 19-40855) in the section 4 (Processes and Properties).

Paper 6. Resistance against Subterranean Termite of Beech Wood impregnated with different derivatives of Glycerol or Polyglycerol and Maleic Anhydride followed by Thermal Modification (Field Test Study)

The Paper 6 investigated an advanced biological durability test of the selected wood modification methods from the Paper 1 to 5 against subterranean termite attacks in the field condition at a tropical area (Indonesia). The paper has been submitted in the European Journal of Wood and Wood Product.

II.2. Results

II.2.1 Paper 1

a. Introduction

In this paper, improvement of European beech wood (*Fagus sylvatica*), known for its low dimensional stability and poor biological durability (EN 350 2016), was performed by combining mild chemical modification and thermal treatment. Mild chemical modification was carried out through impregnation of wood in low concentration of different additive aqueous solution (10% w/w). Followed with different curing temperature at 103, 150, 200, or 220°C, the modified woods were examined and compared for their physical, mechanical, and biological durability properties.

Chapter II (Part I)

The additives used in this paper was based on the vinylic derivatives of glycerol and polyglycerol, which consists of glycerol maleate (Gly-MA), glycerol methacrylate (Gly-GM), polyglycerol maleate (PG-MA), or polyglycerol methacrylate (PG-GM). The use of these kinds of additives was based on the previous works (Salman et al. 2016, 2017), reporting that wood modified with the low concentration of chemicals as additive (PG-MA or PG-GM 10% w/w) followed with thermal modification at 200 or 220°C generated the modified wood with better properties in durability against termite and decay (white rot and brown rot fungi) than untreated wood or thermally modified wood at the same curing temperature. The use of glycerol in this study was based on the analogy that polyglycerol would have similar properties with its monomer form (glycerol). The more easy available in the market and also known as by-product from certain industries (Israel et al. 2008; Leoneti et al. 2012) are also other beneficial aspect of glycerol used in these new additive formulation.

The objective of this study was to investigate the use of glycerol instead of polyglycerol in the additive formulation for wood modification which performing mild chemical and thermal modification. Investigation on the physical and mechanical properties of the modified wood that have not been studied in the previous works (Salman et al. 2016, 2017) was also demonstrated in this paper.

b. Paper 1

Comparison of different treatments based on glycerol or polyglycerol additives to improve properties of thermally modified wood

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Keywords: beech, chemical modification, durability, glycerol, glycidyl methacrylate, maleic anhydride, physical-mechanical properties, polyglycerol, thermal treatment

Abstract

Impregnation of European beech (*Fagus sylvatica*) with 10% w/w aqueous solutions of different additives made from the reaction of glycerol or polyglycerol with glycidyl methacrylate or maleic anhydride followed by thermal modification at 150, 200 or 220°C under inert conditions was investigated to evaluate potential synergies between chemical and thermal treatments. Treated and untreated wood were analysed to evaluate mass changes and bulking values after treatments, resistance of treatment to leaching, wettability, anti-swelling efficiency, modulus of elasticity (MOE), modulus of rupture (MOR), decay resistance against *Coriolus versicolor* and termite resistance against *Reticulitermes flavipes*. Results revealed that synergic effects between combination of light chemical modification and thermal treatments can be observed at higher temperature treatments (200 and 220°C), improving wood dimensional stability (approximately 80%), decay, and termite resistance properties. However, MOE and MOR values decreased by approximately 30% and 60%, respectively. Treated samples resulting from the association of chemical and thermal treatment performed at 220°C present improved durability against termites *Reticulitermes flavipes*.

1. Introduction

Non-biocide wood preservation system has been inquired since several decades. In general, these systems can be derived by the following two types, thermal treatment and chemical modification (Gérardin, 2016). Thermal treatment of wood is one of the alternative processes that have been widely studied and even applied in industrial scale to overcome the problem of wood dimensional stability (Militz 2002; Weiland and Guyonnet 2003; Esteves and Pereira 2009; Dubey et al. 2012) and decay durability (Kamdem et al. 2002; Hakkou et al. 2006). However, thermally modified

woods present poor resistance to termites (Surini et al. 2012; Sivrikaya et al. 2015) limiting their utilization. On the other hand, chemical modifications involving impregnation of active chemical into the wood is the other alternative to overcome biocide substances utilization (Rowell et al. 2009; Esteves et al. 2011; Militz et al. 2011). Chemically modified woods, like furfurylated or acetylated wood, present better characteristics similar to those of most durable tropical wood species. Moreover, treatments can be applied at lower temperature process minimizing degradation of wood comparatively to thermal treatment. The main drawback of these methods is their significant cost due to the large amount of chemicals required to achieve chemical modification. In an attempt to find cost-effective wood modification systems, we have reported the use of the combination of wood thermal modifications in the presence of low concentration of different derivatives of polyglycerol (polyglycerol-maleic anhydride and polyglycerol methacrylate) (Roussel et al. 2001; Soulounganga et al. 2004; Salman et al. 2014, 2016). These modifications allowed not only to improve wood properties similarly to what was generally observed with thermal modifications, but also to improve wood termite resistance in contrary to treatments performed only by heat. The use of polyglycerol in the additive formulations was based on the fact that the reticulated structure of this bio-sourced polyol obtained from glycerol permits the formation of different derivatives able to be fixed in the wood structure, allowing consequently stabilization of wood cell wall polymers as a result of interactions of impregnated polymers with wood hydroxyl groups (Roussel et al. 2001; Soulounganga et al. 2004). However, polyglycerols [such as PG3 used in our previous studies (Roussel et al. 2001; Soulounganga et al. 2004; Salman et al. 2014, 2016, 2017)] which available from industry, present generally a low degree of polymerization, making them not so different from glycerol itself used as starting material. Consequently, utilization of more easily available glycerol could be of interest to substitute PG3 avoiding previous dehydration of glycerol into polyglycerol. In order to evaluate behaviour of the new additives based on glycerol (glycerol-maleic anhydride and glycerol methacrylate), this comparative study has been carried out using either glycerol or polyglycerol-based additives, to develop wood treatments based on combination of light chemical modification with thermal treatments carried out at different temperatures (150, 200, 220°C) under inert condition. As a substrate, European beech (*Fagus sylvatica* L.) known for its poor natural durability and low dimensional stability properties was used in this study. Ultimately, the general goal of this study was also to develop a non-biocide wood preservation system.

2. Experimental

2.1. Sample preparation

A well grained pattern of European beech sapwood samples (moisture content was approximately 10%) with free from knots and defects were used in this experiment. Prior to the experiment, the wood that came from quarter sawn to planks has been air conditioned at ambient condition [20°C/60% of relative humidity (RH)].

All chemicals were purchased from Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France) as reagent grade. Polyglycerol was purchased from Novance (Compiègne, France) as a mixture of compounds with an average molecular weight (Mw) of 242 g mol⁻¹ (degree of polymerization ~3), with 99% in purity.

Four kinds of treatment solutions were investigated: polyglycerol/maleic anhydride adduct (PG-MA), glycerol/maleic anhydride adduct (Gly-MA), polyglycerol/glycidyl methacrylate (PG-GM) and glycerol-glycidyl methacrylate (Gly-GM). Four curing temperatures (103, 150, 200 and 220°C) were tested during this study. For each additive solution, 96 samples measuring 30 × 15 × 5 mm³ and 40 samples measuring 190 × 20 × 5 mm³ (L, R, T) were used for the four curing temperatures. Samples were also treated at the four curing temperatures without any chemical treatments.

2.2. Additive formulation

PG-MA was made according to Roussel et al. (2001). 1 mol of polyglycerol (PG3, Mw = 242 g mol⁻¹) were reacted with 2 mol of maleic anhydride (MAH, Mw = 98.06 g mol⁻¹) into a beaker glass equipped with magnetic stirrer and glass watch, and heated at 80°C for 3 h. The reaction was then stopped after disappearance of ATR-FTIR absorption of carbonyl group (C=O, stretch) of anhydride maleic reagent at about 1780 and 1853 cm⁻¹ and a complete appearance of a characteristic ester band (C=O, stretch) of PG-MA at about 1715 cm⁻¹. The product was directly used without further purification and dissolved into distilled water so that the final concentration of impregnating solution (additive solution) was 10% w/w. Gly-MA was prepared using the same procedure as PG-MA.

PG-GM was made according to Soulounganga et al. (2004). 1 mol of polyglycerol (PG3, Mw = 242 g mol⁻¹) were reacted with 0.02 mol of 4-(dimethylamino)pyridine (4-DMAP, Mw = 122.17 g mol⁻¹) as a catalyst and 2 mol of glycidyl methacrylate (GM, Mw = 142.15 g mol⁻¹) into a beaker glass equipped with magnetic stirrer and glass watch, and heated at 70°C for 15 min. The reaction

was then stopped after a complete appearance of a characteristic ester band (C=O, stretch) of PG-GM by means of ATR-FTIR at about 1716 cm^{-1} , and diminution of hydroxyl group (-OH, stretch) of polyglycerol at 3331 cm^{-1} and epoxy group (stretch) of glycidyl methacrylate at 906 cm^{-1} . The product was directly used without further purification and dissolved into distilled water so that the final concentration of impregnating solution was 10% w/w. Just before impregnation process, about 2% w/w of methylethylketonperoxide was added and mixed. Gly-GM was prepared using the same procedure as PG-GM.

2.3. Wood modification

All oven-dried (103°C until mass stabilization) beech samples were weighed (m_0) and their volumes were recorded (V_0), then exposed under vacuum condition (8 – 10 KPa for 10 min) in an autoclave followed with impregnation process in 10% w/w aqueous additive solution for 1 h under vacuum (5-10 KPa). Afterward, the pressure was brought to 100 KPa (ambient pressure), then exposed under pressure 1200 KPa for 1 h. Finally, the pressure was turned down to ambient condition. All samples were then air conditioned for 24 h, dried at 103°C , weighed until constant mass (m_1) and their volumes were re-recorded (V_1). Samples were then divided in four groups, one group that only dried at 103°C was kept, and the remaining three groups were cured at 150, 200 or 220°C for 20 h under nitrogen. All modified wood were then re-weighed (m_2) and their volumes were re-recorded (V_2). Non-impregnated beech woods were also prepared at each curing temperature as wood controls.

2.4. Leaching test

Leaching tests were conducted according to a procedure adapted from NF X 41-568 (2014). Six samples [$30 \times 15 \times 5\text{ mm}^3$, (L, R, T)] from each treatment (additive-treated wood and wood control from different curing temperatures) were submerged into 72 mL of distilled water and subjected to six leaching periods (1, 2, 4, 8, 16, 48 h) under continuous shaking ($175\text{ linear shakes min}^{-1}$) at 20°C . Between the periods of 4 and 8 h, samples were removed and kept without water for 16 h. After leaching periods were completed, samples were dried at 103°C for 48 h and re-weighed (m_3).

From the wood modification and the leaching test, mass changes were calculated from the following equation (Eq. 1):

$$\Delta m (\%) = 100 \times (m_1 \text{ or } m_2 \text{ or } m_3 - m_0) / m_0 \quad (1)$$

where Δm is the mass changes of additive-treated wood or wood control at different curing temperatures before or after leaching process, m_0 is the initial mass of wood at 103°C before treatment, m_1 is the mass of additive-treated wood at 103°C, m_2 is the mass of additive-treated wood or wood control at higher temperature (150, 200 or 220°C), and m_3 is the mass at 103°C of additive-treated wood or wood control at different curing temperatures after leaching process.

Bulking values during wood modification was calculated from the following equation (Eq. 2):

$$\Delta V (\%) = 100 \times (V_1 \text{ or } V_2 - V_0) / V_0 \quad (2)$$

where ΔV is the percentage of bulking value of additive-treated wood or wood control at different curing temperatures during modification, V_0 is the dry volume of wood before treatment (initial volume), V_1 is the dry volume of additive-treated wood at 103°C, V_2 is the dry volume of additive-treated wood and wood control at 150, 200 or 220°C.

Weight loss due to leaching was calculated from the following equation (Eq. 3):

$$WL_L (\%) = 100 \times (m_1 \text{ or } m_2 - m_3) / m_1 \text{ or } m_2 \quad (3)$$

where WL_L is the percentage of weight loss value of additive-treated wood or wood control at different curing temperatures due to leaching, m_3 is the dry mass (at 103°C) of additive-treated wood or wood control at different curing temperatures after leaching.

2.4. Wettability

Wettability was measured by the water drop test adapted from the method of Engonga et al. (1999). Contact angle of water droplet on the wood surface was measured by means of Drop Shape Analysis system DSA10 MK2 instrument from Krüss. Contact angles of three samples [30 × 15 × 5 mm³, (L, R, T)] of additive-treated wood and wood control at different curing temperatures were measured precisely. For each measurement, contact angle was recorded automatically every 22 seconds until 114 seconds.

2.5. Anti-Swelling Efficiency (ASE)

The method used in this study referred to Pfriem et al. (2012). Wood samples [30 × 15 × 5 mm³, (L, R, T)] from different curing temperatures were dried at 103°C and their volumes were recorded (V_d). Samples were directly immersed into distilled water and placed under vacuum condition (10 KPa) for 30 min. Pressure was then returned to atmospheric pressure, and the samples immersed in water for 24 h. Three cycles of drying-soaking system were conducted so that data of dried volume (V_d) and wet volume (V_w) in every cycle was collected. Swelling (S)

and of Anti-Swelling Efficiency (ASE) values were calculated from the following equations (Eq. 4 and 5), respectively.

$$S (\%) = 100 \times (V_w - V_d)/V_d \quad (4)$$

where S is the percentage of swelling of the wood sample, V_d is the dry volume (at 103°C) of the wood sample, V_w is the wet volume of the wood sample.

$$ASE (\%) = 100 \times (S_0 - S_1)/S_0 \quad (5)$$

where ASE is the percentage of Anti Swelling Efficiency of additive-treated wood or wood control from different curing temperatures, S_0 is the swelling of untreated wood, S_1 is the swelling of additive-treated wood or wood control from different curing temperatures.

2.6. Modulus of Elasticity (MOE) and Modulus of Rupture (MOR)

These three point bending measurements were conducted according to EN 310 (1993). Samples of each additive-treated wood and wood control [$190 \times 20 \times 5 \text{ mm}^3$, (L, R, T)] were conditioned in a climatic chamber with the following conditions, at $22 \pm 2^\circ\text{C}$ and Relative Humidity at $65 \pm 5\%$ RH, until constant mass. Dimension of all samples were re-measured (l, b, t). The increment in load and displacement values of each sample were measured by means of INSTRON 4467 universal testing machine. MOE/MOR values were then calculated as follow (Eq. 6 and 7):

$$\text{MOE (N/mm}^2\text{)} = [l^3(F_2 - F_1)] / [4bt^3(a_2 - a_1)] \quad (6)$$

where l is the distance between the centers of support in millimeters, b is the width of the sample in millimeters, t is the thickness of the sample in millimeters, $F_2 - F_1$ is the increase in load in newton, on the cross section of the load-deformation curve, F_1 should be approximately 10% and F_2 approximately 40% of the breaking load, $a_2 - a_1$ is the increase of deflection at mid-length of the test sample (corresponding to $F_2 - F_1$).

$$\text{MOR (N/mm}^2\text{)} = (3 F_{\text{max}} I)/(2bt^2) \quad (7)$$

where F_{max} is the breaking load in Newton.

2.7. Decay Resistance

This procedure comparable with EN 113 (1996) was referred to Bravery AF (1978). Sterile culture medium prepared from malt (40 g) and agar (25 g) (purchased from Sigma-Aldrich) in distilled water (1 L), was placed in culture 9 cm Petri dishes, inoculated with a small piece of mycelium of

a freshly grown pure culture of *Coriolus versicolor* Quélet (CV) [Linnaeus, CTB 863 A] and incubated for 2 weeks at $22 \pm 2^\circ\text{C}$ and Relative Humidity at $70 \pm 5\%$ RH to allow full colonization of the medium by the mycelium.

Wood samples [$30 \times 15 \times 5 \text{ mm}^3$, (L, R, T)] were sterilized in autoclave at 121°C for 20 min. In each petri dish, three specimens (two treated and one untreated wood) were inserted. Each experiment was repeated three times. Virulence controls were also performed on nine specimens of beech wood. Incubation was carried out for 16 weeks in a climatic chamber (at $22 \pm 2^\circ\text{C}$ and Relative Humidity at $70 \pm 5\%$ RH). Once the fungal exposure was completed, samples were cleaned carefully from the fungus. All samples were then oven dried at 103°C for 48 h and weighed (m_4). Mass loss after decay test was calculated as follow (Eq. 8):

$$\text{ML (\%)} = 100 \times (m_0 \text{ or } m_1 \text{ or } m_2 \text{ or } m_3 - m_4) / m_0 \text{ or } m_1 \text{ or } m_2 \text{ or } m_3 \quad (8)$$

where ML is the mass loss of additive-treated wood or wood control from different curing temperatures before or after leaching due to decay, m_4 is the mass (at 103°C) of wood sample after decay test.

2.8. Termite resistance

Durability against termite was performed by using non-choice screening test based on EN 117 (2013) against *Reticulitermes flavipes* (ex. *santonensis*). All tests were performed on additive-treated wood and wood control from different curing temperatures which previously subjected to leaching as well as untreated wood as virulence. Three replicates from each treatment were tested. Each sample was put in 9 cm diameter Petri dish containing 40 g Fontainebleau sand (4 volume of sand / 1 volume of deionized water). Plastic mesh was used as a support for sample to avoid water saturation. A total amount of 50 termite workers, one nymph, and one soldier were introduced in each Petri dish. The Petri dishes were placed in a dark climatic chamber at $27 \pm 1^\circ\text{C}$ with a relative humidity superior to 75%. After four weeks, the samples were removed and cleaned of the sand and the number of termites still alive (n) were counted to determine their survival rate (Eq. 9). The samples were dried at 103°C , weighed, and mass losses due to termite attacks were calculated (Eq. 10).

$$\text{Survival rate (\%)} = 100 \times n / 50 \quad (9)$$

where n is the number of the remaining live termite worker after test, while 50 is the number of the added termite workers for the test.

$$\text{ML}_t (\%) = 100 \times (m_3 - m_5) / m_3 \quad (10)$$

where ML_t is the mass loss due to the termite attack of additive-treated wood or wood control from different curing temperatures after leaching, m_3 and m_5 are respectively the dried mass (at 103°C) of additive-treated wood and wood control before from different curing temperatures before and after termite attack.

2.9. Thermo-Gravimetric Analysis (TGA)

This analysis was performed to investigate a thermal stability of additive, additive-treated wood, and untreated wood by means of TGA/DSC1-TMA/SDTA 84Xe instrument from Mettler Toledo equipped with STARe v.11 fr System program. Twenty milligram (± 1.00 mg) of pure polyglycerol, glycerol, all types of dried pure additives and dried fine powder samples of additive-treated and untreated wood at 103°C curing condition were placed on alumina crucibles (their exact mass were weighed automatically by the instrument). Afterward, their thermal stabilities (based on the mass loss) at any level of temperatures set were measured by the instrument.

Temperature (T), time (t), and gas flow rate (v) conditions were set as the following steps:

1. T = 25 to 103°C, t = 8 min, air condition (v = 5 ml/min);
2. T = constant at 103°C, t = 15 min, air condition;
3. T = 103 to 220°C, t = 10 min, N₂ condition (v = 10 ml/min);
4. T = constant at 220°C, t = 120 min, N₂ condition (v = 10 ml/min);
5. T = 220 to 300°C, t = 8 min, N₂ condition (v = 10 ml/min);
6. T = constant at 300°C, t = 60 min, N₂ condition (v = 10 ml/min);
7. T = 300 to 25°C, t = 25 min, N₂ condition (v = 10 ml/min).

Mass loss data of the sample in every set of temperatures were recorded automatically. By knowing the mass loss data of each component in treated wood, a mass loss estimation of additive-treated wood could be calculated and a mass loss difference between actual and estimation could be projected as an interaction/behavior of the additive to the wood. Mass loss estimation and its difference with mass loss actual were calculated as follow:

$$\text{Mass loss TGA estimation} = [\text{Additive}] \times \text{MLA} + (1 - [\text{Additive}]) \times \text{MLB} \quad (11)$$

$$\text{Mass loss difference} = \text{Mass loss TGA actual} - \text{Mass loss TGA estimation} \quad (12)$$

where [Additive] is the percentage of additive in treated wood at 103°C curing condition, MLA is the mass loss of pure additive, MLB is the mass loss of untreated beech wood (without additive).

2.10. Statistical Analysis

Statistical analysis was performed by means of Minitab 16 software using one-way ANOVA with Tukey Multiple comparison method ($\alpha=0.05$) for identifying differences in response individually, and two-way ANOVA analysis of variance with $\alpha=0.05$ for identifying differences among the additives and differences among the curing temperatures.

3. Results and Discussion

Data concerning mass changes during the different steps of the treatment and effect of chemical modifications on leaching and bulking properties of additive-treated wood and wood control from different curing temperatures is reported in Table 1.

Replacement of polyglycerol by glycerol in each additive formulation did not affect Δm values after impregnation of 10% w/w aqueous solution of the additives and drying at 103°C. Due to thermal-induced degradation, curing at higher temperatures induced in all cases a decrease of Δm values for both additive-treated wood and wood control, corroborating our previous results using PG-MA and PG-GM at different concentrations and curing temperatures (Salman et al. 2014, 2017). Among the different treatments, treatments involving utilization of glycerol instead of polyglycerol presented the highest mass changes with negative values for higher curing temperatures indicating a stronger effect of thermal degradations due to temperature compared to the increased mass due to additive impregnation. This result might greatly be influenced by the lower molecular mass of glycerol comparatively to polyglycerol. The result corroborates another similar study using glycerol in wood thermal modification quoted that glycerol could accelerate degradation during thermal treatments (Yan and Morrell 2014; Liu et al. 2018). At the same temperature, this effect was more pronounced in Gly-GM treatment compared to Gly-MA. Unlike to the high polarity of carboxylic group of Gly-MA adducts, the lower polarity of methacrylic group of glycidyl methacrylate reduced the penetration of the additive into wood cell wall. The lowest bulking value (ΔV) of Gly-GM wood samples confirms the lower affinity of this additive to penetrate into the wood cell wall. In case of wood modified by maleic anhydride-based additives, the use of glycerol instead of polyglycerol was not obviously different for their Δm values particularly at 103°C and 150°C curing conditions. At 200°C and 220°C curing conditions, the difference became more apparent, where Gly-MA-treated wood showed higher mass loss which confirmed by our TGA results.

Data concerning a thermal stability of all additive-treated woods and their pure additives is presented in the Table 2.

Table 1 Mass changes before and after leaching, bulking values, and mass loss due to leaching of additive-treated wood and wood control at different curing temperatures

Temperature (°C)	Additive	Δm (%)		WL _L ^b (%)	ΔV ^c (%)
		Before leaching ^a	After leaching ^a		
103	PG-MA	10.0 ± 0.6 (ab)	2.0 ± 0.4 (c)	7.3 ± 0.9 (ab)	9.9 ± 1.7 (ab)
	Gly-MA	9.7 ± 0.5 (ab)	2.2 ± 0.4 (bc)	6.8 ± 0.5 (bcd)	11.5 ± 1.8 (ab)
	PG-GM	10.7 ± 0.7 (a)	1.6 ± 0.4 (c)	8.2 ± 0.9 (a)	10.4 ± 1.4 (ab)
	Gly-GM	7.6 ± 0.6 (cd)	0.6 ± 0.5 (cd)	6.4 ± 0.9 (bcd)	4.7 ± 2.3 (def)
	None	0 (h)	-1.4 ± 0.3 (ef)	1.4 ± 0.3 (hi)	0 (gh)
150	PG-MA	8.3 ± 1.2 (bcd)	5.6 ± 1.0 (a)	2.5 ± 0.6 (ghi)	8.9 ± 1.5 (abc)
	Gly-MA	8.9 ± 0.6 (abc)	4.6 ± 0.4 (a)	4.0 ± 0.4 (ef)	11.0 ± 1.3 (a)
	PG-GM	10.2 ± 1.1 (ab)	3.9 ± 0.7 (a)	5.8 ± 0.6 (cd)	11.5 ± 1.4 (a)
	Gly-GM	6.9 ± 0.6 (de)	1.4 ± 0.5 (c)	5.2 ± 0.4 (de)	5.4 ± 2.3 (de)
	None	-0.1 ± 0.2 (h)	-1.8 ± 0.2 (ef)	1.7 ± 0.3 (hi)	0.5 ± 0.2 (gh)
200	PG-MA	3.2 ± 1.5 (fg)	0.9 ± 1.5 (cd)	2.3 ± 0.9 (ghi)	7.4 ± 0.6 (bcd)
	Gly-MA	1.9 ± 1.2 (g)	-0.8 ± 1.9 (de)	2.6 ± 1.2 (fgh)	6.3 ± 0.7 (cd)
	PG-GM	5.0 ± 0.4 (ef)	2.3 ± 0.4 (cd)	2.6 ± 0.6 (ghi)	8.9 ± 0.5 (abc)
	Gly-GM	-1.4 ± 0.9 (hi)	-2.9 ± 0.6 (fg)	1.5 ± 0.4 (hi)	2.1 ± 0.7 (fg)
	None	-2.5 ± 0.4 (ij)	-4.2 ± 0.3 (gh)	1.7 ± 0.1 (hi)	-1.7 ± 0.7 (h)
220	PG-MA	-3.1 ± 1.2 (ij)	-5.3 ± 1.2 (h)	2.4 ± 0.6 (ghi)	2.9 ± 1.0 (efg)
	Gly-MA	-5.6 ± 1.2 (kl)	-8.9 ± 1.1 (i)	3.6 ± 0.4 (fg)	2.8 ± 1.7 (efg)
	PG-GM	-4.0 ± 1.0 (jk)	-5.9 ± 0.7 (h)	1.9 ± 1.0 (hi)	2.9 ± 2.6 (efg)
	Gly-GM	-7.2 ± 1.5 (l)	-8.6 ± 1.3 (i)	1.5 ± 0.7 (hi)	-2.6 ± 0.8 (h)
	None	-10.5 ± 1.1 (m)	-11.6 ± 1.0 (j)	1.2 ± 0.3 (i)	-6.4 ± 0.7 (i)

Value was the average of ^a6 replicates; ^b6 replicates; ^c5 replicates.

Values followed by the same letter in the parentheses do not differ significantly ($\alpha = 0.05$) based on one-way ANOVA test using Tukey multiple comparison.

Table 2 Mass loss of pure additives, additive-treated and untreated wood based on TGA actual measurement and estimation

No	Samples	Mass loss TGA (%)								
		Actual			Estimation			Differences		
		103-220°C (8 min)	220°C (2 h)	Total 103-220°C	103-220°C (8 min)	220°C (2 h)	Total 103-220°C	103-220°C (8 min)	220°C (2 h)	Total 103-220°C
1	PG-MA pure	4.91	7.29	12.2	-	-	-	-	-	-
2	Beech-PG-MA	3.88	10.92	14.8	1.41	9.92	11.33	2.47	1	3.47
3	Gly-MA pure	6.49	14.47	20.96	-	-	-	-	-	-
4	Beech-Gly-MA	4.74	13.13	17.87	1.6	10.64	12.24	3.14	2.49	5.63
5	PG-GM pure	1.22	7.91	9.13	-	-	-	-	-	-
6	Beech-PG-GM	2.37	9.42	11.79	1.06	9.96	11.02	1.31	-0.54	0.77
7	Gly-GM pure	3.47	19.9	23.37	-	-	-	-	-	-
8	Beech-Gly-GM	4.23	10.54	14.77	1.24	10.99	12.23	2.99	-0.45	2.54
9	Beech wood	1.04	10.2	11.24	-	-	-	-	-	-
10	PG pure	0.66	7.91	8.57	-	-	-	-	-	-
11	Gly pure	56.9	94.19	100	-	-	-	-	-	-

Based on TGA data (Table 2), all additive-treated woods present higher mass loss actual than untreated wood in the same analytical condition. The highest mass loss values observed was Gly-MA-treated wood, followed with PG-MA, Gly-GM, and the last was PG-GM. These results confirm our Δm data that mass changes values of wood treated with maleic anhydride-based additives gave higher mass loss than wood treated with glycidyl methacrylate-based additives. According to the mass loss different obtained from the mass loss actual and estimation in TGA data, a higher mass loss difference of Gly-MA and PG-MA-treated wood than Gly-GM and PG-GM-treated wood convinces that the interaction of maleic anhydride-based additives with wood could accelerate wood degradation than the interaction of glycidyl methacrylate-based additive with wood. A more acidic property of maleic-anhydride based-additives presumably was the cause in these phenomena. Similar results was also reported by the related research from Bodirlau et al. (2008) quoting that maleic anhydride-treated wood has lower thermal stability and maleic anhydride in the esterified wood would be eliminated as a volatile products and do not contribute to the carbonized residue.

Based on the leaching data (Table 1), samples treated with PG-MA present slightly higher resistance to leaching (lower WL_L values) than samples treated with Gly-MA, at higher curing temperatures. However, leaching is important especially for samples dried at 103°C and decreased progressively as the curing temperature increased indicating that higher temperatures improved fixation of the product. This condition might be due to higher possibility of polyglycerol to more reticulate within its reaction products than glycerol in the same mol comparison, particularly at higher curing temperatures (150, 200, 220°C). In contrast, PG-GM-treated wood show slightly higher WL_L values than Gly-GM-treated wood at all curing temperatures. The less reactive of methacrylic group in PG-GM or Gly-GM was a possible reason for their difficulties to reticulate within their products or to the wood especially at lower curing temperatures (103 and 150°C). In the other hand, Mass losses (Δm) of wood control treated at 200 or 220°C are more important than mass losses of additive-treated wood at the same temperature indicating that some impregnated additive still remain in wood after curing at high temperature. Considering the quantity of additives impregnated in wood, mass losses observed indicated that some partial degradations of additives occurred during treatment. Nevertheless, the less differences between mass changes (Δm) before and after leaching caused by heat-induced wood degradation at these higher thermal conditions emerged obviously indicating a better additive fixation to the wood.

Table 3 Dimensional stability and mechanical properties of additive-treated wood and wood control at different curing temperatures

Temperature (°C)	Additive	ASE ^a (%)	MOE ^b (N/mm ²)	MOR ^b (N/mm ²)
103	PG-MA	46.1 ± 2.0 (ef)	9479 ± 1088 (c)	96 ± 18 (bcde)
	Gly-MA	46.5 ± 4.9 (e)	9205 ± 876 (c)	89 ± 11 (cde)
	PG-GM	32.1 ± 2.2 (gh)	9837 ± 1009 (c)	119 ± 15 (ab)
	Gly-GM	32.4 ± 1.7 (gh)	9827 ± 1174 (c)	112 ± 14 (abc)
	None	13.1 ± 3.8 (i)	12459 ± 1389 (ab)	132 ± 17 (a)
150	PG-MA	48.1 ± 4.6 (e)	10723 ± 748 (bc)	88 ± 11 (cdef)
	Gly-MA	55.0 ± 4.5 (de)	10392 ± 946 (c)	85 ± 14 (def)
	PG-GM	34.3 ± 7.6 (fg)	10480 ± 915 (c)	116 ± 18 (def)
	Gly-GM	23.6 ± 7.8 (ghi)	10395 ± 816 (c)	112 ± 15 (abc)
	None	21.6 ± 6.3 (hi)	12801 ± 1243 (ab)	134 ± 17 (a)
200	PG-MA	61.7 ± 3.2 (cd)	10328 ± 960 (c)	75 ± 9 (efg)
	Gly-MA	69.0 ± 4.6 (abc)	9283 ± 1381 (c)	63 ± 12 (fgh)
	PG-GM	51.6 ± 7.1 (de)	9904 ± 827 (c)	84 ± 15 (def)
	Gly-GM	54.3 ± 2.2 (de)	10584 ± 1253 (bc)	86 ± 16 (def)
	None	49.4 ± 2.5 (e)	12933 ± 2046 (ab)	102 ± 19 (bcd)
220	PG-MA	74.7 ± 4.4 (ab)	9254 ± 1048 (c)	53 ± 12 (gh)
	Gly-MA	78.2 ± 1.9 (a)	9318 ± 1523 (c)	54 ± 27 (gh)
	PG-GM	73.0 ± 4.2 (abc)	8902 ± 959 (c)	51 ± 7 (gh)
	Gly-GM	75.6 ± 6.7 (ab)	8888 ± 969 (c)	48 ± 11 (h)
	None	63.5 ± 2.3 (bcd)	10490 ± 1880 (c)	58 ± 11 (gh)

Value was the average of ^a4 replicates at 3rd cycle of ASE; and ^b10 replicates.

Values followed by the same letter in the parentheses do not differ significantly ($\alpha = 0.05$) based on one-way ANOVA test using Tukey multiple comparison.

All additives induced an important bulking of wood cell wall with ΔV values comprised between 4.7 and 11.5% in direct connection with Δm values (Table 1). This bulking effect was still obvious after treatments at 150°C, however, due to thermal-induced degradation, it started to decrease for treatments performed at higher temperatures. Samples treated with Gly-GM at 220°C presented high shrinkage similarly to heat-treated samples, while a low bulking effect was still visible for the three other treatments.

Data concerning dimensional stability and mechanical properties of additive-treated wood and wood control at different curing temperatures is presented in Table 3.

ASE values (at the cycle III) increased with the increase of curing temperature (Table 3). Additive-impregnated wood showed higher ASE values than wood control at the same temperature indicating that dimensional stability of wood increased by incorporating chemical and thermal modification treatments. Among the additives, PG-MA and Gly-MA treatments gave higher ASE values than other treatments at all curing temperatures. Similar ASE values were also reported by Epmeier et al. (2004), using impregnation with 15-20% aqueous solution of Gly-MA made from 1/3 molar ratio of glycerol/maleic acid. Other related research that also used maleic anhydride system for wood modification gave ASE values superior to 40% (Iwamoto and Itoh 2005; Liu et al. 2012; Essoua et al. 2015). Glycerol-based additives gave slightly better results than polyglycerol-based additives independently of the curing temperature. This may be due to a better penetration of glycerol-based additives into the wood cell wall leading to a better dimensional stabilization. Yan and Morrell (2014) also gave a similar results that thermal treatment of glycerol-impregnated wood gave higher ASE due to the residual glycerol in wood cell wall and/or in the lumen. In general, a mechanism of the increase in dimensional stability of additive-treated wood combined with heat treatment might be due to possible interactions, chemically [the formation of the new chemical bonds (ester or ether) between additives-wood (especially in maleic anhydride-based additives)] and physically (the formation of anchoring system of additives in wood cell wall/lumen as the result of additive hardening and wood shrinkage at higher thermal process).

MOE and MOR values of the additive-treated wood were always lower than untreated sample cured at the same temperature (Table 3). Indeed, for the same treatment temperature, impregnation of wood samples with the different additives resulted in a slight decrease of MOE and MOR independently of the nature of the additive indicating that interaction of impregnated additives within cell wall polymers induced in wood strength loss. The reduction in these mechanical properties was probably influenced by the acidic property of the 10% aqueous additives solution by which the chemical interactions among wood components (especially the hydrogen bonds

among wood fibers) were disturbed or even accelerated degradation of polysaccharide (especially hemicellulose, amorphous cellulose) during drying. According to Yan et al 2011, the reduction in mechanical properties for glycerol-treated wood above 120°C was assumed that some molecular chains of hemicellulose and/or lignin were cut off and formed new cross-linking. A significant difference for the reduction in MOE for additive-treated wood in comparison with wood control is also presented according to one-way ANOVA test using Tukey multiple comparison at $\alpha = 0.05$. MOR were in all cases more affected by the different treatments (chemical, thermal or thermochemical) than MOE. Effect of curing temperature behave differently according to MOE or MOR and temperature itself, resulted for what is generally described in the literature (Kubojima et al. 2000; Boonstra et al. 2007; Yildiz and Gümüşkaya 2007) that MOE of heat-treated wood increased at certain temperatures and duration then decreased afterward, whereas the MOR will decrease continuously as the increase of temperature. This condition happened at 150°C curing condition, where MOE of the different treated samples increased comparatively to samples treated at 103°C, while at higher temperatures (200 and 220°C) it decreased gradually. On the other hand, MOR values decreased gradually by the increase of curing temperature. No significant differences were observed on MOR and MOE values by replacing polyglycerol by glycerol (based on Tukey comparison method).

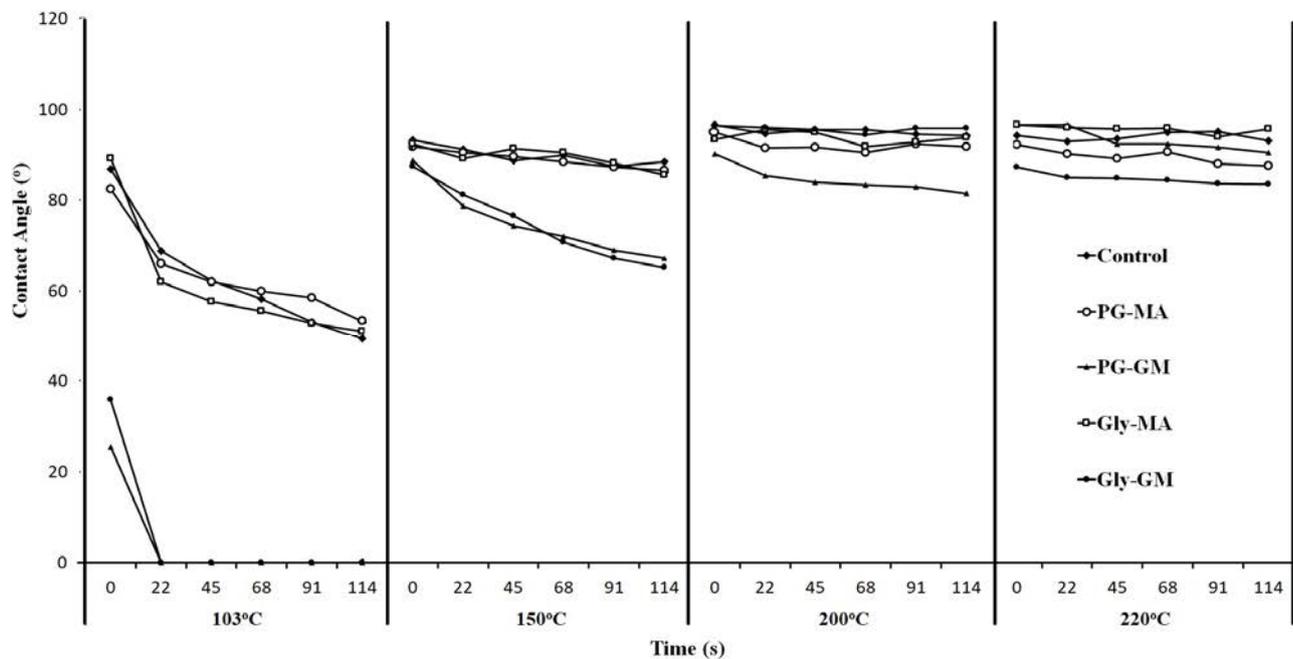


Fig. 1 Evolution of water contact angle on wood samples treated with the different additives and cured at different temperatures

Water contact angle measurement is a possible technique to study the modification performance (Moghaddam 2015). Based on the Fig. 1, wettability of the additive-treated wood and wood control decreased (contact angle increased) by the increase of curing temperature confirming some previous research that the surface of heat-treated wood behaved more hydrophobic (Pétrissans et al. 2003; Hakkou et al. 2005). At 103 and 150°C, maleic anhydride-based additive treated wood, PG-MA and Gly-MA had more hydrophobic properties than glycidyl methacrylate-based additive treated wood. This may be due to a lower penetration of Gly-GM and PG-GM in the wood cell wall due to the lower polarity of these additives compared to Gly-MA and PG-MA resulting in the presence of hydrophilic polyol moiety on the wood surface. Nevertheless, both maleic anhydride- and glycidyl methacrylate-based systems have more or less similar wettability properties independently of the nature of the polyol used at higher thermal treatments. In other words, the most important parameter influencing wettability was the curing temperature.

Results of decay and termite resistance analysis are presented in Table 4.

According to the results (Table 4), durability of additive-treated wood and wood control against *Coriolus versicolor* (CV) was improved with the increase of curing temperature. Even though beech resistance against CV increased as the increase of curing temperature confirming literature data (Hakkou et al. 2006), combination of thermal and chemical treatment improved efficiently its resistance capability. This is particularly obvious for treatments performed at 200°C, where combination of both treatments allowed good protection of un-leached treated samples, while heat-treated samples without additive impregnation at the same temperature presented important mass losses under the experimental condition (according to Tukey comparison method). Additive impregnation permitted in this case to reduce the severity of heat treatment conditions (temperature and duration) to achieve full protection of wood. After leaching, PG-MA and Gly-MA samples heat-treated at 200°C were still resistant to CV degradation, while PG-GM and Gly-GM presented important mass losses resulted probably from the leaching of the impregnated chemicals. In all cases, no significant difference was observed after the replacement of polyglycerol by glycerol. Impregnation of maleic anhydride-based additives followed by heat treatment at 200°C highlighted a synergic effect between chemical and thermal treatments leading to a better decay resistance of wood samples comparatively to those treated at lower curing temperatures. These results are consistent with our previous results (Salman et al. 2017). At 220°C, all treatments permitted good protection of beech samples against CV resulting of the cumulative effect of thermal and chemical modifications. Even if the temperature at 220°C is believed to be responsible for durability improvement (Lekounougou et al. 2009; Gérardin 2016), further experiments will be necessary in this case to evaluate more precisely synergistic effects between both treatments.

Table 4 Decay and termite durability improvement of wood blocks subjected to the different treatments

T (°C)	Additive	Decay resistance		Termite resistance	
		ML (%) before leaching ^a	ML (%) after leaching ^b	ML _t (%) after leaching ^c	Survival Rate ^c (%)
103	PG-MA	7.6 ± 1.1 (cd)	24.1 ± 5.2 (def)	3.9 ± 0.6 (ab)	3 ± 3 (cd)
	Gly-MA	7.85 ± 0.6 (cd)	29.3 ± 6.0 (cde)	3.7 ± 0.8 (ab)	0 ± 0 (d)
	PG-GM	7.8 ± 1.3 (cd)	45.3 ± 5.5 (a)	6.7 ± 3.5 (ab)	61 ± 15 (ab)
	Gly-GM	6.8 ± 0.6 (de)	45.0 ± 9.7 (a)	7.0 ± 1.5 (ab)	67 ± 10 (ab)
	None	24.2 ± 1.7 (a)	42.4 ± 6.3 (abc)	7.9 ± 3.8 (ab)	65 ± 5 (ab)
150	PG-MA	5.3 ± 3.1 (defg)	32.7 ± 3.2 (bcd)	5.4 ± 1.0 (ab)	51 ± 15 (ab)
	Gly-MA	3.5 ± 0.4 (efgh)	21.4 ± 1.9 (ef)	4.5 ± 0.7 (ab)	34 ± 3 (bcd)
	PG-GM	11.3 ± 5.8 (bc)	36.2 ± 2.4 (abc)	3.2 ± 1.1 (b)	29 ± 22 (bcd)
	Gly-GM	5.9 ± 1.0 (def)	30.9 ± 2.3 (cde)	6.9 ± 0.9 (ab)	77 ± 15 (a)
	None	21.2 ± 0.9 (a)	41.8 ± 7.4 (ab)	5.1 ± 1.2 (ab)	57 ± 6 (ab)
200	PG-MA	0.9 ± 0.5 (h)	3.1 ± 3.0 (g)	7.7 ± 1.2 (ab)	64 ± 12 (ab)
	Gly-MA	0.3 ± 0.3 (h)	0.7 ± 0.8 (g)	4.0 ± 1.5 (ab)	46 ± 7 (ab)
	PG-GM	3.6 ± 2.1 (efgh)	15.1 ± 2.3 (f)	4.8 ± 1.4 (ab)	47 ± 2 (ab)
	Gly-GM	2.7 ± 2.3 (fgh)	13.7 ± 7.4 (f)	5.8 ± 1.2 (ab)	63 ± 5 (ab)
	None	14.0 ± 2.1 (b)	21.3 ± 2.6 (ef)	9.7 ± 0.9 (a)	74 ± 2 (a)
220	PG-MA	0.0 ± 0.2 (h)	-0.4 ± 0.2 (g)	3.8 ± 0.7 (ab)	40 ± 7 (abc)
	Gly-MA	-0.3 ± 0.2 (h)	-0.2 ± 0.2 (g)	2.8 ± 1.8 (b)	41 ± 20 (abc)
	PG-GM	0.2 ± 0.3 (h)	3.3 ± 1.0 (g)	5.1 ± 5.3 (ab)	29 ± 30 (bcd)
	Gly-GM	0.2 ± 0.2 (h)	0.6 ± 1.0 (g)	5.8 ± 1.5 (ab)	62 ± 12 (ab)
	None	1.7 ± 1.2 (gh)	1.6 ± 0.9 (g)	8.6 ± 2.2 (ab)	55 ± 13 (ab)
Virulence		29.7 ± 1.3	51.2 ± 3.5	8.0 ± 1.0	81 ± 9

Value was the average of ^a6 replicates with five weeks incubation period; ^b5 replicates with twelve weeks incubation period; and ^c3 replicates.

Values followed by the same letter in the parentheses do not differ significantly ($\alpha = 0.05$) based on one-way ANOVA test using Tukey multiple comparison.

Table 5 Differences among the additives and the curing temperatures according to the results of different parameter analysis using two-way ANOVA analysis of variance with confidence level 95%

Differences	Δm		ΔV^b	WL_L^a	ASE ^c	MOE ^d	MOR ^d	Decay resistance		Termite resistance		
	Before leaching ^a	After leaching ^a						ML before leaching ^a	ML after leaching ^b	MLt after leaching ^c	Survival Rate ^e	
Value	F(157.8) > P(0)	F(83.51) > P(0)	F(197.23) >P(0)	F(22.6) >P(0)	F(38.22) >P(0)	F(31.72) >P(0)	F(24.67) >P(0)	F(64.06) >P(0)	F(23.41) >P(0)	F(6.26) >P(0)	F(9.47) >P(0)	
Additive	PGMA	ab	a	b	b	a	b	c	bc	b	ab	b
	GlyMA	b	b	ab	ab	a	b	c	c	b	ab	b
	PGGM	a	a	a	a	b	b	b	b	a	ab	b
	GlyGM	c	c	c	ab	b	b	b	bc	a	ab	a
	None	d	d	d	c	c	a	a	a	a	a	a
Value	F(641.97) > P(0)	F(457.53) >P(0)	F(150.23) >P(0)	F(65.1) >P(0)	F(164.03) >P(0)	F(16.19) >P(0)	F(123.45) >P(0)	F(69.83) >P(0)	F(223.41) >P(0)	F(1.27) >P(0.295)	F(3.13) >P(0.033)	
T Curing (°C)	103	a	b	a	a	c	b	a	a	a	a	b
	150	b	a	a	b	c	a	a	a	a	a	ab
	200	c	c	b	c	b	ab	b	b	b	a	a
	220	d	d	c	c	a	c	c	c	c	a	ab

Number of samples during analysis were ^a24; ^b20; ^a24; ^c16; ^d40; ^e12; letter(s) in grouping are arranged from the highest (a) to the lowest range of the result values based on two-way ANOVA analysis; the same letter in one parameter analysis column means do not differ significantly ($\alpha = 0.05$) based on confidence interval of two-way ANOVA analysis

Termite resistance analysis was evaluated by non-choice screening test using *Reticulitermes flavipes* (Table 4). All additive-treated wood after leaching presented lower mass loss values against termite than non-impregnated wood cured the same temperature. In this latter case, improvement of curing temperature has less effect on the improvement of durability. Almost all additive-impregnated wood presented lower mass losses than un-impregnated samples even after leaching indicating a potential beneficial effect of chemical treatment in this system. Further, at higher curing temperature, even though additive-treated samples were slightly attacked by the termites, the survival rates of the termites remained with high number indicating that treatment can be considered as non-biocide treatments. Reduction of degradation increased with the increase of curing temperature. Reduction of ML_t comprised between 4 to 65%, depending on the additive used compared to the virulence sample. At 220°C, PG-MA and Gly-MA-treated woods gave quite similar results indicating that no significant difference between glycerol and polyglycerol, while PG-GM-treated wood presented slightly better results than Gly-GM-treated wood. PG-MA and Gly-MA-impregnated samples cured at 103°C presented the lowest mass losses compared to other treatments. Acidity of these additives could also be the possible reason of these better performances. At higher curing conditions, esterification reactions took place favoring fixation of these additives into the wood limiting acidity, which resulted in a decrease of termites durability

According to analysis of variance using two-way ANOVA with 95% confidence level (Table 5), almost all additives made significant difference in all parameter analysis compared to wood without additive (identified as different letters in every column in the table). Among all the additives, wood treated with maleic anhydride-based additives (PG-MA and Gly-MA) made significant differences in ASE, MOR, and ML due to decay test after leaching analysis in comparison with wood treated with glycidyl methacrylate-based additive and wood control. In case of curing temperatures, most of curing temperatures made difference to the properties of the modified woods, however, some of them especially at 103 and 150°C gave similar response in their parameter analysis (bulking, ASE, MOR, and ML due to decay before and after leaching analysis). This condition, on the other words, could mean that treatments at 200 and 220°C gave significant differences on those parameter analysis supporting the observation that the association of light chemical and thermal treatments acted synergistically at these thermal conditions.

4. Conclusions

Results have revealed that replacement of polyglycerol by glycerol did not induce an important change of reactivity of additives prepared from maleic anhydride or glycidyl methacrylate. Depending of the investigated properties, utilisation of glycerol or polyglycerol may offer some slight advantages. In most cases, treatments involving glycerol (Gly-MA and Gly-GM) led to slightly better dimensional stabilisation than treatments with polyglycerol (PG-MA and PG-GM), while more or less similar behaviours were observed for resistance to leaching, wettability, mechanical properties and biological durability tests at higher curing temperatures. Among all additives tested, maleic anhydride-based additives (Gly-MA and PG-MA) showed better performances compared to additives prepared from glycidyl methacrylate. Although in all cases the mechanical properties of the additive-treated woods were slightly lower than wood control, combination of chemical and thermal treatments permitted improvement of durability to *Coriolus versicolor* and *Reticulitermes flavipes* due to synergistic effect between the two kinds of treatments. These effects are particularly obvious at 200°C for decay durability and 220°C for termite durability tests especially for wood treated with maleic anhydride-based additives. However, further experiments will be necessary to investigate more in detail these synergistic effects and their effect on wood durability. Through the various performed measurements, glycerol could be used as a substitute agent for polyglycerol particularly in maleic anhydride-based additive. Ultimately, these results also convince that combination of chemical treatment at low additive concentration and thermal treatment could be an alternative as non-biocide wood preservation treatment.

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c. Conclusion

According to the results of the various parameter analysis, there are some points that considered as characteristics of the modified woods, which could be summarized as follows:

- The wood treated with glycerol-based additive underwent higher thermal degradation than polyglycerol-based additive treated wood.
- The wood treated with maleic anhydride-based additive underwent slightly higher thermal degradation than the wood treated with glycidyl methacrylate-based additive.
- Polyglycerol-based additive treated wood presented slightly higher resistance against leaching than glycerol-based additive treated wood, though no significant difference mostly observed in this case.
- Additive-treated woods, especially the wood treated with maleic anhydride-based additive, presented higher ASE values than untreated wood or thermally treated wood at the same curing condition.
- Wettability study revealed that the wood treated with maleic anhydride-based additive has more or less similar wettability with untreated wood.
- Decay resistance against CV of additive-treated wood were higher and significantly difference than untreated wood or thermally treated wood at the same curing temperature. Maleic anhydride-based additive treated woods presented higher resistance to decay than glycidyl methacrylate-based additive treated woods.
- Termite resistance against *Reticulitermes flavipes* of the additive-treated wood, especially treatment with maleic anhydride-based additive, was higher than untreated wood and thermally treated wood. The survival rate of the termite was higher when treatment underwent at higher curing condition.
- In overall, no significant difference observed for the wood treated either with glycerol-based additives or polyglycerol-based additives, confirming our hypothesis that glycerol would have similar properties with polyglycerol.

II.2.2 Paper 2

a. Introduction

In this paper, a similar modification method by combining mild chemical modification and thermal treatment was also demonstrated. However, the additive used in this study was based on the improvement of certain additives used in the Paper 1. This study used glycerol methacrylate maleate (GM/MA_(2eq)) or polyglycerol methacrylate maleate (PGM/MA_(3eq))-based additive for the

mild chemical modification. Meanwhile, curing temperature was performed with the same condition as the Paper 1 (103, 150, 200, or 220°C).

Due to the low penetration and fixation of glycidyl methacrylate-based additives (Gly-GM and PG-GM) to the wood in comparison with maleic anhydride-based additives (Gly-MA and PG-MA) in the Paper 1, therefore, the Paper 2 introduced improvement of Gly-GM and PG-GM-based additive by the addition of maleic anhydride during formulation of the impregnating solution. Some proposed reactions during formulation and curing process are shown in the Figure 30 and 31.

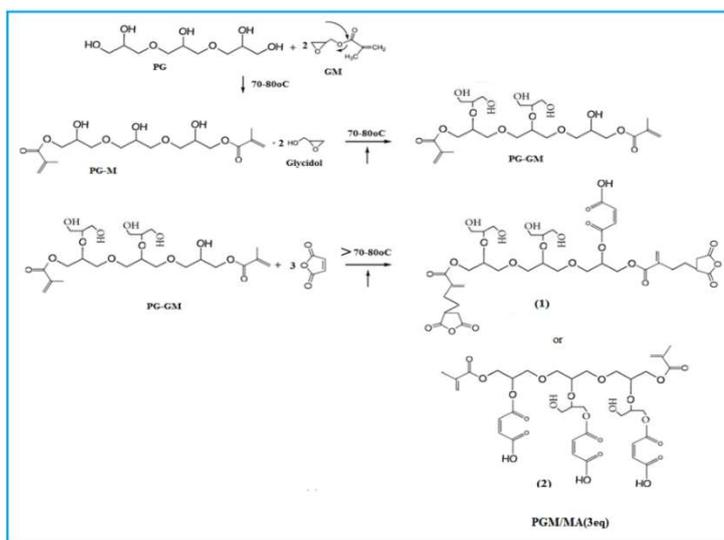


Figure 30: A proposed reaction of *in-situ* three-dimensional structure of PGM/MA_(3eq)

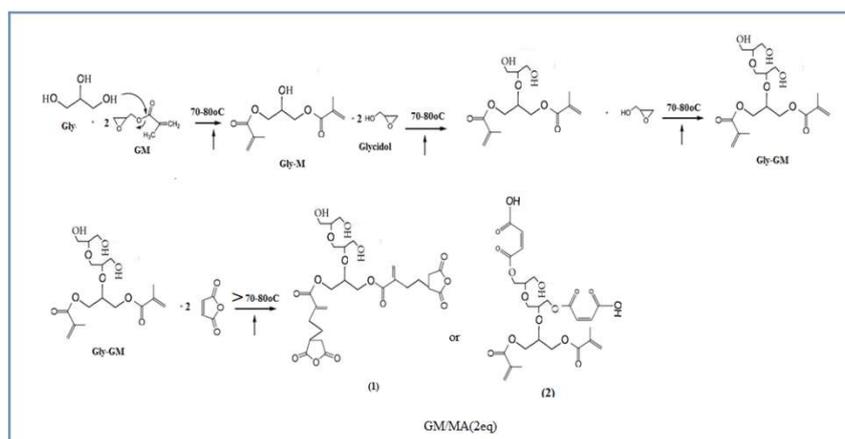


Figure 31: A proposed reaction of *in-situ* three-dimensional structure of GM/MA_(2eq)

In addition, maleic anhydride, a reactive agent in the system, was used in the single form for wood modification as comparison. Various parameter analysis including physical, chemical, mechanical, and biological durability properties of the modified wood were also compared and evaluated.

b. Paper 2

Non-biocide antifungal and anti-termite treatments based on combinations of thermal modification with different chemical additives

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Keywords: chemical modification, durability, *Fagus sylvatica*, glycerol, glycidyl methacrylate, Infrared, maleic anhydride, physical-mechanical properties, thermal treatment, polyglycerol

Abstract

The synergic effect between a mild chemical and thermal modification of beech wood (*Fagus sylvatica*) has been studied. A low concentration of additives based on vinylicpolyglycerol, vinylicglycerol, and maleic anhydride was impregnated into beech wood and followed by curing process under different temperature conditions at 103, 150, 200, and 220°C. The modified wood was then analyzed for its leaching resistance, dimensional stability, wettability, modulus of elasticity (MOE) and modulus of rupture (MOR) in bending, Fourier Transform Infrared (FT-IR) spectroscopy, decay resistance against *Trametes versicolor*, and termite resistance towards *Reticulitermes flavipes*. Results have disclosed that the synergic effect of thermo-chemical wood modification was observed at 200 and 220°C curing conditions. At these curing temperatures, thermo-chemical modified beech presents improved dimensional stability (>60%), better resistance towards both *Trametes versicolor* and *Reticulitermes flavipes* comparatively to control. However, at the same conditions, MOE and MOR values were lowered of approximately 25% and 60%, respectively.

1. Introduction

As a respond to the increasing demands on wood for numerous applications, research on wood thermal and chemical modifications is of interest. Wood modification is considered to be a promising alternative to biocide treatments, in some fields of application (Militz 2002; Schultz et al. 2008; Esteves and Pereira 2009; Rowell et al. 2009; Gérardin 2016). However, even though an increase in wood performance, especially in its dimensional stability and decay resistance, its resistance against termite attacks remains insufficient (Mburu et al. 2007; Militz et al. 2011; Surini

et al. 2012; Sivrikaya et al. 2015; Salman et al. 2016). Therefore, improvement in termite resistance, especially for thermally modified wood, is a challenge. Previous researches have disclosed that the incorporation of low concentrated additives made of a mix of vinylic-polyglycerol compounds into the wood, followed by thermal treatment, could improve timber termite resistance (Salman et al. 2016, 2017). Considering those findings, it was demonstrated that even though chemical and thermal modifications function differently, here they act in such a way that a complete modification can be achieved simultaneously. Based on the work of Salman et al. (2016, 2017), the aim of this paper is to investigate an *in-situ* polymerization of new formulations based on combinations between polyglycerol or glycerol methacrylate with maleic anhydride. These innovative formulations were created by mixing the polyglycerol or glycerol methacrylate adduct with maleic anhydride aqueous solution, which afterwards an impregnation into wood was set at different curing temperatures for an *in-situ* polymerization. The addition of maleic anhydride in the formulation was expected to improve the fixation of the polyglycerol or glycerol methacrylate system within the wood. Even if similar approaches have been carried out on polymerization of glycidyl methacrylate, maleic anhydride, and methylmethacrylate (Li et al. 2011; Liu et al. 2012), impregnation of aqueous mixture of polyglycerol or glycerol methacrylate and maleic anhydride, followed by a thermal treatment have not been studied up to now. In addition, the interest of such systems lies in the potential additional or synergic effects between chemical and thermal treatment. Moreover, this experimental work focused on European beech (*Fagus sylvatica*), a hardwood species needing improvement upon its low durability and dimensional stability to emerge new way of valorization (EN 350, 2016).

2. Experimental

2.1. Sample preparation

Three kinds of aqueous additive solutions were examined: glycerol methacrylate-maleic anhydride (GM/MA_(2eq)), polyglycerol methacrylate-maleic anhydride (PGM/MA_(3eq)), and maleic anhydride (MA). Four curing temperature treatments (103, 150, 200, and 220°C) were investigated. Each additive needed a well grained beech with $12 \pm 2\%$ moisture content with a total number of 96 samples measuring $30 \times 15 \times 5 \text{ mm}^3$ ($L \times R \times T$) and 40 samples measuring $190 \times 20 \times 5 \text{ mm}^3$ ($L \times R \times T$) for four curing temperatures. Wood samples without additives were cured at the four different temperatures as wood control.

2.2. Additive formulation

The basic chemicals used in this research were polyglycerol [PG, as PG3, Inovyn (Belgium) as a mixture of compounds with an average Molecular weight (Mw) of 242 g mol^{-1} (degree of

polymerization ~ 3], glycerol (Gly/G, $M_w = 92.09 \text{ g mol}^{-1}$), 4-(dimethylamino)pyridine (4-DMAP, $M_w = 122.17 \text{ g mol}^{-1}$), glycidyl methacrylate (M, $M_w = 142.15 \text{ g mol}^{-1}$), and maleic anhydride (MA, $M_w = 98.06 \text{ g mol}^{-1}$) [Sigma-Aldrich Chimie SARL (France)]

Polyglycerol methacrylate-maleic anhydride (PGM/MA_(3eq)) was made from 10% w/w aqueous mixture of PGM (polyglycerol-glycidyl methacrylate) adduct and MA (maleic anhydride) with 1:3 molar ratio.

PGM was first made according to Soulounganga et al. (2004). 1 mol of polyglycerol was reacted with 0.02 mol of 4-(dimethylamino)pyridine as a catalyst and 2 mol of glycidyl methacrylate into a beaker glass equipped with a magnetic stirrer and glass watch, and heated at 70°C for 15 min. The reaction was then stopped after a complete appearance of a characteristic ester band (C=O, stretch) at about 1716 cm^{-1} , diminution of hydroxyl group (OH-) of polyglycerol at 3331 cm^{-1} and epoxy group of glycidyl methacrylate at 906 cm^{-1} by means of ATR-FTIR. The product was directly used without further purification.

One mol of PGM product was mixed well into 3 mol of MA aqueous solution so that the final concentration of impregnating additive aqueous mixture was 10% w/w. The final mixture was then directly applied. PGM/MA_(3eq) production was performed in the same manner, GM/MA_(2eq) 10% w/w solution was made by mixing well 1 mol of GM adduct into 2 mol of MA aqueous solution so that the final concentration was 10% w/w. GM adduct was made as similar as PGM adduct production.

MA additive solution was made by dissolving maleic anhydride into distilled water so that the final solution concentration was 10% w/w.

2.3. Wood modification

Beech wood samples were dried at 103°C, weighed (m_0), the dimensions were measured and the volume was calculated (V_0). Wood samples were exposed to the following treatment cycle in an autoclave: vacuum (8 – 10 KPa) for 10 min, impregnation process with 10% w/w aqueous additive solution during 1 h under vacuum (5-10 KPa), pressure was brought up to 100 KPa (ambient pressure), increased to 1200 KPa for 1 h, and finally turned down to 100 KPa. All samples were removed from the autoclave, air conditioned for 24 h, dried at 103°C, weighed until constant mass (m_1) and their dimensions re-measured and volume re-calculated (V_1). For thermal treatments, samples were divided into four groups, one group (dried only at 103°C) was kept, and the remaining three groups were exposed respectively at 150, 200, and 220°C for 20 h under nitrogen condition. All modified woods were then re-weighed (m_2) and their dimensions

were re-measured and volume re-calculated (V_2). The same procedure was also conducted for non-impregnated beech woods as controls.

2.4. Leaching test

Leaching test referred to a method adapted from NF X 41-568 (2014). Six samples [$30 \times 15 \times 5 \text{ mm}^3$ ($L \times R \times T$)] from each treatment (additive-treated wood or wood control at different curing temperatures) were submerged into 72 mL of distilled water and subjected to six leaching periods (1, 2, 4, 8, 16, and 48 h) under continuous shaking (175 linear shakes/min). Between the periods of 4 and 8 h, samples were removed and air-dried for 16 h. After completing the leaching periods, samples were dried at 103°C for 48 h and re-weighed (m_3).

From the wood modification and the leaching test, mass change was calculated from the following equation (Eq. 1):

$$\Delta m (\%) = 100 \times (m_1 \text{ or } m_2 \text{ or } m_3 - m_0) / m_0 \quad (1)$$

where m_0 is the initial mass of wood at 103°C before treatment, m_1 the mass of additive-treated wood at 103°C , m_2 the mass of additive-treated wood or wood control at 150, 200 or 220°C , and m_3 the oven dry mass sample (at 103°C) after leaching of additive-treated wood or wood control at different temperatures.

Bulking value was calculated from the following equation (Eq. 2):

$$\Delta V (\%) = 100 \times (V_1 \text{ or } V_2 - V_0) / V_0 \quad (2)$$

where V_0 is the initial volume of wood at 103°C before treatment (initial volume), V_1 the volume of additive-treated wood at 103°C , V_2 the volume of additive-treated wood or wood control at 150, 200 or 220°C .

2.5. Wettability

Wettability test measured by water drop test adapted from Engonga et al. (1999). Contact angle of water droplet on the wood surface was measured by means of Drop Shape Analysis system DSA10 MK2 instrument from Kruss. Contact angles of samples [$30 \times 15 \times 5 \text{ mm}^3$ ($L \times R \times T$), $n = 3$] before leaching from each additive-treated wood and wood control at different curing temperatures were measured and recorded automatically every 22 seconds until 114 seconds.

2.6. Anti-swelling efficiency (ASE)

This method referred to Pfriem et al. (2012). Additive-treated wood and wood control [$30 \times 15 \times 5 \text{ mm}^3$ ($L \times R \times T$), $n = 4$] at each curing temperature before leaching were re-dried at 103°C and their dimensions were measured and volumes were calculated (V_d). Wood samples were

directly immersed into distilled water and placed under vacuum condition (10 KPa) for 30 min. Pressure was then reset to ambient pressure, and the samples immersed in water for 24 h, followed by their wet volume recording (V_w). Three cycles of drying-wetting system were performed so that data of dried volume (V_d) and wet volume (V_w) in every cycle was collected. Only the ASE of the third cycle is presented in this paper. Swelling (S) and of anti-swelling efficiency (ASE) were calculated from the following equation (Eq. 3 and 4).

$$S = (V_w - V_d)/V_d \quad (3)$$

where V_d is the anhydrous volume of the sample, V_w the wet volume of the sample.

$$ASE = 100 \times (S_0 - S_1)/S_0 \quad (4)$$

where S_0 is the swelling of untreated wood, S_1 the swelling of treated wood.

2.6. Modulus of Elasticity (MOE) and Modulus of Rupture (MOR) in bending

These three point bending measurements referred to EN 310 (1993). Additive-treated wood and wood control at different curing temperatures before leaching [$190 \times 20 \times 5 \text{ mm}^3$ ($L \times R \times T$), $n = 10$] were conditioned [$65 \pm 5\%$ Relative Humidity (RH) and $22 \pm 2^\circ\text{C}$] until constant mass. Dimension of all samples were re-measured. The increment in load and displacement values of each sample were measured by means of INSTRON 4467 universal testing machine. MOE/MOR values were then calculated as follow (Eq. 5 and 6):

$$\text{MOE (N/mm}^2\text{)} = [l^3(F_2 - F_1)] / [4bt^3(a_2 - a_1)] \quad (5)$$

where l is the distance between the center of support in millimeters, b the width of the sample in millimeters, t the thickness of the sample in millimeters, $F_2 - F_1$ the increase in load in newton, on the cross section of the load-deformation curve, F_1 should be approximately 10% and F_2 approximately 40% of the breaking load, $a_2 - a_1$ the increase of deflection at mid-length of the test sample (corresponding to $F_2 - F_1$).

$$\text{MOR (N/mm}^2\text{)} = (3 F_{max} l)/(2bt^2) \quad (6)$$

where F_{max} is the breaking load in Newton.

2.7. Decay resistance

The procedure is derived from EN 113 (1996), according to Bravery (1978). Sterile culture medium prepared from malt (40 g) and agar (25 g) [purchased from Sigma-Aldrich (France)] in distilled water (1 L), was placed in culture 9 cm Petri dishes, inoculated with a small piece of mycelium of a freshly grown pure culture of *Trametes versicolor* Quélet (Tv) [Linnaeus, CTB 863 A] and incubated for 2 weeks at $22 \pm 2^\circ\text{C}$ and $70 \pm 5\%$ RH to allow full colonization of the medium

by the mycelium.

All wood samples [$30 \times 15 \times 5 \text{ mm}^3 (L \times R \times T)$, $n = 11$, for each treatment] were sterilized by steam in an autoclave at 121°C for 20 min. In each petri dish, three specimens (two treated with additive and/or heat and one untreated as control) were inserted. Each experiment was repeated three times. Beech virulence samples, of the same dimensions, were also performed on nine specimens. Incubation was carried out for 12 weeks at $22 \pm 2^\circ\text{C}$ and $70 \pm 5\%$ RH in a climatic chamber. Once the fungal exposure was completed, samples were cleaned carefully from the mycelium. All samples were then oven dried at 103°C for 48 h and weighed (m_4). Mass loss after decay test was calculated as follow (Eq. 7):

$$\text{ML (\%)} = 100 \times (m_0 \text{ or } m_1 \text{ or } m_2 \text{ or } m_3 - m_4) / m_0 \text{ or } m_1 \text{ or } m_2 \text{ or } m_3 \quad (7)$$

where m_0 is the dry mass of untreated wood sample (at 103°C), m_1 the dry mass of additive-treated wood or control sample at 103°C , m_2 the dry mass of additive-treated wood or wood control at 150, 200, or 220°C , m_3 the oven dry mass sample (at 103°C) after leaching of additive-treated wood or wood control at different temperatures, and m_4 the mass of dry mass of wood sample after decay test.

2.8. Termite resistance

Durability against termites was examined based on the non-choice test adapted from EN 117 (2013) against *Reticulitermes flavipes* (ex. *santonensis*). Three replicates of samples after leaching [$30 \times 15 \times 5 \text{ mm}^3 (L \times R \times T)$] from additive-treated wood and wood control at different curing temperatures were tested as well as untreated woods as virulence samples. Each sample was inserted in 9 cm diameter Petri dish containing 40 g of wet Fontainebleau sand (4 volume of sand / 1 volume of deionized water). Plastic mesh was used as a support for sample to avoid water saturation. A total amount of 50 termite workers, one nymph, and one soldier were introduced in each Petri dish. The Petri dishes were placed in a dark climatic chamber at $27 \pm 2^\circ\text{C}$ with a RH superior to 75%. The observations were conducted on a weekly basis in order to add water and check termite behaviour. After four weeks, the samples were removed and cleaned of the sand and the number of termite still alive (n) was counted to determine their survival rate (Eq. 8). The samples were dried at 103°C , weighed (m_5), and mass losses due to termite attacks were calculated (Eq. 9).

$$\text{Survival rate (\%)} = 100 \times n / 50 \quad (8)$$

where n is the number of the remaining live termite worker after the test, while, 50 is the number of the added termite workers for the test.

$$ML_t (\%) = 100 \times (m_3 - m_5)/m_3 \quad (9)$$

where ML_t is the percentage of mass loss due to the termite attacks of additive-treated wood or wood control at different curing temperatures as well as untreated sample after leaching, m_3 and m_5 are respectively the dried mass at 103°C of sample before and after termite attacks.

2.9. Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR spectrums were recorded on an ATR-FTIR Perkin Elmer Spectrum 2000 instrument. The spectrums of the additive-treated wood or wood control sawdust at different curing temperatures were recorded in the range of 4000 – 600 cm^{-1} at a resolution of 4 cm^{-1} with an ATR cell.

3. Results and Discussion

Data concerning mass changes during the different steps of the treatment and effect of chemical modifications are reported in Table 1.

Table 1 Mass changes of additive-treated wood and wood control at different curing temperatures before and after leaching process

Temperature (°C)	Additive	Δm (%)	
		Before leaching ^a	After leaching ^b
103	PGM/MA _(3eq)	11.1 ± 1.2	2.7 ± 0.6
	GM/MA _(2eq)	11.2 ± 0.9	2.9 ± 0.3
	MA	9.3 ± 0.7	2.2 ± 0.7
	Control	0	-1.4 ± 0.3
150	PGM/MA _(3eq)	9.8 ± 1.0	6.5 ± 0.5
	GM/MA _(2eq)	10.2 ± 0.6	6.3 ± 0.4
	MA	7.2 ± 0.8	1.4 ± 0.8
	Control	-0.1 ± 0.2	-1.8 ± 0.2
200	PGM/MA _(3eq)	3.3 ± 1.4	-0.1 ± 1.0
	GM/MA _(2eq)	3.4 ± 0.9	1.5 ± 0.5
	MA	-4.3 ± 0.5	-7.7 ± 0.6
	Control	-2.5 ± 0.4	-4.2 ± 0.3
220	PGM/MA _(3eq)	-2.8 ± 1.0	-5.0 ± 0.6
	GM/MA _(2eq)	-2.1 ± 1.0	-4.6 ± 0.6
	MA	-9.9 ± 0.8	-13.8 ± 1.0
	Control	-10.5 ± 1.1	-11.6 ± 1.0

Value was the average of ^a96 replicates at 103°C and 24 replicates at @150; 200; 220°C; ^b6 replicates

In most cases, mass change (Δm) values decreased as the curing temperatures increase. The amount of Δm values of additive-treated wood appears proportional to their dimensional change values (ΔV) particularly at lower curing temperature (103 and 150°C) indicating that the additives could penetrate into the wood cell wall (Figure 1). PGM/MA_(3eq) and GM/MA_(2eq)-treated wood had similar Δm values for a given curing temperatures, which presumably means that their polarities are conformable between each other. On the other hand, a high decrease on Δm and ΔV

values due to the thermal degradation was observed at 200°C curing condition for both additive-treated wood and wood control.

In the case of MA-treated wood, it gave behaviours as their Δm values were smaller than those of the previous two additive-treated woods. Moreover, the lowest Δm for MA was at 220°C (before and after leaching) (Table 1). This condition indicates some possible factors, an instability of unreacted maleic anhydride (boiling point, 202°C) in MA-treated wood, a lower thermo stability of MA-treated wood at higher temperature (>200°C) and long duration of time (20 h), or combination of both factors which triggered a concentrated acid and accelerated heat-induced wood degradation. At 220°C, an intensive thermal degradation for both additive-treated and untreated wood was undergone where beech control reached about 10% mass loss in this inert condition.

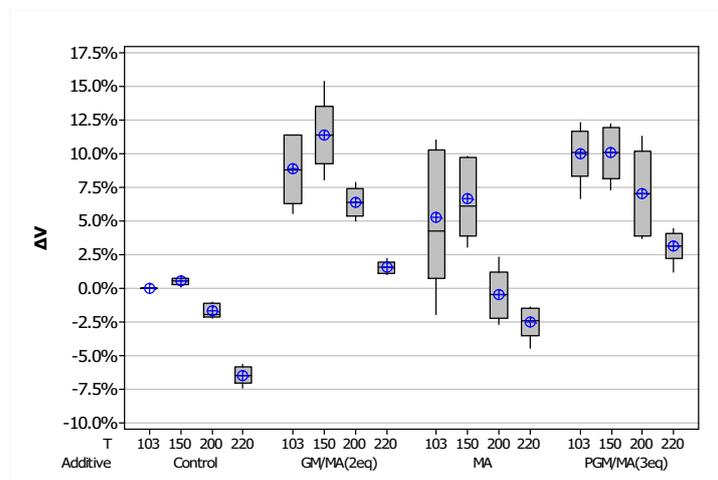


Figure 1 Dimensional changes (bulking) of the additive-treated wood and wood control at different curing temperatures

There is a trend between 103 and 200°C, as mass loss of treated wood after leaching decreased while curing temperatures increase. At 150°C curing condition, PGM/MA_(3eq)- and GM/MA_(2eq)-treated woods gave the highest mass changes (Δm) after leaching indicating that a better fixation of the additives in wood occurred, compared to 103°C curing process. Consequently, mass loss due to leaching at this condition also decreased. Among the additive -treated wood, PGM/MA_(3eq) and GM/MA_(2eq)-treated wood have better leaching resistance than MA-treated wood. A three-dimensional composite system of both methacrylate-based additives was a possible reason for their higher leaching resistance compared to maleic anhydride alone at the same additive concentration. On the other hand, a high decrease of Δm for both before and after leaching due to thermal degradation at 200 and 220°C occurred. However, these conditions, especially at 200°C, allowed additives to better fix in wood, and their differences between Δm before and after leaching also

decreased compared to the lower temperature curing processes. At the highest thermal condition (220°C), an extensive thermal degradation happened, some of the degradation products (particularly for additive-treated wood) were possibly lixiviated during leaching process. Therefore, mass loss due to leaching increased slightly for some treatments at 220°C.

Wettability properties measured as contact angle values of additive-treated wood and wood control at different curing temperatures are presented in Figure 2.

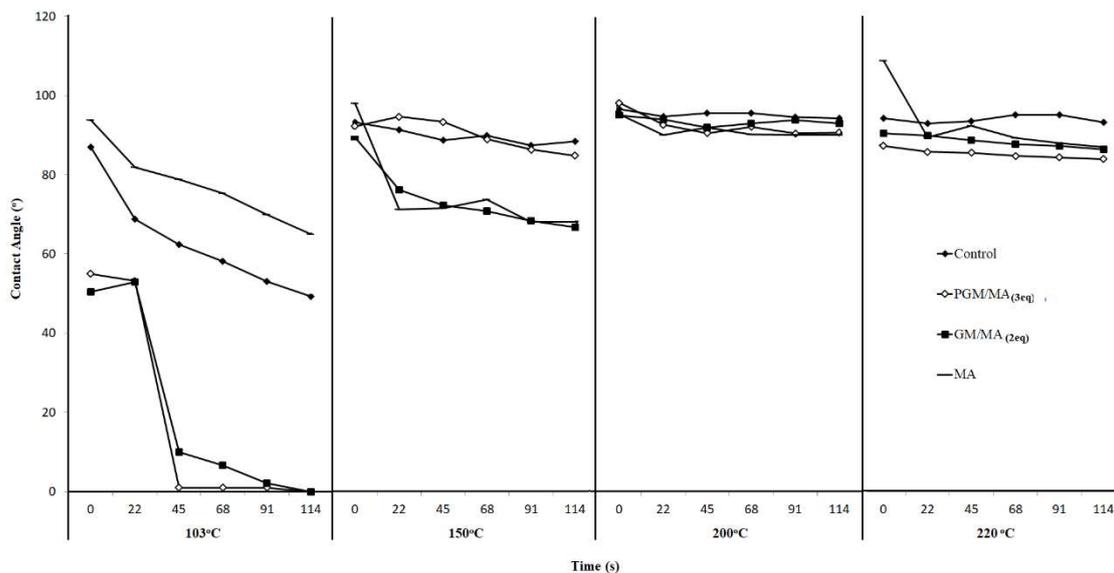


Figure 2 Water contact angle curve on additive-treated wood and wood control at different curing conditions

Wettability of the additive-treated wood and wood control decreased with the increase of curing temperature corroborating some previous research work showing that heat treated wood had higher hydrophobic surface, thus reducing its wettability (Pétrissans et al. 2003; Hakkou et al. 2005a). Among the additive-treated wood, both methacrylate-based additive (GM/MA_(2eq)) and PGM/MA_(3eq) treated woods had a higher wettability (lower contact angle values) than MA-treated wood and wood control at 103°C curing condition. This characteristic might be due to an incomplete reaction of GM/MA_(2eq) and PGM/MA_(3eq)-treated wood at this curing condition. Therefore, some of free hydroxyl groups from both PGM and GM systems remained with a affinity against water. A similar case also happened for GM/MA_(2eq) and MA-treated wood at 150°C curing condition for their incomplete reaction, even though the initial fixation in wood was observed at this temperature (Table 1). An exception for MA-treated wood, where it had the highest contact angle at 103°C curing condition, the double bonds and the cyclic molecule of unreacted MA were believed to be the cause of its lower performance against water in this case. In methacrylate-based additives, because of polyglycerol has higher affinity to reticulate than glycerol, thus, PGM/MA_(3eq)-treated wood polymerized faster and had lower wettability at 150°C curing

condition than other additive-treated wood. At 200°C curing condition, all additive-treated wood and control had approximately a similar wettability. It is assumed that the additives had fully reacted with wood where the effect of thermal degradation to this wettability property was still low. As for the leaching data previously (Table 1), the extensive thermal degradation especially for additive-treated wood at 220°C probably could be the reason for the formation of the light weight degradation product with higher hygroscopicity. Therefore, the additive-treated wood had slightly higher wettability than control at 220°C.

Data concerning the physical and mechanical properties of the additive-treated wood and wood control at different curing temperatures before leaching process are reported in Figure 3 - 5.

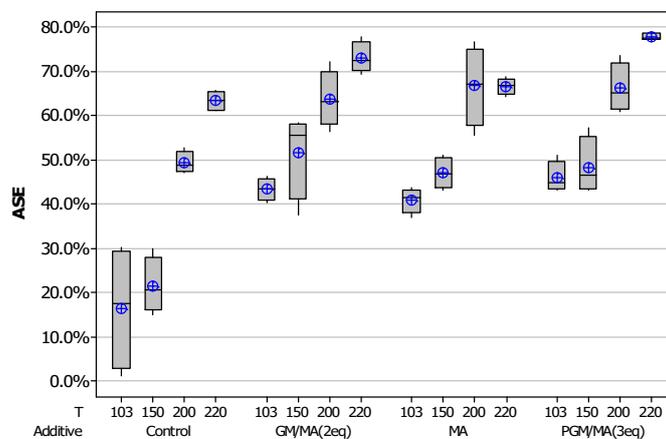


Figure 3 Anti-swelling efficiency (ASE) of additive-treated wood and wood control at different curing temperatures

ASE values after three leaching cycles for both additive-treated wood and wood control increased with the curing temperatures (Figure 3). All additive-treated wood presented better dimensional stability than control at all curing conditions indicating there was a beneficial effect between chemical and thermal modification in additive-treated wood, even though at higher thermal treatments (200 and 220°C), these differences became imminent in general. High ASE values had also been reported by previous related research (Iwamoto and Itoh 2005; Liu et al. 2012; Essoua et al. 2015) with maleic anhydride treated wood showing ASE values above 40%.

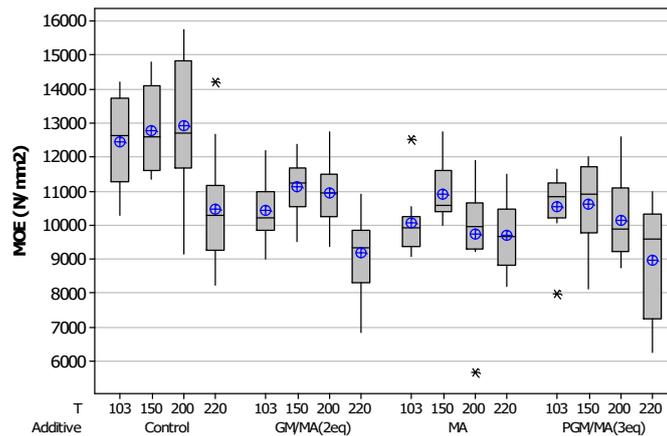


Figure 4 Modulus of elasticity (MOE) of additive-treated wood and wood control at different curing temperatures

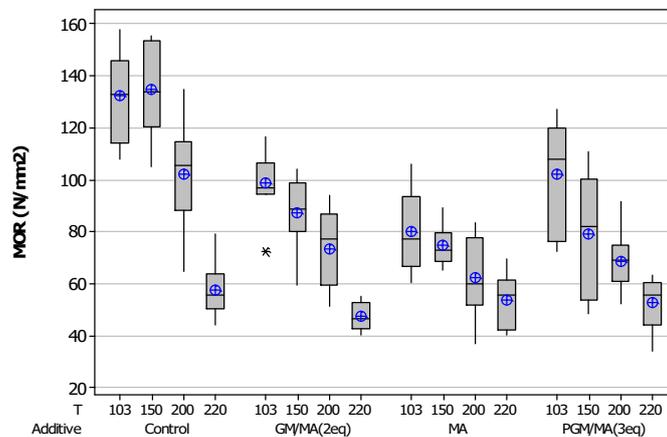


Figure 5 Modulus of rupture (MOR) of additive-treated wood and wood control at different curing temperatures

As a general trend, MOE/MOR values show that all additive-treated wood had lower MOE/MOR values than untreated control at all curing conditions (Figure 4 & 5). The acidic properties of all the additives used probably triggered/accelerated the hydrolysis of some cellulose and hemicelluloses which then led to a decrease in wood mechanical properties. On the other hand, a slight increase of MOE values at 150°C curing condition for all additive-treated wood and controls occurred. These increments were probably rendered by the increase of additive fixation in wood (higher Δm after leaching value) which was observed at this curing condition. The increase of wood crystallinity at this condition was also a potential factor supporting this increment of MOE and appears in accordance with the research from Yildiz and Gümüşkaya (2007) quoted that beech wood reached maximum crystallinity when heated at 180°C for 6 h but decreased for longer durations and higher temperatures, particularly at 200°C for 10 h. Among the additive-treated

wood, MA-treated wood had lower MOE/MOR values at almost all curing conditions. Hydrolysis of MA in water producing maleic acid (Essoua et al. 2015) was the main reason for the lowest MOE/MOR values of MA-treated wood. At 200°C curing condition, the effect of thermal-induced degradation became obvious when MOR values of wood control at the same temperature decreased by 22% compared to control at 103°C. On the other hand, the more thermo-stable (had higher Δm values) and the less acidic properties of PGM/MA_(3eq) and GM/MA_(2eq) compared to MA-treated wood generated a slight decrease of MOE values at this curing condition. However, due to an intense thermal-induced mechanical degradation of all additive-treated wood and control at 220°C curing condition, both MOE and MOR values for all samples were in the same range.

Data concerning decay test against *Trametes versicolor* and termite test against *Reticulitermes flavipes* are reported in Figure 6 - 9.

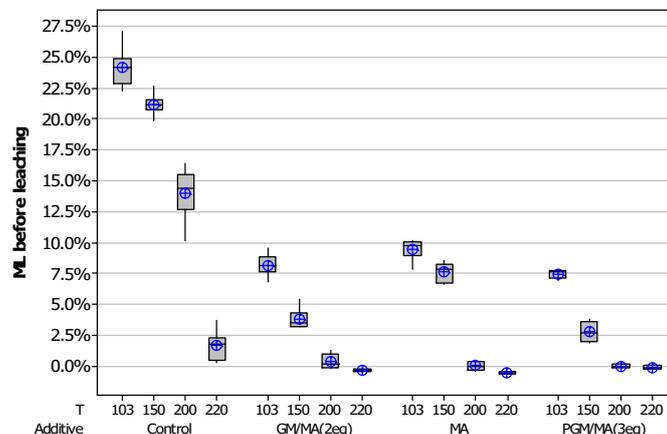


Figure 6 Mass loss due to decay before leaching of additive-treated wood and wood control at different curing temperatures

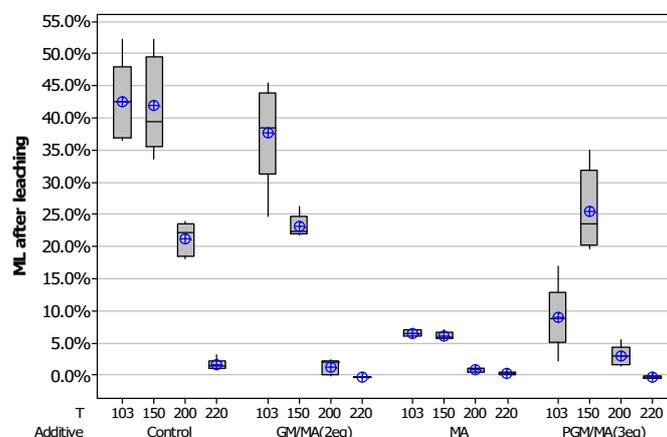


Figure 7 Mass loss due to decay after leaching of additive-treated wood and wood control at different curing temperatures

Trametes versicolor (Tv), is a white rot fungus used in several standards to evaluate both natural (EN 350, 2016) and conferred durability (EN113, 1996) of hardwoods, has been shown to be rather discriminant for beech modified with additives and heat treatment (Salman et al., 2017).

According to data, decay resistance against Tv for all samples before and after leaching of additive-treated wood and controls increased (mass loss decreased) with the increase of curing temperature (Figure 6 & 7). At the same condition, ML of virulence samples observed before and after leaching were 29.7 ± 1.3 and $51.2 \pm 3.5\%$, respectively. Based on the previous leaching data (Table 1), even though PGM/MA_(3eq) and GM/MA_(2eq)-treated wood had better resistance against leaching at 150°C, however, their performance against decay were not enough to reach a high durability [durability class 1 (EN 350 2016)]. On the other hand, the highest acidic properties of the MA-treated wood compared to PGM/MA_(3eq) and GM/MA_(2eq)-treated wood, permitted the treated wood to have more biological resistance even after leaching. At 200°C curing condition, all additive-treated wood before and after leaching presented lower mass losses compared to control, showing that the synergic effect of chemical and thermal modification had taken place at this temperature. Even though decay resistance of wood control at different curing conditions also increased, however its ability to produce efficient decay resistance was still insufficient. Therefore, thermal treatment alone at 200°C under inert condition was not enough to protect beech wood against white-rot fungus. On the other hand, at the highest thermal process (220°C), the increase in decay resistance not only happened on the additive-treated wood (due to the intensive thermochemical modification), but also on wood control convincing a general knowledge that thermally-treated wood has good decay resistance property. Further, the more intensive decay resistance of those additive-treated wood was also similar with the research from Iwamoto and Itoh (2005), reporting that maleic anhydride-treated wood (WPG = 15%) cured at 180°C had better decay resistance than cured at 150°C. Salman et al. (2017) also had similar results for their polyglycerol-methacrylate (PGMA) and polyglycerol-maleic anhydride (AM/PG)-treated wood at the same impregnating solution concentration (10% w/w) and temperature (220°C).

Durability against termite *Reticulitermes flavipes* was evaluated by non-choice test (Figure 8 & 9). Results revealed that all additives-treated wood after leaching have better resistance against termite than wood control without additive at all curing temperatures (Figure 8). Reduction of the mass losses (ML_t) of additive-treated wood for all curing temperatures ranged between 54 – 78% compared to the wood control at 103°C. Similarly, to the results obtained by Salman et al. (2017), the best results were obtained for samples treated at 220°C in the presence of the different additives, while, controls treated at 220°C were more susceptible to degradation by termites.

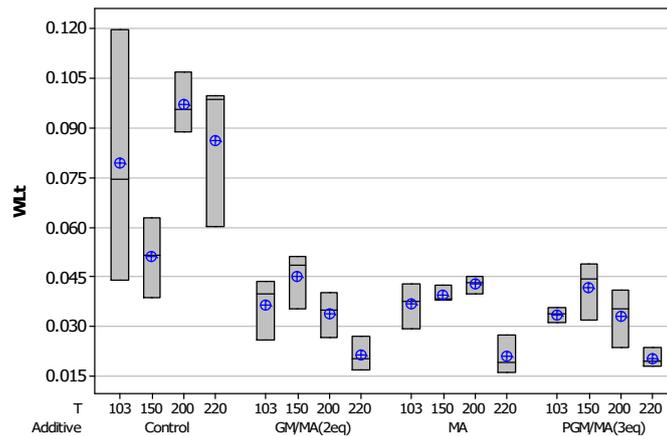


Figure 8 Mass loss due to termite attacks of additive-treated wood and wood control at different curing temperatures after leaching

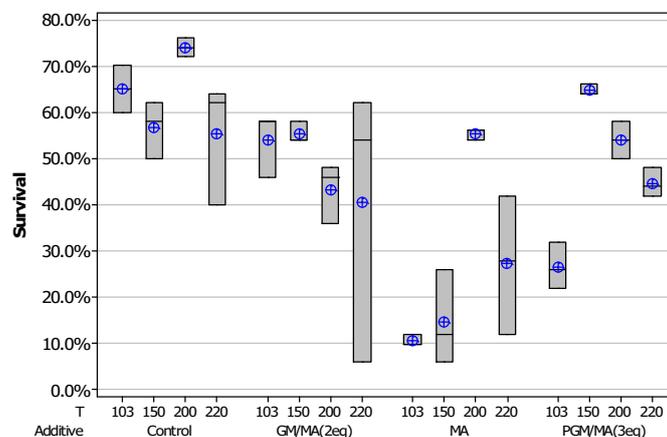


Figure 9 Survival rate of termite after attacking the additive-treated wood and wood control at different curing temperatures

At 103°C curing condition, the mass loss values of additive-treated wood decreased to less than 50% compared to untreated wood (as virulence samples, $ML_t = 8.0 \pm 1.0$ %). The acidic properties of the additive solution could be a possible reason explaining this resistance at this low curing temperature, triggering low survival rate of termites (Figure 9). At 150°C, the resistance values decreased slightly, conversely increased at 200 and 220°C curing condition. In contrast, termite resistance of wood control increased at 150°C compared to other curing temperatures (103, 200 and 220°C). This phenomenon was also reported by Salman et al. (2017), where mass loss values due to the same termite attacks for wood control at 150°C were lower than at 103 (as untreated control), 200 and 220°C curing conditions for both before and after leaching. Further, Unsal et al. (2009) also quoted that pine wood treated at 150°C had significant lower mass loss against termite *Reticulitermes flavipes* (Kollar) than treated and

untreated wood at 120°C. From this research, it is assumed that the increase in termite resistance at 150°C could be related to an increase in wood crystallinity, where a maximum protection against termites for wood control can occur under this experimental condition. On the other hand, higher mass loss values of the control at 200 and 220°C curing condition could be due to the diminution of the hemicelluloses content resulting in weakening of the wood structure during modification process and formation of sugar by-products with appetent properties. Diminution of the hemicelluloses content could trigger effective degradation of the cellulose by the termites (Bignell at al. 2010).

The synergy effect between chemical and thermal modification at 200 and 220°C on decay test results can also be calculated by Colby equation. According to Colby (1967), the additive effect of biocide combined treatments (A and B) can be evaluated according to the following formula:

$$E = X + Y - XY/100$$

where E is the expected protective effect the combination of two treatments A and B, X the measured protective effect of the treatment A, and Y the measured protective effect of the treatment B.

When the observed response is greater than expected, combination is synergy, when less than expected, it is antagonism, and when the observed and the expected response are similar, the combination is additive. By applying this equation on decay and termite test results in this research, a protective effect of the modified wood from different treatments against fungi or termite can be estimated on the measured mass loss after exposure of the treated samples to different degrading agents (Eq. 10).

$$E_{F \text{ or } T} = 100 - ML_{F \text{ or } T} \quad (10)$$

where ML_F is the mass loss after exposure to fungi and ML_T is the mass loss after exposure to termites.

Effect of the chemical modification alone can be estimated on the basis of treatments performed at 150°C, where degradation reactions due to thermal modification are weak (Table 1 & 2). Whereas, effect of thermal modification alone can be evaluated directly by treatment of control at different temperatures (200 and 220°C).

Based on the decay test results, after substituting the protection values of each treatment at 150°C and control at 200 or 200°C to the Colby's equation, almost all the additive-treated wood had higher protection values than the estimated (Table 2). The calculation has confirmed that there was a synergistic effect between chemical and thermal modification at 200 and 220°C curing

temperatures.

Table 2 Effect of additive addition in wood combined with thermal treatment based on Colby equation on the decay test against *Trametes versicolor* data after leaching process

Treatment	ML (%)	Mean Protection Measured (%)	Mean Protection Estimated (%)	Effect
Control 103°C	42.4 ± 7.3		-	-
PGM/MA _(3eq) 150°C	25.5 ± 6.3	74.5	-	-
GM/MA _(2eq) 150°C	23.2 ± 1.8	76.8	-	-
MA 150°C	6.2 ± 0.5	93.8	-	-
Control 150°C	41.8 ± 7.5	58.2	-	-
Control 200°C	21.3 ± 2.6	78.7	-	-
Control 220°C	1.6 ± 0.9	98.4	-	-
PGM/MA _(3eq) 200°C	3.1 ± 1.8	96.9	94.6	Synergy
GM/MA _(2eq) 200°C	1.4 ± 1.2	98.6	95.1	Synergy
MA 200°C	0.8 ± 0.3	99.2	98.7	Synergy
PGM/MA _(3eq) 220°C	-0.2 ± 0.2	100.2	99.6	Synergy
GM/MA _(2eq) 220°C	-0.2 ± 0.1	100.2	99.6	Synergy
MA 220°C	0.4 ± 0.2	99.6	99.9	Antagonist

Because of a low thermal stability of MA-impregnated wood at high temperature (Bodirlau et al. 2008), MA-impregnated wood has lower protection measured than the estimated. Synergistic effects were not shown using Colby's equation in the case of termite test, because of wood control at 200 and 220°C had lower termite resistance than control at 150°C. Therefore, this negative effect of thermal modification on the termite resistance could not be envisaged to play synergistic effect with the chemical modification, which conferred higher durability to wood.

FTIR spectra of wood samples treated with the different additives and subjected to the different curing temperatures indicated in all cases an increase of the band at 1733 cm⁻¹ corresponding to the carbonyl stretching band associated with maleic acid derivatives confirming modification of wood cell wall polymers. It is however difficult to highlight more precisely the reasons of increased biological durability observed with increase of curing temperature on the sole basis of FTIR analysis.

4. Conclusion

Results have disclosed that the addition of low concentration additives based on *in-situ* polymerization reaction (PGM/MA_(3eq) or GM/MA_(2eq)) or MA-based esterification into beech wood combined with thermal treatment permitted some improvements on the properties of the

modified wood compared to thermally modified beech without additive. According to the Colby equation on decay test results, the synergic effect of combination of thermal and chemical wood modification was observed at 200 and 220°C curing condition. At these conditions, thermochemical modified beech have better properties in dimensional stability (>60%), decay resistance after leaching process against *Trametes versicolor*, and termite resistance against *Reticulitermes flavipes* compared to wood control at 103°C. However, due to acidic property of additive solution and the effect of thermal degradation, MOE and MOR values decreased by approximately 25% and 60%, respectively.

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c. Conclusion

Based on the modification performed in this study, characteristics of additives and the modified woods could be summarized as the following:

- Penetration of the additive into the wood was observed by a proportional increase of WPG or mass changes (Δm) values with the increase of bulking or dimensional changes (ΔV).
- PGM/MA_(3eq) and GM/MA_(2eq)-treated wood had similar mass changes (Δm) values for a given curing temperature, indicating presumably a similar polarity between each other.
- The lower flash point (103°C) and boiling point (202°C) of maleic anhydride triggered lower mass changes (Δm) of MA-treated wood in comparison to the others.
- Temperature at 150°C was considered as temperature where the better fixation of the additives in wood occurred, decreasing drastically mass loss due to leaching. PGM/MA_(3eq) and GM/MA_(2eq)-treated wood have better leaching resistance than MA-treated wood.
- At lower curing temperature (103°C), PGM/MA_(3eq) and GM/MA_(2eq)-treated wood tended to have higher wettability than untreated wood or MA-treated wood. While at 150°C, PGM/MA_(3eq)-treated wood have similar wettability with untreated wood, but lower (higher contact angle) than MA or GM/MA_(2eq)-treated wood.
- All additive-treated wood had higher ASE values than untreated wood or thermally treated wood at the same curing temperature. Similar ASE values were observed for all additive-treated wood at the same curing temperature.

- MOE/MOR values of additive-treated wood were lower than untreated wood or thermally treated wood. However, similar MOE/MOR values of additive-treated wood and thermally treated wood were observed at 220°C curing condition.
- Decay resistance against CV was significantly higher for additive-treated wood than untreated wood or thermally treated wood. The highest durability against decay of additive-treated wood was taken place at the temperature of 200 or 220°C.
- Termite resistance against *Reticulitermes flavipes* indicated that all additive-treated wood had higher resistance against termites than untreated wood or thermally treated wood. PGM/MA_(3eq) and GM/MA_(2eq)-treated wood presented higher survival rate of the termites in comparison with MA-treated wood, indicating a possibility to be used as non-biocide wood preservation treatments.
- Modification occurred in wood due to additive was evidenced through characteristic absorptions emerged in FTIR spectra of the modified wood.

II.2.3 Paper 3

a. Introduction

This Paper 3 reported an advanced durability test against termite in the field for the selected additive-based wood modification treatments of the Paper 1, Paper ECWM9 (Appendix 1), and Paper IRG/WP50 (Appendix 2) which also supported by various parameter analysis results (Appendix 3 – 20) and descriptive analysis data of various parameter analysis (Table 4).

The location of the field test was at Arboretum in the Faculty of Forestry, Bogor Agricultural University, Indonesia. Duration for this field test took almost one-year period (347 days). Meanwhile, a dominant termite at the location was from the species of *Macrotermes gilvus* Hagen (Figure 32).

To prove more profoundly the synergistic effect between mild chemical and thermal treatment stated in the Paper IRG/WP50 (Appendix 2), additional temperature at 180°C was also tested in this study. Additive solution concentrations (PG-MA or Gly-MA) were varied at 10 and 40% w/w. During modification, a bigger sample size of wood measuring 190 × 100 × 20 mm³ (L, R, T) was used in this experiment. Meanwhile, prior to the field test, the wood samples (the additive-treated woods, untreated woods, and thermally treated woods) were cut into a specified size, 190 × 20 × 10 mm³ (L, T, R). The wood was buried 150 mm vertically below the ground level. AWWPA E7-07 was used for the rating system of the degradation level undergone on the wood samples after the field test.

Table 4: Descriptive analysis among PG-MA, Gly-MA, and MA-treated wood properties.

No	Parameter Analysis	103°C			150°C			200°C			220°C			Dominant
		PG-MA	Gly-MA	MA										
1	WPG/ Δm	+++	+++	++	+++	+++	++	++	+	-	-	--	---	PGMA
2	ML TGA				+++	++	+	-	--	---	--	--	---	PGMA
3	Bulking (B)/ Volume change (ΔV)	++	+++	++	++	+++	++	++	++	-/+	+	+	-	Gly-MA
4	Swelling (S)	--	--	--	--	--	--	--	--	--	--	--	--	All
5	Density	+++	++	+++	+++	++	+++	++	++	+++	++	++	+++	MA
6	Density Changes (Δd)				-	-	-	--	--	---	---	---	---	PGMA/ Gly-MA
7	Leaching (Leachability)	---	---	---	-	-	---							PGMA/ Gly-MA
8	Δm after leaching	+	+	+	++	++	+	+/-	-	---	--	---	---	PGMA
9	Product Leaching	--	--	--	-	--/+	--	-	-	--	-	--	---	PGMA
10	ASE (Cycle 3)	++	++	++	++	++	++	+++	+++	+++	+++	+++	+++	All
11	Wettability	++	++	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	All
12	MOE	-	-	-	-	-	-	-	--	--	--	--	--	PGMA
13	MOR	-	--	--	-	-	--	---	---	---	---	---	---	PGMA
14	Decay Before Leaching	++	++	++	++	++	++	+++	+++	+++	+++	+++	+++	All
15	Decay After Leaching	+	+	++	+	++	+++	+++	+++	+++	+++	+++	+++	MA
16	Termite	++	++	++	+	++	++	+	++	++	++	+++	+++	Gly-MA/ MA

**Figure 32:** *Macrotermes gilvus* Hagen (Fam. Termitidae) in Bogor, Indonesia

a. Paper 3

Resistance against Subterranean Termite of Beech Wood impregnated with different derivatives of Glycerol or Polyglycerol and Maleic Anhydride followed by Thermal Modification- A Field Test Study

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Keywords: chemical modification, *Fagus sylvatica*, field test, glycerol, maleic anhydride, polyglycerol, termite resistance, thermal treatment

Abstract

Termite resistance of European beech (*Fagus sylvatica*) modified with a combination of chemical and thermal modifications has been investigated in field tests. Modification was performed by impregnating different aqueous solutions of glycerol maleate or polyglycerol maleate at different concentrations (10 or 40%, w/w) into the wood, followed by thermal treatment at different temperatures (180, 200, or 220°C). Field test was conducted for one-year at Bogor the West Java, Indonesia. The results reveal that all wood samples treated by the combination of chemical and thermal modification presented significantly higher termite resistance than thermally modified and untreated wood samples. Among the different curing temperatures tested, the temperatures of 200 and 220°C -resulted in better performances with mass losses due to termite attacks less than 5%.

1. Introduction

European beech (*Fagus sylvatica*) is known as one of the most important hardwood species in Europe. It covers about 12 million ha of territory in the West and Central Europe (CapDecision 2010), and is particularly abundant in Central Europe with an area of more than 300 000 km² (Leuschner et al. 2006). It is used for various applications such as furniture, flooring, decorating material, siding, chairs, table, tools, toys or musical instruments. However, its low dimensional

stability and poor durability to fungi and insects limit its applications, particularly for exterior applications. Numerous research have been conducted to improve wood dimensional stability and biological durability, including thermal and chemical modifications considered as environmentally friendly alternative to classical treatments based on biocides (Schultz et al. 2008; Gérardin 2016). However, even if dimensional stability and decay durability are generally improved, termite durability can be achieved only with chemical modification involving impregnation of wood with huge amounts of chemicals, while, thermal modifications alone have no effect on termite durability improvement. Chemically modified wood such as acetylated, furfurylated or DMDHEU have been reported to be resistant to termite attacks (Hadi et al. 2005; Militz et al. 2011; Bongers et al. 2015). This was not the case for heat-treated wood for which it could be of interest to improve durability of heat-treated wood (Mburu et al. 2007, Shi et al., 2007, Surini et al. 2012, Sivrikaya et al. 2015). Regarding to the above mentioned issues, it has been recently reported that combination of a first wood impregnation with 10% aqueous solution of polyglycerol maleate initially investigated as additive to fix boron (Salman et al. 2014), followed by thermal modification at 200 or 220°C could be an attractive alternative to improve termites durability of heat-treated wood (Salman et al. 2017). Further studies made by the same group indicated that utilization of glycerol maleate instead of polyglycerol maleate leads also to the development of combined treatments involving light chemical modification and thermal modification, improving wood resistance against the subterranean termite *Reticulitermes flavipes* in the laboratory test (Mubarok et al. 2019a, b). In order to evaluate more deeply the efficacy and the potentiality of such treatments, wood samples initially impregnated with a 10 or 40 % glycerol or polyglycerol maleate aqueous solution followed by thermal modification at different temperatures (180, 220 and 220°C) were subjected to termite's attacks under field test condition in tropical area.

2. Experimental

2.1 Synthesis of additive and preparation of impregnation solutions

Polyglycerol (PG) was furnished by Inovyn (Belgium) as a mixture of compounds with an average molecular weight (Mw) of 242 g mol⁻¹ (degree of polymerization ~ 3). Maleic anhydride (MA) and glycerol (Gly) were purchased from Sigma-Aldrich Chimie SARL (France).

Polyglycerol maleate (PG-MA) was made according to the method of Roussel et al. (2001). One mol of polyglycerol was reacted with 2 mol of maleic anhydride and was heated at 80°C for 3

hours. The reaction was stopped after disappearance of ATR-FTIR absorption of carbonyl group from pure anhydride maleic reagent at about 1780 and 1853 cm^{-1} , and appearance of the characteristic ester band of PG-MA product at about 1715 cm^{-1} . The product was directly used without further purification and dissolved into distilled water for the final concentration of additive solution of 10 or 40% w/w.

Glycerol maleate (Gly-MA) additive was made by reacting 1 mol of glycerol with 2 mol of maleic anhydride under continuous mixing at 80°C for 3 hours. The reaction was terminated after disappearance of ATR-FTIR absorption of carbonyl group from pure anhydride maleic reagent at about 1780 and 1853 cm^{-1} , and a clear appearance of a characteristic ester band of Gly-MA product at 1715 cm^{-1} . The product was directly used without further purification and dissolved into distilled water for the final concentration of impregnating solution of 10 or 40% w/w.

2.2 Wood modification

Defect-free beech wood blocks in size of 190 × 100 × 20 mm^3 (L, R, T) were oven dried at 103°C and weighed (m_0) and their volumes were recorded (V_0). Two blocks were placed in an autoclave under vacuum (8 to 10 KPa) for 45 min, then were impregnated with 10 or 40% w/w aqueous additive solution for 1 hour under vacuum (5 to 10 KPa). Afterwards, the pressure was brought up to atmospheric pressure and the samples were placed under pressure (1200 KPa) for 1 hour. Finally, the pressure was released to atmospheric pressure and the samples removed from the autoclave and their wet masses were measured (m_1). The blocks were conditioned for about 60 hours at room condition. The blocks were heated in the autoclave with programmed temperatures under nitrogen condition. The autoclave temperature was increased by 0.5°C min^{-1} to a temperature of 40°C and kept for 10 h, then increased by 0.5°C min^{-1} to temperature of 120°C and kept for 12 h, and increased by 0.5°C min^{-1} to final temperature (180, 200 or 220°C depending on the level of modification desired) and kept for 20 h. Finally, the autoclave temperature was cooled to room temperature, and the blocks were removed and weighed (m_2). Wood blocks were also heat treated at the different temperatures without additives impregnation.

Retention of the additive and mass changes after thermal process (Δm) of untreated and additive-treated wood curing at the different temperatures were calculated as follows (Eq. 1 & 2):

$$\text{Retention (Kg.m}^{-3}\text{)} = [(m_1 - m_0)/V_0] \times ([\text{Additive}]/100) \quad (1)$$

$$\Delta m (\%) = 100 \times (m_2 - m_0)/m_0 \quad (2)$$

where m_0 is the initial mass of wood at 103°C before treatment, m_1 the wet mass of the additive-impregnated wood just after impregnation at room temperature, V_0 the dry volume (103°C) of wood before impregnation, [Additive] the concentration of additive solution (10 or 40% w/w), m_2 the dry mass of additive-treated wood or untreated wood at each curing condition (180, 200, or 220°C).

2.3 Field test



Figure 1. Samples position set during graveyard test

Wood blocks (thermally additive-treated wood, thermally treated, and untreated) of initial size of $190 \times 100 \times 20 \text{ mm}^3$ (L, R, T) were cut to produce sticks of $190 \times 20 \times 10 \text{ mm}^3$ (L, T, R). The sticks were oven dried at 103°C, weighed (m_3) and graveyard tested for almost 1 year (347 days). The samples were buried 150 mm of below the soil level, and the remaining 40 mm being above the soil level. Thermally additive-treated and thermally treated samples were buried randomly with distances among the samples of about 300 mm, while untreated samples were set in every area of the field test (Figure 1). Test site was located at the field test of the Faculty of Forestry Bogor Agricultural University, Bogor, Indonesia. The dominant subterranean termite species identified in this area was *Macrotermes gilvus* Hagen. After the field test period was completed, the samples were removed and cleaned by washing them with water. The samples were room conditioned and

dried at 103°C until constant weight (m_4). Mass loss due to termite attacks was calculated according to following formula (Eq. 3)

$$ML (\%) = 100 \times (m_3 - m_4) / m_3 \quad (3)$$

where, ML is the mass loss due to termite attacks, m_3 the dry mass of wood sample before field test, and m_4 the dry mass of wood sample after field test. Rating of the attack was evaluated according to E7-07 AWP standard (2008) (Table 1).

Table 1. Termite rating scheme according to E7-07 AWP standard (2008)

Rating	Description
10	Sound.
9.5	Trace, surface nibbles permitted
9	Slight attack, up to 3% of cross sectional area affected.
8	Moderate attack, 3 – 10% of cross sectional area affected.
7	Moderate/severe attack and penetration, 10 – 30% of cross sectional area affected.
6	Severe attack, 30 – 50% of cross sectional area affected.
4	Very severe attack, 50 – 75% of cross sectional area affected.
0	Failure.

2.4 Statistical Analysis

Minitab 16 software was used for data processing and analyzing. Two-way ANOVA analysis of variance with ($\alpha=0.05$) was conducted for identifying differences among the additives, the curing temperatures, and interaction between both of them. Tukey multiple range test ($\alpha=0.05$) was chosen for identifying difference in response individually.

3. Results and Discussion

Wood characteristics after the different treatments are presented in Table 2.

Retention value of the impregnated additive increased with the increase in the additive concentration. Based on these retention values, weight percent gain (WPG) at 103°C before thermal modification was estimated to be approximately 11 to 13% and 36 to 56% for additives concentration of 10 and 40%, respectively. Mass change (Δm) of untreated wood subjected to different curing temperatures decreased as the curing temperature increased. At 180°C, the mass change was remained weak with value around -1.4%, while important degradation up to 15.7% were noticed at 220°C. Additive treated wood at 10% presented similar mass change as thermal treated samples. Samples cured at 103°C presented lower mass changes than those treated at

220°C. Additive treated wood at 40% presented similar mass change independently of the curing temperature indicating probably a higher sensitivity of the impregnated polymer to temperature explaining why effect of treatment temperature was not visible on wood components degradation. Between the two additives used, PG-MA-treated wood presented slightly lower degradation than Gly-MA-treated wood, which may be due to the already polymerized structure of PG resulting from etherification reaction of glycerol with the loss of water.

Table 2. Characteristic of treated wood due to modification

Treatment		Retention (Kg m ⁻³)	Δm (%)*
Impregnation Solution	Curing Temperature (°C)		
None	103	-	0.00 ± 0.00
None	180	-	-1.41 ± 0.08
None	200	-	-7.77 ± 0.21
None	220	-	-15.67 ± 0.13
Gly-MA 10%	180	73.41 ± 1.75	-2.55 ± 0.39
Gly-MA 10%	200	73.46 ± 1.52	-4.87 ± 0.19
Gly-MA 10%	220	71.24 ± 1.14	-9.90 ± 0.75
Gly-MA 40%	180	273.2 ± 1.63	22.32 ± 0.24
Gly-MA 40%	200	328.3 ± 16.9	26.53 ± 0.52
Gly-MA 40%	220	315.0 ± 8.27	22.03 ± 1.35
PG-MA 10%	180	69.06 ± 0.40	-2.33 ± 0.53
PG-MA 10%	200	77.59 ± 1.52	-3.70 ± 0.17
PG-MA 10%	220	70.00 ± 0.35	-8.84 ± 0.05
PG-MA 40%	180	247.4 ± 30.8	26.33 ± 4.95
PG-MA 40%	200	301.1 ± 1.45	23.47 ± 0.14
PG-MA 40%	220	301.3 ± 8.79	23.74 ± 0.01

*each value was based on the average of two big samples measuring 190 × 100 × 20 mm³ (L, R, T);

Table 3 presents the aspect of wood samples after graveyard test.

Table 3. Durability of treated and untreated wood samples against termite in the field test

Treatment		ML _t (%) [*]	Mean Area (%) [*]	Mean Depth (%) [*]	Rating
Impregnation Solution	Curing Temperature (°C)				
None	103	99.59 ± 1.43 (a)	100.0 ± 0.0	100.0 ± 0.00	0
None	180	99.77 ± 0.72 (a)	100.0 ± 0.0	100.0 ± 0.00	0
None	200	100.00 ± 0.00 (a)	100.0 ± 0.0	100.0 ± 0.00	0
None	220	48.50 ± 30.71 (b)	16.8 ± 12.7	70.4 ± 33.94	4
Gly-MA 10%	180	14.64 ± 12.36 (c)	12.7 ± 12.4	26.8 ± 23.86	7
Gly-MA 10%	200	4.18 ± 1.15 (cde)	6.9 ± 12.6	17.8 ± 11.49	7
Gly-MA 10%	220	1.05 ± 0.41 (cde)	0.4 ± 0.4	8.6 ± 5.59	8
Gly-MA 40%	180	3.73 ± 1.30 (cde)	0.0 ± 0.0	0.0 ± 0.0	10
Gly-MA 40%	200	0.76 ± 0.14 (de)	0.0 ± 0.0	0.0 ± 0.0	10
Gly-MA 40%	220	0.07 ± 0.34 (e)	0.0 ± 0.0	0.0 ± 0.0	10
PG-MA 10%	180	14.14 ± 8.91 (cd)	5.7 ± 5.2	29.8 ± 21.64	7
PG-MA 10%	200	4.91 ± 1.35 (cde)	7.7 ± 18.1	6.8 ± 4.17	8
PG-MA 10%	220	2.15 ± 0.14 (cde)	0.1 ± 0.1	3.3 ± 3.26	8
PG-MA 40%	180	13.44 ± 13.47 (cde)	11.9 ± 13.0	20.4 ± 30.44	7
PG-MA 40%	200	1.73 ± 0.30 (cde)	0.0 ± 0.0	0.0 ± 0.0	10
PG-MA 40%	220	1.14 ± 0.23 (cde)	0.0 ± 0.0	0.0 ± 0.0	10

*each value was based on the average of 10 – 12 samples measuring 190 × 20 × 10 mm³ (L, T, R), Mean area is the average areas of all sample surfaces due to termite attacks, Mean depth is the average depths on wood surface of all samples due to termite attacks in cross section direction, Rating was based on mean depth area according to AWPA E7-07. Value followed by the same letter in the parentheses do not differ significantly ($\alpha = 0.05$) based on one-way ANOVA test using Tukey multiple comparison.

In all cases, the non-impregnated woods cured at different temperatures presented important mass losses after field test against termites. The non-impregnated woods heat-treated at 180 and 200°C were completely destroyed by termites, while non-additive woods treated at 220°C presented weight loss of 48%. The addition of additive in wood resulted in significantly lower mass losses due to termite attacks in comparison with untreated and thermally treated woods. The termite durability of additive-treated woods increased with treatment temperature and concentration of additive. Effect of additive concentration between solutions at 10 and 40% remains relatively weak, comparatively to the effect of the curing temperature. Similar results obtained from laboratory tests

were reported by Salman et al. (2017). In this study, the authors reported an improvement of termite durability of wood samples impregnated with polyglycerol methacrylate aqueous solution followed by thermal treatment at 220°C. Measurement of termite attacks (surface and depth penetration) and associated rating rate indicated clearly that wood blocks treated with 40% additive solutions presented the better durability against termite (Figure 2).

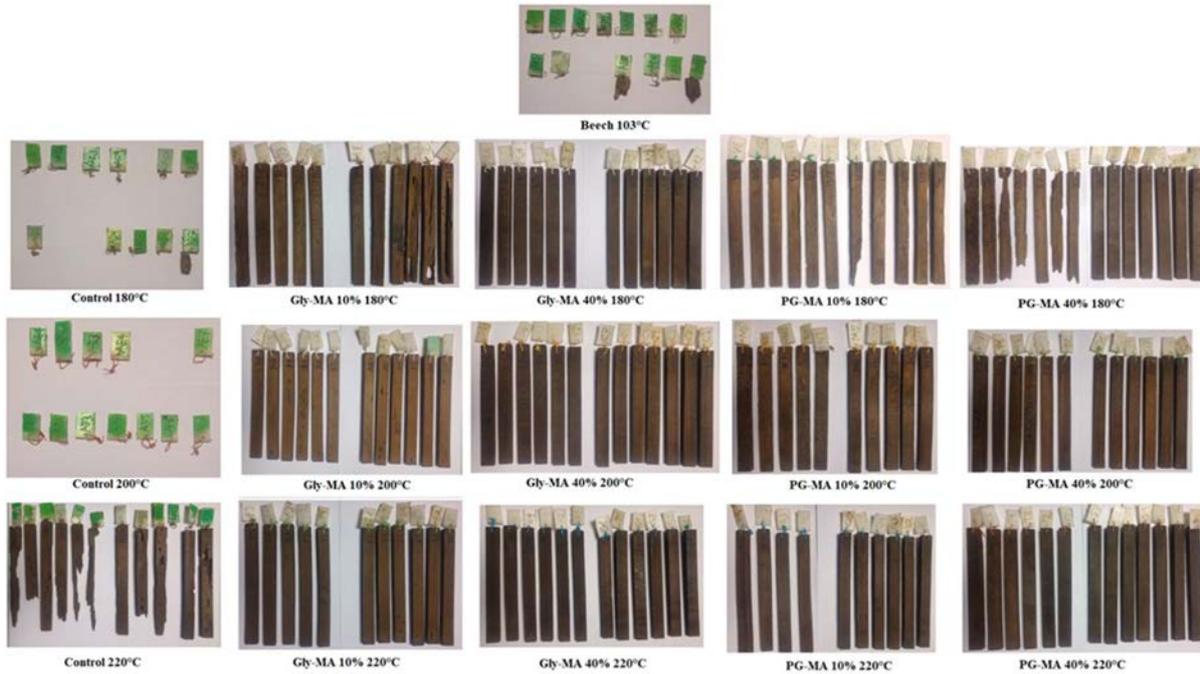


Figure 2. Samples appearance after field tests

Gly-MA presented better performance than PG-MA, wood sample treated with 40% PG-MA solution followed by heat treatment at 180°C being only partially protected. At lower additive concentration (10%), wood samples cured at 220°C presented mass losses of 1.05 and 2.15% for Gly-MA and PG-MA, respectively. Curing at 200°C led to partial protection of additive-treated woods with mass losses of approximately 4 to 5%. Even if improvement in termite resistance of the additive-treated wood at 200 and 220°C has not been clearly understood, it could be considered that the impregnated additives in their initial polymerized form or after thermal degradation could react with wood components or/and wood degradation products formed at these temperatures leading to a new material that termite are not able longer to digest. As a comparison, termite resistance of the additive-treated wood, particularly those impregnated with 40% solutions, followed with thermal modification at 200 or 220°C are similar with furfurylated wood with the highest modification level (WPG > 90%) which had been tested in the similar site area for 1 year

period (Hadi et al. 2005).

Table 4. Two-way ANOVA of wood mass losses (ML_t) due to graveyard test versus additives and curing temperatures (T)

Source	DF	SS	MS	F	P
Additive	4	17.4089	4.35223	487.01	0.000
T	2	1.0576	0.52882	59.17	0.000
Interaction	8	1.3960	0.17449	19.53	0.000
Error	165	1.4745	0.00894		
Total	179	21.3371			

S = 0.09453 R-Sq = 93.09% R-Sq(adj) = 92.50%

Additive	Mean	Individual 95% CIs For Mean Based on Pooled StDev
Control	0.827555	(*)
Gly-MA 10%	0.066221	(-*)
Gly-MA 40%	0.015197	(-*)
PG-MA 10%	0.070669	(*)
PG-MA 40%	0.054356	(*)

T	Mean	Individual 95% CIs For Mean Based on Pooled StDev
180°C	0.291438	(---*---)
200°C	0.223140	(---*---)
220°C	0.105822	(---*---)

Statistical analysis using two-way ANOVA shows that both additives (PG-MA or Gly-MA) and the applied temperatures (180, 200, or 220°C) presented statistically significant for their interactions (F value > P value) (Table 4). These interactions mean that the effect of additive on the mass loss of the modified wood due to termite attacks is dependent on the applied temperature and vice versa. Between the two variables tested (additive and curing temperature), the additives gave higher influence on the mass losses of the modified wood (F value >> P value) than the curing temperatures. Among the applied additives, both PG-MA and Gly-MA with the two applied concentrations (10% or 40%) were not significantly different one and each other on the mass losses of the modified wood. Meanwhile, effect of the three applied curing temperatures presented significant different one and each other on the mass losses of the modified wood.

4. Conclusions

The results revealed that wood impregnated with glycerol or polyglycerol maleate aqueous solution (10% or 40%, w/w) followed by thermal modification at 180, 200, or 220°C presented significantly

higher durability against subterranean termite compared to untreated wood or thermally modified wood. Glycerol maleate and polyglycerol maleate-treated wood presented similar characteristic. Among the applied thermal conditions, additive-treated wood at 200 and 220°C presented better termite resistance property. Based on already existing non-biocide treatments, combination of thermal modification and chemical modification using low concentration of additives permitted to improve durability of heat-treated wood to termites, which was not possible using only thermal modification, while reducing the cost of treatment comparatively to acetylation or furfurylation treatments offering new perspectives for wood protection.

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a. Conclusion

This paper has confirmed our previous decision taken in the Paper IRG/WP50 (Appendix 2), that the synergistic effect between mild chemical and thermal modification was occurred at 200 or 220°C, though the additive-treated woods treated at 180°C were still significantly lower mass loss value due to termite attacks in the field test than untreated wood or thermally modified wood treated at 220°C. Meanwhile, the highest modified wood occurred at the additive concentration of 40% w/w, which rating them as number 10 (no attacks, 1 – 2% small damage). In addition, there were no significant differences observed between the use of glycerol instead of polyglycerol in the formulation at the temperatures where the synergistic effect between mild chemical and thermal

modification occurred.

II.3. Conclusion

Based on the results obtained from the series of treatments in this Part I, the studies have evidenced and confirmed of certain previous research (Salman et al. 2016, 2017) that the incorporation of low quantity of the impregnated chemicals in the wood followed with thermal modification could generate the modified wood with better in physical and biological durability properties than untreated wood or thermally modified wood. However, due to the acidic properties of the chemicals/additives used and the effects of thermal degradation, mechanical properties of the additive-treated wood decreased considerably in comparison with untreated wood. Nevertheless, the decay resistance of thermally modified wood at 220°C presented similar mechanical properties of the additive-treated wood either at 200 or 220°C curing condition. This means that the existence of low quantity of additive could minimize the use of heating energy to improve biological durability properties of thermally modified wood. Among the additive used, Gly-MA and PG-MA-based additive presented better properties either in their modified wood properties or during modification process (easiness in preparation, cost of the process). In addition, in most cases, there were no significant differences between the used of glycerol or polyglycerol-based additives for their modified wood properties, especially for Gly-MA, PG-MA, PGM/MA_(3eq), and GM/MA_(2eq)-based additives.

CHAPTER III (Part II)

WOOD MODIFICATION BASED ON COMBINATION OF CHEMICAL TREATMENT USING GLYCEROL AND POLYGLYCEROL DERIVATIVES AND THERMAL MODIFICATION IN OPENED AND CLOSED SYSTEM, UP-SCALING PROCESS

III.1. Introduction

In this Part II, wood modification was carried out based on the Part I, aimed to perform wood modification into a bigger scale. The work was conducted at the laboratory of Wood Biology and Wood Product Technology, Faculty of Forestry, Göttingen University, in Germany. During this work, some additional wood modifications were also demonstrated, including comparison between wood modification under oven heating (OHT) in opened system and under pressurized steam (HPS) in closed system. The objective of these additional treatments was to improve wood thermo-chemical modification under lower curing condition. Therefore, variation in the chemical concentration and curing temperature under both systems was examined. In general, this Part II was divided into two proposed papers, Paper 4 and Paper 5.

Paper 4. Wood Modification Based on Glycerol-Maleic Anhydride and Maleic Anhydride in Opened and Closed System.

In this paper, the study investigated the screening treatments of wood modification based on the Gly-MA and MA-treated wood followed with different curing processes in opened or in closed system. The study was realized to know the better treatments for the next up-scaling process using the similar equipment, as well as to know the characteristic of wood modification under HPS in the closed system. In order to know the characteristic of these wood modifications, various parameter analysis during and after wood modification were examined, including physical, mechanical, chemical, and biological durability properties.

Paper 5. Properties of Thermo-chemically Modified Wood base on Vinylicglycerol and Vinylicpolyglycerol Derivatives under Oven Heating (OHT) in Opened System and Heat Pressurized Steamed (HPS) in Closed System.

In this paper, the study investigated characteristic of certain selected up-scaling treatments from some series of up-scaling treatments performed either based on the previous works (Paper 1 – 4) or some new developed treatments in bigger sample size. These selected up-scaling treatments were conducted under OHT in opened system or under HPS in closed system. For selecting the better treatments in this study, various parameter analysis during and after wood modification were demonstrated, including physical, mechanical, chemical, and biological durability properties.

III.2. Results

III.2.1 Paper 4

a. Introduction

In this Paper 4, the study investigated wood modification involving combination between chemical and thermal modification performed under oven heating (OHT) in opened system or under heat pressurized steam (HPS) in closed system. Since a thermal degradation undergoes higher in HPS in closed system than under OHT in opened system (Wentzel et al. 2018b), the idea of this comparative study was to investigate whether the modified woods generated from the wood chemical modification under HPS would have similar properties as the modified wood generated under OHT at higher thermal condition (as presented in the previous papers). Another objective of this study was to lower the curing temperature used of the previous papers (200 or 220°C) by increasing the chemical concentration during modification under OHT or by performing thermal treatment under HPS in closed system. Based on these backgrounds, the curing temperature in OHT was set at 120°C or 180°C using a common oven heating equipment under ambient pressure (Figure 33), with varying in chemical solution concentration at 10, 20, or 40% w/w for Gly-MA-based additive and 10, 20, or 30% w/w for MA-based additive. Meanwhile, treatment under HPS in closed system was performed at 150°C (350 KPa, 3 h, 75% RH) or 160°C (600 KPa, 3 h, 100% RH), or 180°C (600 KPa, 6 h, 60% RH) with similar chemical solution concentration used in the OHT. Treatment under HPS was conducted using autoclave which installed tandem with a steam producing boiler (Figure 34). In order to know the characteristic of these wood modifications, various parameter analysis during and after wood modification were conducted.

Due to similar properties of the wood treated either with Gly-MA or PG-MA in the previous papers, hence this study used only Gly-MA-based additive. In addition, MA-based additive as reactive in this system was also demonstrated in the single form.



Figure 33: Oven heating (OHT) equipment, Wood Biology and Wood Technology, Göttingen University, 2018



Figure 34: Autoclave for thermal wood modification, Wood Biology and Wood Technology, Göttingen University, 2018

b. Paper 4

Wood Modification Based on Glycerol maleate and Maleic Anhydride under Opened and Closed System

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Keywords: acidity, chemical modification, closed system, *Fagus sylvatica*, FTIR, glycerol, maleic anhydride, mechanical properties, opened system, physical properties, thermal treatment, *Coriolus versicolor*

Abstract

In this study, wood chemical modification under oven heating (OHT) in opened system and under heat pressurized steam (HPS) in closed system has been investigated. Wood modification was performed by impregnating European beech (*Fagus sylvatica*) in aqueous additive solution made from glycerol maleate (Gly-MA) or maleic anhydride (MA) as additive at different concentrations followed with curing condition under two different systems based on OHT in opened system at 120 or 180°C and HPS in closed system at 150, 160, or 180°C. Certain wood characterizations during and after modification, such as weight percent gain (WPG), mass changes and mass losses values after curing process, bulking values after modification, dimensional stability, weight loss due to leaching, functional group analysis by means of ATR-FTIR, decay durability test after leaching against *Coriolus versicolor*, and mechanical properties of certain HPS-modified wood have been examined. Results have revealed that wood treated under OHT presented higher mass change values (WPG after curing / Δm), higher bulking after curing, lower mass loss due to curing values, lower weight loss due to leaching, and lower acidity than wood treated under HPS. Modulus of elasticity of wood treated under HPS 160 and 180°C were slightly higher than untreated wood, however, modulus of rupture decreased considerably. Wood treated under HPS presented higher modification based on the FTIR analysis than wood under OHT. Decay durability of additive-treated wood under OHT 180°C and HPS mainly at 160 and 180°C at different concentrations were classified as very durable wood.

1. Introduction

It is already known recently that a modified wood, made from a combination of low concentration of chemicals impregnated into the wood followed with thermal modification, has better in biological

durability properties against decay and termites than wood with only undergoes thermal modification (Salman et al. 2016, 2017; Mubarak et al. 2019a, b). Since these observed thermo-chemical modifications effectively/synergistically undergo at higher temperature ($\geq 200^{\circ}\text{C}$) under inert atmosphere, it came to mind, this modification might be related to the minimum limit of mass loss of wood control (untreated chemical) at this thermal condition, in order to induce a preferable degradation with low concentration of the added chemical. In regards to this assumption, it was reported that thermal degradation of wood is higher under atmospheric condition (ambient) than under inert condition (Stamm 1956; Yildiz and Gümüşkaya 2007). Further, since the mass loss due to thermal modification has a proportional relationship with the properties of the thermally modified wood (Welzbacher et al. 2007), it is possible that a similar mass loss between thermal treatment under atmospheric pressure in air condition would be achieved at a temperature lower than treatment under inert condition, minimizing heating energy during modification. A similar effect as treatment under steam condition in closed system, wood degradation at this condition is higher than other treatments (Altgen 2016; Altgen and Militz 2016; Wentzel et al. 2018b, a). Based on this background, incorporation of chemical-impregnated wood with thermal modification under atmospheric pressure in opened system (oven) and under pressurized steam condition in closed system would be of interest and needed to be studied.

The objective of this study was to investigate differences in modification system and characterization between chemical-impregnated wood treated under oven heating system in atmospheric pressure (OHT) and under pressurized steam condition in closed system (HPS). Different chemical concentrations during modification and certain parameter analysis including physical, chemical, mechanical, and decay durability properties were evaluated.

2. Experimental

2.1 Sample preparation

European beach (moisture content, $\pm 11\%$) with free of defects was prepared and cut to specific size [$5 \times 25 \times 25 \text{ mm}^3$ and $180 \times 10 \times 10 \text{ mm}^3$ (L, T, R)]. Prior to the cutting process, the wood was conditioned at approx. $20^{\circ}\text{C}/60\%$ of relative humidity (RH).

2.2 Formulation

Glycerol maleate (Gly-MA) [glycerol was purchased from Sigma-Aldrich Chimie SARL (France)] was made by reacting 1 mol of glycerol with 2 mol of maleic anhydride under continuous mixing at 80°C for 3 hours. The reaction was then terminated after disappearance of ATR-FTIR absorption

of carbonyl group (C=O, stretch) from pure anhydride maleic reagent at about 1780 and 1853 cm^{-1} , and a clear appearance of a characteristic ester band (C=O, stretch) of Gly-MA product at about 1715 cm^{-1} . The product was directly used without further purification and dissolved into demineralized water so that the final concentration of impregnating solution was 10%, 20%, or 40% w/w.

Maleic anhydride/MA additive was made by dissolving maleic anhydride into distilled water so that the final solution concentration was 10%, 20%, and 30% w/w.

2.3 Wood modification

Beech wood samples were dried at 103°C (48 h), weighed (m_0), the volumes were measured (V_0), impregnated into different impregnating solutions under vacuum condition (5-10 KPa, 1 h), and followed by pressure conditions (1200 KPa, 1 h). After the pressure was reset to ambient, all samples were removed from the chamber, an excess of the impregnating solution on the samples was wiped-out, and each sample was re-measured for its wet weight (m_1) and wet volume (V_1). Afterwards, the samples that would be undergone oven heating (OHT) system were re-dried carefully at room condition (2-3 days), 40 (24 h), 60 (24 h), 80 (24 h), and 103°C (24 h), then weighed (m_2), and volumes were re-measured (V_2). Meanwhile, samples that would be undergone heat pressurized steam (HPS) system were dried in room temperature until lower than fiber saturation point. Samples for OHT were cured in normal oven drying at 120 or 180°C for 20 h, while, samples for HPS were undergone heating in closed system at 150°C (350 KPa, 3 h, 75% RH) or 160°C (600 KPa, 3 h, 100% RH), or 180°C (600 KPa, 6 h, 60% RH), followed with open drying at 103°C for 48 h. Finally, each cured sample was re-measured for its weight (m_3) and volume (V_3), then conditioned at room temperature.

From this modification, solution up-take and swelling due to impregnation were calculated as follows (Eq. 1 & 2):

$$\text{Solution up-take (\%)} = 100 \times (m_1 - m_0)/m_0 \quad (\text{Eq. 1})$$

$$\text{Swelling at saturation state (\%)} = 100 \times (V_1 - V_0)/V_0 \quad (\text{Eq. 2})$$

where, m_0 is the initial mass of oven-dry wood at 103°C, m_1 the wet mass of wood just after impregnation, V_0 the initial volume of oven-dry wood at 103°C, and V_1 the wet volume of wood after impregnation.

After drying process at 103°C before thermal treatment, weight percent gain (WPG) and bulking (B) values at 103°C were measured. Further, after curing process either by OHT or HPS, mass changes (Δm), bulking after thermal treatment (ΔV), and weight losses due to curing (WL) at OHT or HPS were calculated as follows (Eq. 3 – 7):

$$\text{WPG (\%)} = 100 \times (m_2 - m_0)/m_0 \quad (\text{Eq. 3})$$

$$\text{B (\%)} = 100 \times (V_2 - V_0)/V_0 \quad (\text{Eq. 4})$$

$$\Delta m (\%) = 100 \times (m_3 - m_0)/m_0 \quad (\text{Eq. 5})$$

$$\Delta V (\%) = 100 \times (V_3 - V_0)/V_0 \quad (\text{Eq. 6})$$

$$\text{WL (\%)} = 100 \times (m_2 - m_3)/m_2 \quad (\text{Eq. 7})$$

where, WPG is the weight percent gain value of impregnated wood at 103°C, B the bulking value of impregnated wood at 103°C, Δm the mass change/WPG value of impregnated wood after curing at OHT or HPS, ΔV volume change/bulking value after curing at OHT or HPS, WL the weight loss value of impregnated wood due to curing at OHT or HPS, m_2 and V_2 are the mass and volume of oven-dry wood at 103°C after impregnation, m_3 and V_3 the mass and volume of oven-dry wood after curing at OHT or HPS.

2.4 Leaching and Anti Swelling Efficiency (ASE) analysis

Leaching test referred to EN 84 (1997). All modified woods and controls were oven dried at 103°C, weighed (m_4), volumes measured (V_4), then submerged into the water in a different chamber with minimum volume five times of the total volume of samples per each treatment. Afterwards, all samples were introduced under vacuum at 5 – 10 KPa for 20 min, 2 h in room condition, changed the water, laid them for 24 h, the water was re-changed, laid them for 24 h, the water was re-changed again, and so forth for the rest seven times of water change in a total leaching period of 14 days. Then, the samples were dried at room temperature (2-3 days), 40 (24 h), 60 (24 h), 80 (24 - 48 h), 103°C (24 h), weighed (m_5), and the volume was measured (V_5). In order to know the acidity of leachate from the leaching test, the weight and pH of the leachate were measured for every water change period. From this leaching test, mass change after leaching (Δm_L), weight losses due to leaching (WL_L), bulking after leaching (ΔV_L), and acidity of the leachate ($[H^+]$) and pH of the total leaching solution were calculated as follows (Eq. 8 – 12):

$$\Delta m_L (\%) = 100 \times (m_5 - m_0)/m_0 \quad (\text{Eq. 8})$$

$$WL_L (\%) = 100 \times (m_4 - m_5)/m_4 \quad (\text{Eq. 9})$$

$$\Delta V_L (\%) = 100 \times (V_5 - V_0)/V_0 \quad (\text{Eq. 10})$$

$$\text{mg eq } H^+ \text{ leachate} = \text{total mol } H^+ \text{ of leachates} \quad (\text{Eq. 11})$$

$$\text{pH leachate} = -\log [H^+] \text{ leachate} \quad (\text{Eq. 12})$$

$$\text{Water capture} = 100 \times (m_6 - m_4)/m_4 \quad (\text{Eq. 13})$$

where, Δm_L is the mass change value of wood sample after leaching, W_{L_L} the mass loss value of wood sample after leaching, ΔV_L the volume change/bulking value of wood sample after leaching, m_4 the dry mass of sample before leaching, m_5 dry mass of sample after leaching, V_5 dry volume of sample after leaching, milligram equivalent H^+ the sum of $10^{-pH} \times \text{volume (ml)}$ of each leachate in each water change, pH leachate the pH calculated as $-\log [H^+]$ of total leachate of the leaching test, $[H^+]$ the sum of $10^{-pH} \times \text{volume}$ of each leachate in each water change then divided by a total volume of leachate from the leaching test, water capture the amount of water captured at saturated state by wood sample, m_6 the mass of wet sample at saturated state at the end of the leaching.

With the same samples as the leaching test, ASE was measured at the end of the leaching test (at water saturated state). By recording the dry and wet volume of modified and untreated wood before and after leaching test, swelling (S) and ASE can be calculated as follows (Eq. 14 & 15):

$$S (\%) = 100 \times (V_w - V_d)/V_d \quad (\text{Eq. 14})$$

where S is the percentage of swelling of wood sample, V_d the dry volume of the sample, V_w the wet volume of the sample.

$$\text{ASE} = 100 \times (S_0 - S_1)/S_0 \quad (\text{Eq. 15})$$

where ASE is the anti-swelling efficiency of treated wood, S_0 the swelling of untreated wood, S_1 the swelling of treated wood.

2.5 Modulus of Elasticity (MOE) and Modulus of Rupture (MOR)

Mechanical properties measurement was referred to DIN 52186 (1978). In this screening test, only HPS samples were measured for their mechanical properties in consideration for their higher underwent thermal degradation than the OHT samples. The HPS modified woods, wood control, and untreated samples measuring $180 \times 10 \times 10 \text{ mm}^3$ (L, T, R) were placed in climatic room with a specific condition, at $20 \pm 1^\circ\text{C}$ and $65 \pm 3\%$ of relative humidity (RH), until constant mass. Prior to the measurement, the dimension of samples was re-measured for data input to the machine program. Afterwards, samples were measured for their increment in load and displacement values by means of ZWICK Z010 universal testing machine equipped with testXpert® II software. MOE and MOR were calculated automatically by the machine.

2.6 Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR spectra of the modified wood, wood control, and untreated wood were recorded on a Bruker Alpha Eco-ATR instrument. The spectra of wood samples powder were recorded in the range of 4000 – 400 cm^{-1} at a resolution of 4 cm^{-1} with an ATR cell.

2.7 Decay resistance properties against white rot

Durability against decay white rot fungus (*Coriulus versicolor*) was performed according to Bravery (1978) for twelve weeks incubation period, while, durability class referred to EN 350 (2016).

3. Result and Discussion

Modification analysis

Data concerning swelling during impregnation process are presented in the Figure 1

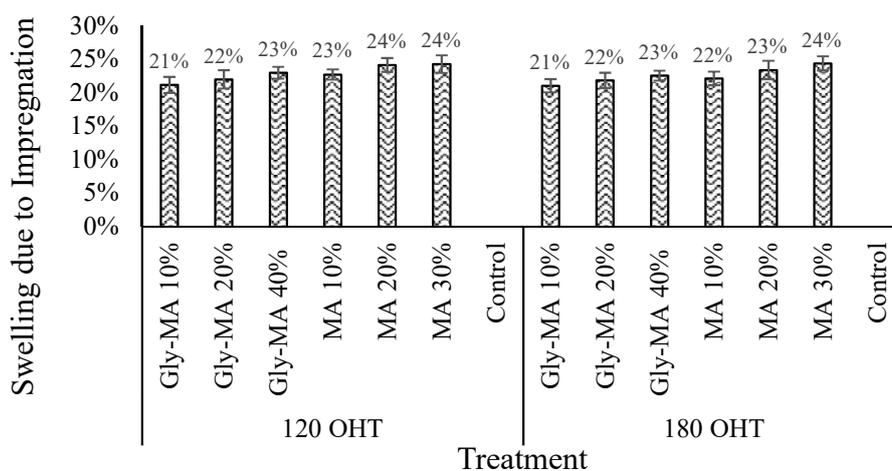


Figure 1 Swelling of the wood samples in different impregnating solutions

Results show that swelling values slightly increased as the increase of impregnating solution concentration. MA-based solution presented slightly higher swelling values than Gly-MA-based solution in the same level of concentration. A lower molecular size of the MA was presumably the main cause for its easy to penetrate into the wood cell wall than its ester form (Gly-MA), however, both of them presented in the similar range swelling values.

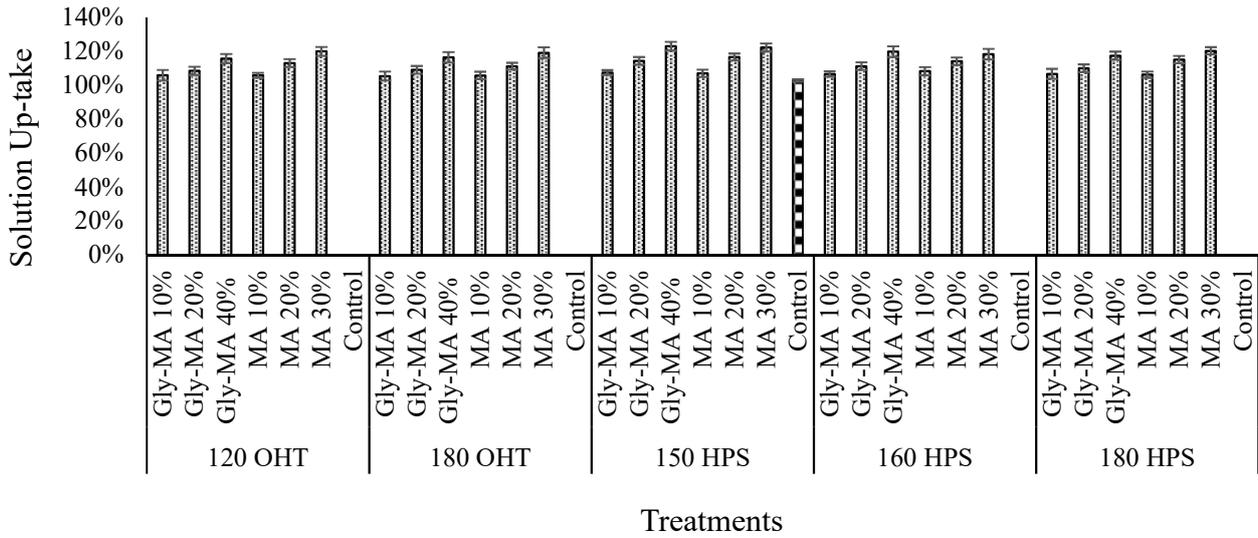


Figure 2 Solution up-take of different impregnating solution during impregnation

Solution up-take would be depended on the polarity, concentration, specific gravity, molecular size, and viscosity of the impregnating solution, the power of vacuum and pressure used, and contact time (aging time) between wood-solution. Similar trends as the swelling data, solution up-take increased as the increase of solution concentration (Figure 2). Even though comparable values between the two additives were observed in these solution up-take values, the higher swelling (penetration) of MA-impregnated wood have made higher solution up-take than Gly-MA-impregnated wood especially at higher concentration, Gly-MA 40% vs MA 30%. In overall, due to the solution densities, solution up-take values of the additive-treated wood were higher than water-impregnated wood.

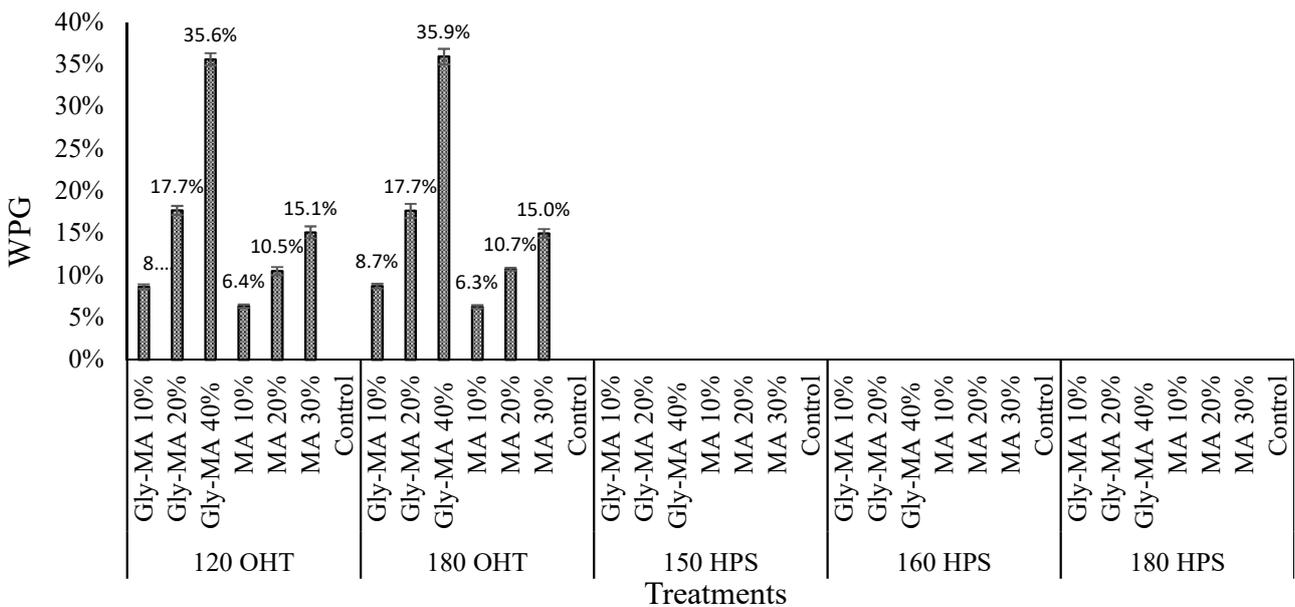


Figure 3 WPG at 103°C of different additive-treated wood with different additive concentrations

In the contrary to the solution up-take values, WPG at 103°C show that Gly-MA-treated wood presented higher WPG value than MA-treated wood at the same level of solution concentration. The lower WPG of MA-treated wood could be due to a lower flash point of MA ($\pm 102^\circ\text{C}$), triggering evaporation of MA during drying process, especially under oven heating (OHT) system. In this observation, treatment was only demonstrated for wood treated under OHT system. Since the wood would undergo water vapor pressure (steam) during HPS system, therefore, wood samples did not follow this pre-drying treatment (103°C).

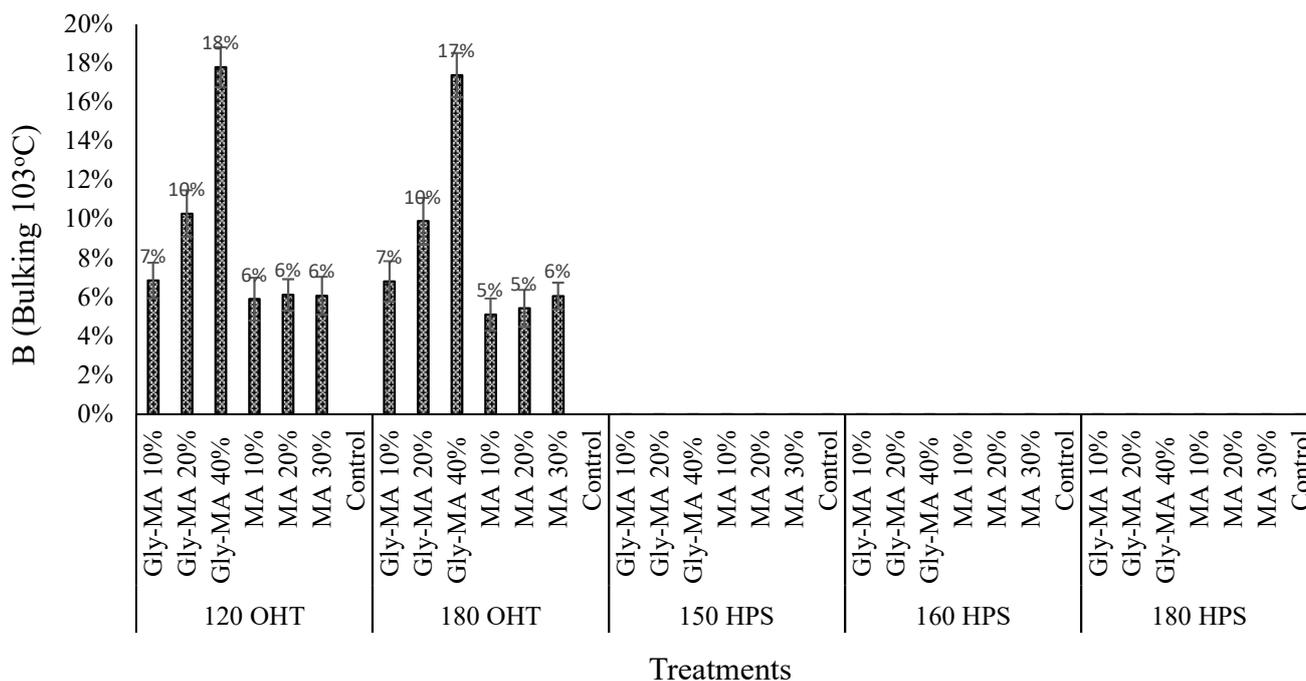


Figure 4 Bulking of different additive-treated wood at 103°C with different additive concentration. Data of bulking values increased as the increase of solution concentration, however, proportional increase was occurred particularly in wood impregnated with Gly-MA solution. Even though MA-treated wood presented slightly higher swelling during impregnation process than Gly-MA, it seems that the amount of MA did not generate higher bulking after drying at 103°C , indicating possibly due to lower in molecular weight of MA compared to Gly-MA in wood in the same level of modification and/or diminution of MA due to evaporation during drying process. The similar reason as WPG data, the wood, which are undergoing HPS system, were not tested for their bulking at 103°C .

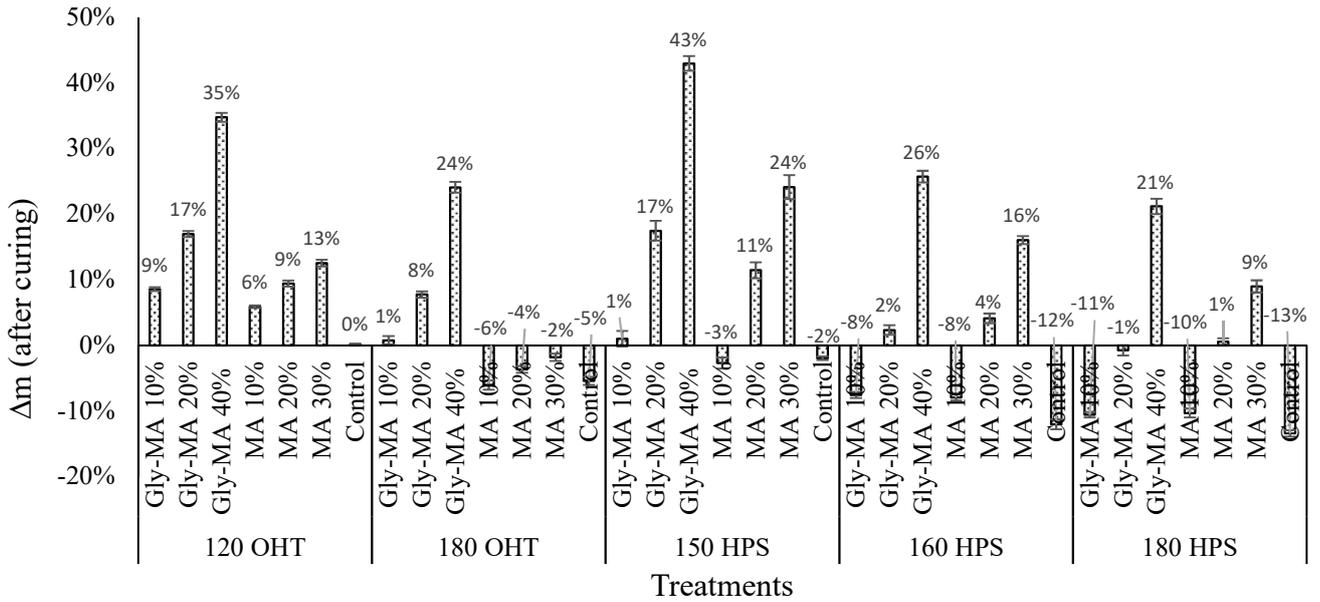


Figure 5 Mass change (WPG after curing process) of different modified wood and wood control

After curing process, in general, mass change (WPG after curing process)/ Δm decreased as the increase of curing temperature and wood treated under OHT system presented higher Δm values than wood treated under HPS (Figure 5). This could be due to an intensive hydrolysis (due to the existence of water, heat, and pressure) occurred in the HPS system, allowing higher degradation undergone on wood than wood treated under OHT system (Ding et al. 2011; Wentzel et al. 2018b). However, under HPS in closed system, evaporation of MA decreased. Further, disintegration of Gly-MA was presumably happened in this condition, presenting lower Δm values, especially in HPS at 180°C.

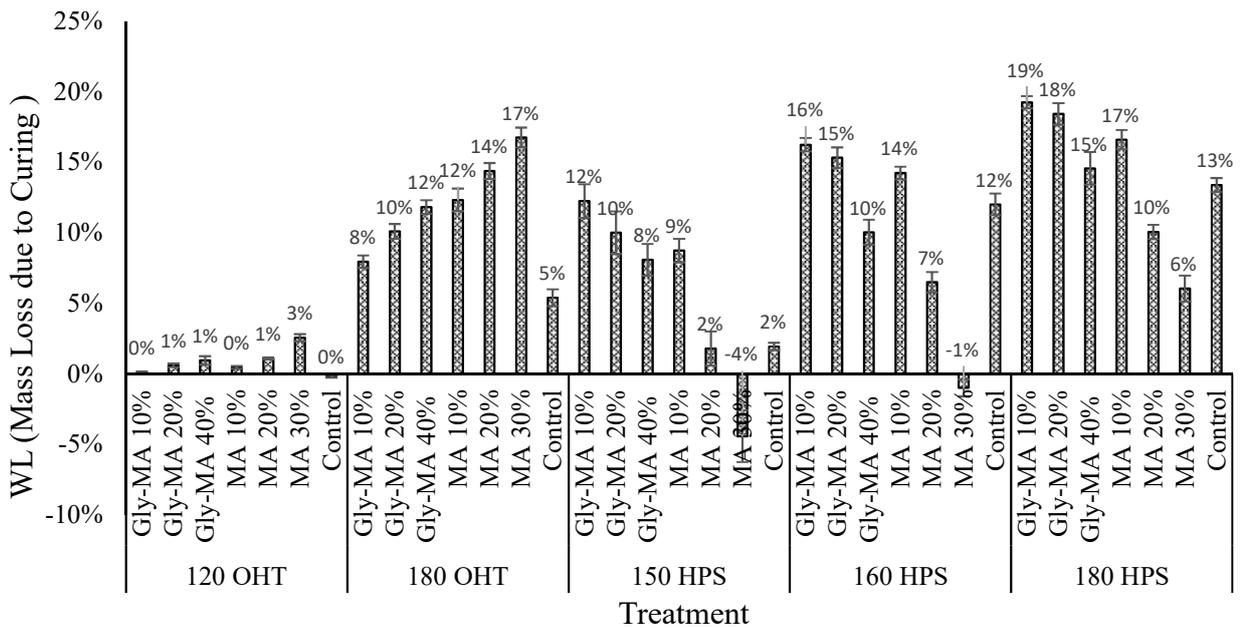


Figure 6 Weight loss due to curing process of additive-treated wood and wood control

Supporting the previous Δm data, weight loss due to curing process (WL) increased as the increase of curing temperature (Figure 6). Wood control underwent higher degradation (higher WL values) in HPS than in OHT. In additive-treated wood, higher concentration of MA would result higher WL in OHT system. In contrast, treatment under HPS in closed system could diminish evaporation of MA, remaining higher Δm values than treatment under OHT system. The results seem in accordance with some research, reporting that thermal treatment under closed system can reduce evaporation of some volatile wood degradation products (Altgen et al. 2016; Wentzel et al. 2018b), including reduction of evaporation of unreacted MA in our case.

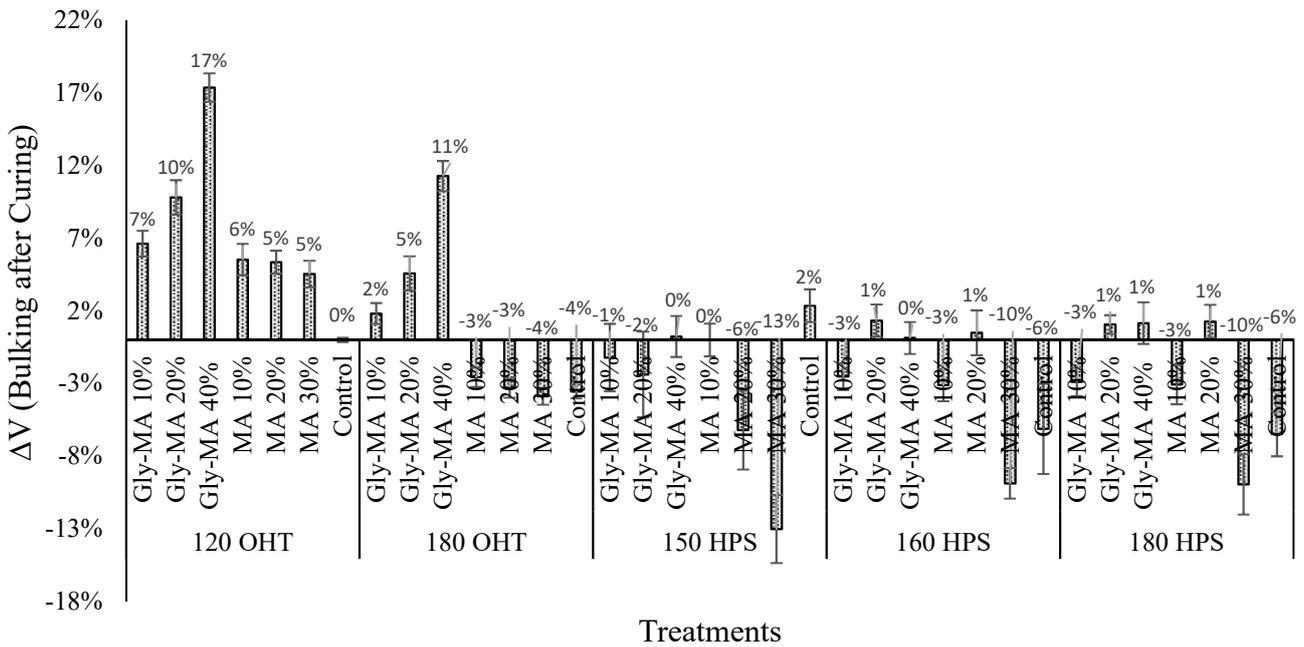


Figure 7 Bulking after curing (ΔV) of additive-treated wood and wood control

In general, bulking after curing process (ΔV) shows that wood treated under OHT remained higher ΔV values than wood treated under HPS (Figure 7). The lower ΔV values in HPS condition could be also due to an intensive degradation/hydrolysis of wood components and/or the formation of esterified products that might happen in this condition with wood components or with wood degradation products. The decrease in bulking values could trigger higher density of the modified wood, however, this condition would affect to higher wood pricing if it is marketed in the unit volume.

Dimensional stability

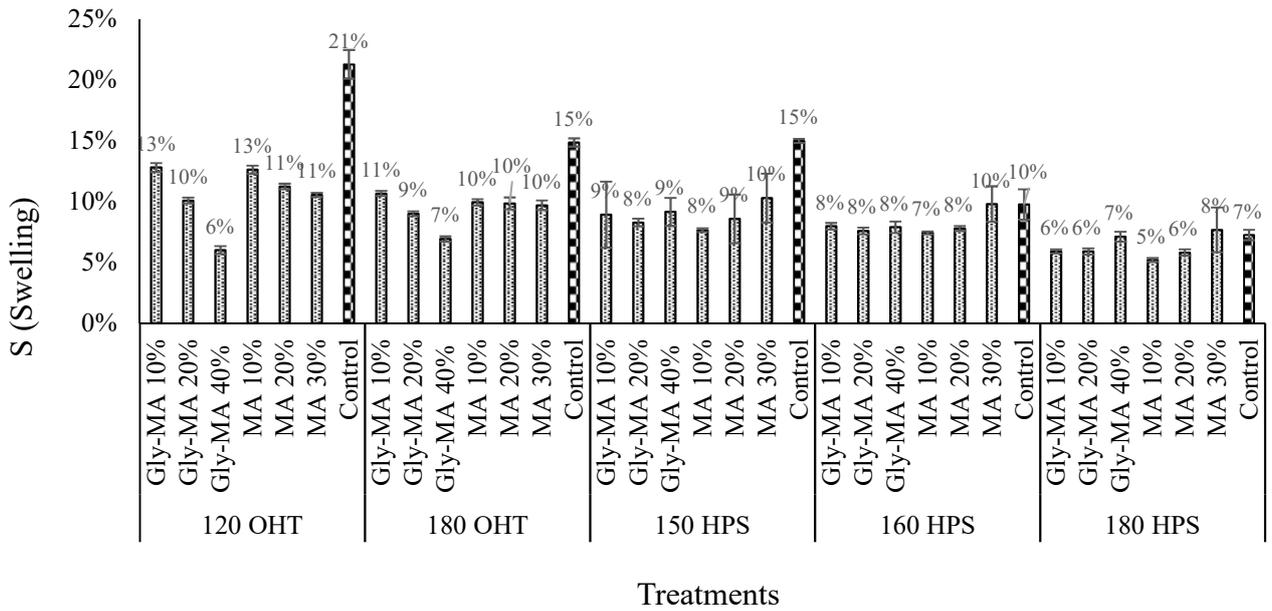


Figure 8 Swelling during ASE test of additive-treated wood and wood control

Swelling values due to water immersion decreased as the increase of treatment temperatures (Figure 8). Swelling of the modified wood was observed higher in OHT than HPS system, depending on the additive concentration. Wood treated under HPS presented lower swelling than OHT, indicating improvement in dimensional stability. Similar to the common effects of thermal degradation reported by Chaouch et al. (2013), higher degradation of hemicelluloses and modification in lignin in this HPS system could be the cause for improvement in this dimensional stability.

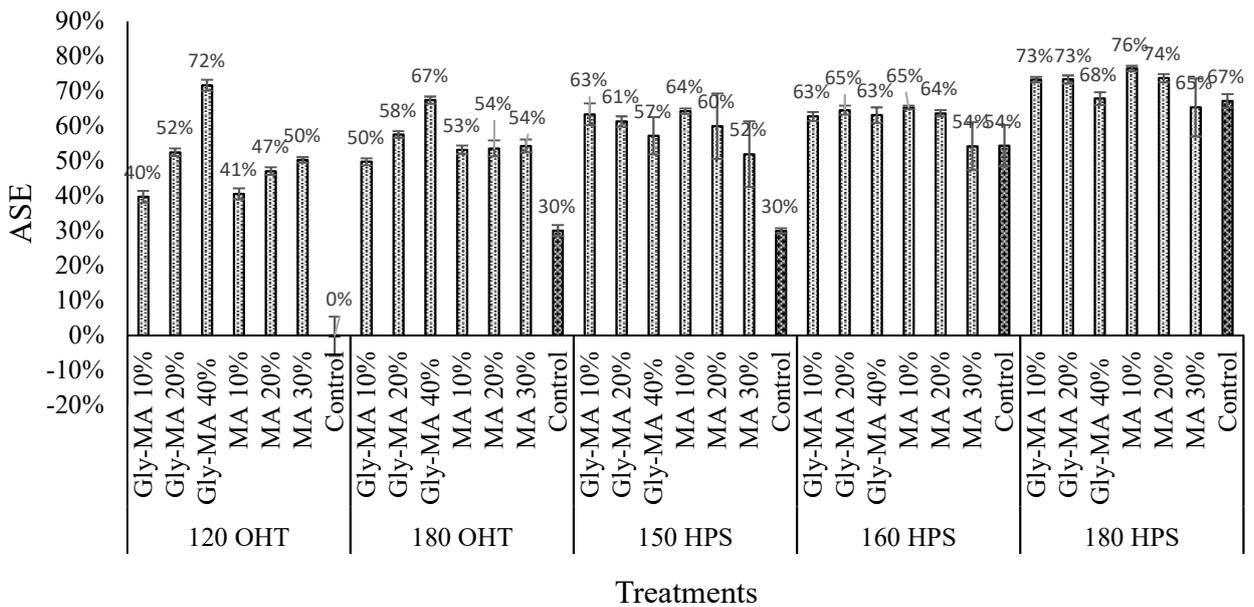


Figure 9 Anti-swelling efficiency (ASE) of additive-treated wood and wood control

In general, ASE increased as the increase of curing temperature and the addition of additive made positive response in ASE improvement (Figure 9). As a consequent of the previous swelling values, ASE under HPS presented higher value than that of OHT system, corroborating a research reporting that wood treated under HPS has higher dimensional stability than under atmospheric steam (Ding et al. 2011). ASE of wood control under OHT 180°C was similar with wood control of under HPS 150°C. ASE under OHT increased as the increase of additive concentration. In contrast, ASE tends to decrease as the increase of additive concentration under HPS. This phenomenon presumably indicated that higher concentration of additive in wood under HPS could trigger higher degradation of wood components which not only hemicellulose but possibly decreasing cellulose crystallinity that might affect higher affinity against water.

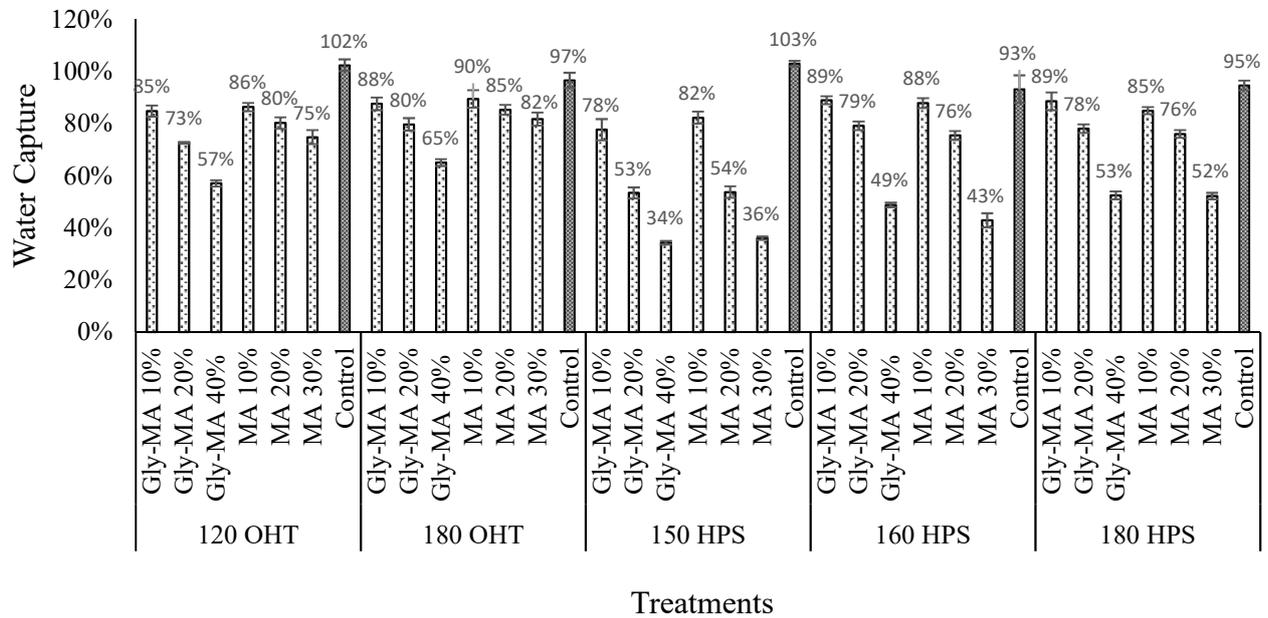


Figure 10 Water capture during the end of the ASE

Water capture decreased as the increase of curing temperature (Figure 10). Water capture decreased higher under HPS, especially at 160 and 180°C, which is in harmony with a study reporting that hygroscopicity of wood treated under HPS was lower than under atmospheric steam (Ding et al. 2011). The increase of additive concentration made lower water capture capacity, indicating possibly due to the bulking (especially in OHT system), degradation of hemicellulose, and/or the formation of the new chemical bonds between additive-wood (Esteves and Pereira 2009).

Leaching analysis

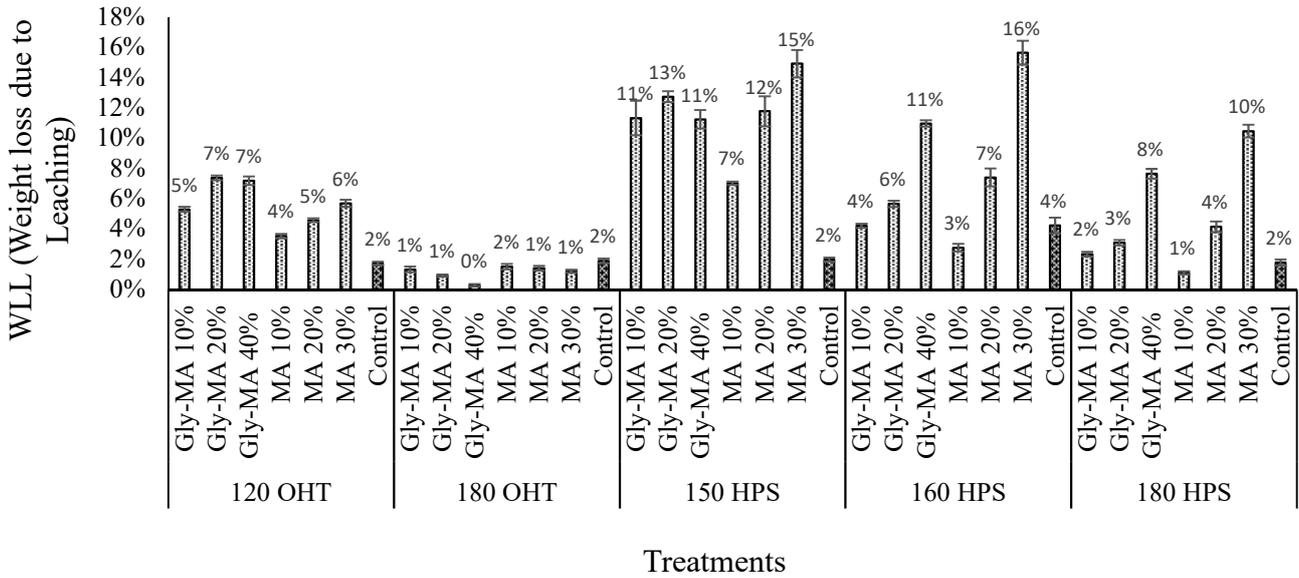


Figure 11 Weight loss due to leaching (W_L) of additive-treated wood and wood control

Mass loss due to the leaching test decreased as the increase of treatment temperature (Figure 11). Treatment under HPS presented higher W_L than under OHT. Higher wood degradation as previously mentioned in HPS, which then released during leaching process, was a main cause here. On the other hand, an incomplete polymerization of the additive and grafting to the wood under OHT 120°C were the possible factors for their higher W_L values than OHT 180°C. The results also in accordance with a study reporting that leaching value of MA-treated wood under oven drying system (OHT) was higher at 140°C than at 180°C curing temperature (Essoua et al. 2015).

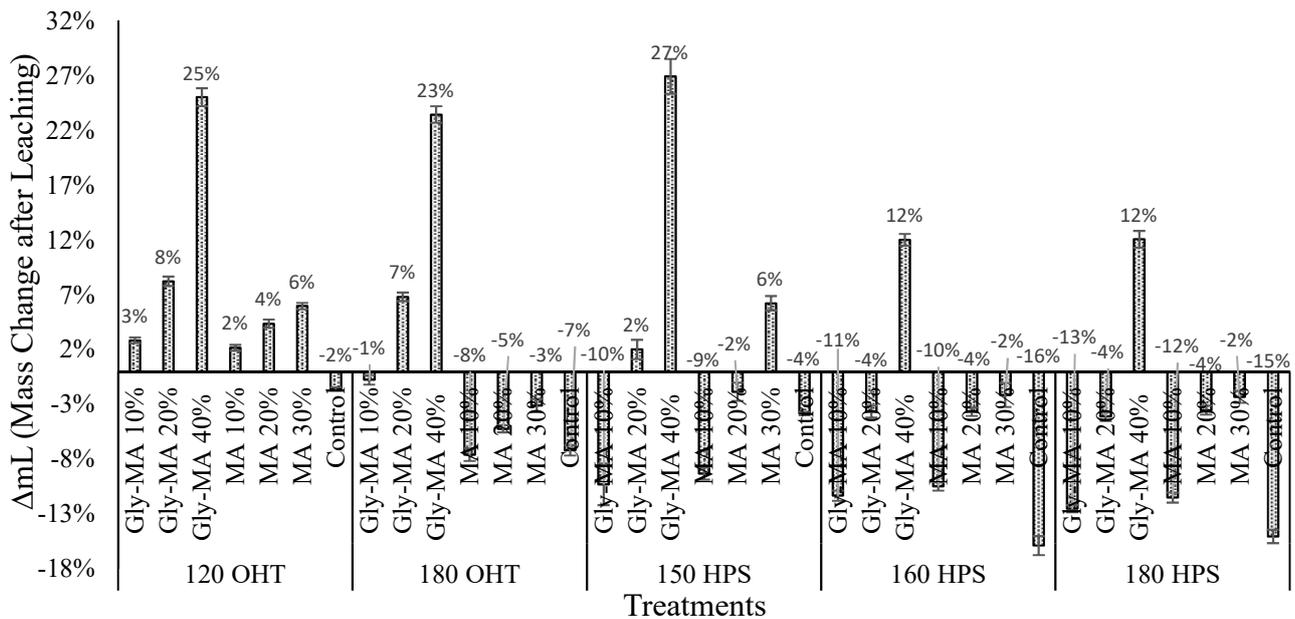


Figure 12 Mass change after leaching (Δm_L) of additive-treated wood and wood control

Mass changes after leaching (WPG after leaching) decreased as the increase of treatment temperature (Figure 12). Almost all treatments under HPS presented very low ΔV_L , confirming for its higher degradation occurred during process. Among the additive treated wood, MA-treated wood presented the lowest ΔV_L than Gly-MA-treated wood. The lower molecular weight, the lower flash point, and higher acidic properties of MA (Figure 14 – 15) could be a main cause for the lower ΔV_L values of its modified wood.

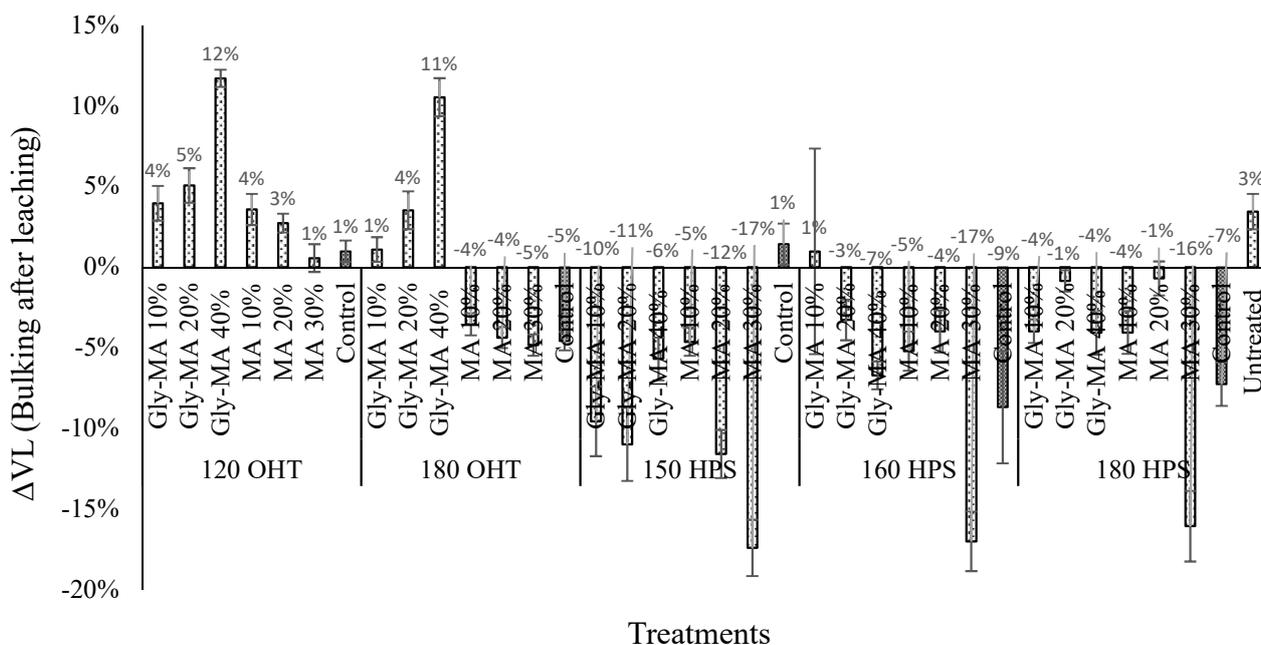


Figure 13 Bulking after leaching process (ΔV_L) of additive-treated wood and wood control

Bulking after leaching values show that treatment under HPS presented the lowest ΔV_L , indicating for its higher wood degradation occurred in this system (Figure 13). Among the additive-treated woods, MA-treated wood presented lower ΔV_L values than Gly-MA treated wood. The higher degradation of wood due to higher acidic properties and a possible formation of double bonds reaction between MA and wood could be the cause here, allowing the modified wood to shrink severely.

Acidity measurement

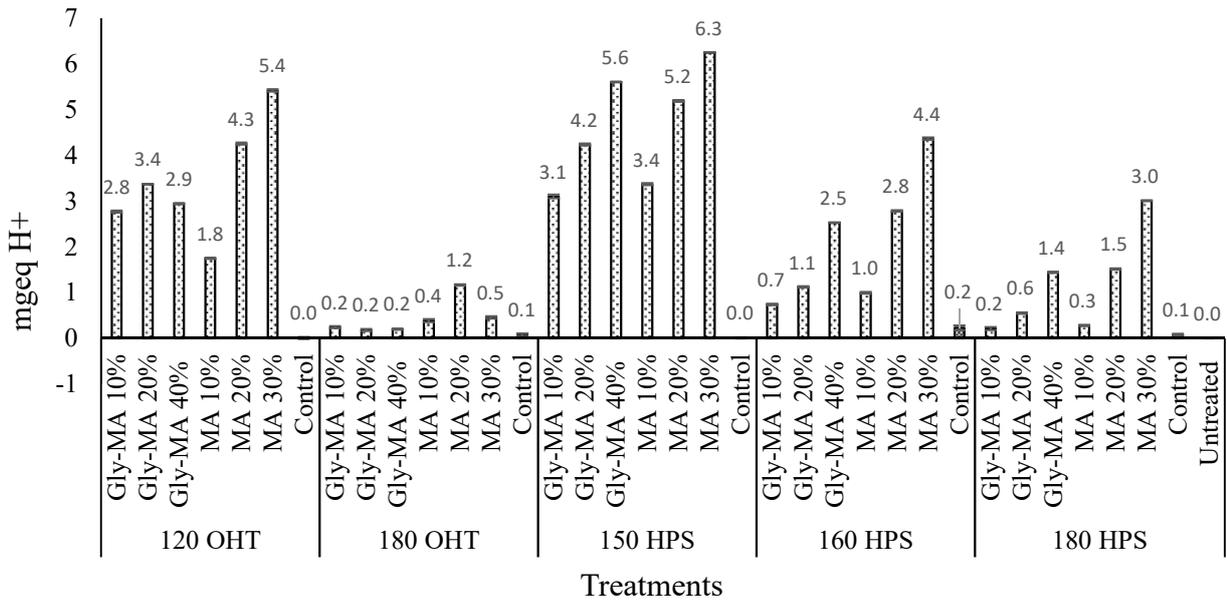


Figure 14 Milligram equivalent of H⁺ measured in the leachate during leaching test

Acidity calculated as milligram equivalent of H⁺ of the leachate during leaching test decreased as the increase of curing temperature (Figure 14). This could be due to an intensive polymerization of additive/grafting of additive to the wood at higher curing temperature. Among the two systems, treatment under HPS presented higher acidity than OHT. Combination of the water vapor during the process under HPS, accumulation of the acids as part of wood degradation products, and the existence of the additive in wood made higher degradation of wood which then released during leaching test, including unreacted additive owing acidic property.

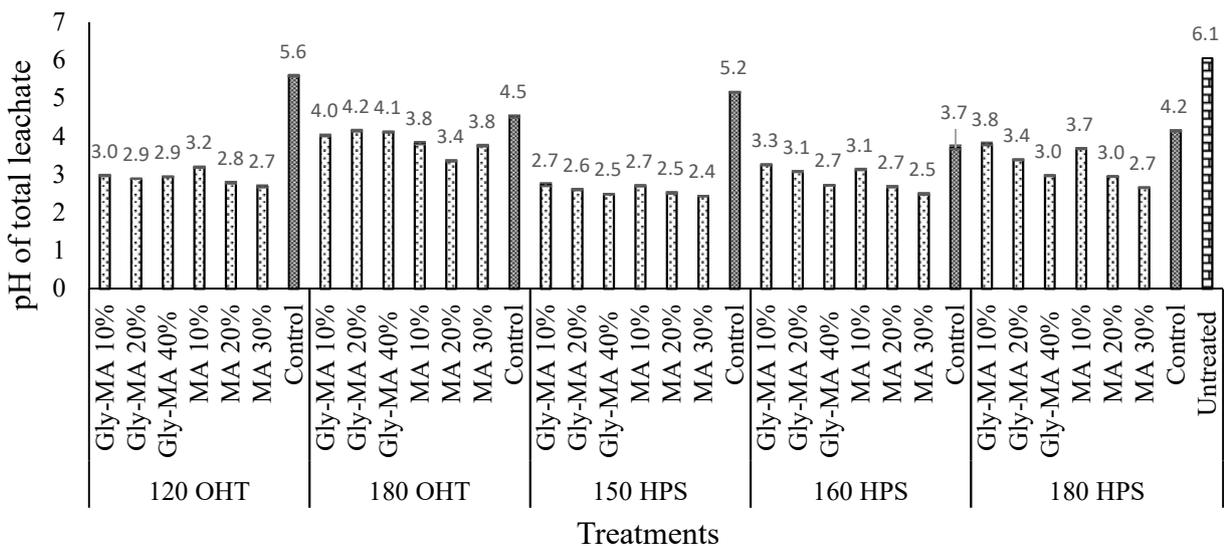


Figure 15 pH of the leachate during leaching test

Related to the mgeq H^+ , pH values of the leachate were higher in treatment at higher curing temperature. Treatment under HPS presented lower pH values (more acidic property) than under OHT. This results also corroborate research from Essoua et al. (2015), reporting that pH value of MA-treated wood cured at 180°C was higher (less acidic property) than at 140°C.

Table 1 Mechanical properties of additive-treated wood and wood control under HPS 160 and 180°C

	Treatment	Density (Kg/m³)	MOE (N/mm²)	MOR (N/mm²)
160 HPS	Gly-MA 10%	643 ± 38	13825 ± 1436	80 ± 26
	Gly-MA 20%	699 ± 59	12733 ± 1176	76 ± 9
	Gly-MA 40%	884 ± 90	12185 ± 929	69 ± 5
	MA 10%	658 ± 33	14054 ± 1522	77 ± 12
	MA 20%	778 ± 73	13139 ± 1252	67 ± 14
	MA 30%	970 ± 08	15396 ± 1327	64 ± 8
	Control	605 ± 74	15528 ± 1416	85 ± 19
	180 HPS	Gly-MA 10%	633 ± 59	12672 ± 2298
Gly-MA 20%		711 ± 69	12830 ± 1091	70 ± 13
Gly-MA 40%		902 ± 68	12153 ± 1096	68 ± 5
MA 10%		616 ± 53	12362 ± 1013	54 ± 6
MA 20%		762 ± 56	13105 ± 353	57 ± 7
MA 30%		911 ± 41	11827 ± 1859	41 ± 12
Control		602 ± 71	14062 ± 1535	72 ± 8
Untreated		650 ± 20	11602 ± 538	108 ± 4

Due to the highest wood degradation during modification, mechanical properties measurement in this preliminary test was conducted only for sample underwent HPS 160 and 180°C. In general, mechanical properties (MOE/MOR) decreased as the increase of curing temperature. All additive-treated wood presented lower MOE/MOR value than wood control at the same curing temperature. These lower mechanical properties could be due to degradation of some wood components, mainly hemicellulose as the cross-linking agent between cellulose and lignin (Salmén et al. 2012). Disturbance among the hydrogen bond interactions among polysaccharide in wood due to acidic property of the additive could also be the cause in contributing reduction in these mechanical properties of the additive-treated wood. In addition, even though density of additive-treated wood increased, their mechanical properties remained lower than wood control or untreated wood. In most cases, both additives presented in the same range of MOE/MOR values for both HPS conditions.

FTIR Analysis

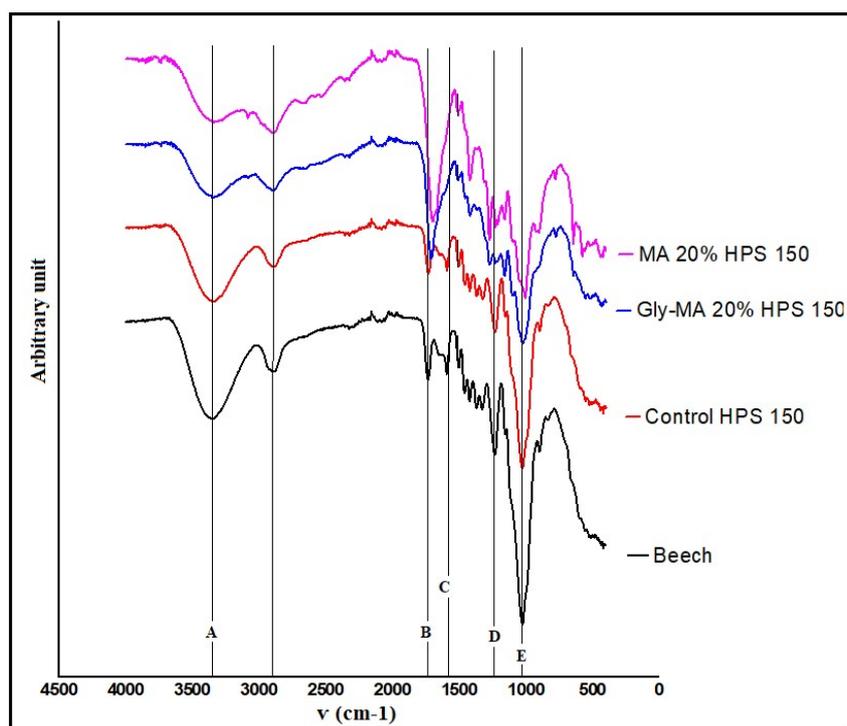


Figure 16 Beech wood, Wood Control HPS 150°C, Gly-MA 20%-Wood HPS 150°C, MA 20%-Wood HPS 150°C

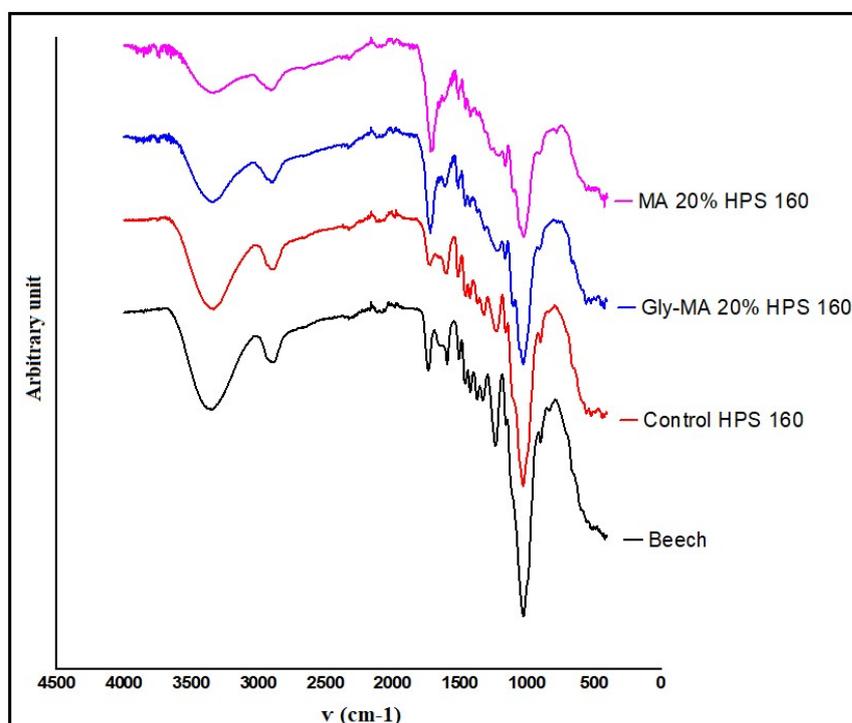


Figure 17 Beech wood, Wood Control HPS 160°C, Gly-MA 20%-Wood HPS 160°C, MA 20%-Wood HPS 160°C

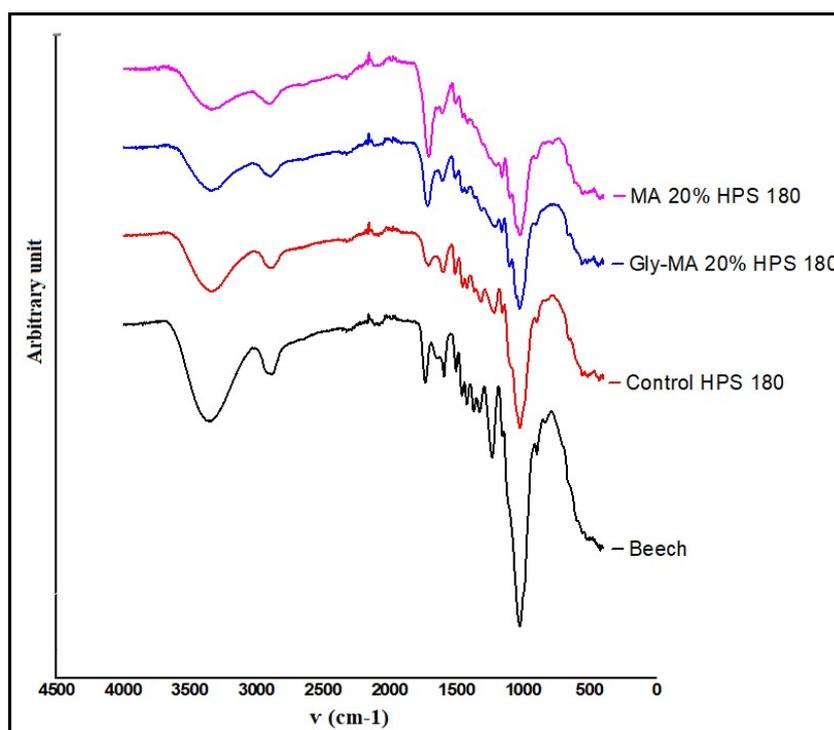


Figure 18 Beech wood, Wood Control HPS 180°C, Gly-MA 20%-Wood HPS 180°C, MA 20%-Wood HPS 180 °C

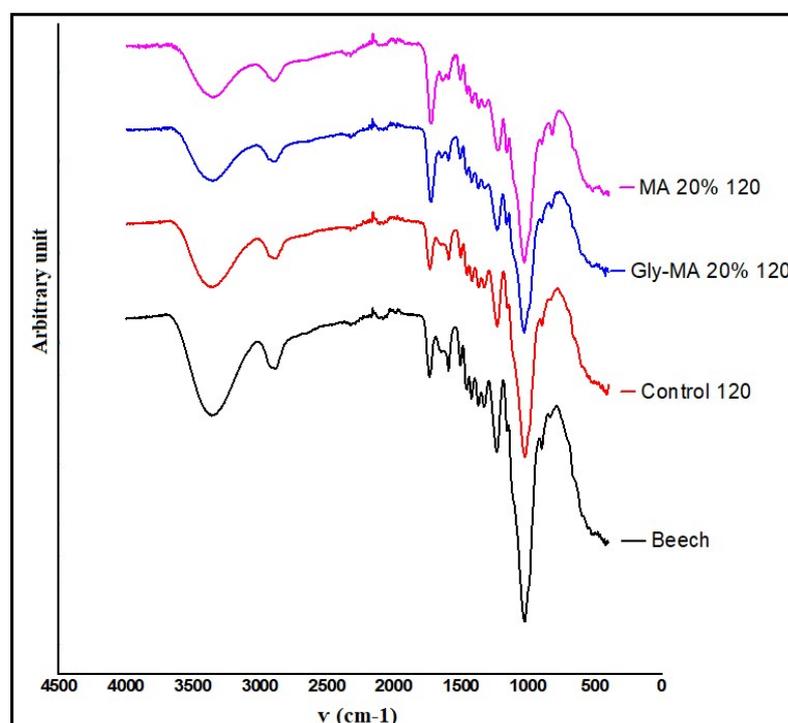


Figure 19 Beech wood, Wood Control 120°C, Gly-MA 20%-Wood 120 °C, MA 20%-Wood 120°C

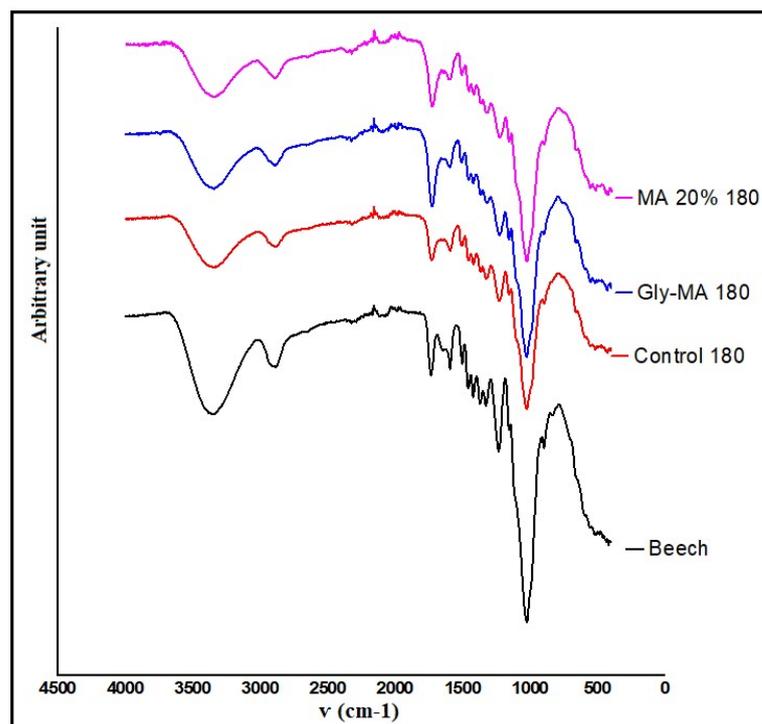


Figure 20 Beech wood, Wood Control 180°C, Gly-MA 20%-Wood 180 °C, MA 20%-Wood 180°C

Table 2 Major FTIR absorption of beech wood and additive-treated wood under different curing systems.

Peak	Approx. ν (cm^{-1})	Assignment
A	3356	OH str, alcohol
A - B	2899	CH str, alkane
B	1737/1715 ^a	C=O str ester / C=O, α , β -unsaturated (hemicellulose + lignin) ^b
B - C	1652	C=C str, alkene cis/alkene conjugate/hemicellulose
C	1590	C=C str, aromatic ring (lignin) ^b
C - D	1504	C=C str, aromatic ring (lignin) ^b
C - D	1456	CH bend, lignin
C - D	1424	CH bend, crystallized cellulose and amorphous cellulose ^{b,c}
C - D	1372	CH bend, holocellulose or lignin
C - D	1327	OH bend, phenol lignin
D	1232	C-O str, alkyl aryl ether (lignin) or C-O str hemicellulose
D - E	1153	C-O str, cellulose ^b
E	1024	C-O primary alcohol

^a1715 was the approx. wave length (ν) almost appeared only in additive-treated wood; ^bColom et al. (2003); ^cHakkou et al. (2005)

In general, at 20% additive concentration, all additive-treated woods presented different absorption compared either to untreated wood or wood control under different curing systems (Figure 16 – 20). The difference took place generally at 1737/1715 cm^{-1} (increased), which assigned as absorption of carbonyl bond (C=O) formed due to the existence of additives in wood and/or the new ester bond formation between wood and additive. Reduction absorption at 1232 cm^{-1} , which assigned as C-O signal of alkyl aryl ether (lignin) or hemicellulose (Table 2), also took place due to degradation of wood components (mainly hemicellulose) in additive treated wood in both curing systems (OHT and HPS) and in wood control at higher curing temperature (OHT 180 and HPS). Further, modification of lignin was also observed in the range of absorption from 1590 – 1327 cm^{-1} , particularly under HPS system. Due these modifications, additive-treated under HPS appeared with darker in color than wood control at the same condition (Figure 21).



Figure 21 Additive-treated wood and wood control under HPS system at 160°C

Decay durability properties

Decay durability against white rot fungus (*Coriolus versicolor*) revealed that the additive-treated wood presented higher resistance than untreated wood or wood control (Table 3). Decay resistance increased as the increase of curing temperature. Even though Δm_L (WPG after leaching) of additive-treated woods under OHT 120°C were higher than other curing treatments, their decay resistances were not enough to protect the wood, compared to other conditions. This lower decay resistance could be due to an incomplete grafting of the additive to the wood or wood degradation level at this condition is still low, allowing the fungus is still capable of degrading its substrates.

Table 3 Decay durability against white rot fungus (*Coriolus versicolor*) after leaching process

Treatment		Humidity (%)	ML (%)	Specification
120 OHT*	Gly-MA 10%	59.23 ± 4.16	10.32 ± 2.56	moderately durable
	Gly-MA 20%	55.92 ± 6.95	9.63 ± 4.61	moderately durable
	Gly-MA 40%	50.24 ± 3.96	6.38 ± 1.26	moderately durable
	MA 10%	61.99 ± 2.94	10.78 ± 2.34	moderately durable
	MA 20%	67.21 ± 11.10	10.38 ± 4.43	moderately durable
	MA 30%	82.27 ± 8.66	8.47 ± 0.46	moderately durable
	Control	47.91 ± 7.81	16.14 ± 6.58	slightly durable
180 OHT*	Gly-MA 10%	38.64 ± 0.96	0.76 ± 0.15	very durable
	Gly-MA 20%	35.07 ± 3.20	0.35 ± 0.27	very durable
	Gly-MA 40%	24.37 ± 2.72	0.17 ± 0.14	very durable
	MA 10%	43.56 ± 1.67	1.01 ± 0.83	very durable
	MA 20%	39.03 ± 1.89	0.78 ± 0.32	very durable
	MA 30%	34.52 ± 10.63	0.99 ± 0.39	very durable
	Control	55.66 ± 13.19	10.92 ± 7.75	moderately durable
150 HPS**	Gly-MA 10%	65.67 ± 4.30	2.99 ± 0.74	very durable
	Gly-MA 20%	70.30 ± 7.24	4.40 ± 0.88	durable
	Gly-MA 40%	62.97 ± 9.13	9.05 ± 1.76	moderately durable
	MA 10%	62.96 ± 7.18	2.25 ± 0.37	very durable
	MA 20%	68.49 ± 10.70	4.08 ± 1.33	durable
	MA 30%	63.71 ± 6.00	7.45 ± 2.89	moderately durable
	Control	48.38 ± 7.15	6.93 ± 1.46	moderately durable
160 HPS**	Gly-MA 10%	51.65 ± 2.21	1.43 ± 0.46	very durable
	Gly-MA 20%	49.90 ± 1.05	1.83 ± 0.15	very durable
	Gly-MA 40%	62.66 ± 3.55	4.49 ± 0.41	durable
	MA 10%	43.72 ± 2.20	1.03 ± 0.20	very durable
	MA 20%	58.75 ± 2.16	2.18 ± 0.10	very durable
	MA 30%	70.58 ± 3.90	4.27 ± 0.68	durable
	Control	52.52 ± 8.68	8.01 ± 3.65	moderately durable
180 HPS**	Gly-MA 10%	35.80 ± 3.87	0.62 ± 0.33	very durable
	Gly-MA 20%	39.22 ± 1.47	1.19 ± 0.10	very durable
	Gly-MA 40%	40.71 ± 2.22	2.50 ± 0.23	very durable
	MA 10%	30.85 ± 3.59	0.29 ± 0.07	very durable
	MA 20%	39.84 ± 1.51	0.92 ± 0.21	very durable
	MA 30%	49.89 ± 4.83	1.68 ± 0.11	very durable
	Control	42.68 ± 8.07	3.97 ± 2.72	durable
Virulence		88.88 ± 15.50	30.93 ± 2.92	not durable

*Each value was based on the average of 6 samples; **Each value was based on the average of 5 samples; Virulence samples was based on the average of 16 samples; Durability class was based on EN 350-1

In term of the additive-treated wood under HPS, it seems that the increase of the additive concentration tended to decrease decay resistance at lower temperature of HPS (at 150°C and 160°C). This decrease could be due to the excessive reaction between additive and wood components in wet condition, not

only hemicelluloses but also part of the celluloses (either amorphous or crystalline celluloses). Afterwards, some of these product reactions would be released during leaching test, remaining more degradable wood components against decay of the leached wood sample.

Conclusions

The study has presented certain characteristics of wood modification based on different concentration of Gly-MA and MA under OHT and HPS systems, which most of them could be summarized as the following:

1. Before curing process, Gly-MA-treated wood presented higher WPG and bulking at 103°C than MA-treated wood, even though both additives had similar penetration during impregnation. Bulking value of Gly-MA-treated wood was proportional with the increase of Gly-MA concentration.
2. After curing process, in most cases, wood treated under OHT presented higher mass change values (WPG after curing / Δm), higher bulking after curing (ΔV), lower mass loss due to curing values (WL), lower weight loss due to leaching, and lower acidity than wood treated under HPS.
3. MOE of wood treated under HPS was slightly higher than untreated wood and lower than wood control at the same condition. On the other hand, MOR decreased sharply due to this modification.
4. Wood treated under HPS presented higher modification based on the FTIR analysis than wood under OHT.
5. Decay durability of additive-treated wood under OHT 180°C and HPS mainly at 160 and 180°C at different concentrations were classified as very durable wood. While at these conditions, wood controls were classified as moderately durable wood under OHT 180°C, and durable wood under HPS 180°C.

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c. Conclusion

Through this variation in wood modification treatments, certain characteristics of wood during and after modification could be summarized as the following:

During modification

- MA-impregnated wood showed slightly higher swelling due to impregnation than Gly-MA-impregnated wood at the same solution concentration. Meanwhile, no significant difference observed between the two additives used at the same solution concentration level for their solution up-take values.
- WPG at 103°C presented that Gly-MA-treated wood had higher WPG and bulking values than MA-treated wood at the same concentration level. There were no significant differences in bulking values observed among the applied MA solution concentrations.
- In most cases, mass change values (Δm) or WPG after curing at higher temperature of the wood treated with Gly-MA under OHT were higher than the wood treated under HPS. In contrast, due to the limited evaporation of MA, the wood treated with MA under HPS in closed system presented higher Δm values than under OHT in open system.
- In most cases, mass loss due to curing values (WL) under OHT increased linearly with the increase of additive concentration and MA-treated wood had higher WL value than Gly-MA-treated woods. In contrast, due to possible intensive hydrolysis occurred under HPS, WL values decreased with the increase of additive concentration and Gly-MA treated wood presented higher WL values than MA-treated wood.

- In general, the wood treated under HPS presented negative bulking values after curing (ΔV) (underwent shrinking). Meanwhile, the wood treated under OHT presented remained have positive ΔV , except the wood treated with MA at 180°C.

After modification

- Swelling values of the wood treated under OHT decreased (ASE values increased) by the increase of additive concentration. Meanwhile, the swelling values / ASE values of the wood treated under HPS were more or less similar one and each other in the same treatment independently with the additive concentration. At the same curing temperature, treatment under HPS generated lower swelling (higher ASE values) than treatment under OHT.
- Water capture values in saturated condition decreased as the increase of additive concentration. At the same curing temperature, the wood treated under HPS had slightly lower water capture than treatment under OHT.
- Weight loss due to leaching (WL_L) values under HPS increased as the increase of additive concentration. While at higher curing temperature under OHT, WL_L decreased as the increase of additive concentration. In general, WL_L decreased as the increase of curing temperature.
- Acidic properties of the wood treated HPS were higher (lower pH values) than under OHT at the same curing temperature. Acidity values increased (pH decreased) as the increase of additive concentration.
- In most cases, MOE of the wood treated under HPS 160°C or 180°C were slightly higher than untreated wood. Unfortunately, MOR values plunged from 21 to 62%.
- FTIR study revealed that the wood treated under HPS underwent higher structural changes in comparison with the wood treated under OHT.
- Decay resistance against CV revealed that the wood treated at lower curing temperature/lower severity condition under HPS tended to decrease its decay resistance as the increase of additive concentration. In general, decay resistance of the wood treated at higher curing temperature either under HPS or OHT were higher than treatment at lower curing temperature.

III.2.8 Paper 5

a. Introduction

Paper 5 reported the selected up-scaling treatments from some series of up-scaling treatments performed either based on the previous papers or from newly developed treatments detailed in a part of up-scaling treatments below. Based on the Gly-MA and PG-MA-based additive, treatments in this paper implemented curing process under OHT and HPS. Treatments under OHT were performed by varying in curing temperatures at 120, 150, and 220°C. Meanwhile, to avoid higher wood degradation, treatment under HPS was processed only at 150°C with the specific pressure of 4.66 MPa and humidity at 100% RH.

b. The up-scaling treatments

In this section, some series of up-scaling treatments were based on the selected treatments in the Part I and certain treatments improved from the previous screening treatments in the Paper 4. In addition, other treatments were also tested for their possibility in the up-scaling treatment through which prediction for biological durability improvement could be performed.

The sample size used in these up-scaling treatments were $1000 \times 20 \times 80 \text{ mm}^3$ and $650 \times 20 \times 50 \text{ mm}^3$ (L, T, R) with a mean dried wood density was $650 \pm 20 \text{ Kg/m}^3$. The moisture content of the wood before impregnation was about 9 - 11%. During modification, impregnation of the chemicals into the wood was performed in a bigger vacuum-pressure impregnation chamber with capacity of $\pm 0.8 \text{ m}^3$ (Figure 35). Detail of particular selected treatments procedures, parameter analysis, and characteristics of the modified woods are presented in the Paper 5.

In the curing processes, certain processes were conducted using the similar machine used in the previous screening test (Figure 34) for thermal modification under OHT at 220°C in opened system and under HPS in closed system. Meanwhile, for thermal modification at lower curing temperature under OHT, a bigger size of common drying oven was used.



Figure 35: Vacuum-pressure impregnation chambers during up-scaling, Wood Biology and Wood Technology, Göttingen University, 2018

1) Results and Discussion

In terms of thermal modification under HPS system, the samples were directly dried at 103°C soon after the HPS process (humidity was recorded), aimed to remove the remaining moisture of the samples due to steaming process in the HPS. In overall, wood modification trials performed in these up-scaling treatments are listed in the Table 5. Meanwhile, appearances of the wood samples from these trials are shown in the Figure 36. Among these treatments, there were certain treatments that expected would have better properties, particularly in biological durability and dimensional stability. This estimation was initially based on their appearances, mass losses, and FTIR spectra. These selected treatments are listed in the Table 6 – 10.

Table 5: Wood modification trials performed during up-scaling treatments

No	Up scaling Treatment	Condition	MC initial (%) [*]	Δm (%) [*]	Mass Loss (%) [*]
1	Gly-MA 20%	150°C; 4.6 bar; 100% RH	21.14 ± 0.85	7.34 ± 1.09	13.77 ± 0.70
2	Control positive	150°C; 4.6 bar; 100% RH	9.49 ± 0.15	-3.81 ± 0.45	3.81 ± 0.45
3	Gly-MA 20%	160°C; 6 bar; 100% RH	20.91 ± 1.33	4.60 ± 0.60	16.16 ± 0.47
4	Control positive	160°C; 6 bar; 100% RH	9.74 ± 0.35	-7.70 ± 0.55	7.70 ± 0.55
5	Gly-MA 10%	150°C; 4.6 bar; 100% RH	18.44 ± 1.53	-5.87 ± 0.94	17.94 ± 0.48
6	Gly-MA 10%	180°C; 6 bar; 60% RH	17.31 ± 0.92	-9.41 ± 0.86	21.07 ± 0.62
7	Gly-MA 20%	120°C; 5 days; OHT	8.78 ± 2.86	18.98 ± 2.85	6.15 ± 1.96
8	Gly-MA 20%	120°C; 5 days; OHT + Al foil	6.07 ± 1.78	10.86 ± 1.35	12.23 ± 0.94
9	Gly-MA 40%	120°C; 5 days; OHT	20.03 ± 0.78	40.58 ± 2.14	4.91 ± 0.57
10	Gly-MA 40%	120°C; 5 days; OHT + Al foil	18.46 ± 1.30	37.46 ± 4.45	7.31 ± 0.83
11	MA 20%	120°C; 5 days; OHT + Al foil	19.42 ± 2.55	14.06 ± 1.02	8.94 ± 0.40
12	MA 30%	120°C; 5 days; OHT	38.12 ± 2.49	20.54 ± 1.73	3.14 ± 1.32
13	MA 30%	120°C; 5 days; OHT + Al foil	36.18 ± 3.15	26.14 ± 0.50	-1.02 ± 0.22
14	Gly-MA 20%	150°C; 2 days; OHT + Al foil	7.99 ± 0.28	10.79 ± 0.11	12.60 ± 0.06
15	Gly-MA 40%	150°C; 2 days; OHT + Al foil	18.43 ± 0.00	23.82 ± 0.00	10.41 ± 0.00
16	MA 20%	150°C; 2 days; OHT + Al foil	16.97 ± 2.03	8.48 ± 1.05	13.04 ± 0.38
17	MA 30%	150°C; 2 days; OHT + Al foil	32.68 ± 0	16.50 ± 0.00	6.68 ± 0.00
18	Gly-MA 10%	220°C; Steam; + Al foil	17.37 ± 1.51	-6.84 ± 1.04	18.53 ± 0.71
19	Gly-MA 20%	120°C; 5 days OHT, 220°C; Steam; + Al foil	8.78 ± 2.86	3.75 ± 2.69	13.73 ± 0.55
20	Gly-MA 40%	120°C; 5 days OHT, 220°C; Steam; + Al foil	20.03 ± 0.78	22.55 ± 1.51	12.54 ± 0.34
21	MA 20%	150°C; 4.6 bar; 90% RH	18.50 ± 1.20	13.03 ± 0.55	9.36 ± 0.34
22	PG-MA 20%	150°C; 4.6 bar; 100% RH	15.81 ± 0.61	3.16 ± 1.09	21.81 ± 0.84
23	PG-MA 20%	120°C; 5 Days; OHT + Al foil	16.11 ± 1.38	12.13 ± 1.39	10.27 ± 0.65
24	PG-MA 20%	180 HPS; 6 Bar; 60% RH	15.95 ± 0.61	0.23 ± 1.68	24.76 ± 0.77
25	PG-MA 10%	220°C, steam, + Al foil	24.92 ± 2.01	-3.91 ± 0.56	15.43 ± 0.59
26	Untreated Beech	Oven drying at 103°C	9.59 ± 0.17	0.00 ± 0.00	0.00 ± 0.00
27	PG-MA (1:3) 10%	220°C steam	18.62 ± 1.68	-6.93 ± 0.44	19.01 ± 0.44
28	PG-MA (1:3) 20%	150°C; 4.6 bar; 100% RH	17.02 ± 1.66	5.20 ± 1.41	17.83 ± 0.11
29	PG-MA (1:3) 20%	120°C; 5 days; OHT + Al foil	22.71 ± 3.48	13.02 ± 0.58	12.25 ± 0.19
30	PG-MA (1:3) 20%	150°C; 2 days; OHT + Al foil	18.55 ± 0.43	10.10 ± 0.55	13.77 ± 0.16
31	PG-MA (1 :2) 20%	150°C; 2 days; OHT + Al foil	17.36 ± 0.97	10.81 ± 1.79	11.48 ± 0.09
32	PG-MA (1:3) 10%	150°C; 4.6 bar; 100% RH	15.95 ± 2.08	-6.05 ± 0.66	17.88 ± 0.59

*Each value was based on the average of 1 – 10 samples (varied).



Figure 36: Appearance of wood samples from certain treatments in the up-scaling processes

Dimensional stability

According to selected treatment in the Table 6. It is shown that all additive/chemical-treated woods have ASE values higher than 60%, compared to wood control treated under HPS 150 or 160°C at certain conditions. This higher dimensional stability indicates that hydrophobicity of wood increased by the addition of these chemicals through which mechanism of the dimensional stability

improvement could be as the result of the formation of new chemical bonds between additive-wood, wood bulking (particularly for additive with 40% w/w), degradation of hemicellulose, and modification of lignin, as similar characteristic as the previous screening test (Paper 4).

Table 6: Swelling, anti-swelling efficiency (ASE), and shrinkage of certain selected wood modification treatments during up-scaling

ID	Additives	System	Swelling (%)*	ASE (%)*	Shrinkage (%)*
A	Gly-MA 20%	150°C; 4.6 bar; 100% RH	7.98 ± 0.6	68.83 ± 2.43	2.2 ± 0.43
B	Control positive	150°C; 4.6 bar; 100% RH	14.57 ± 0.5	43.07 ± 2.12	3.8 ± 0.70
C	Gly-MA 20%	160°C; 6 bar; 100% RH	8.13 ± 0.3	68.22 ± 1.35	1.5 ± 1.39
D	Control positive	160°C; 6 bar; 100% RH	11.30 ± 0.9	55.84 ± 3.75	4.0 ± 0.73
E	Gly-MA 20%	120°C; 5 days; OHT + Al foil	6.32 ± 0.2	75.32 ± 1.08	2.2 ± 0.10
F	Gly-MA 40%	120°C; 5 days; OHT	6.03 ± 0.4	76.43 ± 1.60	1.7 ± 0.34
G	Gly-MA 40%	120°C; 5 days; OHT + Al foil	6.23 ± 0.3	75.65 ± 1.38	3.2 ± 0.67
H	MA 20%	120°C; 5 days; OHT + Al foil	6.22 ± 0.2	75.70 ± 0.80	1.7 ± 0.14
I	Gly-MA 10%	220°C; steam; + Al foil	7.78 ± 0.2	69.62 ± 0.95	0.3 ± 0.11
J	MA 20%	150°C; 4.6 bar; 90% RH	7.73 ± 0.2	69.79 ± 1.07	1.6 ± 0.17
K	PG-MA 20%	150°C; 4.6 bar; 100% RH	9.52 ± 0.2	62.79 ± 1.11	3.3 ± 2.24
L	PG-MA 20%	120°C; 5 days; OHT + Al foil	8.70 ± 0.2	65.99 ± 0.95	2.2 ± 0.30
M	PG-MA 10%	220°C, steam, + Al foil	8.47 ± 0.2	66.90 ± 1.11	1.0 ± 0.12
N	Beech wood	Oven drying at 103°C	25.59 ± 3.6	0	0.0 ± 0.63
P	Pine wood	Oven drying at 103°C	-	-	-

*each value was based on the ten samples and twenty samples for untreated wood (beech)

Leaching resistance and acidity

In general, leaching resistance of the additive-treated wood were high (low loss values), indicating a better fixation of the additive in wood, a modified wood structure, and/or a possibility have low wood degradation products that could leach out during leaching (Table 7). Among the additive-treated woods, Gly-MA 40%-treated wood cured under OHT 120°C with aluminum foil covering had the highest leaching value. This could be due to unreacted additive in wood/uncomplete reaction between additive-wood or higher degradation of wood components due to higher additive concentration that might leach out during leaching test.

Table 7: Leaching and acidity properties of certain selected wood modification treatments during up-scaling

ID	Additives	System	Leaching (%)*	[H ⁺](M)*	pH*
A	Gly-MA 20%	150°C; 4.6 bar; 100% RH	3.00 ± 0.37	7.90E-05	4.1
B	Control positive	150°C; 4.6 bar; 100% RH	3.78 ± 0.32	1.20E-06	5.92
C	Gly-MA 20%	160°C; 6 bar; 100% RH	2.33 ± 0.13	5.50E-05	4.26
D	Control positive	160°C; 6 bar; 100% RH	4.50 ± 0.92	3.50E-06	5.46
E	Gly-MA 20%	120°C; 5 days; OHT + Al foil	3.73 ± 0.32	1.40E-04	3.84
F	Gly-MA 40%	120°C; 5 days; OHT	3.22 ± 0.64	4.10E-04	3.38
G	Gly-MA 40%	120°C; 5 days; OHT + Al foil	4.39 ± 0.95	3.20E-04	3.49
H	MA 20%	120°C; 5 days; OHT + Al foil	4.13 ± 0.32	3.70E-04	3.43
I	Gly-MA 10%	220°C; steam; + Al foil	0.72 ± 0.09	1.30E-07	6.89
J	MA 20%	150°C; 4.6 bar; 90% RH	3.77 ± 0.31	6.80E-04	3.17
K	PG-MA 20%	150°C; 4.6 bar; 100% RH	3.70 ± 0.43	1.50E-05	4.83
L	PG-MA 20%	120°C; 5 days; OHT + Al foil	3.33 ± 0.43	1.10E-05	4.94
M	PG-MA 10%	220°C, steam, + Al foil	1.43 ± 0.09	1.80E-07	6.74
N	Beech wood	Oven drying at 103°C	1.30 ± 0.40	1.10E-07	6.96
P	Pine wood	Oven drying at 103°C	-	8.70E-08	7.06

*each value was based on the ten samples, leaching process referred to EN 84 (1997)

In terms of acidity of the leachate during leaching test, MA 20%-treated wood cured under HPS 150°C at specified condition had higher total acidity than others ($[H^+] = 6.8E-04$ M), indicating possibly due to unreacted MA that hydrolyzed in the water to become maleic acid, the release of its product reaction with wood components, and/or as the release of wood degradation products owing acidic properties. Hence, pH value decreased due to this higher acidic property.

Mechanical properties

Mechanical properties measured as MOE, MOR, and work to maximum load in bending (WMLB) show that in most cases MOE of the additive-treated wood increased slightly in comparison to untreated wood (Table 8). The increase in MOE is possibly happened by an increase in cross-linking of the lignin network, which then enhance the cell wall matrix stiffness. In relation to this, MOR values decreased until 45%. Moreover, as a function of stress and strain, the work to maximum load is commonly affected long before significantly affected strength properties or properties related to the proportional limit (e.g. MOE) (Winandy and Rowell 2005). Therefore,

WMLB decreased considerably for both additive-treated wood under all specified conditions and wood control under specified condition in HPS 150 and 160°C.

Table 8: Density and mechanical properties of certain selected wood modification treatments during up-scaling

ID	Additives	System	Density (Kg/m ³)*	MOE (N/mm ²)*	MOR* (N/mm ²)*	WMLB* (N/mm ²)*
A	Gly-MA 20%	150°C; 4.6 bar; 100% RH	767 ± 18	11680 ± 1107	80 ± 17	459 ± 180
B	Control positive	150°C; 4.6 bar; 100% RH	654 ± 28	13800 ± 994	110 ± 16	1121 ± 363
C	Gly-MA 20%	160°C; 6 bar; 100% RH	753 ± 45	11943 ± 1965	66 ± 11	291 ± 70
D	Control positive	160°C; 6 bar; 100% RH	641 ± 29	14933 ± 1039	105 ± 18	759 ± 270
E	Gly-MA 20%	120°C; 5 days; OHT + Al foil	739 ± 14	13180 ± 816	88 ± 20	495 ± 186
F	Gly-MA 40%	120°C; 5 days; OHT	-	-	-	-
G	Gly-MA 40%	120°C; 5 days; OHT + Al foil	861 ± 23	13406 ± 1171	86 ± 9	504 ± 98
H	MA 20%	120°C; 5 days; OHT + Al foil	765 ± 34	13753 ± 1568	72 ± 11	320 ± 84
I	Gly-MA 10%	220°C; steam; + Al foil	654 ± 22	14246 ± 1035	83 ± 12	379 ± 102
J	MA 20%	150°C; 4.6 bar; 90% RH	767 ± 21	11708 ± 1041	60 ± 13	259 ± 108
K	PG-MA 20%	150°C; 4.6 bar; 100% RH	750 ± 27	14293 ± 1317	100 ± 27	593 ± 305
L	PG-MA 20%	120°C; 5 days; OHT + Al foil	746 ± 21	14080 ± 1212	87 ± 14	491 ± 132
M	PG-MA 10%	220°C, steam, + Al foil	678 ± 29	14193 ± 1436	86 ± 12	408 ± 98
N	Beech wood	Oven drying at 103°C	655 ± 16	12475 ± 712	110 ± 6	2599 ± 369
P	Pine wood	Oven drying at 103°C	-	-	-	-

*each value was based on at least fifteen samples, mechanical test method referred to DIN 52186 (1978)

Similar causes as the previous Part I and the screening test in this Part II (Paper 4), acidic properties and wood thermal degradation could be the main factors in this reduction in mechanical properties. Boonstra et al. (2007a) suggested that the reduction in toughness and strength of thermally modified wood is resulted from the loss of substances (wood components) during thermal modification. Therefore, since the external load is applied on the thermally modified wood, the resulted stresses are distributed over the less wood cell wall material. Higher losses of wood components due to the existence of the additive might contribute these higher strength losses. Nevertheless, the reduction of the toughness and strength is somehow considerably higher than the corresponding reduction of the wood components (mass losses) (Esteves et al. 2007; Borrega and Kärenlampi 2008b). Therefore, a considerable reduction on mechanical properties of the thermally modified wood, especially additive-treated wood, is not only caused by the higher mass losses

values but also probably caused by the changes in chemical and ultra-structural composition of the wood cell wall (Boonstra et al. 2007a; Arnold 2010; Hughes et al. 2015).

Decay resistance properties

Decay resistances against *Coniophora puteana* (CP) and *Trametes versicolor* (TV) of additive-treated woods, wood control, and untreated wood (virulence) after leaching are presented in the Table 9 & 10 (Figure 37).

Table 9: Decay resistance against brown rot fungus *Coniophora puteana* (CP) of certain modified woods after leaching from selected treatments during up-scaling

ID	Additives	Humidity CP (%) [*]	Mass loss CP (%) [*]	Med CP (%) [*]	x	Specification
A	Gly-MA 20% HPS 150	21.98 ± 1.56	4.11 ± 0.82	4.02	0.11	durable
B	Control HPS 150	37.29 ± 7.07	20.82 ± 4.44	20.84	0.59	slightly durable
C	Gly-MA 20% HPS 160	18.95 ± 4.32	3.69 ± 0.72	3.59	0.1	durable
D	Control HPS 160	28.16 ± 3.52	11.42 ± 3.07	11.91	0.34	moderately durable
E	Gly-MA 20% 120 OHT+Al	15.24 ± 3.26	2.13 ± 0.34	2.15	0.06	very durable
F	Gly-MA 40% 120 OHT	27.26 ± 4.26	4.45 ± 0.94	4.54	0.13	durable
G	Gly-MA 40% 120 OHT+Al	28.31 ± 2.84	4.34 ± 0.71	4.34	0.12	durable
H	MA 20% 120 OHT+Al	20.91 ± 1.65	3.99 ± 0.87	3.97	0.11	durable
I	Gly-MA 10% 220 Al	12.37 ± 0.65	-0.32 ± 0.15	-0.35	-0.01	very durable
J	MA 20% HPS 150	24.11 ± 3.40	4.54 ± 1.32	4.35	0.12	durable
K	PG-MA 20% HPS 150	25.22 ± 1.89	3.39 ± 1.20	3.46	0.1	very durable
L	PG-MA 20% 120 OHT+Al	19.39 ± 1.33	3.10 ± 1.39	3.19	0.09	very durable
M	PG-MA 10% 220 Al	14.53 ± 1.13	0.00 ± 0.26	-0.04	0	very durable
N	Beech wood	36.44 ± 9.43	34.08 ± 6.28	35.16%	1	not durable
P	Pine wood	45.80 ± 2.43	41.49 ± 5.99	42.79%	1.22	not durable

^{*}each value was based on the twenty samples; method referred to CEN/TS 15083-1 2005; Med CP is the median mass loss due to CP; x is the x-value calculated according to CEN/TS 15083-1 2005



Figure 37: Decay test against *Coniophora puteana* (CP) and *Trametes versicolor* (TV), Wood biology and Wood Technology, Gottingen University, 2019

Table 10: Decay resistance against brown rot fungus *Trametes versicolor* (TV) of certain modified woods after leaching from selected treatments during up-scaling

ID	Additives	Humidity TV (%) [*]	Mass loss TV (%) [*]	Med TV (%) [*]	x	Specification
A	Gly-MA 20% HPS 150	25.19 ± 1.92	2.77 ± 0.55	2.91%	0.13	durable
B	Control HPS 150	28.41 ± 3.53	18.87 ± 2.36	18.99%	0.83	not durable
C	Gly-MA 20% HPS 160	24.14 ± 8.85	2.94 ± 1.48	2.58%	0.11	durable
D	Control HPS 160	22.44 ± 2.95	13.92 ± 1.71	14.19%	0.62	slightly durable
E	Gly-MA 20% 120 OHT+Al	16.29 ± 3.21	2.10 ± 0.26	2.10%	0.09	very durable
F	Gly-MA 40% 120 OHT	26.06 ± 2.97	3.58 ± 0.79	3.44%	0.15	durable
G	Gly-MA 40% 120 OHT+Al	29.88 ± 3.27	3.44 ± 0.86	3.50%	0.15	durable
H	MA 20% 120 OHT+Al	19.93 ± 2.18	2.26 ± 0.43	2.18%	0.1	very durable
I	Gly-MA 10% 220 Al	14.65 ± 2.12	0.67 ± 0.40	0.55%	0.02	very durable
J	MA 20% HPS 150	22.04 ± 5.41	2.57 ± 0.42	2.39%	0.1	durable
K	PG-MA 20% HPS 150	25.55 ± 3.24	2.78 ± 0.54	2.77%	0.12	durable
L	PG-MA 20% 120 OHT+Al	21.46 ± 2.64	3.62 ± 1.66	3.12%	0.14	durable
M	PG-MA 10% 220 Al	17.20 ± 3.01	2.68 ± 0.62	2.75%	0.12	durable
N	Beech wood	34.13 ± 1.40	23.30 ± 4.53	22.83%	1	not durable
P	Pine wood	35.91 ± 8.55	13.35 ± 4.43	12.31%	0.54	slightly durable

^{*}each value was based on the twenty samples; method referred to CEN/TS 15083-1 2005; Med TV is the median mass loss due to TV; x is the x-value calculated according to CEN/TS 15083-1 2005

In general, all additive-treated woods have lower mass loss values (< 5%) than untreated wood or wood control under HPS 150 and 160°C. Between the two fungi, the virulence (the untreated wood)

underwent higher attacks from the CP than TV, however, the additive-treated wood and wood control under HPS 150 and 160°C have more or less similar mass losses due to both fungi attacks, allowing slight differences in the given specification according to CEN/TS 15083-1 2005.

Among the additive-treated woods, wood treated with Gly-MA 10% 220 Al or Gly-MA 20% 120 OHT+Al presented as very durable wood against both fungi. The result have confirmed that Gly-MA 10% 220°C-treated wood has very good decay resistance properties (Mubarok et al. 2019a, b), even though duration of the peak temperature (220°C) was only 3 hours without inert condition in these up-scaling trials. On the other hand, the very good decay resistance wood treated with Gly-MA 20% 120 OHT+Al has given novel insight that at lower curing condition under opened system with aluminum covering, the modified wood has far better decay properties than treatment without aluminum covering (Paper 4). Appearance of these modified woods is shown in the Figure 38. Further, the increase in Gly-MA concentration to become 40% seems did not give better decay resistance, indicating possibly higher acid-induced thermal degradation that might make wood degradation product became easy to degrade by the fungi after leaching process.

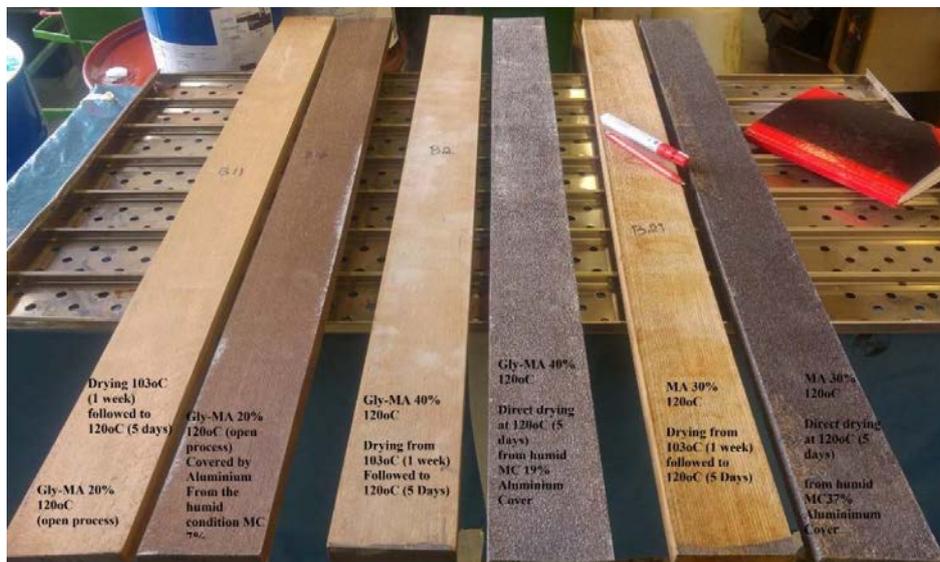


Figure 38: Appearance of Gly-MA and MA-treated wood with and without aluminum covering cured at 120°C

Under the same condition as Gly-MA 10% 220 Al-treated wood, however, PG-MA 10% 220 Al-treated wood has lower decay resistance against CV. This condition could be due to the less severe thermal condition than treatment in the Part I with 20 hours duration at same peak temperature 220°C. Due to this difference, additional molar of MA as the reactive in the formulation of PG-

MA was used to form the new PG-MA (1 : 3) in the further treatments. In overall, improvement in durability against decay could be due to the changes in chemical composition of the modified wood. Similarly as the effect of wood thermal modification, the most possible factors suggested for this improvement are the degradation of hemicellulose as the nutrition for the decaying fungi (Hakkou et al. 2006), unrecognizable of the enzyme of the fungi to degrade the modified wood polymer due to treatment (Weiland and Guyonnet 2003; Hakkou et al. 2006), the penetration hindrance of wood cell wall caused by the previous factors (e.g. bulking due to additives, shrinkage due to HPS) that makes difficulties for fungi to penetrate into the modified wood (Boonstra et al. 2007c; Thybring 2013; Hosseinpourpia and Mai 2016).

From these results, further treatments were performed by varying the temperature and condition as listed in the Table 11, while, the concentration was not varied to higher portion, avoiding higher wood degradation that might have reverse results in durability. With these certain new modification treatments, an advanced biological durability test was destined for soft-rotting micro fungi test and field test.

Soft-rotting micro fungi test

Durability against soft-rotting micro fungi was conducted by planting wood samples after leaching in unsterile soil medium with controlled humidity and placed in indoor condition for 4 months period (minimum limit of mass losses of reference wood must reach 20%) (Figure 39). Appearances of the samples after test are shown in Figure 40. According to the results, in general, the additive-treated woods have significantly far lower mass loss values due to soft rot decay than untreated wood (Table 11).



Figure 39: Samples set in soft-rotting micro fungi test, after 4 months period



Figure 40: Appearance of wood samples after 4 months soft-rotting micro fungi test

Table 11: Leaching properties and decay resistance against soft-rotting micro fungi (SR) of certain modified woods after leaching from selected treatments during up-scaling

No	Treatment	Leaching (%) [*]	Humidity (%) [*]	ML due to soft rot (%) [*]
A	PG-MA (1 : 2) 20% HPS 150	2.92 ± 0.30	62.50 ± 7.13	6.23 ± 0.37
B	PG-MA (1:3) 20% HPS 150	2.33 ± 0.41	65.49 ± 2.61	5.71 ± 0.53
C	Gly-MA 20% HPS 150	6.55 ± 0.41	69.61 ± 6.04	10.80 ± 0.60
D	PG-MA (1:2) 20% 120 OHT+Al	3.13 ± 0.28	51.31 ± 3.74	4.66 ± 0.30
E	PG-MA (1:3) 20% 120 OHT+Al	3.07 ± 0.35	51.34 ± 4.62	4.72 ± 0.35
F	Gly-MA 20% 120 OHT+Al	2.41 ± 0.37	48.32 ± 3.64	4.98 ± 0.26
G	PG-MA (1:2) 20% 150 OHT+Al	1.08 ± 0.19	49.91 ± 4.68	2.29 ± 0.27
H	PG-MA (1:3) 20% 150 OHT+Al	0.74 ± 0.16	41.84 ± 2.30	1.56 ± 0.15
I	Gly-MA 20% 150 OHT + Al	0.58 ± 0.18	34.92 ± 3.73	2.04 ± 0.45
J	PG-MA (1:2) 10% OHT 220	1.04 ± 0.16	40.01 ± 4.90	1.54 ± 0.24
K	PG-MA (1:3) 10% OHT 220	0.28 ± 0.18	39.64 ± 3.17	0.96 ± 0.22
L	Gly-MA 10% OHT 220	0.39 ± 0.18	38.19 ± 2.29	0.70 ± 0.15
M	PG-MA (1:3) 10% HPS	1.76 ± 0.17	75.81 ± 6.47	5.05 ± 0.36
N	MA 20% 150 OHT + Al	2.01 ± 0.38	40.91 ± 2.09	2.63 ± 0.46
P	Gly-MA 10% HPS	2.81 ± 0.36	80.40 ± 6.87	6.49 ± 0.94
R	Beech wood	0.97 ± 0.35	168.31 ± 22.41	35.77 ± 4.92

^{*}each value was based on the ten samples and fifteen samples for untreated wood (beech); leaching referred to EN 84 (1997); decay method referred to CEN/TS 15083-2 2005

Among the additive treated woods, treatment under OHT at 220°C with 10% w/w concentration and under OHT at 150°C + Al with 20% w/w concentration had lower mass loss values than others, indicating a robust treatment that fit for wood biological durability improvement. Similar as what have been mentioned previously, improvement in biological durability could be due to the formation of new chemical bonds between additive-wood/the chemical changes of wood components, the acidic properties of the modified wood (mainly due to additives), modification of the wood polymeric structure, penetration hindrance due to treatments or/and degradation of decay-susceptible wood components during modification (hemicellulose).

Table 12: Specification given for decay resistance against soft-rotting micro fungi (SR) of certain modified woods after leaching from selected treatments during up-scaling

No	Treatment	Median (%)*	x value	Specification
A	PG-MA (1 : 2) 20% HPS 150	6.32	0.18	durable
B	PG-MA (1:3) 20% HPS 150	5.57	0.16	durable
C	Gly-MA 20% HPS 150	10.84	0.31	moderately durable
D	PG-MA (1:2) 20%120 OHT+Al	4.67	0.13	durable
E	PG-MA (1:3) 20% 120 OHT+Al	4.68	0.13	durable
F	Gly-MA 20% 120 OHT+Al	5.06	0.14	durable
G	PG-MA (1:2) 20% 150 OHT+Al	2.19	0.06	very durable
H	PG-MA (1:3) 20% 150 OHT+Al	1.57	0.04	very durable
I	Gly-MA 20% 150 OHT + Al	2.06	0.06	very durable
J	PG-MA (1:2) 10% OHT 220	1.53	0.04	very durable
K	PG-MA (1:3) 10% OHT 220	1.03	0.03	very durable
L	Gly-MA 10% OHT 220	0.68	0.02	very durable
M	PG-MA (1:3) 10% HPS	4.90	0.14	durable
N	MA 20% 150 OHT + Al	2.64	0.08	very durable
P	Gly-MA 10% HPS	6.34	0.18	durable
R	Beech wood	35.23	1	not durable

*each value was based on median of ten samples and fifteen samples for untreated wood (beech); method referred to CEN/TS 15083-2 2005

Through these wood modification treatments, in most cases, the modified woods were specified as durable to very durable wood according to CEN/TS 15083-2 2005 (Table 12). Very durable wood is given for wood treated under OHT at 220°C with 10% w/w concentration and under OHT at 150°C with 20% w/w concentration. In terms of PG-MA-treated wood, higher portion of MA in PG-MA (1 : 3)-based additive shows slightly better resistance of the modified wood than the usual PG-MA (1 : 2)-based additive. However, both additives generated the modified woods with the same specification.

Field test

Further advanced biological durability test was performed through field test (Figure 41). The field test is conducted with the same location as the previous work in Part I, in Arboretum of Faculty of Forestry, Bogor Agricultural University, Indonesia. Similar with a furfurylated wood tested in the same location by Hadi et al. (2005), the samples were cut to a specified dimension, 200 mm × 20 mm × 8 mm (L, T, R). Further, the samples were buried vertically 150 mm below ground level and positioned/separated with ± 300 mm of a distance with other samples. However, up to now, the samples are still under ground, the results would be available later.



(a)



(b)

Figure 41: Wood samples (a) and samples setting during field test (b), Bogor, Indonesia

2) Conclusion

The main results in these series of up-scaling treatments can be summarized as follows:

- Impregnation of the chemicals/additives into the wood worked without any issues during this up-scaling process, penetration of the additive solutions into a bigger wood sample size was more or less similar with when using a small wood sample size. However, due to higher affinity of maleic acid (product hydrolysis of maleic anhydride) to hold water and might cover the moisture beneath wood surface, maleic anhydride impregnated wood with higher concentration (20/30% w/w) needed longer duration for conditioning to reach lower moisture content before curing process.
- Curing process can be operated under oven heating in opened system (OHT) or heat pressurized steam in closed system (HPS). However, due to higher wood degradation undergone when using HPS process and had slightly lower biological durability of the modified wood, system under OHT with aluminum covering is considered as the better treatment in this research, especially when wood treated using chemicals addition.
- Due to the acidic properties of the additives and effect of thermal degradation, mechanical properties of the modified wood decreased considerably.
- The results also confirmed the previous work in Part I that wood treated under OHT at 220°C with low concentration of chemicals addition (10% w/w) had better biological durability, especially against decay (white rot, brown rot, and soft rot fungi).
- The new findings were also found in this up-scaling treatments evidencing that additive-treated woods cured under OHT at 150°C with 20% w/w chemicals addition (PG-MA or Gly-MA) had more or less similar biological durability against decay (white rot, brown rot, and soft rot fungi) as the treatment under OHT at 220°C in the Part I or in this up-scaling treatment.
- The more advanced biological durability against termite in the field test is still under ongoing process.

c. Paper 5

Properties of Thermo-chemically Modified Wood base on Vinylicglycerol and Vinylicpolyglycerol Derivative under Oven heating (OHT) in Opened System and Heat Pressurized Steam (HPS) in Closed System

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Abstract

Incorporation of chemical as additive in wood thermal modification could improve dimensional stability and biological durability properties of thermally modified wood. In this study, thermo-chemical wood modification based on additive of vinylicglycerol or vinylicpolyglycerol derivative under oven heating (OHT) in opened system and heat pressurized steam (HPS) in closed systems has been investigated. European beech (*Fagus sylvatica*) known for its low dimensional stability and poor biological durability has been the subject for this improvement. Impregnation of beech wood in certain additive concentrations (10 and 20% w/w) followed with different curing temperatures (at 120, 150, or 220°C) under OHT in opened system or under HPS (150°C, water vapor pressure of 4.66 MPa, relative humidity of 100% RH) in closed system have been evaluated. Various parameter analysis including physical, chemical, mechanical, and biological durability properties has been examined. Based on the results, at the same curing temperature, mass loss due to curing temperature (ML) was higher under HPS than under OHT system. Comparable results in dimensional stability were obtained for additive-treated wood under both systems. Modulus of elasticity (MOE) increased slightly, modulus of rupture (MOR) rested the same, however, the work to maximum load in bending (WMLB) decreased 57% for wood control under HPS. Under the same additive concentration, MOR and WMLB values of additive-treated wood were comparable between both systems, however, lower MOE values were observed under HPS. Durability against *Coniphora puteana* (CP) and *Coriolus versicolor* (CV) of wood control under HPS increased by 39% and 19%, respectively. At the same curing temperature and additive concentration, durability against soft-rotting micro fungi (SR) of additive-treated wood was higher under OHT system, while, durability against CP and CV was comparable between both systems. Thermogravimetric

analysis revealed that the additive-treated wood under both systems increased the initial degradation temperature, and certain treatments could decrease the end temperature point, promoting the possibility as self-fire-retardant. FTIR have disclosed differences of the modified wood under both systems. Additive-treated wood under HPS was black in color, while, under OHT was in dark pale brown.

1. Introduction

Wood thermal modification has been investigated extensively for decades. It is already well-known that thermally modified wood has good in dimensional stability and decay durability properties, as reviewed by Militz (2002a, b), Hill (2006), Esteves and Pereira (2009), and Gérardin (2016). The changes in structural configuration on wood components as the results of the heat-induced physical-chemical transformation are believed to be a fundamental factor on the properties improvement of thermally modified wood. In principal, those transformations of the chemical wood structure are caused by the autocatalytic reactions of the cell-wall constituents (Tjeerdsma et al. 2005). Lignin is depolymerized partially and undergo to thermo-reticulate (Tjeerdsma et al. 1998, 2005; Brosse et al. 2010), hemicellulose strongly degraded (Nuopponen et al. 2004; Inari et al. 2007), and cellulose crystallinity modified (Sivonen et al. 2002; Hakkou et al. 2005). Practically, in this thermal treatment, there are not only the peak temperature and duration that influence the level of modification, but wood moisture content or heat transfer media (Mitchell 1988; Alén et al. 2002; Tjeerdsma et al. 2005; Candelier et al. 2013) and environmental pressure during process, such as in sub-atmospheric (e.g., Vacu³®), atmospheric (e.g., ThermoWood®) or elevated pressure condition (e.g., FirmoLin®, WTT) also could affect this method. On the other hand, as the respond to the high temperature condition, however, mechanical properties of wood decreased as degradation of wood components had taken place (Kubojima et al. 2000; Boonstra et al. 2007). Under sub-atmospheric pressure, Hofmann et al. (2013) reported that at this condition wood degradation products become volatile and constantly removed by the reactor. This condition might trigger the shrinkage stress due to wood anisotropy reach a maximum due to uncontrolled relative humidity (Altgen et al. 2016). In closed reactor system, the moisture content of wood and the high pressure of unsaturated steam condition would be dependent on the relative water vapor pressure (Lenth and Kamke 2001; Kubojima et al. 2003; Ishikawa et al. 2004). Other studies reported that thermal-induced wood degradation takes place faster at elevated pressure in close reactor system

than at atmospheric pressure in opened system (Stamm 1956; Ding et al. 2011; Rautkari and Hill 2014). Further, confirmed study was also performed by Altgen et al. (2016) recently as reporting that water vapor pressure was determined as the dominant variable in wood degradation process, rather than the applied peak temperature. Moreover, according to their results, the combined factors due to a better in heat transfer in a compressed gas atmosphere, reduction in evaporative cooling, and accumulation of organic acids as well as the presence of water in wood during the process were accused to be the main aspect triggering this higher wood degradation under water vapor pressure condition. Regarding to this higher wood degradation at relatively lower temperature in closed system than in opened system, it could be predicted that the modified wood might enable to have better in dimensional stability and decay durability.

On the other hand, the addition of certain chemicals as additive at low concentration into the wood incorporated with thermal modification process can also be another alternative to improve wood dimensional stability and biological durability at lower temperature than wood undergone with only thermal modification, as reported recently by Salman et al. (2016, 2017). According to their studies, termite resistance of impregnated wood with vinylicpolyglycerol 10% w/w [polyglycerol maleate (PG-MA) or polyglycerol methacrylate (PG-GM)] associated with thermal process at 220°C under inert condition gave significantly better results than wood control at the same temperature. Further, they also reported that PG-MA 10% w/w-impregnated beech thermal-treated at 200°C under inert atmosphere [mass loss due to thermal process recorded (ML) was $9.31 \pm 1.82\%$] after leaching process could improve decay durability of thermally modified control at the same condition (ML was $6.92 \pm 2.34\%$) to about 61% against *Trametes versicolor* and 92% against *Coniophora puteana*. Meanwhile, termite resistance improved about 53% with still remaining 40% of the survival rate, allowing possibly to be used as non-biocide wood preservation method. From these results, even though improvements were predominantly happened on its biological durability properties and great possibility would have contributed on its physical properties, the new knowledge on this thermo-chemical wood modification might trigger other studies to find out more the characteristic of these thermo-chemically modified wood or even to seek new methods aiming to have better properties on this path.

Regarding to the research of Salman et al. (2017) above, it was interesting to know how if the thermo-chemical wood modification is carried out under specific water vapor pressure condition (HPS) in closed system as Altgen et al. (2016) performed previously, minimizing the heating

temperature during thermal modification. Responding to this question, this paper would explain a comparative study of thermo-chemical wood modification based on certain additives made from vinylicglycerol and vinylicpolyglycerol derivatives under different specific curing conditions, in opened (oven heating) or in closed (water vapor pressure/heat pressurized steam) system. The use of vinylicglycerol was based on analogy that glycerol has similar properties to its polymer form, polyglycerol, a renewable chemical used by Roussel et al. (2001) and Salman et al. (2017) for making polyglycerol maleate (PG-MA). In order to compare effects between both systems, treatment departed based on the same mass loss value due to thermal degradation (ML), a parameter known has direct correlation with the severity of the thermal treatment (Stamm et al. 1946; Inari et al. 2009; Altgen et al. 2016) and as one of the main parameter influencing wood decay durability (Hakkou et al. 2006; Chaouch et al. 2010, 2013). This mass loss value was selected based on the mass loss value of wood control which thermally modified at 200°C under OHT in opened system, as Salman et al. (2017) reported previously. Further, for better understanding effects between both systems, certain parameter analysis including physical, chemical, mechanical, and biological properties were also examined.

2. Experimental

2.1 Material preparation

European beach (*Fagus sylvatica*) sapwood (moisture content, $\pm 11\%$) was prepared and cut to specific size [$1000 \times 20 \times 80 \text{ mm}^3$ and $650 \times 20 \times 50 \text{ mm}^3$ (L, T, R)]. Prior to the cutting process, the wood material was air conditioned at 20°C/60% of relative humidity (RH).

A technical grade of maleic anhydride pellet and glycerol (approx. 99% in purity) was purchased from Fisher Scientific Chemical. Polyglycerol was purchased from Inovyn ineos (France) as a mixture of compounds with an average molecular weight (Mw) of 242 g mol^{-1} (degree of polymerization ~ 3), with 99% in purity.

2.2 Additive formulation based on vinylicpolyglycerol or vinylicglycerol derivative

PG-MA was made according to Roussel et al. (2001). 1 mol of polyglycerol (PG as PG3, Mw = 242 g mol^{-1}) were reacted with 2 mol of maleic anhydride (MA, Mw = 98.06 g mol^{-1}) into a beaker glass equipped with magnetic stirrer and glass watch, and heated at 80°C for 3 h. The reaction was then stopped after disappearance of ATR-FTIR absorption of carbonyl group (C=O, stretch) of anhydride maleic reagent at about 1780 and 1853 cm^{-1} and a complete appearance of a characteristic ester band (C=O, stretch) of PG-MA at about 1715 cm^{-1} . The product was directly

used without further purification and dissolved into distilled water so that the final concentration of impregnating solution (additive solution) was 10% or 20% w/w. Gly-MA was prepared using the same procedure as PG-MA. Before impregnation process, these diluted additive solutions were measured for their solid content (SC) by means of SARTORIUS MA 35.

2.3 Wood modification

Each wood sample [moisture content (MC), $\pm 11\%$] was cut by 20 mm at the edge in longitudinal direction for determining the precise MC of each sample (oven drying at 103°C). Meanwhile, the rest of the large wood sample chunks was weighed (W_1) and painted with water-proof at the edge of its longitudinal direction to avoid an excessive discharge of the impregnated solution after impregnation and evaporation in the longitudinal direction during curing, minimizing crack. The samples were then impregnated in additive solution (10% or 20% w/w) under vacuum condition (5-10 KPa, 2 h), followed under pressure condition (1200 KPa, 2 h), and then aging for three days for making sure that the impregnating solution penetrated completely into the wood. After aging period, all samples were removed (an excess of the impregnating solution on the samples was wiped-out) and weighed (W_2). Afterward, the samples were pre-dried at room condition/oven drying at 40°C until MC under 30% known by weighing the humid samples (W_3). The samples were then covered by aluminum paper then heated at different curing conditions. Curing condition was adjusted according to which treatment used as follows:

Curing under oven heating system at 120°C (OHT 120)

The pre-dried samples were heated directly in the oven at 120°C for five days under atmospheric pressure.

Curing under heat pressurized steam at 150°C (HPS 150), water vapor pressure at 4.66 MPa, and humidity at 100% RH

The reactor and the selected setting condition in this curing process referred to Altgen et al. (2016). The pre-dried samples were heated under water vapor (steam) in the reactor at 50°C and kept for 55 min, then continue heated with $12^{\circ}\text{C}/\text{min}$ to 150°C and kept for 180 min under the steam pressure 4.66 MPa and 100% RH, and finally decreased by $20^{\circ}\text{C}/\text{min}$ to room temperature. The samples were then weighed (W_4), dried at 103°C in oven until constant mass, and finally weighed for knowing their moisture due to HPS.

Curing under opened system at 220°C (OHT 220)

Under atmospheric pressure, the pre-dried samples were heated at 50°C and kept for 55 min,

then continue heated with 12°C/min to 220°C and kept for 180 min, and finally decreased by 20°C/min to room temperature.

After curing process, each modified wood was weighed (W_5) and conditioned at room temperature.

During this modification, certain variables were calculated as follows:

Moisture content of wood after impregnation and pre-drying before curing process

$$MC_i (\%) = 100 \times [(W_3 - W_0) - ((W_2 - W_0) \times SC)] / W_0$$

where, MC_i is the initial moisture content of the impregnated wood just before curing process, W_0 the anhydrous mass of wood before impregnation calculated from the corrected moisture of humid mass of initial wood (W_1) [$W_0 = W_1 / (MC + 1)$], W_2 the mass of wood just after impregnation, W_3 the mass humid of impregnated wood before curing, SC the percentage of solid content of the solution.

Moisture content of wood just after HPS process before drying at 103°C at the end

$$MC_t (\%) = 100 \times (W_4 - W_5) / W_5$$

Where MC_t is the moisture content of the modified wood just after HPS process before drying, W_4 is the wet mass of the modified wood just after HPS process before drying at 103°C, W_5 the mass of modified wood after curing process.

Weight percent gain after curing process/mass changes (Δm)

$$\Delta m (\%) = 100 \times (W_5 - W_0) / W_0$$

where Δm is the weight percent gain/mass change of the modified wood at different curing conditions.

Mass loss due to curing process (ML)

$$ML (\%) = 100 \times [((WPG \times W_0) + W_0) - W_5] / ((WPG \times W_0) + W_0)$$

where ML is the mass change of the modified wood at different curing conditions, WPG the weight percent gain of wood at 103°C which calculated as $WPG = 100 \times [(W_1 - W_0) \times SC] / W_0$.

2.4 Characterization

For the characterization, the modified wood was cut to the specific dimension according to the parameter analysis. In brief, the main parameters analysis tested in this study, dimension, and number of samples used are listed in the Table 1.

Table 1 The main analytical parameter, size, and number of samples used in this study

No	Parameter	Dimension L, T, R (m ³)	N	Standard
1	Leaching	50 × 20 × 15	20	Adapted to EN 84 (1997)
2	MOE/MOR/WMLB*	180 × 10 × 10	15	DIN 52186 (1978)
3	Decay test against <i>Coriolus versicolor</i>	50 × 20 × 15	20	CEN/TS 15083-1:2004
4	Decay test <i>Coniophora puteana</i>	50 × 20 × 15	20	CEN/TS 15083-1:2004
5	Soft-rot test	100 × 10 × 5	10	CEN/TS 15083-2:2004

*Wood material for MOE/MOR/WMLB test had prepared before modification; Decay and soft-rot test samples were based on the samples after leaching process

Additional parameters were also investigated in this characterization as listed as follows:

Swelling, Anti-swelling efficiency (ASE), and Shrinkage

These measurements were based on the samples used during the leaching test [EN 84 (1997)] at which dimensions of all samples were recorded before, during, and after leaching test. Calculation for the ASE value referred to Rowell and Ellis (1978). Swelling value was calculated based on the increase in wood volume wet at the end of the leaching test compared to the initial dried wood volume (103°C) before leaching. Whereas, the shrinkage was based on the decrease of dried volume (103°C) of sample after leaching test compared to the initial volume of sample before leaching.

Acidity as pH value of the leachate during leaching test

Acidity of the total leachate during the leaching test was measured by pH meter (Mettler Toledo, calibrated by two buffer solution 4.00 and 7.00 from ChemSolute®).

Thermogravimetric analysis (TGA)

TGA was performed by means of TG 209 F1 Iris instrument. Sample powder (± 15 mg) were placed in alumina (Al₂O₃) crucible. Thermogram were recorded using a heating rate of 10°C/min from 50 to 700°C under a nitrogen purge (20 ml.min⁻¹).

Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR spectra were recorded on a Bruker Alpha Eco-ATR instrument. The spectra of the treated or untreated wood sawdust was recorded in the range of 4000 – 400 cm⁻¹ at a resolution of 4 cm⁻¹ with an ATR cell.

Microscopic observation

Images of the sample's surface were investigated by means of Axioplan 2 imaging microscope with Zeiss optic equipped with Nikon D5-Fi2 Digital Sight and NIS-element imaging software. Image was taken at certain magnification on the cross-section surface, which prepared by cutting very smoothly the cross-section surface of treated and untreated samples.

3. Results and Discussion

Data concerning wood properties during modification is presented in the Table 2.

During the modification, penetration of the impregnating solution of both additive solutions (Gly-MA or PG-MA) in different concentrations performed without any issues, allowing water uptake reached more than 100% w/w (data is not presented here) for all sample size. The easily treatable of beech wood (EN 350 2016), the good polarity, and relatively low molecular size of the additives as well as its low solution concentration (10/20% w/w) were the main factors supporting this process.

In the post-impregnation process and just before curing, initial moisture content (MC_i) of the impregnated wood was kept not to be higher than 30%, avoiding higher effect of wood degradation through hydrolysis at high temperature (Garrot et al. 1999; Ishikawa et al. 2004) and crack formation of wood during curing process. The wood crack/split in this case, were not only caused by the changing moisture between wood – environment (oven/heating reactor) or wood anatomy (Lamb 1992), but might also by the chemical/additive properties used. To minimize this issue, the pre-dried wood was un-tightly covered by the aluminum paper to lower the evaporation rate during curing/drying, allowing wood probably to be soften and minimizing stress strain due to moisture change. Chow and Pickles (1971) reported regardless to the species, oven-dry wood start to soften at 180°C. When the MC_i of wood > 10%, the softening temperature would decrease to 160°C, and the absolute softening condition happened at the MC about 30%. Therefore, in this study, the MC_i was kept under 30%, especially for impregnated wood. Further, Rautkari and Hill (2014) reported that the initial moisture content (MC_i) before thermal treatment under high-pressure saturated steam could influence the mass loss (ML) and anti-swelling efficiency (ASE) of the modified wood through which the excessive ML value (17%) due to high initial moisture content (26%) could decrease ASE values. Regarding to this issue, however, the existence of the additives and different wood species (*Fagus sylvatica*) in this study might result differently according to the obtained results. Based on the observation

(Table 2), MCi values of both impregnated wood and control were under 30%. Technically, these values were dependent on the pre-drying period before curing process. The concentration of the impregnating solution and its composition influenced the duration of the pre-drying process at which the lowest concentration of the impregnating solution and the lowest composition in mass of the maleic anhydride (MA) in the additive formulation would faster the period to reach MCi values < 30%. Therefore, due to lower portion in mass of MA in PG-MA than in Gly-MA, under the same solution concentration and pre-drying period, PG-MA-impregnated wood dried faster than Gly-MA-impregnated wood. This condition presumably indicated that beside the hygroscopic properties of MA, it might also avert/minimize the evaporation of water from the inner side of the wood (by surface covering) through its less polar double bonds structure.

Table 2 Moisture content of impregnated wood before and after thermal process, mass change, and mass loss of the modified wood due to curing process

ID	Treatment	MCi (%)*	MCt (%)*	Δm (%)*	ML (%)*
A	Untreated	9.49 ± 0.15	< 1%	0	0
B	Gly-MA 20% 120 OHT	6.07 ± 1.78	< 1%	10.86 ± 1.35	12.23 ± 0.94
C	PG-MA 20% 120 OHT	16.11 ± 1.38	< 1%	12.13 ± 1.39	10.27 ± 0.65
D	Gly-MA 20% 150 OHT	7.99 ± 0.28	< 1%	10.79 ± 0.11	12.60 ± 0.06
E	PG-MA 20% 150 OHT	17.36 ± 0.97	< 1%	10.81 ± 1.79	11.48 ± 0.09
F	Gly-MA 10% 220 OHT	17.37 ± 1.51	< 1%	-6.84 ± 1.04	18.53 ± 0.71
G	PG-MA 10% 220 OHT	24.92 ± 2.01	< 1%	-3.91 ± 0.56	15.43 ± 0.59
H	Control HPS 150	9.49 ± 0.15	4.61 ± 0.13	-3.81 ± 0.45	3.81 ± 0.45
I	Gly-MA 20% HPS 150	21.14 ± 0.85	12.38 ± 1.32	7.34 ± 1.09	13.77 ± 0.70
J	PG-MA 20% HPS 150	16.09 ± 0.82	10.78 ± 1.77	3.54 ± 1.19	20.52 ± 2.50
K	Gly-MA 10% HPS 150	18.44 ± 1.53	15.99 ± 1.48	-5.87 ± 0.94	17.94 ± 0.48
L	PG-MA 10% HPS 150	15.95 ± 2.08	13.08 ± 1.59	-6.05 ± 0.66	17.88 ± 0.59

*each value was based on the average of 2, 3, or 4 samples (size: 998 × 20 × 80 mm³, L, T, R) or the average of 3, 6, or 10 samples (size: 648 × 20 × 50 mm³, L, T, R)

In the curing process, concentration of the impregnated additives and process condition were considered as the critical factors influencing the modified wood properties. In this section, there was not only fixation of the chemical needed to achieve, but also a minimum wood degradation as well as the minimum formation of crack that sometime happens in particular condition (e.g., wood anatomy and defects, uncontrolled humidity). In HPS curing condition, the reactor and setting referred to Altgen et al. (2016), proceed in closed system at 150°C under water vapor

pressure over 4.66 MPa and 100% RH. This condition was selected based on the consideration that beech wood had mass loss around 4% (based on the dry weight), the equal mass loss of beech wood proceed at 200°C with OHT under nitrogen flow condition (Salman et al. 2017). With the similar mass loss value ($\pm 4\%$) from the selected HPS condition in closed system above, the wood properties especially its dimensional and biological durability properties were expected to be similar with the results of Salman et al. (2017).

According to data in the Table 2, in most cases, thermo-chemical wood modification under HPS 150°C in closed system generated higher mass loss values (ML) than treatment under OHT system in the same peak temperature (150°C), corresponding to some previous studies quoting that thermal degradation takes place faster at elevated temperature in closed system than in atmospheric pressure in opened system (Stamm 1956; Ding et al. 2011; Rautkari and Hill 2014). As comparison, we also report treatment under lower temperature (120°C OHT) and higher temperature (220°C OHT). The latest treatment was performed based on the best treatment (PG-MA) known for its excellent biological durability properties from Salman et al. (2017), it was made also as a comparison for its lower molecular size, Gly-MA. However, treatment at 200°C in OHT system, as the comparison for HPS 150 in closed system based on the similar mass loss values of wood control, was not conducted in this study and the data will refer to Salman et al. (2017).

Based on the observation, it is shown that due to low thermal degradation (lower ML values), weight percent gain after curing/mass change values (Δm) of additive-treated wood cured at 120°C were higher than other curing processes. At this lower curing condition, both additives had more or less similar Δm values. However, due to higher ratio in mass of MA in Gly-MA than in PG-MA-based additive and a more reticulate product of PG-MA, Δm of Gly-MA-treated wood had slightly lower value than PG-MA-treated wood at this OHT system. A similar respond also happened in additive-treated wood under curing condition at 150 and 220°C with OHT system. This condition was assumed that the higher portion in mass of MA in additive might trigger a higher acidity of the additive, promoting higher effect on wood degradation by which under OHT system the wood degradation products might easily to evaporate. In contrast, under HPS 150°C in closed system, the higher portion in mass of MA in additive 20% w/w might react intensively with wood components as well as wood thermal degradation products [e.g., furfural, organic acid, hydroxymethyl furfural, etc (Chaouch et al. 2010; Karlsson et al. 2012; Altgen et al. 2016)] to form

new stable compounds, presenting higher Δm values of Gly-MA-treated wood than PG-MA. However, at this HPS system, wood degradation was more obvious than at 120 and 150°C under OHT system. The moisture content values of the modified wood just after HPS 150°C (Mct) also indicated the moisture content of wood during process which could relate to its mass loss value (Altgen et al. 2016), however, with the existence of the additive, it seems the relation was not consistence. Comparing to treatment with PG-MA 10% w/w at 200°C under OHT system from Salman et al. (2017), treatment with HPS 150°C in closed system also gave higher ML values ($17.88 \pm 0.59\%$) than theirs ($6.92 \pm 2.34\%$). Regarding to the ML data above, thermo-chemical wood modification under HPS 150°C in closed system seems similar to treatment at 220°C under OHT system, generating similar mass loss values between both system under the same additive concentration, 10% w/w. Even though the mass loss values were similar for the latest treatments, the characteristic of the modified wood still must to be examined. In the case of PG-MA 10%-treated wood at 220°C with OHT system under inert atmosphere, ML values in our study (15.43 ± 0.59) also confirmed the one reported by Salman et al. (2017) (13.21 ± 2.25 %). At this highest curing temperature, even though ML values of wood control reached about 15% (Salman et al. 2017), three time higher than wood control cured under HPS. However, with the existence of the additive, treatment under HPS 150°C gave similar ML values between both systems.

Data concerning mass loss of the modified wood due to leaching, pH of the leachate from the leaching test, and dimensional stability of the modified wood is presented in the Table 3.

According to data from the leaching test, in most cases, mass loss due to leaching (ML_L) values of the treatment under HPS 150°C were higher than others. This condition probably was the result of the curing under wet circumstance, promoting the unevaporated wood degradation products that might release during leaching test. Under this condition, wood control reached WL_L values around $3.78 \pm 0.32\%$, almost three time higher than WL_L values of wood control at 200°C with OHT system from Salman et al. (2017) ($1.28 \pm 0.40\%$). In this case, water soluble compounds, mainly carbohydrate and furfural that accumulated during process (Karlsson et al. 2012; Altgen et al. 2016), could be a main factor for higher WL_L values of wood control under HPS 150°C in closed system. In the case of additive-treated wood, the unreacted additives or the product reaction between additive and the wood degradation products might also be released during the test, decreasing pH value of the leachate. A similar ML_L value was also happened at 120°C under OHT

curing condition, however, effect of the unreacted/unfixed additive to the wood at this lower curing condition might contribute much on this. On the other hand, this study also confirmed that WL_L values of PG-MA 10%-treated wood at 220°C with OHT system had the same value as the one obtained by Salman et al. (2017) ($1.44 \pm 0.46\%$). Under this highest thermal condition, it was assumed that some of the volatile wood degradation products (e.g., organic acid, furfural) had evaporated during thermal process, releasing non-volatile wood degradation products with similar pH value as untreated wood to the leachate.

Table 3 Swelling, anti-swelling efficiency, and shrinkage values of the modified wood

ID	Treatment	ML_L (%)	pH	Swelling (%) ^b	ASE (%) ^b	Shrinkage (%) ^b
A	Untreated	1.30 ± 0.40	6.93	25.59 ± 3.6	0	0
B	Gly-MA 20% 120 OHT	3.73 ± 0.32	3.83	6.32 ± 0.28	75.32 ± 1.08	2.26 ± 0.10
C	PG-MA 20% 120 OHT	3.33 ± 0.43	4.93	8.70 ± 0.24	65.99 ± 0.95	2.29 ± 0.30
D	Gly-MA 20% 150 OHT ^a	0.58 ± 0.18	NT	NT	NT	NT
E	PG-MA 20% 150 OHT ^a	1.08 ± 0.19	NT	NT	NT	NT
F	Gly-MA 10% 220 OHT	0.72 ± 0.09	6.87	7.78 ± 0.24	69.62 ± 0.95	0.37 ± 0.11
G	PG-MA 10% 220 OHT	1.43 ± 0.09	6.71	8.47 ± 0.29	66.90 ± 1.11	1.02 ± 0.12
H	Control HPS 150	3.78 ± 0.32	5.92	14.57 ± 0.54	43.07 ± 2.12	3.84 ± 0.70
I	Gly-MA 20% HPS 150	3.00 ± 0.37	4.09	7.98 ± 0.62	68.83 ± 2.43	2.20 ± 0.43
J	PG-MA 20% HPS 150	3.70 ± 0.43	4.83	9.52 ± 0.28	62.79 ± 1.11	3.30 ± 2.24
K	Gly-MA 10% HPS 150 ^a	2.81 ± 0.36	NT	NT	NT	NT
L	PG-MA 10% HPS 150 ^a	1.76 ± 0.17	NT	NT	NT	NT

ML_L is the mass loss due to leaching process referred to EN 84 (1997); ^a ML_L data was based on the sample size $100 \times 10 \times 5 \text{ mm}^3$ ($n = 20$); ^bdata was based on the sample size $100 \times 10 \times 5 \text{ mm}^3$ ($n = 10$); NT is not tested

Dimensional stability, measured as swelling, ASE, and shrinkage values, revealed that the incorporation of the additives with thermal modification can improve dimensional stability of untreated wood or thermally modified wood (wood control HPS 150°C). ASE of wood control under HPS 150°C reached $\pm 43\%$, two times higher than ASE under OHT system at 150°C in our preliminary test ($WL = 0.1\%$; ASE = $\pm 22\%$) (Mubarok et al. 2019a, b). This higher ASE values of wood control under HPS 150°C could be due to its higher mass loss values than OHT system, even though this condition would depend on the initial moisture content (MCi) of wood before HPS as previously reported by Rautkari and Hill (2014). In additive-treated wood, swelling decreased for about three to four times, ASE reached more than 60%, and shrinkage reached to maximum value around 2 – 3%. Between two kinds of additives, Gly-MA-treated wood tends to have higher stability than PG-MA-treated wood. In this case, the higher portion in mass of MA

in Gly-MA than in PG-MA was also believed as the main cause for its better dimensional stability, confirming previous studies working with MA-based wood modification (Bodirlau et al. 2008; Essoua et al. 2015; Mubarok et al. 2019a, b). Similarly as what has been reviewed by Esteves and Pereira (2009), improvement in this dimensional stability was suggested as the result of not only the degradation of hemicellulose and modification of lignin (Chaouch et al. 2013) but also the formation of the new chemical bonds between additive and hydroxyl groups of wood, decreasing hygroscopicity of the wood. Even though some treatments were not tested for their dimensional stability, the study could estimate that their ASE values might reach more than 60% due to their higher thermally modified than treatment at 120°C curing condition.

Data concerning the mechanical properties of the modified wood is presented in the Table 4.

Table 4 Density, modulus of elasticity, modulus of rupture, and work to maximum load in bending values of the modified wood

ID	Treatment	Density (Kg.m ⁻³)	MOE (N.mm ⁻²)	MOR (N.mm ⁻²)	WMLB (Nmm)
A	Untreated	654.5 ± 15.6	12475 ± 712	110 ± 6	2599 ± 369
B	Gly-MA 20% 120 OHT	739.3 ± 13.8	13180 ± 816	87 ± 20	496 ± 186
C	PG-MA 20% 120 OHT	746.3 ± 21.1	14080 ± 1212	87 ± 14	491 ± 132
D	Gly-MA 20% 150 OHT	760.5 ± 20.5	14586 ± 1323	100 ± 17	581 ± 158
E	PG-MA 20% 150 OHT	733.8 ± 28.8	13533 ± 955	95 ± 13	547 ± 145
F	Gly-MA 10% 220 OHT	653.6 ± 21.8	14247 ± 1036	83 ± 12	379 ± 102
G	PG-MA 10% 220 OHT	678.0 ± 29.1	14193 ± 1437	86 ± 12	408 ± 98
H	Control HPS 150	654.5 ± 28.1	13800 ± 995	110 ± 16	1121 ± 363
I	Gly-MA 20% HPS 150	766.8 ± 18.4	11680 ± 1107	80 ± 17	459 ± 180
J	PG-MA 20% HPS 150	749.9 ± 27.4	14293 ± 1317	100 ± 27	593 ± 305
K	Gly-MA 10% HPS 150	654.4 ± 29.9	13760 ± 1257	81 ± 18	435 ± 216
L	PG-MA 10% HPS 150	649.4 ± 25.6	13253 ± 1269	77 ± 22	419 ± 257

According to the mechanical properties, in most cases, the three-points bending MOE of the additive-treated wood increased as well as wood control under HPS 150°C. The increase in MOE value, however, was also accompanied by the increase of density. In contrast, due to the acidic properties of the applied additives and combined with thermal-induced wood degradation, MOR and work to maximum load in bending (WMLB) values decreased until approx. 30% and 84%, respectively. In general, MOE, MOR, and WMLB values of additive-treated woods under OHT were comparable with the additive-treated woods under HPS, independently to their

concentrations and curing temperatures. With the absence of additive, wood control under HPS 150 presents the same value in MOR at the same density level, however, WMLB values decreased for about 57% due to the intensive thermal degradation, deteriorating of fracture properties due to the diminution of amorphous polysaccharide content (Esteves and Pereira 2009). In overall, the addition of both kinds of additives at different concentrations gave similar responds in mechanical properties.

Data concerning durability of the modified wood and wood control against brown-rot fungi *Coniophora puteana* (CP) is presented in the Table 5.

Table 5 Durability of the modified wood after leaching against *Coniophora puteana* based on CEN/TS 15083-1:2004

ID	Treatments	HR CP (%)	ML CP (%)	Med CP (%)	x value	Description
A	Untreated	36.44 ± 9.43	34.08 ± 6.28	35.16	1	not durable
B	Gly-MA 20% 120 OHT	15.24 ± 3.26	2.13 ± 0.34	2.15	0.06	very durable
C	PG-MA 20% 120 OHT	19.39 ± 1.33	3.10 ± 1.39	3.19	0.09	very durable
D	Gly-MA 20% 150 OHT	NT	NT	NT	NT	NT
E	PG-MA 20% 150 OHT	NT	NT	NT	NT	NT
F	Gly-MA 10% 220 OHT	12.37 ± 0.65	-0.32 ± 0.15	-0.35	-0.01	very durable
G	PG-MA 10% 220 OHT	14.53 ± 1.13	0.00 ± 0.26	-0.04	0	very durable
H	Control HPS 150	37.29 ± 7.07	20.82 ± 4.44	20.84	0.59	slightly durable
I	Gly-MA 20% HPS 150	21.98 ± 1.56	4.11 ± 0.82	4.02	0.11	durable
J	PG-MA 20% HPS 150	25.22 ± 1.89	3.39 ± 1.20	3.46	0.1	very durable
K	Gly-MA 10% HPS 150	NT	NT	NT	NT	NT
L	PG-MA 10% HPS 150	NT	NT	NT	NT	NT
M	Pine (control CP)	45.80 ± 2.43	41.49 ± 5.99	42.79	1.22	not durable

HR CP is the humidity of sample during decay test against CP; ML CP the mass loss of sample due to decay against CP; Med CP the median of ML CP data; x value the value calculated from the reduction mass loss due to decay of sample in comparison with untreated sample; description the classification of durability class based on x value according to CEN/TS 15083-1:2004

According to the CEN/TS 15083-1:2004, durability test against brown-rot fungus (CP) would be valid if the softwood (*Pinus sylvestris*) as virulence sample reached mass loss more than 30%. Based on the experiment, the virulence sample (Pine wood) reached mass loss 41.49%, thus the decay test against CP was valid. Based on the observation, all additive-treated woods after leaching process [EN 84 (1997)] presented their good resistance against CP, even though some of the treatments were not tested. Compared to the untreated beech, mass loss due to decay CP

(ML CP) of additive-treated wood in overall decreased until more than 85%, allowing them to be classified mostly as very durable wood according to CEN/TS 15083-1:2004. In the case of OHT system, Salman et al. (2017) reported that beech control and beech treated by PG-MA 10% w/w at 150°C under OHT system only reduced mass loss against CP and CV (*Coriolus versicolor*) about 1.5% and 0% for beech control and about 14.37% and 22.79% for PG-MA-treated wood, respectively. Based on their results, therefore, it could be assumed that wood control under OHT system either heated at 120°C or 150°C would be failed in decay test, due to low effect of thermal degradation at these conditions. However, with higher additive concentration (20% w/w), treatment under 120°C could decrease ML CP value until almost 94% (classified as very durable wood) in comparison with untreated wood, indicating that chemical modification played dominant role in this condition. Regarding to this result, it could be estimated that ML CP for additive-treated wood cured at 150°C with OHT system would be better than at 120°C.

On the other hand, under HPS 150°C in closed system, wood control could decrease ML CP until around 38% (classified as slightly durable) in comparison with untreated beech or wood control treated at 150°C with OHT system (Salman et al. 2017). Meanwhile, comparing to higher temperature under OHT system, HPS 150°C brought the wood control to have almost similar durability against CP with wood control at 200°C OHT system from Salman et al. (2017), which ML CP decreased until 45% (Salman et al. 2017). Regarding to this latest case, it seems that under the similar mass loss due to curing process (ML) values between both systems (as mentioned previously), durability properties against CP of both systems could also the same. However, due to higher effect of thermal degradation at 220°C, Salman et al. (2017) reported that mass loss due to decay CP and CV of beech wood control decreased until about 98% and 92%, respectively. In other words, through these results, improvement in durability against decay could be due to several factors which some of them have been reviewed by Esteves and Pereira (2009) for thermally treated wood, including the transformation of hemicellulose from hydrophilic and easily digestible to become hydrophobic molecule and the formation of the new chemical bonds between additive – wood by which the enzyme do not recognize them, and the lower fiber saturation point as shown by the lower humidity values (HR CP) due to the structural transformation of wood components in the treated wood over the untreated wood.

Data concerning durability of the modified wood and wood control against white-rot fungi *Coriolus versicolor* is presented in the Table 6.

Table 6 Durability of the modified wood against *Coriolus versicolor* based on CEN/TS 15083-1:2004

ID	Treatments	HR CV (%)	ML CV (%)	Med CV (%)	x value	Description
A	Untreated	34.13 ± 1.40	23.30 ± 4.53	22.83	1	not durable
B	Gly-MA 20% 120 OHT	16.29 ± 3.21	2.10 ± 0.26	2.1	0.09	very durable
C	PG-MA 20% 120 OHT	21.46 ± 2.64	3.62 ± 1.66	3.12	0.14	durable
D	Gly-MA 20% 150 OHT	NT	NT	NT	NT	NT
E	PG-MA 20% 150 OHT	NT	NT	NT	NT	NT
F	Gly-MA 10% 220 OHT	14.65 ± 2.12	0.67 ± 0.40	0.55	0.02	very durable
G	PG-MA 10% 220 OHT	17.20 ± 3.01	2.68 ± 0.62	2.75	0.12	durable
H	Control HPS 150	28.41 ± 3.53	18.87 ± 2.36	18.99	0.83	not durable
I	Gly-MA 20% HPS 150	25.19 ± 1.92	2.77 ± 0.55	2.91	0.13	durable
J	PG-MA 20% HPS 150	25.55 ± 3.24	2.78 ± 0.54	2.77	0.12	durable
K	Gly-MA 10% HPS 150	NT	NT	NT	NT	NT
L	PG-MA 10% HPS 150	NT	NT	NT	NT	NT
M	Pine (control CP)	35.91 ± 8.55	13.35 ± 4.43	12.31	0.54	slightly durable

HR CV is the humidity of sample during decay test against CV; ML CV the mass loss of sample due to decay against CV; Med CV the median of ML CV data; x value the value calculated from the reduction mass loss of sample due to decay in comparison with untreated sample; description the classification of durability class based on x value according to CEN/TS 15083-1:2004

Validity of decay test against white-rot fungi *Coriolus versicolor* was proven by the mass loss of virulence sample (beech wood) reached more than 20%. Based on the observation, mass loss due to decay CV of additive-treated wood after leaching process decreased for more than 84%, allowing them to be classified mostly as durable wood according to CEN/TS 15083-1:2004. Between the additive-treated woods, Gly-MA-treated wood seems had higher durability than PG-MA-treated wood under OHT system, presenting lower mass loss due to CV (ML CV) and classified as very durable wood. The higher portion in mass of MA in Gly-MA than in PG-MA might also influence its durability improvement, reducing the pH value of the modified wood (can be seen in the pH of the leachate) and the hygroscopicity (diminution in humidity, HR CV) through the transformation of the hemicellulose or the new chemical bonds (especially the ester bond) between additive and wood, as presented in FTIR analysis forwards. Under HPS 150°C curing condition, however, both additives gave the similar responds, presenting lower resistance against CV. This condition was assumed that under HPS system, the additives was diluted due to the wet condition (water vaporized steam, 100% HR) and degraded intensively the wood components

through hydrolysis in acidic condition, generating the products that could be released during leaching. In the same time, however, this condition could minimize the formation of the new chemical bond between additive and hydroxyl group of the main polysaccharide, which needing dehydration process (releasing water as by product reaction). Even though drying process at 103°C after HPS could evaporate moisture in wood, the condition might not enough to make intensively new chemical bonds, allowing the unreacted OH group of the main polymer in wood remained have higher affinity against moisture (high HR CV).

In the case of wood control under HPS 150°C, the treatment reduced ML CV only about 19% in comparison with untreated wood. Compared to Salman et al. (2017), the HPS 150°C made wood more durable than wood control treated at 150°C OHT (no reduction in ML CV at this condition) but less durable than 200°C OHT system against CP (ML CV reduced 40% at this condition).

Data concerning the durability against soft-rotting micro-fungi is presented in the Table 7.

Since the soft-rot attacks wood differently than the previous decay tests, this durability test is usually performed for wood/treated wood before testing them in the field/exterior area. In soft-rot test, the existence of the tunneling bacteria in the soil fertile media could aggravated the attacks on wood and even hardly to remove after the test, as shown in the Figure 1a.

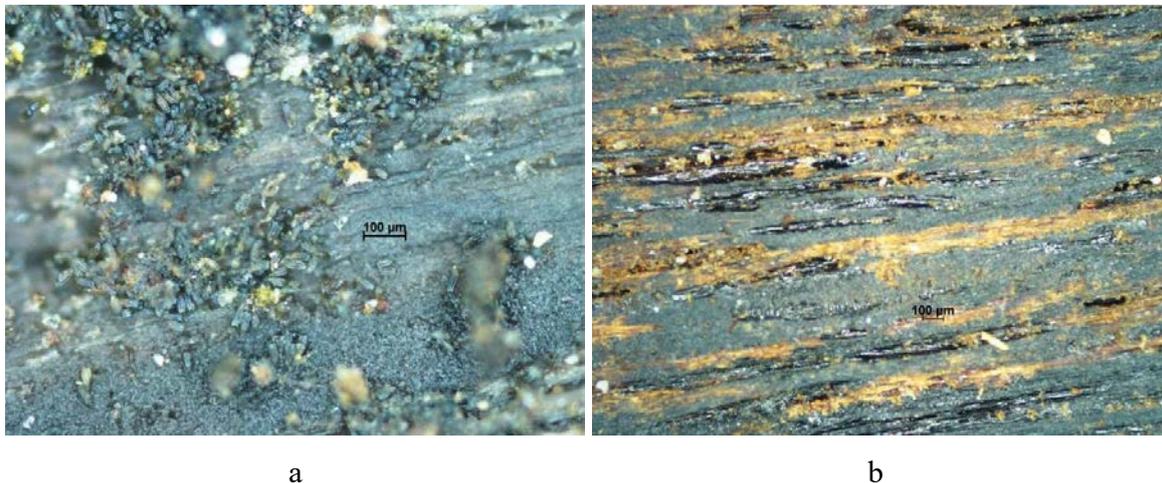


Figure 1 The appearance of some tunneling bacteria on the untreated wood (a) and the appearance of wood treated with Gly-MA 20% HPS 150°C (b) at the end period of soft-rot test in fertile soil media after cleaning process

According to the results, among the additive-treated wood after leaching process, treatment with additive 20% at 150°C and additive 10% at 220°C under OHT system have classified the modified

wood as very durable wood against soft-rot due to the double effects of chemical and thermal modification based on the classification given by CEN/TS 15083-2:2004. Even though classification were based on the median value, the reduction in mass loss due soft rot (ML SR) values reached more than 93%, in comparison with untreated wood. However, under HPS 150°C, most treatments with additives were in category as durable wood, the same as treatment under 120°C under OHT system due to its dominant effect of chemical modification, reducing the WL SR values maximum until approx. 87%. The cause for durability improvement in these additive-treated woods were similar with what has been discussed in the previous decay test (CP and CV). Further, it seems that the existence of the additive made the modified wood were well preserved from the attacks of the tunneling bacteria, as there were not any tunneling bacteria observed under the light microscope on the additive-treated wood after cleaning process (Figure 1b).

Table 7 Durability of the modified wood against soft-rotting micro-fungi based on CEN/TS 15083-2:2004

ID	Treatments	HR SR (%)	ML SR (%)	Med SR (%)	x value	Description
A	Untreated	168.31 ± 22.41	35.77 ± 4.92	35.23	1	not durable
B	Gly-MA 20% 120 OHT	48.32 ± 3.64	4.98 ± 0.26	5.06	0.14	durable
C	PG-MA 20% 120 OHT	51.31 ± 3.74	4.66 ± 0.30	4.67	0.13	durable
D	Gly-MA 20% 150 OHT	34.92 ± 3.73	2.04 ± 0.45	2.06	0.06	very durable
E	PG-MA 20% 150 OHT	49.91 ± 4.68	2.29 ± 0.27	2.19	0.06	very durable
F	Gly-MA 10% 220 OHT	38.19 ± 2.29	0.70 ± 0.15	0.68	0.02	very durable
G	PG-MA 10% 220 OHT	40.01 ± 4.90	1.54 ± 0.24	1.53	0.04	very durable
H	Control HPS 150	NT	NT	NT	NT	NT
I	Gly-MA 20% HPS 150	69.61 ± 6.04	10.80 ± 0.60	10.84	0.31	moderately durable
J	PG-MA 20% HPS 150	62.50 ± 7.13	6.23 ± 0.37	6.32	0.18	durable
K	Gly-MA 10% HPS 150	80.40 ± 6.87	6.49 ± 0.94	6.34	0.18	durable
L	PG-MA 10% HPS 150	75.81 ± 6.47	5.05 ± 0.36	4.9	0.14	durable

HR SR is the humidity of sample during decay test against SR; ML SR the mass loss of sample due to decay against SR; Med SR the median of ML SR data; x value the value calculated from the reduction mass loss of sample due to decay in comparison with untreated sample; description the classification of durability class based on x value according to CEN/TS 15083-2:2004

Data concerning thermogravimetric analysis is presented in the Table 8

According to thermogravimetric analysis, the addition of the additives could increase an onset temperature (an initial degradation temperature) of all additive-treated wood by the range of 18

– 35°C higher than untreated wood. Between the additives used, most of Gly-MA-based additive made slightly higher in onset temperature than PG-MA-based additive but then made the lower in the end temperature, indicating that Gly-MA-treated wood has self-fire-retardant properties. This unique characteristic of Gly-MA-treated wood could be due to higher portion in mass of MA in Gly-MA than in PG-MA. A higher content of MA was assumed could trigger higher degradation of wood components (e.g., hemicellulose) during wood modification. Furthermore, its acidic properties might act as a dehydrating agent and leads to increased yield of char (some char are produced at lower temperature than charring temperature of the wood) and reduced the volatiles, a similar reason explained by Rowell and Diertenberger (2012) for chemical as coating-based fire retardant. As the result of this early wood degradation, the modified wood would have higher onset temperature, lower in the end temperature, and lower mass changes during TGA. Although the end temperature would also depend on which additive used, in this case, glycerol (as monomer form of polyglycerol) seems has lower thermal stability than polyglycerol in the form of their esterified products (Gly-MA and PG-MA).

Table 8 Thermogravimetric (TG) analysis of the modified wood and wood control

ID	Treatment	Onset (°C)	Mid (°C)	Inflection (°C)	End (°C)	Mass changes (%)
A	Untreated	307.1	337.8	356	374.2	-67.93
B	Gly-MA 20% 120 OHT	334.1	348.2	350.3	352.1	-59.51
C	PG-MA 20% 120 OHT	332.8	352.8	356.4	372.8	-65.51
D	Gly-MA 20% 150 OHT	NT	NT	NT	NT	NT
E	PG-MA 20% 150 OHT	325.8	350.1	355.8	374.8	-65.53
F	Gly-MA 10% 220 OHT	342.1	348.4	348.8	355.1	-60.74
G	PG-MA 10% 220 OHT	331.8	353.5	355.7	375.3	-57.49
H	Control HPS 150	311.9	341	357.3	372.1	-69.55
I	Gly-MA 20% HPS 150	334.6	346.1	345.2	357.2	-49.16
J	PG-MA 20% HPS 150	333.1	352.2	355.5	371.1	-58.19
K	Gly-MA 10% HPS 150	342.9	349.1	350.3	356.5	-53.56
L	PG-MA 10% HPS 150	332.3	352.8	357.1	373	-60.55

Onset is the initial temperature during TG; Mid the middle temperature profile of sample during TG; inflection the inflection temperature of sample during TG; Mass changes the reduction mass of sample during TG.

FTIR spectra of additive-treated wood and wood control is presented in Figure 2, while, the

assignment and the difference in peak absorptions between the modified wood in comparison with untreated wood are presented in the Table 9 and 10, respectively.

FTIR was found as an appropriate technique to determine the intensity of the specific bonds and functional groups within the polymeric structure (Nuopponen et al. 2004; Tjeerdsma et al. 2005). Functional group analysis by FTIR have shown that there are many differences between untreated wood and the treated wood, especially for additive-treated wood under different curing conditions. For easily differentiating and interpreting the spectra, four zones from approximative peaks have been put in the Figure 2 (a – e) and interpreted in Table 9. Based on the main observed peaks (Table 9), the difference absorption between untreated wood and the treated woods could be obtained (Table 10).

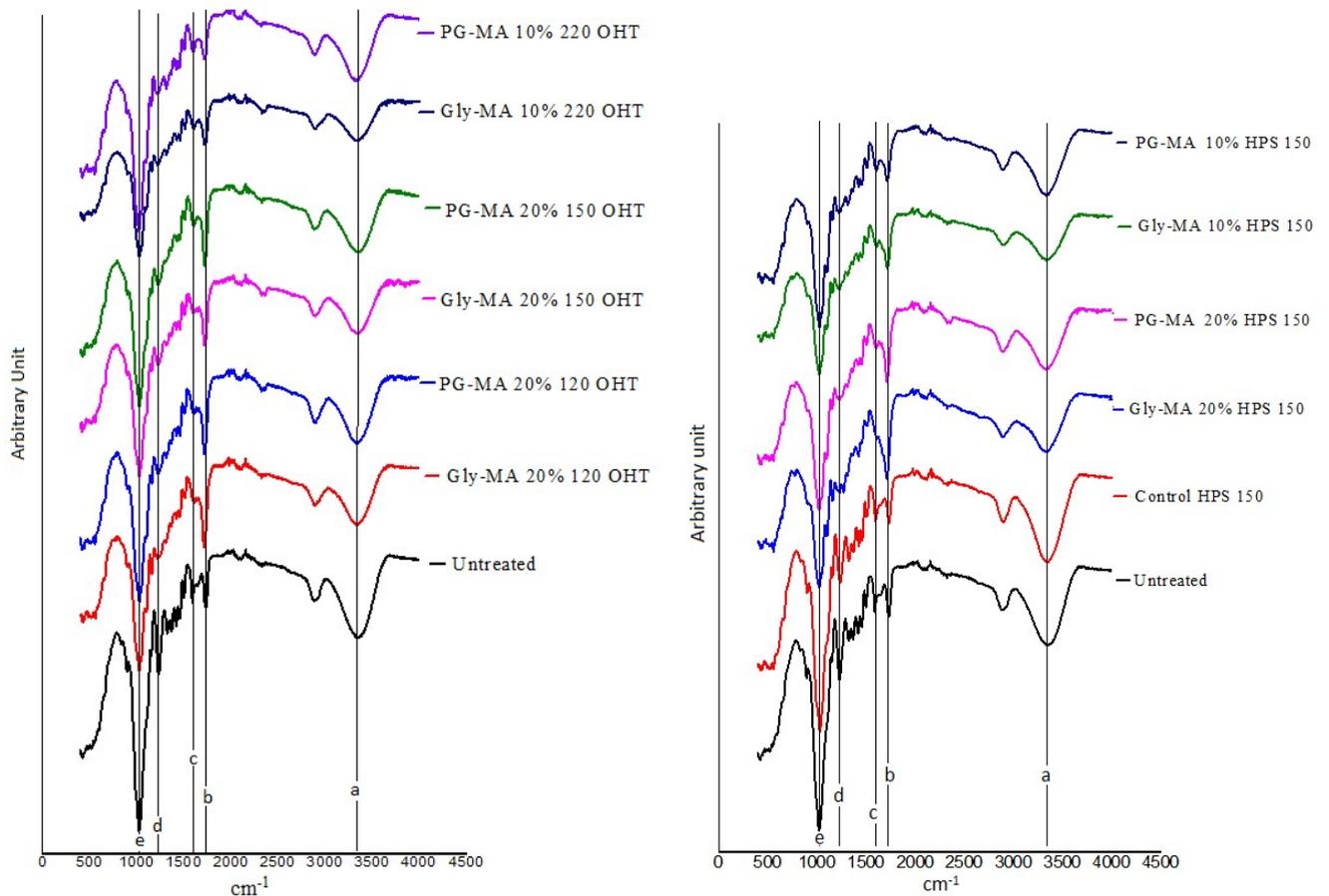


Figure 2 FTIR spectra of the modified wood compared untreated wood

Table 9 The main observed peak zone and their approximative wave number (ν) and suggested assignment

Peak	Approx. ν (cm^{-1})	Assignment
a	3356	OH str, alcohol
a - b	2899	CH str, alkane
b	1737/1715 ^a	C=O str ester / C=O, α , β -unsaturated (hemicellulose + lignin) ^b
b - c	1652	C=C str, alkene cis/alkene conjugate/hemicellulose
c	1590	C=C str, aromatic ring (lignin) ^b
c - d	1504	C=C str, aromatic ring (lignin) ^b
c - d	1456	CH bend, lignin
c - d	1424	CH bend, crystallized cellulose and amorphous cellulose ^{b,c}
c - d	1372	OH bend, holocellulose or lignin
c - d	1327	OH bend, phenol lignin
d	1232	C-O str, alkyl aryl ether (lignin) or C-O str hemicellulose
d - e	1153	C-O str, cellulose ^b
e	1024	C-O primary alcohol

^a1715 was the approx. wave length (ν) almost appeared only in additive-treated wood; ^bColom et al. (2003); ^cHakkou et al. (2005)

Table 10 Percentage of absorbance difference between the treated wood (ID: B – J) in comparison with untreated wood

Peak	Approx. ν (cm^{-1})	Treatment ID and difference value compared to untreated beech (%)										
		B	C	D	E	F	G	H	I	J	K	L
a	3356	-22	-14	-29	-21	-41	-14	3	-19	-15	-36	-15
a - b	2899	-3	3	-15	-10	-26	-5	0	2	5	-24	-7
b	1737/1715*	34	31	12	25	-15	-9	-9	45	33	-1	-2
b - c	1652	5	9	-3	-8	-21	-9	-6	55	21	1	11
c	1590	-15	-13	-23	-20	-30	-14	47	-2	-6	-25	-11
c - d	1504	-16	-7	-14	-23	-25	-12	-6	-12	-4	-25	-10
c - d	1456	-13	-4	-18	-17	-29	-11	-1	-11	-3	-25	-9
c - d	1424	-19	-11	-24	-22	-34	-16	-1	-5	-9	-28	-15
c - d	1372	-16	-8	-22	-17	-34	-15	-1	-10	-8	-28	-14
c - d	1327	-1	3	-14	-8	-26	-4	7	7	6	-19	-2
d	1232	-18	-15	-25	-18	-39	-26	-8	-10	-15	-31	-24
d - e	1153	5	5	-10	0	-25	-3	-1	9	5	-19	-8
e	1024	-23	-17	-27	-21	-40	-20	-4	-4	-21	-37	-24

*1715 was the approx. wave number (ν) appeared only in additive-treated wood; Negative value means that the absorption of the treated wood decreased (lower than the untreated wood), vice versa.

Among the treated woods, due to the highest effect of thermo-chemical degradation, it shows that wood treated using Gly-MA 10% w/w at 220°C under OHT system (F) made the highest difference in the absorbance of each selected peak in comparison with untreated wood (Table 10). These evidences might also be the cause for its good properties in dimensional stability and biological durability. On the other hand, an increase in C=O bond absorption at approx. 1715 cm^{-1} (>12%) on Gly-MA 20% or PG-MA 20%-treated wood at 120 or 150°C under OHT system was assumed as the existence of the ester bonds of the additives (Figure 3c) / and the formation of the new chemical bonds between hydroxyl group of wood and carboxylic acid from the additive. Under HPS 150°C with additive 20%, the increase in absorption of C=O bond at approx. 1715 cm^{-1} could be due to combined substances, such as the additive itself (ester bond), some thermal degradation products (e.g., carboxylic acid, aldehydes), or the new ester bond created between additive – wood/wood degradation products. Meanwhile, the increase absorption at approx. 1652 cm^{-1} (1669 cm^{-1}) could be due to the absorption of C=C bond from the additives in the form of trans conformation or from certain group of hemicellulose (as the result of intensive hydrothermal degradation). Under the same condition, it seems that wood treated with the additive 10% w/w gave higher absorbance difference than with additive 20% w/w. Even though this evidence seems opposite with the common theory, however, the dilute concentration could be the reason for its easier to penetrate into wood cell wall. On the other hand, wood control under HPS 150 presented higher absorption at 1590 cm^{-1} (46.9%), which was assigned as absorption of C=C bond of the aromatic ring from lignin at which modification/re-condensation of the lignin might have been taken place. In overall, the results have shown that modification on wood structural components had been taken place and supported to their physical, mechanical, and biological durability properties.

Appearance of untreated beech and certain modified woods is presented in the Figure 3

As the result of the modification under HPS 150°C in closed system above, the color of wood pores of untreated wood (Figure 3a) was changed into dark color (Figure 3b). Between the additive-treated wood, the wood treated with PG-MA 20% under OHT system still remained much PG-MA deposit lying in the wood porous. Meanwhile, smaller amount of PG-MA deposit was observed on the wood modified under HPS 150°C in closed system, which probably due to intense reaction between additive – wood in humid condition during HPS. As a consequence, the modified wood color was changed into black (Figure 3d), in comparison with modified wood under OHT (Figure 3c).

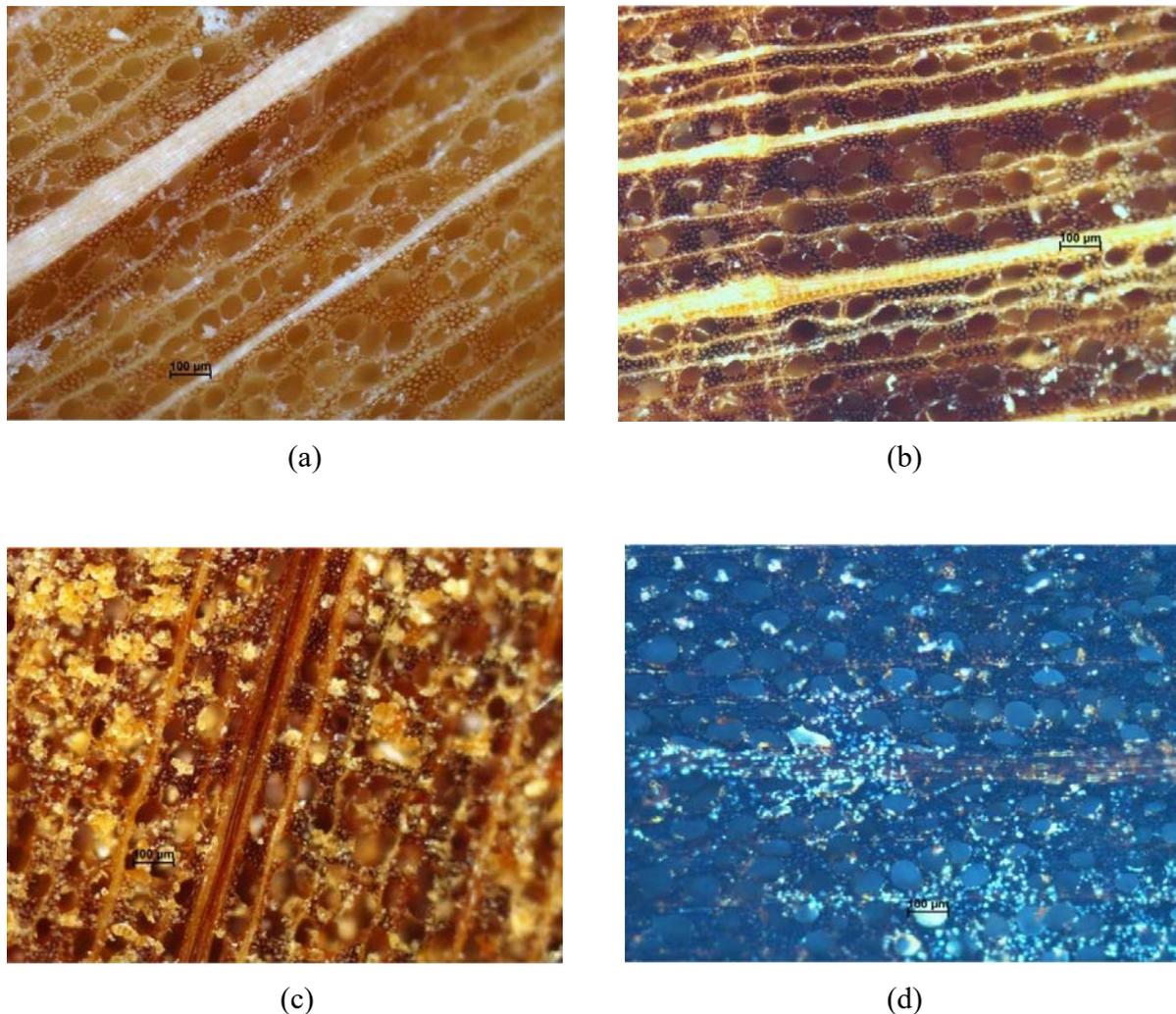


Figure 3 Cross section appearance of untreated beech (a), beech under HPS 150°C in closed system (b), PG-MA 20%-treated beech at 150°C with OHT system (c), and PG-MA 20%-treated beech under HPS 150°C in closed system (d) under light microscope with 10x magnification

4. Conclusion

1. Chemical modification of European beech wood by additives based on vinylicglycerol and vinylicpolyglycerol can be carried out under specific opened (OHT) or closed (HPS) system.
2. At the same peak temperature, both wood control and additive-treated wood under specific HPS had higher mass loss due to thermal process (ML) and leaching (ML_L) values than wood treated under OHT system.
3. Dimensional stability of wood under the specific HPS increased about 43% (ASE). However, comparable results were obtained for additive-treated wood under both OHT and HPS system.

4. MOE values of wood control treated under the specific HPS above increased slightly, MOR values were the same, however, work to maximum load bending (WMLB) values decreased for about 57%. Meanwhile, at the same additive concentration, additive-treated wood under the specific HPS above had lower MOE specific values than under OHT system, but giving comparable results in MOR and WMLB values. Compared to untreated wood, additive-treated wood had comparable result in MOE specific values, $\pm 30\%$ lower in MOR, and max. $\pm 85\%$ lower in WMLB values.
5. Compared to untreated wood, wood control treated under the specific HPS above could increase durability against CP and CV by 39% and 19%, respectively. At the same mass loss due to thermal process (ML) value, the wood control treated under the specific HPS above had comparable durability against CP but had far lower durability properties against CV than wood control treated under OHT system.
6. At the same peak temperature, the wood treated with the same additive concentration had higher durability against soft-rot under OHT system than under HPS system, while, durability against CP and CV were comparable between both systems.
7. Thermogravimetric analysis revealed that additive-treated wood under both OHT and the specific HPS systems above could increase the initial degradation temperature (onset temperature) of the modified wood by the range of 18 – 35°C. Further, Gly-MA treated wood gave lower value in the end temperature, promoting the possibility as self-fire-retardant wood.
8. FTIR analysis have revealed the difference between untreated wood and the treated wood. Under the same temperature and additive concentration, additive-treated wood under HPS system made higher modification at the hemicellulose absorption especially at C=O (approx. at 1715 and 1232 cm^{-1}) and C=C (1669). Meanwhile, under OHT system, higher modification took place at hydroxyl group (approx. at 3356 cm^{-1}), lignin (1590 cm^{-1}), and hemicellulose (approx. at 1715 and 1232 cm^{-1}).
9. Additive-treated wood under the specific HPS above was black in color, while, it was dark pale brown under OHT system.

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d. Conclusion

Based on the characteristics of the modified woods derived from the selected up-scaling treatments, the study has confirmed results of certain previous papers in the Part I that the wood impregnated with 10% w/w of Gly-MA or PG-MA-based additive followed with the thermal modification under OHT at 220°C presented excellent biological durability properties. On the other hand, treatments with higher additive concentration, 20% w/w of Gly-MA or PG-MA-

based additive, followed with curing under OHT at 150°C could be other alternatives for generating the modified wood with very good in biological durability properties, though field test study of these treatments is still ongoing process realized at the similar location as the previous field test (Paper 3). Similar as what have been reported in the previous papers, due to the acidic properties of the additive and effect of the thermal degradation, mechanical properties of the modified woods particularly work to maximum load in bending plunged significantly in comparison with untreated wood.

III.3. Conclusion

Based on the series of treatments performed in this Part II, and in relation with the Part I, improvement in biological durability and physical properties of European beech could be conducted through the addition of chemicals/additives impregnated into the wood followed with thermal treatment either under OHT in opened system or under HPS in closed system. Among the additives used, Gly-MA and PG-MA-based additives generated better properties in terms of the up-scaling process or in the modified wood properties than MA-based additive. Confirming the previous works in Part I, the wood treated with low concentration of additive (10% w/w) followed thermal treatment under OHT at 220°C in the opened system generated the modified wood with much better in biological durability. According to the results, similar resistance in biological durability could also implemented at lower curing condition (150°C) with higher additive concentration (20% w/w). Curing at 120°C under OHT with 20% w/w of additive could also another alternative in this opened system, though the decay resistance against soft rot was only specified as durable wood. On the other hand, due to higher wood degradation undergone under HPS in closed system, the additive-treated wood under HPS presented lower biological durability properties than the additive-treated wood under OHT in the opened system. In overall, the additive treated wood presented significantly higher biological durability properties than untreated wood or the wood with only underwent thermal treatment under OHT or HPS. However, as a common drawback for acidic-based treated wood, the mechanical properties particularly the work to maximum load in bending (WMLB) of the additive-modified wood decreased considerably.

CHAPTER IV (Part III)
**WOOD MODIFICATION BASED ON *IN-SITU* POLYMERIZATION OF SORBITOL
AND CITRIC ACID IN OPENED SYSTEM**

IV.1. Introduction

In this part, modification of European beech was carried out through *in-situ* polymerization of sorbitol and citric acid in opened system. Even though the chemicals used were difference with the previous chemicals used in the Part I and Part II, the type of chemical reactions occurred in wood was more or less similar, through polyesterification-based bulk impregnation wood modification. The use of sorbitol and citric acid in this work was based on an easy availability in the market, renewable, safer chemicals which commonly used in foods and beverages industries (green chemicals), relatively cheap, soluble in water, odorless, impregnating solution can be re-useable, and citric acid is a weak acid which expected could minimize mechanical degradation of wood. In principle, this study was based on a research of Doll et al. (2006) who studied the optimum condition of polyesterification between sorbitol and citric acid, and a research of Larnøy et al. (2018) who studied the modification of pine wood through *in-situ* polyesterification of sorbitol and citric acid at high applied concentration (55 % w/w) and different curing temperatures. Based on these research, this recent study aimed to investigate the optimum concentration of sorbitol-citric acid solution for modifying European beech at different curing temperatures, as well as various parameter analysis of wood during and after modification. From this study, one paper as Paper 6 has been submitted in the Wood Science and Technology journal.

IV.2. Results

IV.2.1 Paper 6

a. Introduction

Research on wood esterification has been performed since a couple decades (Rowell 1983). However, an easily practiced and obtained reagent, cheap, and relatively low toxic chemical used in this process are some critical factors promoting the implementation of this technique in considerable amounts. Wood acetylation as an example, the well-known wood esterification process based on the reaction of acetic anhydride and wood, has been commercialized recently by

ACCOYA company. In addition, the stricter on environmental concern since the last decade especially for the utilization of artificial biocide for wood preservation (Schultz et al. 2008), therefore, a benign or even the safest chemicals in wood modification would become a substantial matter that still scrutinized intensively by many stakeholders in this field. Further, the utilization of renewable chemicals instead of the limited sources of petroleum-based chemicals also give much valuable attention in the recent research.

Due to a high crystallinity of cellulose and a compact wood structure that sometime need reactive chemicals/catalysts in order the chemical reaction can be taken place in wood esterification method, therefore, research on esterification-based bulk impregnation method has got many interests nowadays. Principally, esterification-based bulk impregnation works by filling all wood cell wall, lumen, and cavities through the addition of chemical deposit on them. The addition of the chemical deposit can be performed by impregnation of ester/polyester product with low molecular weight into the wood (Roussel et al. 2001; Soulounganga et al. 2004; Mubarok et al. 2016, 2019a, b) or by impregnation of some basic agents that would be esterified (*in-situ*) in wood during curing process (Berube et al. 2017; L'hostis et al. 2017; Larnøy et al. 2018). Through this method, the reactivity/toxicity of the chemicals used is ordinarily lower than chemicals used for wood esterification. Thus, handling process during modification would not become an issue. Unfortunately, in order to have good modified wood properties, a relatively high amount of chemical needed and their good resistance against leaching would be other challenges that should be taken in to account. Therefore, a relatively cheap chemicals or renewable-based chemical would be more advantageous in this aspect, minimizing a limited source of petroleum-based chemicals and respecting to the global concern on environment.

As possible, studies were performed with renewable-based chemicals (glycerol and citric acid) for their esterification-based bulk impregnation and destined for wood protection. L'hostis et al. (2017) reported that beech wood impregnated with 44% w/w of glycerol-citric acid (1:1.63 molar ratio) aqueous solution followed with different temperature condition at 120 – 160°C gave good results on decay resistance against *Coriolus versicolor*, leaching, ASE, and bending strength. On the other hand, Essoua et al. (2016) reported that pine wood impregnated with 80% w/w of glycerol-citric acid (1:1.44 molar ratio) aqueous solution and acid catalyst followed with curing at 180°C for 2 and 4 h gave good results in decay resistance (*Postia placenta*), ASE, and hardness. Also with the same high solution concentration, Berube et al. (2017) reported that pine wood treated with approx.

80% w/w of glycerol-citric acid (1:0.6-1.4 molar ratio) aqueous solution followed with curing at 150°C also gave good result in ASE particularly when using TSA catalyst.

In addition, Larnøy et al. (2018) have tried to make *in-situ* polyesterification of pine wood using sorbitol and citric acid under aqueous solution. Citric acid, a relatively cheap bio-based chemical used commonly for food and beverage industries, is manufactured commercially through fermentation of sucrose-glucose-containing medium using *Aspergillus niger*. Meanwhile, sorbitol is a cheap bio-based chemical which produced commercially from reduction of glucose. Initially, polyesterification of sorbitol and citric acid was investigated by Doll et al. (2006). The study varied the molar ratio of citric acid to sorbitol and found the optimum condition at which sorbitol and citric acid with 1:3 molar ratio followed with curing at 150°C gave a partial soluble ester product in water ($54 \pm 8\%$), indicating that a complete esterification has accomplished. Using the same formulation of citric acid and sorbitol with the ratio of 3/1 as Doll et al. (2006) created above, Larnøy et al. (2018) has initiated to use it to modify wood (pine wood). Experimentally, the pine wood was impregnated in the aqueous solution of sorbitol and citric acid under high concentration (approx. 55% w/w) and followed with curing process at 103 or 140°C. The study reported that curing at 140°C gave significant increase of WPG after leaching, almost undetected leaching components (sorbitol or citric acid), better in dimensional stability, very good in decay resistance (*Postia placenta* and *Trametes versicolor*), and better resistance against blue stain fungi than samples cured at 103°C and untreated wood. Even though the optimum ratio of sorbitol and citric acid had been found more than a decade ago and *in-situ* polyesterification on wood has been done recently, the optimum concentration of the chemical during application in relation with the modified wood properties are unknown and needed to be studied.

The objective of this recent study was to investigate an *in-situ* esterification of sorbitol and citric acid (SorCA) on European beech (*Fagus sylvatica*), known for its low dimensional stability and poor natural durability wood species (EN 350 2016). Since every wood species has a different anatomical structure and in order to avoid an excessive chemical use as well as to find the optimum conditions to modification, different concentrations of SorCA during impregnation (10, 20, 30, and 55% w/w in the water) were also evaluated under varying temperatures (140 and 160°C). The use of two different curing temperatures, 140°C or 160°C, was based on the solubility characteristic of the cured SorCA. During preliminary test, SorCA pure cured at 140°C was still soluble during continuous stirring in water for 24 h. SorCA pure cure at 150°C was also slightly soluble during

this solubility test. Meanwhile, SorCA pure cured at 160°C was not visually soluble during this solubility test, indicating a complete polyesterification has been undergone at this curing process. In general, polyesterification reaction between sorbitol and citric acid is shown in the Figure 42. Some physical, mechanical, chemical, and decay durability analysis against white rot, brown rot, and soft rot of the modified wood were demonstrated and evaluated in the Paper 6.

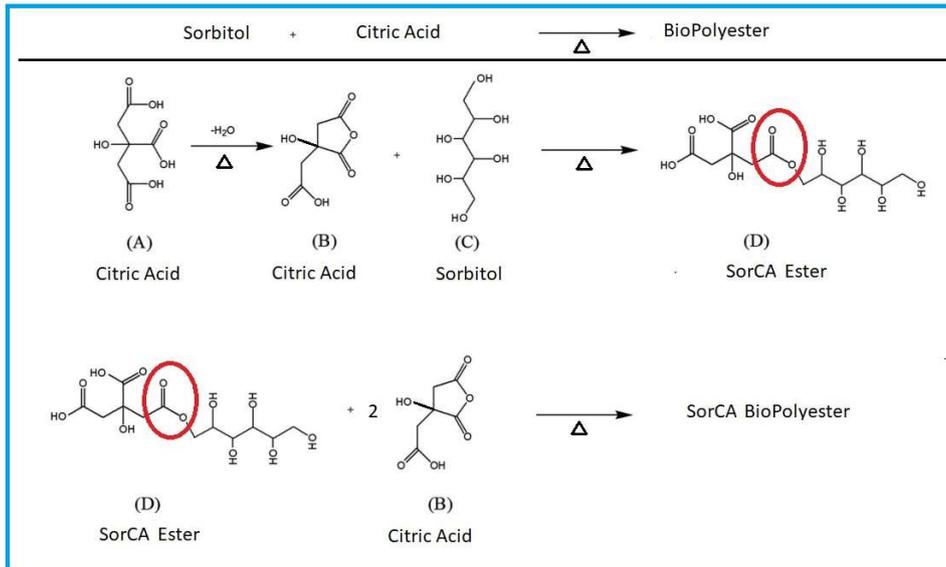


Figure 42: Polyesterification of SorCA during curing process modified from Doll et al. (2006)

According to the Figure 42, polyesterification reaction is initially formed through the reaction of anhydride form of citric acid (formed by heating and evaporating water) to sorbitol. The complete reaction would be occurred at enough curing temperature and duration to evaporate completely the water as by product of the reaction.

b. Paper 6

Beech wood modification based on *in-situ* esterification with sorbitol and citric acid

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Abstract

In this study, modification of European beech wood (*Fagus sylvatica*) through *in-situ* esterification of sorbitol and citric acid (SorCA) has been investigated under two curing temperatures, 140 and 160°C. In order to determine the optimum condition for modification, aqueous solution of SorCA at varying concentration were evaluated (10, 20, 30, and 55% w/w). Physical, mechanical, chemical, and decay durability properties of the modified wood were evaluated. Results have disclosed that among different SorCA concentrations, treatment with SorCA at 30% w/w was considered as the optimum concentration independently of the curing temperature. Under these conditions, anti-swelling efficiency (ASE) increased to approx. 55% and modulus of elasticity (MOE) increased slightly with approx. 9% in comparison to untreated wood. Decay resistance against white rot (*Trametes versicolor*), brown rot (*Coniophora puteana*), and soft-rotting micro fungi classified the SorCA-30%-impregnated wood as very durable wood. In addition, thermogravimetric study evidenced that SorCA 30%-impregnated wood has a lower mass loss value and lower the end thermal decomposition temperature in comparison to untreated wood/wood control by 20°C difference, indicating the SorCA-modified wood possibly has certain fire-retardant properties. However, due to acidic properties of SorCA solution, modulus of rupture (MOR) and mainly work to maximum load in bending (WMLB) decreased considerably.

1. Introduction

Esterification is one of the most common chemical reactions applied in wood modification. Under

practical conditions, this technique generally can be applied in two types, wood esterification and esterification-based bulk impregnation wood modification (Hill 2011). In wood esterification, the reaction is commonly based on the reaction of anhydride/carboxylic acid/isocyanate/ester groups of a modifying agent (chemical) and hydroxyl groups of wood (Rowell 1983; Hill et al. 2007). Meanwhile, in esterification-based bulk impregnation, esterification is usually based on the reaction of anhydride/carboxylic acid/isocyanate groups of one modifying agent and hydroxyl groups from other modifying agents/and wood (Essoua et al. 2016; Mubarok et al. 2016; Berube et al. 2017; L'hostis et al. 2017; Larnøy et al. 2018). Even though both techniques work with the same principle as the formation of ester bonds, in terms of the modified wood properties, they show different characteristics.

With a relatively lower reactivity of chemicals needed to undergo esterification-based bulk impregnation wood modification, this technique has got many interests in recent years. As part of this technique, polyesterification of sorbitol and citric acid, as using relatively cheap chemicals used commonly in foods and beverages industries, can be another alternative for environmentally friendly wood modification method. Actually, wood modification based on *in-situ* esterification of sorbitol and citric acid has been initially demonstrated in recent year (Larnøy et al. 2018; Mubarok et al. 2019). Based on the optimum condition for the esterification of sorbitol-citric acid developed by Doll et al. (2006), Larnøy et al. (2018) have used the formula to modify pine wood with high concentration, 55% w/w. The study reported that the sorbitol-citric acid-impregnated wood treated at 140°C curing condition gave significant increase in weight percent gain after leaching, improvement in leaching resistance and dimensional stability, a high decay resistance (*Postia placenta* and *Trametes versicolor*), and better resistance against blue stain fungi than samples cured at 103°C and untreated wood. Even though the optimum ratio of sorbitol and citric acid had been found more than a decade ago and *in-situ* polyesterification on wood has been conducted recently, the optimum concentration of the chemicals during application in relation with the modified wood properties are still unknown and needed to be studied.

The objective of this study was to investigate an *in-situ* esterification of sorbitol and citric acid (SorCA) on European beech (*Fagus sylvatica*), known for its low dimensional stability and poor natural durability wood species (EN 350 2016). Since every wood species has a different anatomical structure and in order to avoid an excessive chemical use as well as to find the optimum conditions for modification, different concentrations of SorCA during impregnation were also

evaluated under varying temperatures (140 and 160°C). Moreover, some physical, mechanical, chemical, and decay resistance analysis against white rot, brown rot, and soft rot of the modified wood were demonstrated.

2. Experimental

2.1 Sample preparation

Visual defect-free European beech (*Fagus sylvatica*) sapwood (moisture content, $\pm 11\%$) was prepared and cut to sample sizes [$5 \times 25 \times 25 \text{ mm}^3$ and $180 \times 10 \times 10 \text{ mm}^3$ (L, T, R)]. Prior to the cutting process, the wood material was air conditioned at approx. 20°C/60% of relative humidity (RH).

A technical grade of citric acid crystal (approx. 97% in purity) was purchased from PanReacAppliChem. A laboratory grade of sorbitol crystal (approx. 99% in purity) was purchased from Chemsolute®Bio.

2.2 Formulation

Four concentrations (10, 20, 30, and 55% w/w) of sorbitol-citric acid (SorCA) aqueous solutions were prepared. The solution was made by diluting 1 mol of sorbitol and 3 mol of citric acid crystal into the deionized water until it reaches a homogenous destined concentration. pH, total solid (TS), and density (D) were measured for all SorCA solutions. pH was measured by means of pH meter from Mettler Toledo, calibrated by two buffer solution 4.00 and 7.00 from ChemSolute. Total solid was measured by means of total solid meter SARTORIUS MA 35. Density was measured by means of analytical balance SARTORIUS and volumetric pipette 10 ml, pyrex.

2.3 Wood modification

Beech wood samples were dried carefully to avoid crack formation at an increased temperature and proper time, 40 (24 h), 60 (24 h), 80 (24 h), and 103°C (24 h), weighed (m_0), the volumes were measured by means of flat-bed micrometer (V_0), impregnated into different SorCA solution under vacuum condition (5-10 KPa, 1 h), and followed by pressure conditions (1200 KPa, 1 h). Impregnation for wood samples in the water was also conducted as a control for a following step. Once the impregnation completed, all samples were removed, an excess of the impregnating solution on the samples was wiped-out, and each sample was re-measured for its

wet weight (m_1) and wet volume (V_1). Afterward, the samples were re-dried carefully at room condition (2-3 days), 40 (24 h), 60 (24 h), 80 (24 - 48 h), and 103°C (24 h), then weighed (m_2), and volumes were re-measured (V_2). All SorCA-impregnated samples and controls were then divided by two groups for further curing process. One group was cured at 140°C and another group was at 160°C with the same curing period, 24 h. Finally, each cured sample was re-measured for its weight (m_3) and volume (V_3), then conditioned at room temperature.

During this modification, solution up-take and swelling caused by the impregnating solution were calculated as follows (Eq. 1 & 2):

$$\text{Solution up-take (\%)} = 100 \times (m_1 - m_0)/m_0 \quad (\text{Eq. 1})$$

$$\text{Swelling at saturation state (\%)} = 100 \times (V_1 - V_0)/V_0 \quad (\text{Eq. 2})$$

where, m_0 is the initial mass of oven-dry wood at 103°C, m_1 the wet mass of wood just after impregnation, V_0 the initial volume of oven-dry wood at 103°C, and V_1 the wet volume of wood after impregnation.

After drying process at 103°C before thermal treatment, weight percent gain (WPG) and bulking (B) values at 103°C were measured. Further, after thermal process at 140/160°C, mass changes (Δm), bulking after thermal treatment (ΔV), and weight losses due to curing (WL) at 140/160°C were calculated as follows (Eq. 3 – 7):

$$\text{WPG (\%)} = 100 \times (m_2 - m_0)/m_0 \quad (\text{Eq. 3})$$

$$\text{B (\%)} = 100 \times (V_2 - V_0)/V_0 \quad (\text{Eq. 4})$$

$$\Delta m (\%) = 100 \times (m_3 - m_0)/m_0 \quad (\text{Eq. 5})$$

$$\Delta V (\%) = 100 \times (V_3 - V_0)/V_0 \quad (\text{Eq. 6})$$

$$\text{WL (\%)} = 100 \times (m_2 - m_3)/m_2 \quad (\text{Eq. 7})$$

where, WPG is the weight percent gain value of impregnated wood at 103°C, B the bulking value of impregnated wood at 103°C, Δm the mass change/WPG value of impregnated wood after curing at 140/160°C, ΔV volume change/bulking value after curing at 140/160°C, WL the weight loss value of impregnated wood due to curing at 140/160°C, m_2 and V_2 are the mass and volume of oven-dry wood at 103°C after impregnation, m_3 and V_3 the mass and volume of oven-dry wood after curing at 140/160°C.

2.4 Leaching and Anti Swelling Efficiency (ASE) analysis

Leaching test referred to EN 84 (1997). All SorCA-treated samples, controls, and untreated samples [$5 \times 25 \times 25 \text{ mm}^3$ (L, T, R), $n = 10$] were oven dried at 103°C , weighed (m_4), volumes measured (V_4), and followed the leaching procedure according to standard. Afterwards, the samples were dried at room temperature (2-3 days), 40 (24 h), 60 (24 h), 80 (24 - 48 h), 103°C (24 h), weighed (m_5), and the volume was measured (V_5). In order to know the acidity of leachate from the leaching test, the weight and pH of the leachate were measured for every water change period. From this leaching test, mass change after leaching (Δm_L), weight losses due to leaching (WL_L), bulking after leaching (ΔV_L), and acidity of the leachate ($[\text{H}^+]$) and pH of the total leaching solution can be calculated as follows (Eq. 8 – 12):

$$\Delta m_L (\%) = 100 \times (m_5 - m_0)/m_0 \quad (\text{Eq. 8})$$

$$WL_L (\%) = 100 \times (m_4 - m_5)/m_4 \quad (\text{Eq. 9})$$

$$\Delta V_L (\%) = 100 \times (V_5 - V_0)/V_0 \quad (\text{Eq. 10})$$

$$[\text{H}^+] \text{ leachate (M)} = \text{mol total H}^+/\text{L of leachate} \quad (\text{Eq. 11})$$

$$\text{pH leachate} = -\log [\text{H}^+] \text{ leachate} \quad (\text{Eq. 12})$$

where, Δm_L is the mass change value of wood sample after leaching, WL_L the mass loss value of wood sample after leaching, ΔV_L the volume change value of wood sample after leaching, m_4 the dry mass of sample before leaching, m_5 dry mass of sample after leaching, V_5 dry volume of sample after leaching, $[\text{H}^+]$ the acidity of the leachate in molar (M) unit, mol H^+/L the concentration which obtained as the sum of $10^{-\text{pH}} \times \text{volume}$ of each leachate in each water change then divided by a total volume of leachate from the leaching test, pH leachate the pH calculated as $-\log [\text{H}^+]$ of total leachate of the leaching test.

ASE was measured with the same samples as the leaching test. Because the first cycle of the ASE can be measured at the end of the leaching test, the second and the third cycle of ASE was measured by continuing the remaining two times of re-wetting under water (exposed to vacuum at 5 – 10 KPa for 20 min, and 24 h in room condition) and re-drying [at room condition (2-3 days), 40 (24 h), 60 (24 h), 80 (24 - 48 h), 103°C (24 h)] processes. By recording the dry and wet volume of treated and untreated wood in each cycle, swelling (S) and ASE can be calculated as follows (Eq. 13 & 14):

$$S (\%) = 100 \times (V_w - V_d)/V_d \quad (\text{Eq. 13})$$

where S is the percentage of swelling of wood sample, V_d the dry volume of the sample, V_w the wet volume of the sample.

$$\text{ASE} = 100 \times (S_0 - S_1)/S_0 \quad (\text{Eq. 14})$$

where ASE is the percentage of anti-swelling efficiency of treated wood, S_0 the swelling of untreated wood, S_1 the swelling of treated wood.

A recorded dry weight (m_6) of samples after three leaching cycles during ASE test can be used for calculating weight losses due to leaching after ASE (WL_{ASE}) as follows (Eq. 15):

$$WL_{\text{ASE}} (\%) = (m_4 - m_6)/m_4 \quad (\text{Eq. 15})$$

where, WL_{ASE} is the weight loss after three leaching cycles during ASE test, m_6 the dry mass at 103°C of samples after three leaching cycle of ASE test.

2.5 Modulus of Elasticity (MOE), Modulus of Rupture (MOR), and work to maximum load in bending (WMLB)

This measurement referred to DIN 52186 (1978). Treated and untreated samples measuring $180 \times 10 \times 10 \text{ mm}^3$ (L, T, R) were placed in climatic room, at $20 \pm 1^\circ\text{C}$ and $65 \pm 3\%$ of relative humidity (RH), until constant mass. Prior to the measurement, the dimension of samples was re-measured for data input to the machine program. Afterwards, samples were measured for their increment in load and displacement values by means of ZWICK Z010 universal testing machine equipped with testXpert® II software. MOE, MOR, and WMLB was calculated automatically by the machine.

2.6 Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR spectra were recorded on a Bruker Alpha Eco-ATR instrument. The samples were prepared by grinding the treated and untreated wood into fine powder. Spectra were recorded in the range of $4000 - 400 \text{ cm}^{-1}$ at a resolution of 4 cm^{-1} with an ATR cell.

2.7 Thermogravimetric (TG) Analysis

Thermogravimetric analysis was performed on a TG 209 F1 Iris instrument. Sample powder ($\pm 15 \text{ mg}$, 40-60 mesh) were placed in alumina (Al_2O_3) crucible. Thermogram were recorded using

a heating rate of 10°C/min from 50 to 700°C under a nitrogen purge (20 ml/min).

2.8 Microscopic observation

Microscopic observation of the wood samples was investigated by means of Axioplan 2 imaging microscope with Zeiss optic equipped with Nikon D5-Fi2 Digital Sight and NIS-element imaging software.

2.9 Stability observation for the impregnating solution

Stability test of the impregnating solution was carried out by monitoring the ex-impregnating solutions from precipitation/and fungi.

2.10 Decay resistance properties against white rot, brown rot, and soft rot fungi

Durability against decay was performed according to CEN/TS 15083-1:2004 and EN 113 (1996) for Basidiomycetes with durability class referred to EN 350 (2016). Meanwhile, durability against soft-rotting micro fungi was performed according to CEN/TS 15083-2:2004, including its durability classification.

3. Result and Discussion

Formulation and Modification analysis

Data concerning total solid (TS), pH, and density (D) of different SorCA solution are presented in Table 1. Meanwhile, data concerning solution up-take, swelling, weight percent gain (WPG), and bulking (B) before curing at 140/160°C are presented in Figure 1.

Table 1 Data of total solid, pH, and density of different SorCA solution during preparation

SorCA (% w/w)	TS (% w/w)	pH	D (Kg/m ³)
10	13.72	1.75	1034
20	22.12	1.62	1073
30	34.59	1.51	1123
55	58.00	1.11	1229

TS is the total solid of the solution measured under temperature 120°C with automated duration, D is the density of the solution measured as the weight of 10 ml solution at 22°C room condition.

Results show that solution up-take increased as the SorCA concentration increased. Similar solution up-take was observed between water-impregnated wood (control) and SorCA 10% / 20%-impregnated wood. At higher concentration, due to the weight of chemicals (density),

solution up-take values appear somewhat higher. Even though a minor increase in swelling (1-2%) was observed when applying SorCA 30 and 55%, a higher amount of the polar groups in SorCA solution (-OH and -COOH) might trigger an additional swelling in impregnated wood beside water-induced swelling. At the highest SorCA concentration, solution up-take reached around 151%, which was lower than results from Larnøy et al. (2018) for *Pinus sylvestris* ($162 \pm 17\%$). This was expected and can be explained by differences in anatomy and density of the used wood species.

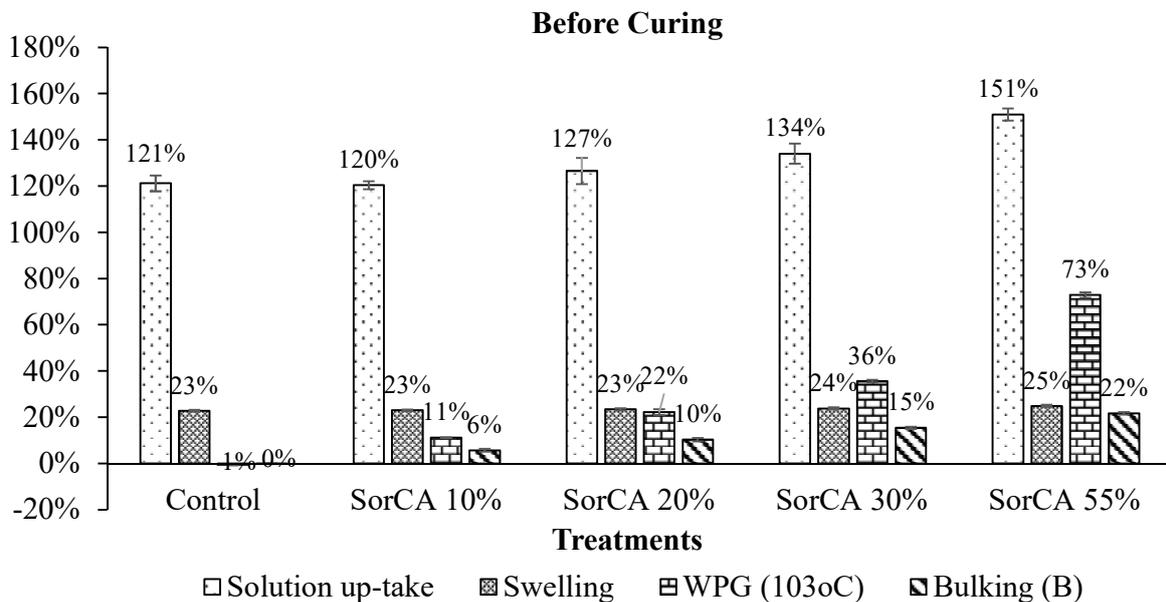


Figure 1 Data of solution up-take, swelling at saturated state (S), weight percent gain (WPG), and bulking (B) before curing at 140/160°C (each value was based on the average of 10 samples)

In similar trends as for the density of SorCA solution, WPG and bulking value (B) increased linearly until concentration of SorCA 30%, however, due to probably a maximum bulking was achieved, B increased slightly, while WPG increased drastically at SorCA 55%, indicating a higher deposition of SorCA in the lumen cell/and in the wood cavities.

Data concerning mass change (Δm), weight loss (WL), and volume change/bulking (ΔV) values after curing at 140/160°C is presented in the Figure 2.

After curing at 140/160°C, mass change values (Δm) (WPG after curing at 140/160°C) increased as the SorCA concentration increased. Due to a low effect of thermal degradation at 140°C, where weight loss (WL) for the wood control was only 1%, Δm increased linearly until concentration of SorCA 30% and drastically increased at SorCA 55%. WL values ranged from

2 – 6%, and the highest WL values were observed in SorCA 30 and 55%-impregnated woods, indicating mainly due to release of water as by product of esterification reaction between sorbitol and citric acid (Larnøy et al. 2018). At the same curing temperature, Larnøy et al. (2018) obtained approx. 15% of WL value. Curing duration, wood species, and its variabilities might explain these differences.

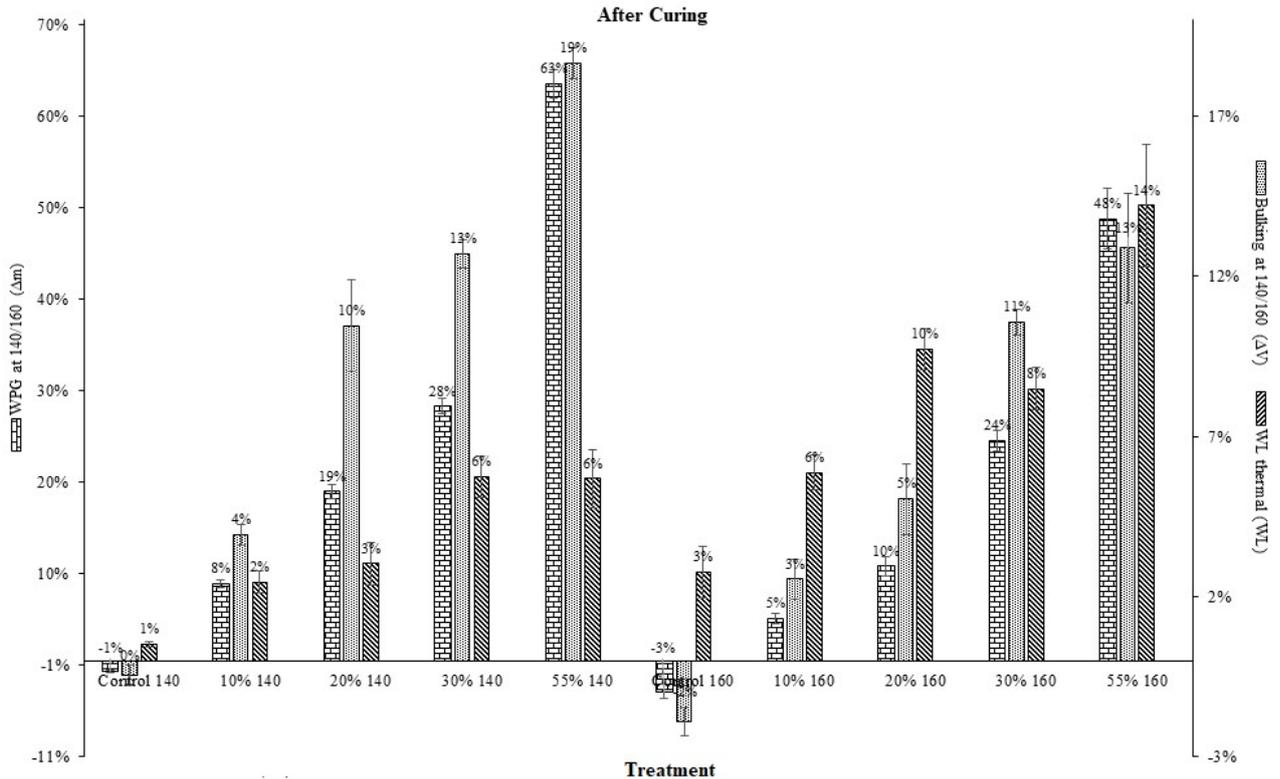


Figure 2 Data of mass change (Δm), weight loss (WL), and volume change (ΔV) values after thermal process (curing at 140/160°C) (each value was based on the average of 10 samples)

On the other hand, at the highest curing condition (160°C) and stronger effects of thermal degradation (WL values of wood control was $\pm 3\%$), Δm of all SorCA-impregnated wood decreased for about 22 – 50% compared to curing at 103°C. A lower amount of SorCA attached in wood (less shielding effect) and a mild thermal degradation in acidic condition presumably induced for the highest decrease of Δm values ($\pm 50\%$) in SorCA 10 and 20%-impregnated wood. In contrast, due to the excessive amount of SorCA in wood which possibly deposited in the cell lumen/and the wood cavities, combination effects with an extensive polyesterification reaction (by releasing water), and mild thermal degradation in acidic condition, Δm values of SorCA 55%-impregnated wood decreased for about 30% in comparison with pre-curing

condition (at 103°C). As the consequent, WL values observed at this condition reached about 14%. However, due to a proportional amount of SorCA to embed and polymerize in wood, minimizing from those influenced factors, SorCA 30%-impregnated wood appeared with the lowest decrease in Δm values ($\pm 22\%$).

Leaching analysis

Data concerning mass change after leaching (Δm_L), weight loss due to leaching (WL_L), and bulking values after leaching (ΔV_L) is presented in Figure 3.

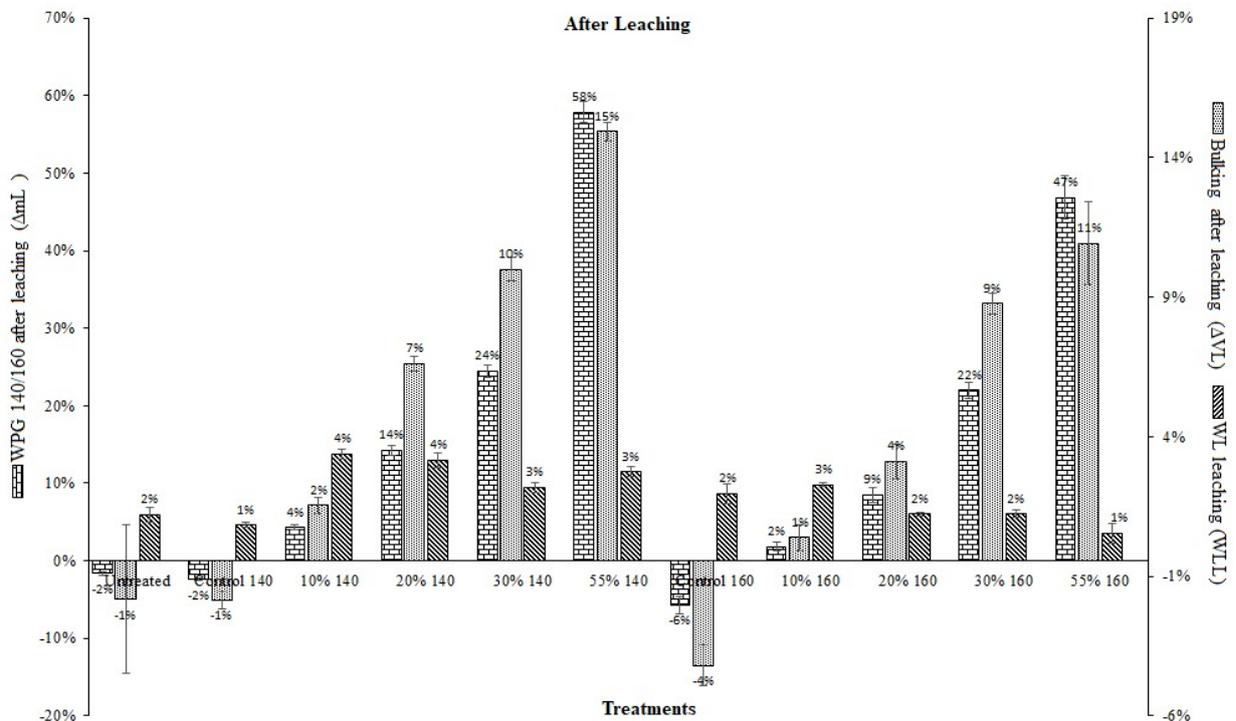


Figure 3 Data of mass change after leaching (Δm_L), weight loss due to leaching (WL_L), and bulking values after leaching (ΔV_L) (each value was based on the average of 10 samples)

After leaching process, a decrease in mass change (Δm) values was observed for all wood samples, where wood control and SorCA 10%-impregnated wood for both 140 and 160°C curing conditions reached the highest decrease for approx. 50% (the difference between Δm and Δm_L). A lower amount of SorCA was also a main factor in this matter, inducing the intensive decrease in Δm values either due to the thermal or to the leaching process. In terms of mass loss due to leaching values (WL_L), almost in all cases, SorCA-impregnated wood cured at 160°C gave the lowest leaching, indicating an intensive polyesterification had occurred at this curing

temperature. This explanation is in accordance with Doll et al. (2006), reporting that polymerization between sorbitol and citric acid takes place faster at 150°C than 110°C. Among the treatments, SorCA 30% and 50%-impregnated wood appeared with the lower decrease in Δm values for both curing and leaching processes. On the other hand, a similar volume change/bulking after leaching value (ΔV_L) for SorCA 30%-impregnated wood indicated a similar stability of this system for both curing processes.

Dimensional stability analysis

Data concerning anti-swelling efficiency (ASE), and weight loss due to leaching (WL_{ASE}) after three cycles of drying-wetting process in ASE test is presented in Figure 4.

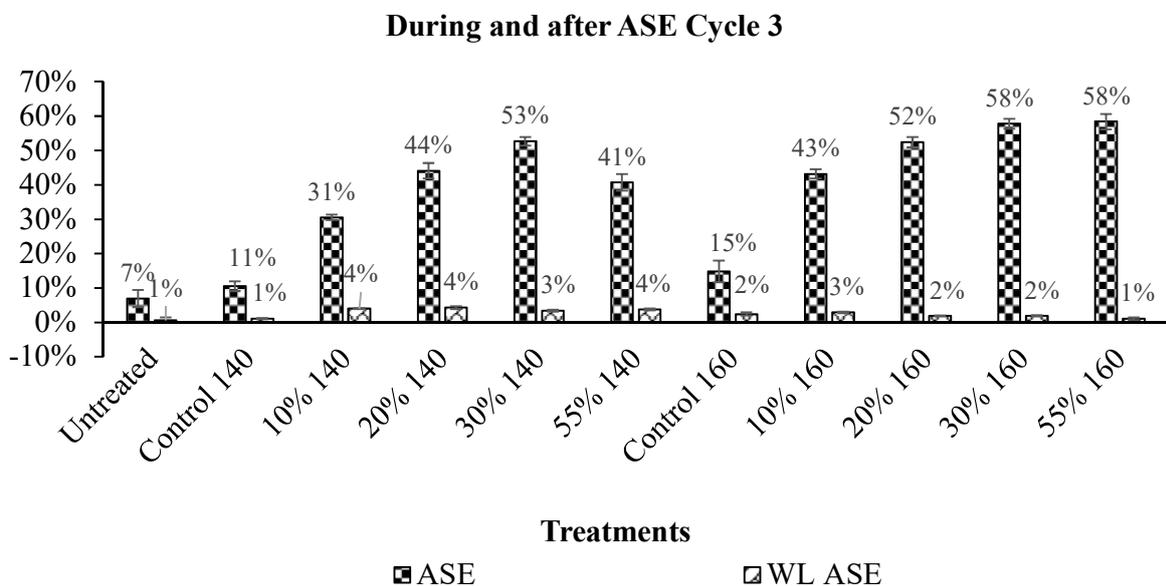


Figure 4 Data of anti-swelling efficiency (ASE) and weight loss due to leaching after three cycles of drying-wetting in ASE test (WL_{ASE}) (each value was based on the average of 10 samples).

After three leaching cycles of drying-wetting process (total wetting time was at least 16 days), in general, ASE values increased with increased SorCA concentration and curing temperature. The increase in ASE values also appear linearly until the concentration of SorCA 30%, then increased slightly afterward or even did not increase in SorCA 55% at 160°C, indicating that treatment with SorCA 30% was assumed as the optimum condition for this system due to saturation of the wood cell wall. In case of SorCA 55%-impregnated wood cured at 140°C, Larnøy et al. (2018) found no significant difference in volume for sample before and after soaking in water (no swelling). However, due to a different wood species and method used

during soaking, the results could not be compared with ours. Supporting the ASE values, weight loss due to leaching during ASE (WL_{ASE}) remained with the similar values as the first wetting process (data after leaching process), indicating there was no leaching during the ASE test.

Acidity analysis during leaching

Data concerning acidity values of the leachates during leaching test of SorCA-impregnated wood and wood control at 140 and 160°C curing conditions is presented in the Table 2

Table 2 Data of acidity values of the leachates during leaching test of SorCA-impregnated wood and wood control at 140 and 160°C curing conditions

Treatment	mmol total H⁺	[H⁺] leachate (M)	pH
Untreated	0.0014	4.961E-07	6.30
Control 140	0.0012	4.192E-07	6.38
10% 140	0.0976	3.399E-05	4.47
20% 140	0.3681	0.0001279	3.89
30% 140	0.4365	0.0001517	3.82
55% 140	3.2995	0.0011465	2.94
Control 160	0.0043	1.504E-06	5.82
10% 160	0.0367	1.281E-05	4.89
20% 160	0.0631	2.191E-05	4.66
30% 160	0.0731	2.506E-05	4.60
55% 160	0.3433	0.000118	3.93

Acidity values measured by pH measurement of the leachates of each treatment during leaching test show that acidity values of SorCA-impregnated woods cured at 140°C curing condition were higher than that of treatments cured at 160°C. An incomplete polyesterification reaction of SorCA cured at 140°C was presumably the main cause, permitting the release of H⁺ ion from unreacted carboxylic acid groups of citric acid/SorCA into the water as hydronium ion (H₃O⁺) decreasing the pH of the leachate. This incomplete polyesterification was also in harmony with research from Doll et al. (2006), reporting that some amount of acid is still found (0.6 milliequivalent of acid/g material) during the reaction of citric acid-sorbitol (3:1 molar ratio) at 150°C for 20 h and a weak band peak at 1406 cm⁻¹ is still emerged in FTIR spectra which probably due to C-O stretching in unreacted acid. Among the applied concentrations, SorCA 55%-impregnated wood gave the lowest pH (the highest acidity of the leachate), indicating the large amount of SorCA can trigger higher release of H⁺ ion which originally come from the

citric acid/SorCA (particularly at 140°C curing condition).

Mechanical properties

Data concerning modulus of elasticity (MOE), modulus of rupture (MOR), and work to maximum load in bending (WMLB) values are presented in Table 3.

Table 3 Data concerning modulus of elasticity (MOE), modulus of rupture (MOR), and work to maximum load in bending (WMLB) values

Treatments	Density (Kg/m³)	MOE (N/mm)	MOR (N/mm)	WMLB (KNmm)
Untreated	873 ± 23	13988 ± 1680	124 ± 12	3.15 ± 0.95
Control 140	840 ± 30	13424 ± 1358	115 ± 14	1.84 ± 0.47
10% 140	863 ± 25	13982 ± 1234	106 ± 13	0.85 ± 0.20
20% 140	901 ± 30	14106 ± 1133	112 ± 15	0.88 ± 0.22
30% 140	947 ± 27	15200 ± 1226	106 ± 15	0.73 ± 0.21
55% 140	1091 ± 32	16700 ± 987	116 ± 15	0.77 ± 0.17
Control 160	820 ± 30	13476 ± 1106	97 ± 14	0.89 ± 0.34
10% 160	835 ± 13	12835 ± 3520	81 ± 8	0.34 ± 0.52
20% 160	860 ± 25	14171 ± 1854	92 ± 17	0.54 ± 0.18
30% 160	926 ± 31	15206 ± 1478	102 ± 12	0.63 ± 0.14
55% 160	1030 ± 38	14653 ± 1379	96 ± 9	0.54 ± 0.08

Each value was based on the average value of 17 samples.

In general, MOE/MOR and WMLB values decreased with increase in curing temperature. The acidity and a thermal-induced mechanical degradation are the main factors for this at which WMLB values decreased more severely. Work to maximum load in bending as an ability to absorb shock with some permanent deformation is a measure of the combined strength and toughness of wood under bending stress (Ross and USDA Forest Service. 2010). This property which is related to the brittleness of the material can decrease as a deterioration of fracture properties due to the loss of amorphous polysaccharides (hemicellulose degradation is most important for this factor) and might also supported by crystallization of amorphous cellulose (Esteves and Pereira 2009). Therefore, in this study, the acidic property of the SorCA solution might play a main role in degrading of the amorphous polysaccharide (especially hemicellulose), while effect of higher curing temperature (140 and 160°C) might affect not only to degradation

of amorphous polysaccharides but also could increase wood crystallinity (Yildiz and Gümüşkaya 2007). Based on the observation, a proportional composition of SorCA 30%-impregnated wood also triggered a similar respond in its mechanical properties for both curing temperatures and gave the highest values among all SorCA concentrations at 160°C curing condition.

FTIR analysis

FTIR spectra of certain treatments is presented in Figure 5.

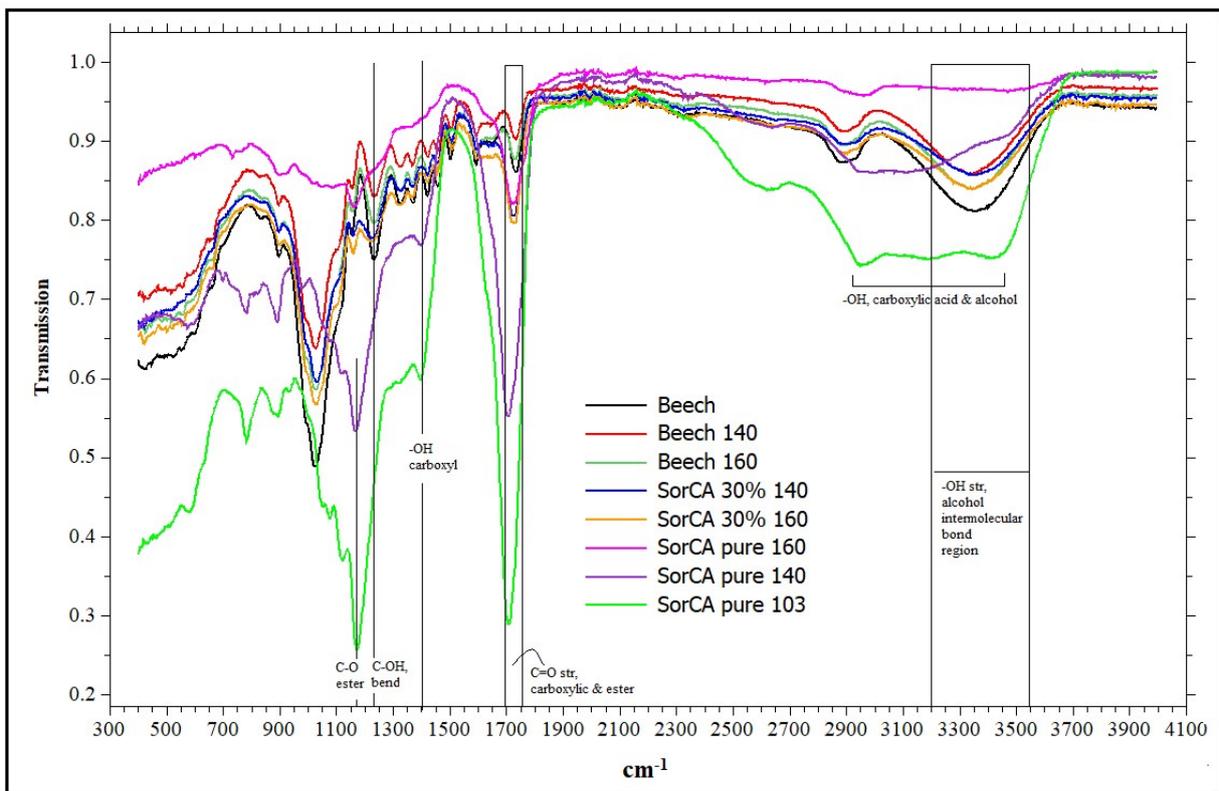


Figure 5 FTIR spectra of certain treatments

FTIR spectra of SorCA 30%-impregnated wood for both curing processes shows an increasing absorption at around 1735 and 1188 cm^{-1} which are assigned as C=O stretching and C-O stretching of the ester bond from SorCA (Doll et al. 2006). Together with the formation of ester bond, there are recorded as well some changes in wood structure, such as a decreasing/broadening absorption at around 1236 cm^{-1} which assigned as C-OH bending bond assuming as degradation/modification of hemicellulose. Minor modification of lignin also presumably occurred at this condition as some changes observed in the area between 1300 –

1600 cm^{-1} [1594 and 1503 cm^{-1} , assigned as vibrations of aromatic rings present in lignin; 1458 cm^{-1} , assigned as CH_3 deformation in lignin (Kuo et al. 1987); 1424 cm^{-1} , assigned as vibration of the C-H group in aromatic (Kudzin and Nord 1949)]. In addition, it seems there are no big differences observed between wood control heated at 140 and 160°C. From these evidences, it is clear that the addition of SorCA into the wood have made different absorptions on its FTIR spectra by which some properties of the modified wood have been changed. There are obvious differences between spectra of SorCA pure cured at 103, 140, and 160°C, confirming that a complete polyesterification at 160°C curing condition took place. The evidences of this reaction are shown by a decrease almost completely of the existing hydroxyl groups (-OH groups) at around 3000 – 3500 cm^{-1} of both sorbitol and citric acid, which is also supported by diminution of absorption at 1420 cm^{-1} as -OH group from carboxylic acid.

Thermogravimetric analysis

Data concerning thermogravimetric analysis is presented in Figure 6 [thermogravimetry (TG) curves], Figure 7 [differential thermogravimetry (DTG) curves], and Table 4 (Data of TG and DTG analysis).

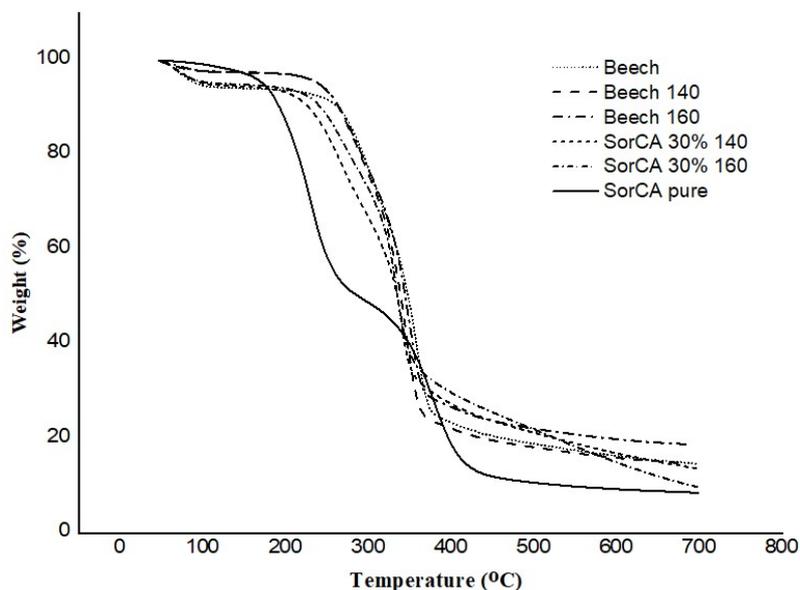


Figure 6 Thermogravimetry (TG) curves of certain treatments

Thermogravimetric investigation (Figure 6 and Table 4) shows that treatment with SorCA 30%-impregnated wood for both curing processes present lower mass losses [53% (140°C) and 55% (160°C)] than wood control [72% (140°C) and 68% (160°C)], untreated beech wood (68%), or

even the pure SorCA (67%) for the total heating process. This condition represented that the addition of SorCA into the wood triggered the formation of more char as the product reaction between SorCA and wood at high temperature and reducing the end temperature of total heating process to around 343-350°C, more than 20°C lower than untreated beech and beech control. A lower onset temperature (initial change/degradation temperature) of SorCA 30%-impregnated wood at 140°C than at 160°C curing condition in the stage I could be due to the release of water of incomplete polymerization and degradation of unreacted citric acid with lower thermal decomposition at 188°C (Berube et al. 2017). Therefore, SorCA-impregnated wood cured at 140°C appeared with higher mass loss value than treatment cured at 160°C. Nevertheless, both curing processes gave comparable results in their mass loss values in the total process.

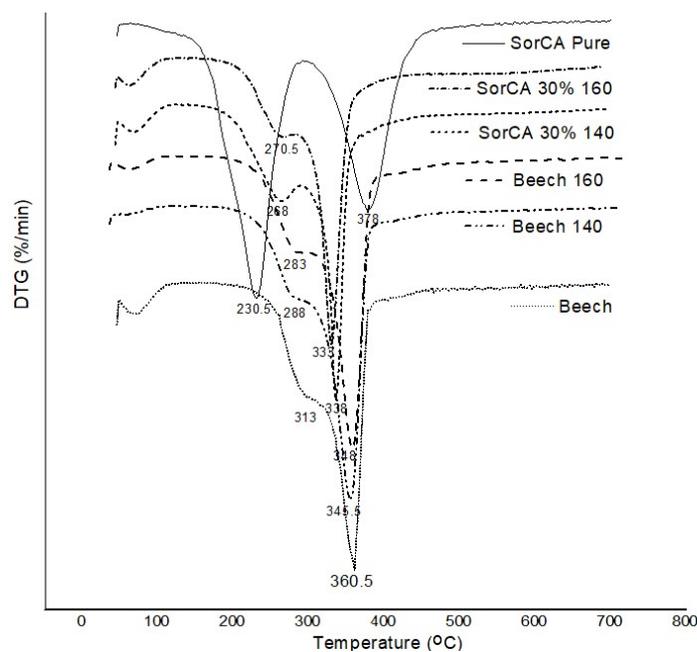


Figure 7 Differential Thermogravimetry (DTG) curves of certain treatments

Study on the DTG (Figure 7 and Table 4) shows that SorCA pure gave the highest mass loss rate (v) value in the stage I at 230°C, indicating mainly as the release of water of incomplete polyesterification at 103°C and degradation part of the polymer product. Further, the second highest v value occurred at 376°C (stage II), presenting thermal degradation of the remaining polymer and carbonization.

Table 4 Data of thermogravimetry (TG) and differential thermogravimetry analysis (DTG) of certain treatments and control

Peak	TG						DTG	
	Treatment	Onset (°C)	Mid (°C)	Inflection (°C)	End (°C)	Mass loss (%)	T(°C)	v (%/min)
Stage I	SorCA pure	192.2	221.2	230.8	253.1	34.72	230.2	7.13
	Control 140	-	-	-	-	-	-	-
	Control 160	258.0	273.8	290.0	289.6	5.88	290.0	3.88
	SorCA 30% 140	225.4	257.0	260.3	288.5	12.21	268.0	3.87
	SorCA 30% 160	232.8	231.4	236.1	230.1	1.16	270.3	3.24
	Beech	-	-	-	-	-	-	-
Stage II	SorCA pure	347.3	382.3	375.2	409.3	24.72	376.2	4.87
	Control 140	-	-	359.1	-	-	359.5	12.52
	Control 160	-	-	355.0	-	-	355.0	11.61
	SorCA 30% 140	334.4	340.6	336.6	341.2	18.05	337.9	11.66
	SorCA 30% 160	320.5	337.3	333.5	349.7	26.64	333.1	11.46
	Beech	-	-	356.0	-	-	356.0	11.56
Total process	SorCA pure	195.5	301.2	230.8	311.2	66.64	-	-
	Control 140	314.8	343.9	359.1	376.1	72.12	-	-
	Control 160	309.4	339.2	355.0	372.3	68.16	-	-
	SorCA 30% 140	324.3	325.9	336.6	343.3	53.49	-	-
	SorCA 30% 160	298.5	322.3	333.5	349.9	54.86	-	-
	Beech	307.1	337.8	356.0	374.2	67.93	-	-

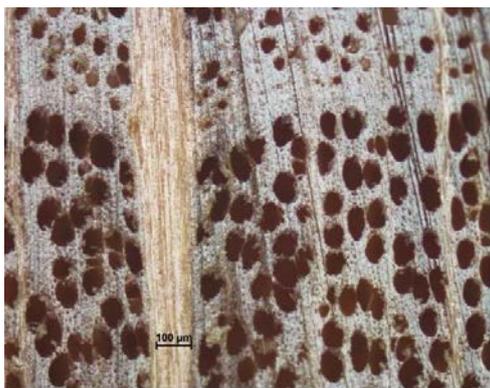
v is the rate of the mass loss per minute, values in the total process were based on the automatic calculation by device from the initial until the end of the process.

In terms of SorCA 30%-treated wood, the highest v values occurred between SorCA pure and wood control 160 in the stage I, however, it placed at the lowest temperature in the stage II, about 20°C lower than untreated beech and beech control, confirming the previous TG data. Regarding to these phenomena, Rowell and Diertenberger (2012) reported that hydrolysis of glycosidic bonds of polysaccharide in wood could increase the amount of residual char and lower the initial temperature of thermal decomposition of wood, representing part of mechanism in fire retardant properties. Similarly with our results, the hydrolysis of glycosidic bonds of wood polysaccharide by the acid (mainly from SorCA), the formation of esterified wood at high temperature, and the thermal-induced degradation during curing process were believed as the main factor that increase the residual char during heating process (reducing mass loss in total) and lower the end thermal decomposition temperature of SorCA-impregnated wood. In other

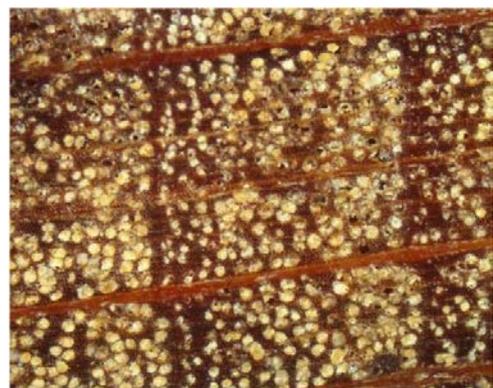
words, through this thermogravimetric investigation, the results show that SorCA modified wood has a certain fire-retardant property.

Microscopic observation

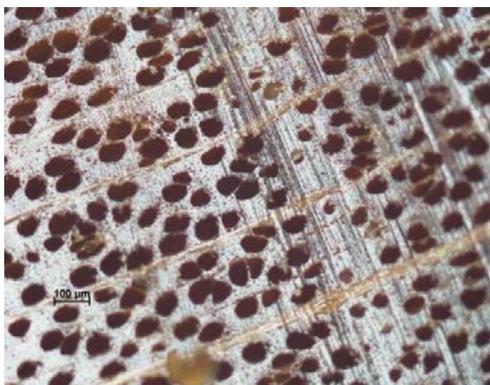
Microscopic observation of wood control and SorCA 30%-impregnated wood are presented in Figure 8.



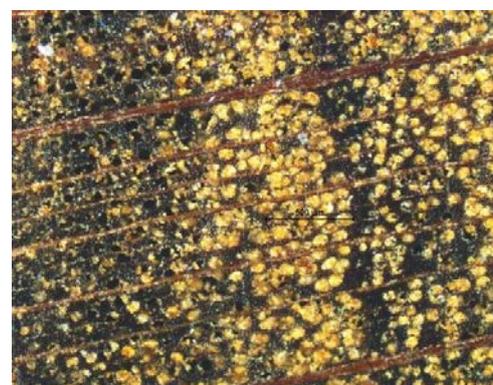
Beech Control 140°C 10x



Beech-SorCA 30% 140°C 5x



Beech control 160°C 10x



Beech-SorCA 30% 160°C 5x

Figure 8 Microscopic observation of SorCA 30%-impregnated wood

There are no big differences visually observed between wood control cured at 140°C and 160°C. Clear differences were observed between wood controls and SorCA 30%-impregnated wood for both curing conditions. A blackish in color of wood cell wall was observed in SorCA 30%-treated wood at 160°C, indicating that thermo-chemical wood modification obviously occurred under these conditions. As an addition, the appearance of the SorCA 30%-impregnated wood cured at 140 and 160°C in comparison with untreated wood are shown in the Figure 9.



Figure 9 Beech and SorCA 30%-impregnated wood cured at 140 and 160°C

Stability test of SorCA impregnating solution

After 4 months observation, SorCA 30 and 55% w/w solution presented a good stability, appearing neither precipitation nor fungi growth in the solution.

Decay test against white rot, brown rot, and soft rotting micro fungi

Based on the decay test against the white rot fungus (*Trametes versicolor*/Tv), decay resistance of SorCA modified wood after leaching increased as the increase of SorCA concentration or curing temperature (Table 5). However, the increase of curing temperature did not change the durability of wood control, indicating that at this condition, thermal-induced decay resistance of wood was still low. Among SorCA-treated woods, SorCA 30%-impregnated wood presented high durability against Tv for both curing temperatures, confirming its proportional concentration for the modification.

Table 5 Decay resistance of varied SorCA-treated wood and wood control at 140 and 160°C curing condition against *Trametes versicolor*.

Sample ^a	T (°C)	Humidity (%) ^b	ML _D (%) ^b	x-value ^c	Class ^d
SorCA 10%	140	107.83 ± 5.40	30.91 ± 2.01	0.649	slightly durable
	160	81.29 ± 3.94	16.26 ± 1.29	0.341	moderately durable

SorCA 20%	140	117.25 ± 15.50	25.29 ± 3.45	0.531	moderately durable
	160	54.83 ± 5.55	7.56 ± 1.31	0.159	durable
SorCA 30%	140	73.28 ± 7.43	6.48 ± 1.06	0.136	very durable
	160	52.43 ± 5.67	4.40 ± 0.48	0.092	very durable
SorCA 55%	140	76.56 ± 1.91	9.81 ± 0.75	0.206	durable
	160	46.33 ± 6.57	2.36 ± 0.65	0.049	very durable
Control	140	66.05 ± 11.27	48.56 ± 6.77	1.020	not durable
	160	82.69 ± 18	43.76 ± 3.99	0.919	not durable
Virulence		79.45 ± 30.48	47.62 ± 5.96	1.000	not durable

^aSample size: 10 × 25 × 25 mm³ (L, T, R) prepared before wood modification; ^beach value was based on the average of ten samples; ^cx-value = [(μ mass loss of virulence - μ mass loss of sample) / μ mass loss of virulence]; ^dClassification was based on EN 350. ML_D is the mass loss due to decay [*Trametes versicolor* (L.:Fr.) Pilat CTB 863A)]; Humidity is the humidity of the wood sample measured at the end of decay test. Incubation period was 12 weeks.

Further tests were also undertaken for SorCA 30%-impregnated wood against brown rot fungi (*Coniophora puteana*/Cp) and white rot fungi (*Trametes versicolor*/Tv) with higher sample replication after leaching process [NF X 41-568 (2014)] (Table 6). As in latest test, SorCA 30%-impregnated wood was very durable properties for both curing temperatures.

Table 6 Decay resistance of SorCA 30%-impregnated wood and wood control at 140 and 160°C curing condition against *Trametes versicolor* and *Coniophora puteana*

Sample ^a	W _L ^b (%)	Fungus	N	Humidity (%) ^c	ML _D (%) ^c	x-value ^d	Class ^e
SorCA 30% Beech 140°C	0.55 ± 0.13		20	40 ± 6	1.03 ± 0.15	0.02	very durable
SorCA 30% Beech 160°C	0.93 ± 0.20	<i>Trametes versicolor</i>	20	53 ± 6	1.69 ± 0.67	0.04	very durable
Control medium	1.41 ± 0.13		20	156 ± 48	56.20 ± 5.52	1.33	not durable
Virulence	1.40 ± 0.14		9	84 ± 20	42.14 ± 5.43	1	not durable
SorCA 30% Beech 140°C	0.85 ± 1.31		19	40 ± 5	0.74 ± 1.69	0.02	very durable
SorCA 30% Beech 160°C	0.92 ± 0.31	<i>Coniophora puteana</i>	20	47 ± 9	1.38 ± 0.65	0.03	very durable
Control medium	1.38 ± 0.13		16	115 ± 53	55.53 ± 9.24	1.3	not durable
Virulence	1.40 ± 0.10		9	125 ± 54	43.70 ± 5.29	1	not durable

^aSample size: 25 × 15 × 5 mm³ (L, T, R) was cut from modified sample size 250 × 50 × 20 mm³ (L, R, T); ^bweight loss due to leaching based on NF X 41-568 (2014); ^ceach value was based on the average of N samples; ^dx-value = [(μ mass loss of virulence - μ mass loss of sample) / μ mass loss of virulence];

[°]Classification was based on EN 350. ML_D is the mass loss due to decay [*Trametes versicolor* ((L.:Fr.) Pilat CTB 863A) or *Coniophora puteana* ((Schum.:Fr.) P. Karsten BAM Ebw. 15)], Humidity the humidity of the wood sample measured at the end of decay test. Incubation period was 12 weeks.

However, further test against soft-rotting micro fungi presented only SorCA 30%-impregnated wood at 160°C curing conditions show high durability (Table 7). This indicates that the higher curing temperature for SorCA 30%-impregnated wood could give higher conferred durability of the modified wood against soft-rotting micro fungi.

Table 7 Decay resistance of SorCA 30%-impregnated wood and wood control at 140 and 160°C curing condition against soft-rotting micro fungi

Sample ^a	N	WPG 103°C (%) ^b	Δm (%) ^b	WL _L (%) ^b	Humidity (%) ^b	ML _s (%) ^b	x-value ^c	Class ^d
SorCA 30% 160	14	62.71 ± 2.41	44.67 ± 2.12	0.22 ± 0.07	51 ± 1	0.46 ± 0.12	0.02	very durable
SorCA 30% 140	14	61.21 ± 6.46	55.47 ± 6.07	0.93 ± 0.08	60 ± 4	2.86 ± 0.43	0.13	durable
Beech 160°C	15	-	-1.85 ± 0.31	1.11 ± 0.16	124 ± 12	26.70 ± 3.44	1.20	not durable
Beech 140°C	15	-	-0.65 ± 0.15	0.87 ± 0.25	136 ± 7	26.21 ± 2.36	1.14	not durable
Untreated Beech	30	-	-	1.38 ± 0.49	133 ± 6	23.71 ± 3.22	1.00	not durable

^aSample size: 100 × 10 × 5 mm³ (L, T, R) prepared before modification; ^beach value was based on the average of N samples; ^cx-value = median value of mass loss of sample / median value of mass loss of virulence; ^dClassification was based on CEN/TS 15083-2 (2006). Δm is the WPG after thermal treatment, WL_L weight loss due to leaching based on EN 84 (1997), ML_s the mass loss due to soft-rotting micro fungi, Humidity the humidity of the wood sample measured at the end of decay test. Incubation period was 16 weeks in unsterile soil medium in laboratory.

4. Conclusions

The study has revealed that modification of European beech through *in-situ* esterification of sorbitol and citric acid leads to greatly changed wood properties at 140 and 160°C curing conditions, though curing at 160°C presented highly modified wood with better physical and decay properties. Among different concentrations applied in this research, SorCA 30% shows good properties of the modified wood independently of the curing temperature. At this condition, a high WPG, low leaching in water leaching trials, high dimensional stability (up to 55%) are reached. Under these conditions, MOE is slightly increased, however, MOR and WMLB are decreased. Decay resistance against white rot (*Trametes versicolor*), brown rot

(*Coniphora puteana*), and soft-rotting micro fungi classified the SorCA-30%-impregnated wood is very high. In addition, thermogravimetric study evidenced that SorCA 30%-impregnated wood has lower thermal decomposition temperature in comparison to untreated wood/wood control by 20°C difference, indicating the modified wood possibly has certain fire-retardant properties.

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c. Conclusion

Based on various parameter analysis, wood characteristics during and after modification could be summarized as follows:

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During modification

- SorCA 55% was considered as an excessive SorCA concentration by which higher deposition of SorCA in the lumen cell/and in the wood cavities took place and triggered higher weight loss due to curing values (especially at 160°C) than SorCA 30%-treated wood.

After modification

- SorCA 30% or 50%-treated wood presented lower leaching values than others.
- SorCA 30%-treated wood had higher ASE cycle 3 values than others, especially at 140°C curing condition.
- Acidity of the leachate of treatments at 160°C were lower than at 140°C. SorCA 55%-treated wood had the highest acidity values (lowest pH) for both curing temperatures.
- SorCA 30%-treated wood presented higher MOE values than others. However, MOR and especially WMLB decreased considerably for all SorCA-treated wood or wood control for both curing temperatures.
- FTIR spectra revealed differences of SorCA-treated wood with untreated wood or wood control at different curing temperatures.
- TGA have disclosed that SorCA 30%-treated wood generated lower mass losses than untreated wood, wood control, or pure SorCA. This thermal property of SorCA 30%-treated wood at both curing temperatures might bring it to be self-fire-retardant properties.
- Microscopic observation showed that SorCA 30%-treated wood at 160°C presented higher modification in comparison with SorCA 30%-treated wood at 140°C.
- Decay resistance property against *Trametes versicolor* revealed that SorCA 30%-treated wood treated at both curing temperatures and SorCA 55% treated at 160°C were specified as very durable wood.
- Confirmed test also shown that SorCA 30%-treated were very durable not only against *Trametes versicolor* but also against *Coniophora puteana*.
- Decay durability test against soft rot have revealed that SorCA 30%-treated wood at 160°C was specified as very durable wood, while SorCA 30%-treated wood at 140°C was specified as durable wood.

IV.3. Conclusion

This study has disclosed that the optimum condition for wood modification based on *in-situ* esterification of sorbitol and citric acid was occurred at the solution concentration of 30% w/w, presenting good properties of the modified wood independently of the curing temperature, though curing at 160°C presented highly modified wood with better in decay and physical properties. Under these optimum conditions, MOE is slightly increased, however, MOR and WMLB are decreased. Decay resistance against white rot (*Trametes versicolor*), brown rot (*Coniphora puteana*), and soft-rotting micro fungi classified the SorCA-30%-impregnated wood is very high. In addition, thermogravimetric study revealed that SorCA 30%-impregnated wood has lower thermal decomposition temperature in comparison to untreated wood/wood control by 20°C difference, indicating the modified wood possibly has certain fire retardant.

GENERAL CONCLUSION

In the first part of the study, the obtained results have demonstrated that the combination of low amounts of chemicals impregnated into European beech (*Fagus sylvatica*) followed by thermal modification, allowed to increase biological durability and certain physical properties of the modified wood. Through this thermo-chemical wood modification method, dimensional stability increased considerably in comparison to untreated wood. However, it increased slightly compared to wood control heat treated at the same temperature. Improvement in biological durability was not only undergone in decay durability properties but also especially against termite attacks, which was not owned by the thermally modified wood. These properties improvements were not only due to similar effects of thermal modification, such as degradation of hemicelluloses and modification of lignin, but also due to chemical modification of the impregnated chemicals in the wood cell walls. Some possible new reactions between wood cell wall polymers or wood degradation products and the impregnated chemicals are also probably involved to explain the synergistic effects between thermal and chemical modifications.

The additives used in this study were based on different glycerol or polyglycerol derivatives chosen for their ability to interact with wood cell wall polymers. Substitution of the polyglycerol used in the previous studies on the laboratory scale by the glycerol did not influence significantly the properties of wood modified with the different investigated treatments. Among the developed treatments, maleic anhydride-based additives (PG-MA, Gly-MA, PGM/MA_(3eq), GM/MA_(2eq), and MA) presented better improvement on the properties of the modified woods than others.

Among the different temperatures tested, the temperature at 200 and 220°C were considered as the better temperatures to increase wood durability against biological degrading agents, especially against termites. However, due to the acidity of the chemicals used and to the curing temperature, different degradations occurred under these conditions. Mechanical properties decreased considerably similarly to what was generally observed for heat-treated wood.

Termites durability investigated in the field test, held in Indonesia against *Macrotermes gilvus* Hagen for almost one year, indicated that the wood sticks impregnated with 10% polyglycerol or glycerol maleate (w/w) followed by thermal modification at 200 or 220°C presented improved durability with essentially no mass losses contrary to control and heat-treated samples which were heavily degraded by the termites.

In the second part of the study, up-scaling trials with lower curing temperatures under oven heating (OHT) in opened system at 120 or 180°C or under pressurized steam (HPS) in closed system at

150, 160, or 180°C with involving specific pressure and humidity were carried out. Variation of additives concentration (Gly-MA or MA at 10, 20, and 30% w/w) have disclosed that wood treated in opened systems (OHT) presented lower mass change (Δm after curing), higher bulking after curing (ΔV), lower weight loss due to leaching, and lower acidity than wood treated in closed systems (HPS). Modulus of elasticity of wood treated under pressurized system at 160 and 180°C were slightly higher than those of untreated wood, however, modulus of rupture decreased considerably. Decay durability of 10% (w/w) additive-treated wood under OHT at 180°C and HPS at 150, 160, or 180°C permitted to classify the corresponding treated wood as very durable.

Tests performed with a bigger sample size confirmed the results obtained on the smaller size samples. Comparable results in dimensional stability were obtained for additive-treated woods under both systems. In comparison to untreated wood, wood control under HPS presented slightly higher in MOE values, however, the work to maximum load in bending (WMLB) decreased. Under the same additive concentration, MOR and WMLB values of additive-treated wood were comparable between both systems, however, lower MOE values were observed under HPS. Durability against *Coniphora puteana* (CP) and *Coriolus versicolor* (CV) of wood control under HPS increased by 39% and 19%, respectively. At the same curing temperature and additive concentration, durability against soft-rot fungi of additive-treated wood was higher under OHT system, while, durability against CP and CV was comparable between both systems. Thermogravimetric analysis revealed that the additive-treated wood under both systems increased the initial degradation temperature, and certain treatments could decrease the end temperature point, promoting the possibility as self-fire-retardant. FTIR have disclosed differences of the modified wood under both systems. Additive-treated wood under HPS was black in color, while, under OHT was in dark pale brown.

In the third part of the study, properties improvement of European beech was performed based on the *in-situ* polyesterification of sorbitol and citric acid (SorCA). Under varying concentrations (10, 20, 30, and 55% w/w) of aqueous solution of sorbitol-citric acid (1/3 molar ratio) and curing temperatures of 140 or 160°C, the trials disclosed that SorCA 30% was considered as the optimum condition for the modification, independently of the curing temperature. Under these conditions, anti-swelling efficiency increased to approximately 55%, while, modulus of elasticity increased only slightly (9%) in comparison to untreated wood. Decay resistance against white rot (*Trametes versicolor*), brown rot (*Coniphora puteana*), and soft rot fungi classified the SorCA-30%-impregnated wood as very durable wood. In addition, thermogravimetric study evidenced that SorCA 30%-impregnated wood has a lower thermal decomposition temperature in comparison to untreated wood/wood control by 20°C difference, indicating the SorCA-modified

wood possibly has certain fire-retardant properties. However, due to acidic properties of SorCA solution, modulus of rupture and mainly work to maximum load in bending decreased considerably. Nevertheless, this environmentally friendly wood modification method is ready to be up-scaled and the modified could be used either for interior or exterior above ground service area.

CONCLUSION GENERALE

Dans la première partie de la thèse, les résultats obtenus ont montré que la combinaison d'une première étape d'imprégnation du bois de hêtre (*Fagus sylvatica*) utilisant de faibles quantités de réactifs suivi d'une étape de traitement thermique permettait d'améliorer la durabilité du bois aux attaques biologiques et certaines propriétés du bois. La stabilité dimensionnelle du bois est fortement améliorée suite à ce traitement thermo-chimique. Cependant, cette dernière n'augmente que faiblement par rapport à un traitement thermique réalisé à la même température. L'amélioration de la durabilité aux agressions biologiques ne concerne pas seulement la résistance aux champignons de pourritures, mais surtout aux termites, cette dernière n'étant généralement pas possible dans le cas d'un traitement thermique seul. L'amélioration des propriétés du bois modifié sont comme dans le cas du traitement en partie due à des changements structuraux des polymères constitutifs des parois cellulaires suite à la dégradation des hémicelluloses et la modification des lignines, mais aussi en partie due à l'imprégnation de réactifs dans les parois cellulaires. Des réactions entre les constituants des parois cellulaires ou les produits de dégradation thermique du bois et les additifs chimiques imprégnés dans le bois sont probablement également impliquées expliquant le fort effet de synergie observé entre traitement chimique et thermique.

Les additifs utilisés dans cette étude sont basés sur l'utilisation de glycérol et de polyglycérols choisis pour leur capacité à interagir avec les polymères pariétaux du bois. Le remplacement du polyglycérol utilisé dans les études précédentes réalisées au laboratoire par du glycérol ne modifie pas de manière importante les propriétés des bois modifiés par les différents traitements développés. Parmi les traitements développés, les additifs basés sur l'utilisation de l'anhydride maléique (PG-MA, Gly-MA, PGM/MA_(3eq), GM/MA_(2eq), and MA) présentent les meilleures performances.

Les températures de 200 et 220°C correspondent aux meilleures conditions parmi les différentes températures testées, permettant une nette amélioration de la durabilité du bois aux agents de dégradation biologique dont notamment vis-à-vis des termites. Cependant, du fait des propriétés acides des réactifs et de la température utilisée, différentes réactions de dégradation peuvent se produire. Les propriétés mécaniques diminuent d'une manière similaire à ce qui est observé pour le bois traité thermiquement à 220°C. Des essais termites réalisés en champs contre *Macrotermes gilvus* Hagen en Indonésie indiquent une amélioration importante de la durabilité des éprouvettes traitées avec des solutions à 10% de maléate de glycérol ou de polyglycérol (w/w) suivi d'un traitement thermique à 200 ou 220°C.

Dans la seconde partie de la thèse, des essais de changement d'échelle impliquant des températures

de cuisson plus bases en systèmes ouverts (OHT) à 120 et 180°C, ou en systèmes fermés en réacteurs sous pression de vapeur d'eau à 150, 160 ou 180°C avec des valeurs spécifiques de pression et d'humidité ont été réalisés (HPS). La modification des teneurs en réactifs (Gly-MA ou MA at 10, 20, et 30% m/m) a mis en évidence que les bois traités en systèmes ouverts (OHT) présentaient après traitement des pertes de masse (Δm) plus faibles, des valeurs de gonflement plus importantes, une meilleure résistance au lessivage et une acidité plus faible que ceux traités en systèmes fermés (HPS). Les modules d'élasticité des bois traités sous pression à 160 et 180°C sont légèrement plus élevés que ceux du bois non traité, cependant les modules de rupture diminuent considérablement. La durabilité mesurée des bois traités avec des solutions à 10% des différents additifs (m/m) en systèmes ouverts à 180°C ou sous pression à 150, 160 ou 180°C permet de classer ses derniers comme très durable.

Les essais réalisés sur des échantillons de plus grande taille confirment les résultats obtenus sur des échantillons de petite taille. Des résultats similaires de stabilité dimensionnelle ont été obtenus avec les différents additifs. Comparativement au bois non traité, les échantillons traités sous pression en système fermés présentent des MOE légèrement supérieurs, cependant la résistance à la charge maximale (WMLB) diminue. Pour une même concentration en additifs, MOR et WMLB sont comparables pour chaque système, des MOE plus faibles étant obtenus pour les traitements réalisés sous pression.

La durabilité vis à vis de *Coniphora puteana* (CP) et de *Coriolus versicolor* (CV) des bois traités en système fermés augmente de 39% et 19%, respectivement. Pour une même température de traitement et concentration en additif, la durabilité contre les pourritures molles est meilleure pour les échantillons traités en réacteurs ouverts, alors qu'elle est comparable pour CP et CV quel que soit le type de système utilisé (OHT ou HPS). Des analyses thermogravimétriques montrent que la température initiale de dégradation des bois traités est plus importante, et que certains traitements peuvent diminuer la température finale de dégradation ouvrant des possibilités en tant que matériaux ignifugeants. Les bois traités en système fermé présentent une coloration noire, alors que ceux traités en système ouverts présentent une coloration brun pâle foncée.

Dans la troisième partie du travail, l'effet de traitements impliquant une polyesterification *in-situ* du sorbitol et de l'acide citrique (SorCA) a été envisagé pour stabiliser le bois de hêtre. Différentes concentrations (10, 20, 30, et 55% m/m) dans l'eau de sorbitol-acide citrique (1/3 mole/mole) et des températures de traitement de 140 ou 160°C ont été envisagées. Les résultats montrent que des concentrations de SorCA de 30% conduisent aux meilleurs résultats indépendamment de la température de traitement. Dans ces conditions, l'efficacité anti gonflement augmente de 55%,

alors que le module d'élasticité n'augmente que légèrement (9%) comparativement au bois non traité. La résistance aux champignons de pourriture blanche (*Trametes versicolor*), de pourriture brune (*Coniophora puteana*), et de pourriture molle montrent que les bois traités avec une solution de SorCA à 30% peuvent être considérés comme très durables. De plus, les analyses thermogravimétriques indiquent également des propriétés ignifuges intéressantes comparativement au bois non traités. Cependant, du fait de l'acidité de l'acide citrique, le module de rupture et la résistance à la charge maximale diminuent fortement. Toutefois, le caractère non biocide de ce type de traitement présente différents intérêts justifiant de poursuivre des études à plus grande échelle pour mieux cerner les propriétés de ces nouveaux matériaux.

Perspectives

Chapter II

- Due to the simple chemical preparation, a relatively cheap and low hazard chemical used, and good in impregnability, the selected treatments are feasible for up-scaling treatment.
- Due to the synergistic effect between chemical and thermal modification, some efforts to find other possible chemicals that could improve wood properties would be interesting to study.
- Further research to work with low acidic properties of the chemicals would be interesting to investigate, reducing degradation of wood mechanical properties while improving its biological durability.

Chapter III

- A field test with a longer period would be more convincing the biological durability of the selected modified wood.
- Another mechanical testing such as shear strength, impact bending, bonding strength would give additional information for the properties of the modified woods.
- Compatibility test with coating materials would become valuable information for the market.
- Since the modified woods have good in biological durability, dimensional stability, and potentially has self-fire-retardant properties, application of the modified woods would be suited for cladding and roofing.

Chapter IV

- Due to a simple wood modification performed by *in-situ* polyesterification of sorbitol and citric acid, the optimum condition of the wood modification with SorCA 30% would be feasible to be implemented in up-scaling treatment.
- Durability against termite either in the laboratory or in the field test would be interesting to investigate.
- Other mechanical tests (e.g. shear strength, impact banding, bonding strength) and coating test would become beneficial information for the characteristic of the modified wood, especially during application.
- Application of all wood modification treatments above on a low durability and dimensional stability of fast growing Indonesian wood species, such as Jabon (*Anthocephalus cadamba*) and teak (*Tectona grandis*), would be interesting to study.

Perspectives

Chapitre II

- Poursuivre les essais d'up-scaling du fait de la simplicité de la préparation chimique, de l'utilisation d'une substance chimique relativement peu coûteuse et peu dangereuse, ainsi que d'une bonne imprégnabilité,
- En raison de l'effet de synergie entre les modifications chimiques et thermiques, il serait intéressant d'étudier certains efforts visant à trouver d'autres produits chimiques susceptibles d'améliorer les propriétés du bois.
- Il serait intéressant d'étudier de manière plus approfondie les travaux visant à exploiter les propriétés peu acides des produits chimiques, en réduisant la dégradation des propriétés mécaniques du bois tout en améliorant sa durabilité biologique.

Chapitre III

- Un essai sur le terrain avec une période plus longue serait plus convaincant de la durabilité biologique du bois modifié sélectionné.
- D'autres tests mécaniques tels que la résistance au cisaillement, la flexion par impact, la résistance de la liaison fourniraient des informations supplémentaires sur les propriétés des bois modifiés.
- Réaliser des tests de compatibilité avec des finitions pour pouvoir répondre aux marchés visés.
- Étant donné que les bois modifiés ont une bonne durabilité biologique et une bonne stabilité dimensionnelle, ainsi que des propriétés potentiellement ignifuges, développer des applications vers le bardage et la toiture.

Chapitre IV

- En raison d'une simple modification du bois effectuée par polyestérification in situ du sorbitol et de l'acide citrique, il serait possible d'appliquer la condition optimale de la modification du bois avec SorCA à 30% au traitement à grande échelle.
- Il serait intéressant d'étudier la durabilité contre les termites en laboratoire ou sur le terrain.
- D'autres tests mécaniques (résistance au cisaillement, bande d'impact, force de liaison) et de revêtement deviendraient des informations utiles pour les caractéristiques du bois modifié, en particulier lors de l'application.
- Il serait intéressant d'étudier l'application de tous les traitements de modification du bois ci-dessus sur la faible durabilité et la stabilité dimensionnelle d'essences indonésiennes à croissance rapide, telles que Jabon (*Anthocephalus cadamba*) et le teck (*Tectona grandis*).

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APPENDIXES

Appendix 1

Valorization of Beech Wood through Development of Innovative Friendly Environmentally Chemical Modification Treatments

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Keywords: chemical modification, *fagus sylvatica*, glycerol, maleic anhydride, polyglycerol, thermal treatment

ABSTRACT

A comparative study of some wood chemical modification combined with thermal treatments has been examined. European beech (*Fagus sylvatica*), known for its poor natural durability and low dimensional stability, was treated to improve its quality. Three types of additives based on 10% aqueous solution of vinylicpolyglycerol or vinylicglycerol derivatives, and maleic anhydride were impregnated into beech wood, followed by a thermal treatment at 150, 200, and 220°C under inert condition. Treated and untreated wood were then analysed for their mass changes after curing process (Δm), mass loss due to leaching (WL_L), anti-swelling efficiency (ASE), modulus of elasticity (MOE)/modulus of rupture (MOR) and decay resistance against *Coriolus versicolor* (CV) before and after leaching. The main results of this research revealed that the synergic effects of the applied chemical and thermal treatments at 200°C could improve wood dimensional stability up to 62 – 69% and the decay resistance before and after leaching to very durable class (EN BS 350-2 1994) compared to untreated wood, however MOE/MOR values decreased by 17 – 26%/43 – 53%. As a response to the increasing environmental pressure since a decade ago, these treatments could also be used as non-biocide wood preservation treatment.

INTRODUCTION

Non-biocide wood preservation system has been researched for several decades. In general, this system can be separated into two types, thermal and chemical modification, as reviewed by Gérardin (2016). Thermal treatment of wood is one of the alternative processes that have been widely studied and even applied in industrial scale to overcome the problem of wood dimensional stability (Tjeerdsma *et al.* 1998; Militz 2002; Esteves and Pereira 2009; Rowell *et al.* 2009) and biological durability (Kamdem *et al.* 2002; Hakkou *et al.* 2006; Rowell *et al.* 2009). On the other hand, chemical modifications involving impregnation of active chemical into the wood can also be an alternative to overcome those problems (Rowell *et al.* 2009; Militz *et al.* 2011) and even some of them generated products with better characteristic than thermal treated wood (Epmeier *et al.* 2004). Moreover, chemical treatments can be applied at lower temperature, minimizing the degradation of wood compared to thermal treatment. Unfortunately, some of these techniques sometimes need very reactive chemicals/additives, some of which require high concentration chemicals or use of organic solvent during the application. This causes a high cost for the application, which will become a decisive parameter.

In an attempt to find alternatives for easy applied wood modification systems and minimize the costs there are recent investigations on comparative studies of some wood chemical modification

treatments based on the utilization of low concentration waterborne solution of vinylicpolyglycerol (Roussel *et al.* 2001; Salman *et al.* 2017) and the new developed formulation based on vinylicglycerol and maleic anhydride. The use of glycerol was based on the thought that it has similar characteristics with already used polyglycerol (PG3) and that it presents a better availability. Both Glycerol and PG3 are renewable chemicals derived from oilseeds easily available as industrial byproducts from soap manufactures and biodiesel production, which could minimize the utilization of petroleum-based chemicals. In order to know their reactivity with the wood and the properties of modified wood, a combination of varied thermal treatments (150, 200, 220°C) under inert condition was performed to investigate synergic effect on the way for generating the best modified wood performance. These type of combined chemical/thermal modifications have been studied recently based on highly concentrated additives made from *in situ* formation of citric acid and glycerol (Essoua *et al.* 2016) and maleic anhydride alone (Geraud *et al.* 2015) into pine wood, yet the use of low concentration of additives combined with thermal treatment into European beech wood has not been studied. Ultimately, the general goal of this study is also to develop a non-biocide wood preservation system.

MATERIAL AND METHOD

Additive formulation

Polyglycerol-maleic anhydride/PG-MA was made according to Roussel *et al.* (2001) method. 1 mol of polyglycerol (PG3, MR = 242 g/mol) was reacted with 2 mol of maleic anhydride (MA, MR = 98.06 g/mol) and heated at 80°C for 3 h. The reaction was then stopped after disappearance of ATR-FTIR absorption of anhydride and a complete appearance of a characteristic ester band at about 1715 cm⁻¹. The product was directly used without further purification and dissolved into distilled water so that the final concentration of impregnating solution (additive solution) was 10% w/w. Glycerol-maleic anhydride/Gly-MA additive was also made by the same mol comparison and condition as PG-MA. Maleic anhydride/MA additive was made by directly dissolving maleic anhydride into distilled water so that the final solution concentration was 10%w/w.

Wood modification

Oven-dried beech wood samples measuring 3 × 1.5 × 0.5 and 19 × 2 × 0.5 cm³ (L x R x T) were weighed and placed under vacuum condition (80 – 100 mbar for 10 minutes) in an autoclave (Figure 1) followed with impregnation process with 10%w/w aqueous additive solution for 30 min under vacuum. Afterwards, the pressure was liberated up to 1 bar, the samples were then placed under pressure (10 – 12 bar) for 30 min, and then the pressure was turned down to 1 bar. The samples were then placed under vacuum again (5 – 10 mbar for 10 min), returned back to 1 bar pressure, place to general vacuum (70 – 100 mbar for 1 h), and finally the pressure was liberated to 1 bar. Samples were then removed and air conditioned for 24 hours, dried at 103°C and weighed until constant mass so that their mass changes (Δm) could be calculated (Eqn. 1). Dried impregnated samples were then divided by four groups, one group (dried at 103°C only) was kept, and the remaining three groups were exposed each at 150, 200, and 220°C for 20 h under nitrogen condition. All modified wood were then reweighed for their mass changes (Δm) after thermal treatment. General analysis for modified wood were also performed, such as leaching test (Eqn. 2 & 3), anti-swelling efficiency (ASE), mechanical test (MOE/MOR), and decay resistance test for the different samples before and after leaching. The same procedure was also conducted for untreated samples/control.



Figure 1: Autoclave for vacuum-pressure impregnation and thermal treatment

$$\Delta m (\%) = 100 \times (M_1 - M_0) / M_0 \quad (1)$$

where Δm is the mass change after curing process at 103, 150, 200, or 220°C, M_1 is the mass of treated wood at 103, 150, 200, or 220°C and M_0 is the initial mass of wood before modification.

$$\Delta m_{AL} = 100 \times (M_2 - M_0) / M_0 \quad (2)$$

where Δm_{AL} is the mass change after leaching process, M_2 is the dry mass of additive-treated or untreated wood at each curing condition after leaching process.

$$WL_L = 100 \times (M_1 - M_2) / M_1 \quad (3)$$

where WL_L is the mass loss due to the leaching test.

RESULTS AND DISCUSSION

Mass changes (Δm) analysis

Table 1 shows that the mass changes (Δm) values decreased as the curing temperature increases. At 103°C, the polarity of PG-MA and Gly-MA additives was the reason of similar Δm values of the treated wood. On the other hand, the absence of hydroxyl group and the less polar double bond of the MA additive system led to the less bulking effect of wood cell wall. Therefore, Δm values of MA-treated wood were lower than that of PG-MA and Gly-MA-treated wood.

At 200 and 220°C, MA-treated wood had the lowest mass changes values and the highest mass loss during thermal treatment. These modification conditions could be explained by the instability of MA-treated wood due to higher acidity of the treatment compared to other treatments with polyols leading to esters formation (Bodirlau *et al.* 2008; Geraud *et al.* 2015). Higher temperatures (>180 - 200°C) and the long duration of treatment (20 h) or combination of both factors are also the origin of accelerated heat-induced wood degradation.

Leaching analysis

Leaching test referred to procedure adapted from NF X 41-569 standard (2014). According to the leaching data in the Table 1, percentage of mass loss of additive-treated and untreated wood after leaching/ WL_L (Eqn. 3) decreased by the increase of curing temperature.

At 150°C curing condition, almost all treated wood have higher mass changes after leaching values/ Δm_{AL} (Eqn. 2) than other curing conditions. It indicates that at this curing temperature the PG-MA and Gly-MA additives have begun to fix better into the wood than at 103°C curing condition and the problem of heat-induced degradation of the additive and wood was minimal.

Therefore, mass losses of the additives treated wood after leaching (WL_L) were also decreased. On the other hand, even at higher curing temperatures, MA-treated wood remains with a lower Δm AL and the highest WL_L values. The reaction between water and unreacted MA to form soluble maleic acid during leaching process was the most possible factor for this problem. Some possible factors presented in Δm analysis previously were also might contribute to the leaching character of this MA-treated wood.

At higher curing condition (200 and 220°C), the reduction of mass changes for both before and after leaching (Δm AL) caused by heat-induced wood degradation emerged. These conditions made a better additive fixation into the wood, and WL_L values were also diminished, especially at 200°C curing condition.

Table 1: mass change, mass change after leaching test, mass loss due to leaching, and 3rd cycle of anti-swelling data at different curing conditions

T(°C)	Additives 10%	Δm^a (%)	Δm AL ^b (%)	WL_L^b (%)	3 rd Cycle ASE ^c
103	PG-MA	10.3 (1.2)	2.0 (0.4)	7.3 (0.9)	46.1 (2.1)
	Gly-MA	10.0 (0.9)	2.2 (0.4)	6.8 (0.5)	46.5 (4.9)
	MA	9.3 (0.7)	2.2 (0.7)	6.4 (0.9)	41 (2.8)
	Control	0	-1.4 (0.3)	1.4 (0.3)	13.9 (8.0)
150	PG-MA	8.8 (1.0)	5.6 (1.0)	2.5 (0.6)	48.1 (4.6)
	Gly-MA	8.6 (0.8)	4.6 (0.4)	4.0 (0.4)	55.0 (4.5)
	MA	7.2 (0.8)	1.4 (0.8)	5.3 (0.8)	47.7 (3.3)
	Control	-0.1 (0.2)	-1.8 (0.2)	1.7 (0.3)	21.6 (6.3)
200	PG-MA	3.8 (1.6)	0.9 (1.5)	2.3 (0.9)	61.7 (3.2)
	Gly-MA	1.1(1.0)	-0.8 (1.9)	2.6 (1.2)	69.0 (4.6)
	MA	-4.3 (0.5)	-7.7 (0.6)	3.7 (0.7)	66.9 (9.0)
	Control	-2.6 (0.5)	-4.2 (0.3)	1.7 (0.1)	49.4 (2.5)
220	PG-MA	-3.2 (1.2)	-5.4 (1.2)	2.4 (0.6)	74.7 (4.4)
	Gly-MA	-5.7 (1.2)	-9.0 (1.1)	3.6 (0.4)	78.2 (1.9)
	MA	-9.9 (0.8)	-13.8 (0.9)	4.2 (1.3)	66.7 (2.2)
	Control	-10.5 (0.8)	-11.6 (1.0)	1.2 (0.3)	63.5 (2.3)

^aEach value was based on the average of ninety six samples at 103°C and twenty four samples for each thermal treatment (150, 200, 220°C), ^bEach value was based on the average of six samples, ^cEach value was based on the average of four samples. Standard deviation is in parentheses

Anti-swelling efficiency (ASE)

ASE test refers to drying-wetting cycle system adapted from Pfriem *et al.* (2012). Based on the Table 1, all ASE values increased with the increase of curing temperature, with the additive-treated woods presenting higher ASE values than control. This indicates that there were some chemical (*e.g.* reaction between additives and components in wood cell wall, degradation of hemicellulose) and physical interactions (*e.g.* anchoring system of the cured additives into wood cell wall, the increase in surface tension) due to the high temperature curing. These ASE results were similar some previous research (Iwamoto and Itoh 2005), where maleic anhydride treated wood had ASE values > 40% in the first drying-wetting cycle.

Modulus of elasticity (MOE) and modulus of rupture (MOR) analysis (EN 310 1993)

Based on the results in Table 2, both MOE and MOR values of the additive-treated wood were lower than control at all curing conditions. Each additive-treated wood had MOE/MOR values which were proportionally approximate with their Δm values. MOE values decreased gradually as the curing temperature increased.

Table 2: MOE/MOR values of treated and untreated wood and MOE/MOR reduction values compared to untreated wood at different curing condition

T (°C)	Additives 10%	Δm (%)*	MOE (N/mm ²) / MOE Red (%)*	MOR (N/mm ²) / MOR Red (%)*
103	PG-MA	9.1 (0.4)	9479 (1089) / -23.9	96 (19) / -27.5
	Gly-MA	9.3 (0.4)	9205 (876) / -26.1	89 (11) / -32.6
	MA	8.4 (0.4)	10070 (971) / -19.2	80 (16) / -39.4
	Control	0.0 (0.0)	12460 (1390) / 0.0	133 (17) / 0.0
150	PG-MA	8.0 (0.3)	10723 (748) / -13.9	89 (11) / -33.2
	Gly-MA	8.2 (0.3)	10393 (946) / -16.6	85 (15) / -35.9
	MA	5.9 (0.4)	10916 (850) / -12.4	75 (6) / -43.3
	Control	-0.4 (0.0)	12801 (1243) / 2.7	135 (18) / 1.6
200	PG-MA	3.7 (0.8)	10329 (960) / -17.1	75 (10) / -43.4
	Gly-MA	-0.0 (1.3)	9283 (1382) / -25.5	64 (13) / -51.9
	MA	-2.5 (0.8)	9760 (1663) / -21.7	62 (15) / -52.9
	Control	-3.6 (0.4)	12934 (2047) / 3.8	102 (20) / -22.7
220	PG-MA	-8.7 (0.7)	9255 (1049) / -25.7	54 (13) / -59.3
	Gly-MA	-12.1 (2.2)	9318 (1523) / -25.2	55 (27) / -58.9
	MA	-10.7 (0.9)	9701 (1025) / -22.1	54 (10) / -59.2
	Control	-17.5 (0.9)	9441 (3761) / -24.2	52 (21) / -60.7

*Each value was based on the average of ten samples; standard deviation is in parentheses

On the other hand, MOE of treated wood increased slightly at 150°C curing condition, even though these increments were not significant compared to the samples at 103 and 200°C. The higher positive mass changes after leaching (Δm AL) (Table 2) at this temperature indicated that the interaction between additive and wood had been well constructed by minimizing the heat-induced mechanical degradation of wood.

In addition, the low concentration of applied additive solution might contribute for the small differences in their mechanical properties, especially among additive-based woods. Compared to untreated wood and thermal treated controls, the acidic properties of the applied additives solution in the additive-treated wood might contribute to destabilize or even to hydrolyse some glycosidic bond of hemicellulose and amorphous cellulose, which eventually would reduce the mechanical properties (e.g MOE and MOR) of wood. Nevertheless, both thermal treated control and additive-treated wood gave a similar respond on those mechanical properties at 220°C curing condition.

Decay resistance analysis (EN 113 1996)

In general, durability values (EN BS 350-2 1994) of both treated and untreated wood against *Coriolus versicolor* (CV) attacks increased (mass loss decreased) by the increase of curing temperature (Table 3). At 200°C, all treated wood with additives for before and after leaching had lower mass loss values against CV (Class 1, very durable) than control (Class 3, moderately durable). These phenomena indicated that in this curing condition, the synergic effect of both applied chemical and thermal modification gave better decay durability properties of modified wood than at lower curing conditions.

These results corroborate the previous research from Salman *et al.* (2017), which revealed that a significant decrease in mass loss of PG-MA-treated wood against CV began at 200°C curing condition. On the other hand, Iwamoto and Itoh (2005) and Geraud *et al.* (2015) also quoted that MA-treated wood cured at 180°C had better decay resistance than at lower curing condition. Furthermore, thermal treatment at 220°C gave best results on this decay resistance for all additive-

treated and untreated wood before and after leaching. Thus at 220°C, thermal modification of wood played dominant rule in this condition.

Table 3: Mass losses and durability due to decay test against *Coriolus versicolor* for treated and untreated wood at different curing condition before and after leaching

T (°C)	Additives 10%	Before Leaching ^a		After Leaching ^b	
		Δm (%)	MLDB (%) / Durability Class	Δm AL (%)	MLDA (%) / Durability Class
103	PG-MA	10.6 (2.2)	7.6 (1.1) / 3	3.6 (0.7)	24.1 (5.2) / 3
	Gly-MA	9.7 (1.3)	7.8 (0.6) / 3	4.4 (0.8)	29.3 (6.0) / 4
	MA	8.9 (1.2)	9.50 (0.9) / 3	2.8 (0.4)	6.6 (0.6) / 2
	Control	0.0 (0.0)	24.2 (2.6) / 5	-1.0 (0.2)	42.4 (7.3) / 5
150	PG-MA	8.7 (1.02)	5.3 (3.1) / 2	6.2 (1.3)	32.7 (3.2) / 4
	Gly-MA	8.2 (1.10)	3.5 (0.4) / 1	6.3 (0.6)	21.4 (1.9) / 3
	MA	7.0 (0.4)	7.7 (0.8) / 3	1.2 (0.7)	6.2 (0.5) / 2
	Control	-0.2 (0.2)	21.2 (1.4) / 4	-0.9 (0.1)	41.8 (7.5) / 5
200	PG-MA	4.1 (1.6)	0.9 (0.5) / 1	-1.0 (1.1)	3.1 (3.0) / 1
	Gly-MA	0.6 (1.0)	0.32 (0.3) / 1	-1.2 (2.7)	0.7 (0.8) / 1
	MA	-4.5 (0.2)	0.1 (0.4) / 1	-8.5 (1.1)	0.8 (0.3) / 1
	Control	-2.3 (0.2)	14.0 (2.4) / 3	-6.8 (0.3)	21.3 (2.6) / 3
220	PG-MA	-2.8 (1.2)	0.0 (0.2) / 1	-6.7 (3.1)	-0.4 (0.2) / 1
	Gly-MA	-6.2 (1.1)	-0.3 (0.2) / 1	-6.8 (1.4)	-0.2 (0.2) / 1
	MA	-9.8 (0.8)	-0.5 (0.1) / 1	-13.5 (1.1)	0.4 (0.2) / 1
	Control	-10.3 (0.8)	1.7 (1.2) / 1	-13.7 (0.4)	1.6 (0.9) / 1

^aIncubation process in five weeks and each value was the average of six samples; ^bIncubation process in twelve weeks and each value was the average of five samples; MLDB = mass loss after decay test for treated and untreated wood before leaching process; MLDA = mass loss after decay test for treated and untreated wood after leaching process; Durability class referred to N BS 350-2 1994 regulation (1= very durable, 2= durable, 3= moderately durable, 4=slightly durable, 5= non durable); standard deviation is in parentheses

CONCLUSION

Based on the results, some additive-treated wood have shown their properties improvement by the increase of curing temperature compared to untreated wood. The synergic effect of thermochemical modification was observed at 200°C. PG-MA, Gly-MA, and MA-treated wood presented better improvement in dimensional stability (62 – 69%) and decay durability for before and after leaching process (Class 1, very durable) against *Coriolus versicolor* than the control. Unfortunately, at this temperature, MOE/MOR values decreased by 17 – 26%/43 – 53% compared to untreated wood. Nevertheless, these non-biocide wood preservation treatments results could be the basis for further work and other advanced analytical tests.

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THE INTERNATIONAL RESEARCH GROUP ON WOOD PROTECTION

Section 4

Processes and Properties

**Development of beech wood thermo-chemical modification
treatments based on different vinylic derivatives of glycerol and
polyglycerol**

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ABSTRACT

In this study, a combination between chemical and thermal wood modification has been investigated. Seven types of a low concentration of 10% aqueous additive solution of vinylicglycerol [glycerol-maleic anhydride (Gly-MA), glycidyl methacrylate (GM), and Glycerol methacrylate-maleic anhydride (GM/MA_(2eq))], vinylicpolyglycerol [polyglycerol-maleic anhydride (PG-MA), polyglycerol methacrylate (PGM), and polyglycerol methacrylate-maleic anhydride (PGM/MA_(3eq))], and maleic anhydride (MA) were impregnated into European beech wood (*Fagus sylvatica*), known for its low dimensional stability and poor natural durability. Varied with different curing temperatures at 103, 150, 200, and 220°C under inert condition, the modified wood and control were then characterized for their physical, mechanical, decay, and termite resistance properties. We found that, at the same initial weight percent gain (WPG) value (8 – 11%), mass changes (Δm) after thermal treatment, bulking (B), weight loss due to leaching (W_L), swelling (S), wettability, modulus of elasticity (MOE), and modulus of rupture (MOR) values of the additive-treated wood decreased as the curing temperature increased. In contrast, anti-swelling efficiency (ASE), decay resistance against *Coriolus versicolor*, and termite resistance against *Reticulitermes flavipes* values of additive-treated wood increased considerably for some treatments as the curing temperature increased, with better results at 200 and 220°C. In other words, the study has disclosed that the addition of some selected additives combined with thermal treatment can improve wood decay resistance and termite resistance better than untreated wood or wood with only underwent thermally modified treatment.

Keywords: chemical modification, decay resistance, *Fagus sylvatica*, glycerol, glycidyl methacrylate, maleic anhydride, termite resistance, thermal treatment, polyglycerol.

1. INTRODUCTION

As an increase on environmental concern in many aspects, especially in the field of wood preservation technology, wood modification has been considered as an alternative method to overcome this issue since the last decade (Schultz *et al.* 2008). Moreover, numerous methods of wood modification which categorized as a non-biocide wood preservation system for some treatments could be used for a wider service area, exterior or interior applications. Based on the same principle by altering the wood properties through intervening the wood cell wall, wood modification consists of three methods: thermal, chemical, and impregnation modifications (Hill 2011; Gerardin 2016). Thermal modification, a well-known method for decades, is believed to improve dimensional stability (Stamm *et al.* 1946; Tjeerdsma *et al.* 1998; Militz

2002; Esteves and Pereira 2009; Rowell *et al.* 2009) and decay durability (Kamdem *et al.* 2002; Weiland and Guyonnet 2003; Hakkou *et al.* 2006; Rowell *et al.* 2009; Mburu *et al.* 2007) of the modified wood. However, even though the modification process occurred at elevated temperature (150 – 280°C) (Boonstra *et al.* 2007), its durability against termite attacks for some wood species is still low (Shi *et al.* 2007; Sivrikaya *et al.* 2015; Surini *et al.* 2012), limiting its application especially for exterior service area. On the other hand, chemical and impregnation modifications, the methods which involve the utilization of some reactive chemicals in the process, are believed to improve not only the wood physical properties and decay resistance, but also wood resistance against termites for some treatments (Rowell *et al.* 1997; Ibach *et al.* 2000; Lande *et al.* 2004; Hadi *et al.* 2005; Militz *et al.* 2011; Bongers *et al.* 2015). However, due to a considerable cost of the chemical and process used, some of these methods are ordinarily used for only specific applications. Based on these limitations, certain research had tried to find other alternatives for wood modification including the use of combination of two methods, thermal and chemical modification simultaneously. Salman *et al.* (2016, 2017) have applied a low concentration of additives (to minimize cost of chemical used) based on vinylic derivatives of polyglycerol followed with thermal treatments at certain elevated temperatures. This research has given a novel insight into how the addition of relatively low concentration of chemicals in thermally modified wood treatments can improve not only decay resistance but also termite resistance properties.

Based on the same principle as the research from Salman *et al.* (2016, 2017), this study investigated the new additive formulations based on vinylic derivatives of glycerol (glycerol-maleic anhydride, glycerol methacrylate, and glycerol methacrylate-maleic anhydride) combined with different curing temperatures. The use of glycerol in this study was based on the expectation that it has similar properties as polyglycerol (a polymer form of glycerol) and similar properties of their modified wood. Further, a huge amount in availability, glycerol would be more advantageous for an up-scaling treatment or a commercial purpose. As comparison for the new developed additives, vinylic derivatives of polyglycerol (polyglycerol-maleic anhydride, polyglycerol methacrylate, and polyglycerol methacrylate-maleic anhydride) and maleic anhydride in the single form were also used in this research. General testing for modified wood properties such as physical, mechanical, decay, and termite durability properties was also undertaken for a complete understanding of the new developed wood products. Because of a huge abundance in Europe, European beech (*Fagus sylvatica*) known for its low dimensional stability and poor natural durability (EN 350 2016) was used as a substrate in this experiment.

2. EXPERIMENTAL METHODS

A defect-free of European beech wood (*Fagus sylvatica*) raw material (moisture content, $\pm 11\%$) was prepared and cut according to specific size based on each parameter analysis and conditioned at 20°C/60 of Relative Humidity (RH). Seven additive solutions [polyglycerol-maleic anhydride (PG-MA), glycerol-maleic anhydride (Gly-MA), polyglycerol methacrylate (PGM), glycerol methacrylate (GM), polyglycerol methacrylate-maleic anhydride (PGM/MA_(3eq)), glycerol methacrylate-maleic anhydride (GM/MA_(2eq)), maleic anhydride (MA)] and four curing temperature treatments (103, 150, 200, and 220°C) were applied in this study.

2.1 Additive formulation

Polyglycerol-maleic anhydride additive (PG-MA) was made according to the method of Roussel *et al.* (2001). 1 mol of polyglycerol/PG [purchased from Inovyn (Belgium) as a mixture of compounds with an average molecular weight (Mw) of 242 g mol⁻¹ (degree of polymerization ~ 3)] was reacted with 2 mol of maleic anhydride/MA [purchased from Sigma-Aldrich Chimie SARL (France) with Mw = 98.06 g mol⁻¹] and heated at 80°C for 3 hours. The reaction was then stopped after disappearance of ATR-FTIR absorption of anhydride [carbonyl group (C=O, stretch) at about 1780 and 1853 cm⁻¹] and a complete appearance of a characteristic ester band (C=O) at about 1715 cm⁻¹. The product was directly used without further purification and dissolved into distilled water so that the final concentration of impregnating solution (additive solution) was 10 % w/w. Whereas, glycerol-maleic anhydride additive (Gly-MA) additive

[glycerol was purchased from Sigma-Aldrich Chimie SARL (France)] was also made by the same mol comparison and condition as PG-MA.

Polyglycerol methacrylate additive (PGM) was made according to the method of Soulonganga *et al.* (2004). 1 mol of polyglycerol were reacted with 0.02 mol of 4-(dimethylamino)pyridine (4-DMAP, $M_w = 122.17 \text{ g mol}^{-1}$) as a catalyst and 2 mol of glycidyl methacrylate ($M_w = 142.15 \text{ g mol}^{-1}$) [purchased from Sigma-Aldrich Chimie SARL (France)] into a beaker glass equipped with magnetic stirrer and glass watch, and heated at 70°C for 15 min. The reaction was then stopped after a complete appearance of a characteristic ester band (C=O) of PGM by means of ATR-FTIR at about 1716 cm^{-1} and diminution of hydroxyl group (-OH, stretch) of polyglycerol at 3331 cm^{-1} and epoxy group (stretch) of glycidyl methacrylate at 906 cm^{-1} . The product was directly used without further purification and dissolved into distilled water so that the final concentration of impregnating solution was 10% w/w. Just before impregnation process, about 2% w/w of methylethylketone peroxide [purchased from Sigma-Aldrich Chimie SARL (France)] was added and mixed. Glycerol methacrylate additive (GM) was also made by the same mol comparison and condition as PGM production.

Polyglycerol methacrylate-maleic anhydride additive (PGM/MA_(3eq)) was made by mixing 1 mol of PGM adduct into 3 mol MA aqueous solution so that the final concentration of impregnating additive aqueous mixture was 10% w/w. The final mixture was then directly applied. The same manner as PGM/MA_(3eq) aqueous mixture, GM/MA_(2eq) 10% w/w additive aqueous mixture was made by mixing well 1 mol of GM adduct into 2 mol of MA aqueous solution so that the final concentration was 10% w/w.

Maleic anhydride (MA) additive aqueous solution was made by dissolving maleic anhydride solid into distilled water so that the final solution concentration was 10% w/w.

2.2 Wood modification

Beech wood samples [$30 \times 15 \times 5 \text{ mm}^3$ and $190 \times 20 \times 5 \text{ mm}^3$ (L, R, T)] were dried at 103°C , weighed (m_0), the volume was recorded (V_0), exposed under vacuum condition (pressure (P) = 8 – 10 KPa, time (t) = 10 min) in an autoclave followed with impregnation process in 10% w/w aqueous additive solution for 1 h under vacuum (P = 5-10 KPa). Further, the pressure was brought up to 100 KPa (room pressure), then exposed under pressure (P = 1200 KPa, t = 1 h). Finally, the pressure was turned down to room pressure. All samples were then air conditioned for 24 h, dried at 103°C , weighed until constant mass (m_1), and their volumes were re-recorded (V_1). For thermal modification, samples were divided by four groups, one group (samples that dried only at 103°C) was kept, and the remaining three groups were exposed each at 150, 200, and 220°C under nitrogen condition for 20 h. The mass (m_2) and volume (V_2) of all modified woods at different curing temperatures were then recorded. Samples for non-additive impregnated wood/control were also conducted with the same procedure as the additive-treated wood previously.

2.3. Leaching process

Based on the method adapted from NF X 41-568 (2014), leaching test for some samples (destined for decay and termite test) [$30 \times 15 \times 5 \text{ mm}^3$, (L, R, T)] of additive-treated wood and wood control was performed. Samples were soaked into the distilled water (min 5 times volume of total wood samples). Samples were then subjected to six leaching periods (1, 2, 4, 8, 16, 48 h) under continuous shaking ($175 \text{ shakes min}^{-1}$). Between the periods of 4 and 8 h, samples were removed and kept without water for 16 h. After all leaching periods were complete, samples were finally dried at 103°C for 48 h and re-weighed (m_3).

Mass change as the result of the wood modification previously and the leaching process was calculated from the following equation (Eq. 1):

$$\Delta m (\%) = 100 \times (m_1 \text{ or } m_2 \text{ or } m_3 - m_0) / m_0 \quad (1)$$

where m_0 is the initial mass of wood at 103°C before modification, m_1 the dry mass of additive-treated wood at 103°C, m_2 the dry mass of additive-treated wood or wood control cured at higher temperature (150, 200, or 220°C), and m_3 the dry mass at 103°C of additive-treated wood or wood control after leaching process. Bulking value as the result of the wood modification was calculated from the following equation (Eq. 2):

$$\Delta V (\%) = 100 \times (V_1 \text{ or } V_2 - V_0) / V_0 \quad (2)$$

where V_0 is the dry volume of wood before modification (103°C), V_1 the dry volume of additive-treated wood at 103°C, V_2 the dry volume of additive-treated wood or wood control after thermal process at 150, 200 or 220°C.

Mass loss due to leaching process was calculated according to the following equation (Eq. 3):

$$WL_L (\%) = 100 \times (m_1 \text{ or } m_2 - m_3) / m_1 \text{ or } m_2 \quad (3)$$

where m_3 is the dry mass of additive-treated wood or wood control from different curing temperatures after leaching process.

2.4 Wettability

Water droplet contact angle measurement (Sessile drop test) adapted from Engonga *et al.* (1999) was conducted for predicting wettability properties of the modified wood and control. Contact angle of water droplet on the wood surface was measured by means of Drop Shape Analysis system DSA10 MK2 instrument from Kruss. Contact angles of three samples [$30 \times 15 \times 5 \text{ mm}^3$, (L, R, T)] from each additive-treated wood and wood control were measured and recorded automatically every 22 seconds until 114 seconds.

2.5 Anti-Swelling Efficiency (ASE)

This measurement was adapted to the method of Pfriem *et al.* (2012). Samples [$30 \times 15 \times 5 \text{ mm}^3$, (L, R, T)] of additive-treated wood and wood control at different curing temperatures were dried at 103°C, then their volumes were recorded (V_d). Afterwards, samples were soaked into distilled water and exposed under vacuum 10 KPa for 30 min. Then, the pressure was brought up to room pressure, and the samples were kept soaking in the water for 24 h followed with recording the wet volume at the end (V_w). This drying-wetting cycle was repeated three times. From these volume data, swelling (S) (Eq. 4) and anti-swelling efficiency (ASE) (Eq. 5) of samples were calculated as follow:

$$S = (V_w - V_d) / V_d \quad (4)$$

where V_d is the dry volume of the sample at 103°C, V_w the wet volume of the sample.

$$ASE (\%) = 100 \times (S_0 - S_1) / S_0 \quad (5)$$

where S_0 is the swelling of untreated wood, S_1 the swelling of treated wood.

2.6 Modulus of Elasticity (MOE) and Modulus of Rupture (MOR)

In brief, mechanical properties measurement (MOE and MOR) of the additive-treated woods and wood controls [$190 \times 20 \times 5 \text{ mm}^3$ (L, R, T)] at different curing temperatures was performed by means of INSTRON 4467 universal testing machine. Sample preparation, conditioning, a three point bending test measurement, and calculation of the MOE and MOR data were adapted from EN 310 (1993).

2.7 Decay resistance

This decay test comparable with EN 113 (1996) was undertaken according Bravery (1978). *Coriolus versicolor* Quélet (CV) [Linnaeus, CTB 863 A] was used as decay-degrading fungi for the additive-treated

wood and wood control [30 × 15 × 5 mm³, (L, R, T)] from different curing temperatures before and after leaching process as well as untreated woods as virulence samples. In brief, all wood samples were sterilized in autoclave at 110-120°C for 20 min and exposed on a pure well grown CV on a culture medium (containing 4% malt and 2.5% agar). Afterward, all samples were then incubated for 12 weeks at 22 ± 2°C and 70 ± 5% RH in a climatic chamber. Once the incubation period was completed, samples were cleaned carefully from the fungus. All samples were then dried at 103°C for 48 h and weighed (m₄). Finally, mass loss (ML) due to decay attacks was calculated according to the following formula (Eq. 6):

$$ML (\%) = 100 \times (m_0 \text{ or } m_1 \text{ or } m_2 \text{ or } m_3 - m_4) / m_0 \text{ or } m_1 \text{ or } m_2 \text{ or } m_3 \quad (6)$$

where m₄ is the dry mass at 103°C of wood sample after decay test.

2.8 Termite resistance

This procedure was based on the non-choice test according to EN 117 (2013) against *Reticulitermes flavipes* (ex. *santonensis*). Samples [30 × 15 × 5 mm³, (L, R, T)] of additive-treated wood and wood control were previously subjected to leaching. Three replicates from each treatment and control were tested. Each sample was put in 9 cm diameter Petri dish containing 40 g Fontainebleau sand (4 volume of sand / 1 volume of deionized water). Plastic mesh was used as a support for sample to avoid water saturation. A total amount of 50 termite workers, one nymph, and one soldier were introduced in each Petri dish. The Petri dishes were placed in a dark climatic chamber at 27°C with a relative humidity superior to 75%. After four weeks, the samples were removed and cleaned of the sand and the number of termites still alive (n) were counted to determine their survival rate (Eq. 7). The samples were dried at 103°C, weighed (m₅), and mass losses due to termite attacks (ML_t) were calculated (Eq. 8).

$$\text{Survival rate } (\%) = 100 \times n / 50 \quad (7)$$

where n is the number of the remaining live termite worker after test, while 50 the number of the added termite workers for the test.

$$ML_t (\%) = 100 \times (m_3 - m_5) / m_3 \quad (8)$$

where m₃ and m₅ are respectively the dry mass at 103°C of sample before and after termite attacks.

3. RESULTS AND DISCUSSION

3.1 Mass changes and leaching values

Based on the results in Table 1, in general, weight percent gain/mass changes (Δm) values of all additive-treated wood before leaching decreased as the curing temperature increased, and it happened intensively at 200 and 220°C curing conditions (due to an intensive thermal degradation). Among all impregnated additives, certain additives (PG-MA, Gly-MA, PGM, PGM/MA_(3eq), and GM/MA_(2eq)) have shown their good penetration into the wood (indicated by a higher Δm values before leaching process) and in parallel with the increase of their bulking values (ΔV). This condition can be observed particularly at 103 and 150°C curing condition. Polarity and molecular structure of the impregnated additives are believed to be the cause of their different penetration and bulking values.

Even though polarity of glycerol is similar with polyglycerol, the difference in molecular structure between both of them caused the difference in reactivity during additive synthesis. Further, the product synthesis might have different properties as well. In one case, PG-MA and Gly-MA have not much differences for their polarities (observed by their similar Δm and ΔV values). In the other case, PGM and GM have different polarities between both of them (difference in Δm and ΔV values), even though they were created by the same mol comparison of reactants during synthesis. In this system, glycidyl methacrylate as the non-polar

agent, had made clear difference between glycerol and polyglycerol. To minimize this difference, the addition of maleic anhydride (MA) into both systems (PGM and GM) increased their polarities and reactivities to the wood. These three compositions appear made batter fixation in wood, and made slightly higher penetration and stability during thermal treatments (150, 200, 220°C) among all impregnated additives in the same level of concentration (10% w/w).

Table 1: Data of mass changes before and after leaching, bulking values, and weight loss values due to leaching process of additive-treated wood and wood control at different curing temperatures

T(°C)	Additive	Δm (%)		ΔV^c (%)	WL _L ^b (%)
		Before leaching ^a	After leaching ^b		
103	PG-MA	10.0 ± 0.6	2.0 ± 0.4	9.9 ± 1.7	7.3 ± 0.9
	Gly-MA	9.7 ± 0.5	2.2 ± 0.4	11.5 ± 1.8	6.8 ± 0.5
	PGM	10.7 ± 0.7	1.6 ± 0.4	10.4 ± 1.4	8.2 ± 0.9
	GM	7.6 ± 0.6	0.6 ± 0.5	4.7 ± 2.3	6.4 ± 0.9
	PGM/MA _(3eq)	11.1 ± 1.2	2.7 ± 0.6	10.0 ± 2.4	7.6 ± 0.6
	GM/MA _(2eq)	11.2 ± 0.9	2.9 ± 0.3	8.8 ± 3.0	6.6 ± 0.9
	MA	9.3 ± 0.7	2.2 ± 0.7	7.0 ± 3.2	6.4 ± 0.9
	None	0	-1.4 ± 0.3	0	1.4 ± 0.3
150	PG-MA	8.3 ± 1.2	5.6 ± 1.0	8.9 ± 1.5	2.5 ± 0.6
	Gly-MA	8.9 ± 0.6	4.6 ± 0.4	11.0 ± 1.3	4.0 ± 0.4
	PGM	10.2 ± 1.1	3.9 ± 0.7	11.5 ± 1.4	5.8 ± 0.6
	GM	6.9 ± 0.6	1.4 ± 0.5	5.4 ± 2.3	5.2 ± 0.4
	PGM/MA _(3eq)	9.8 ± 1.0	6.5 ± 0.5	10.1 ± 2.3	3.2 ± 0.4
	GM/MA _(2eq)	10.2 ± 0.6	6.3 ± 0.4	11.4 ± 3.1	3.6 ± 0.4
	MA	7.2 ± 0.8	1.4 ± 0.8	6.7 ± 3.0	5.3 ± 0.8
	None	-0.1 ± 0.2	-1.8 ± 0.2	0.5 ± 0.2	1.7 ± 0.3
200	PG-MA	3.2 ± 1.5	0.9 ± 1.5	7.4 ± 0.6	2.3 ± 0.9
	Gly-MA	1.9 ± 1.2	-0.8 ± 1.9	6.3 ± 0.7	2.6 ± 1.2
	PGM	5.0 ± 0.4	2.3 ± 0.4	8.9 ± 0.5	2.6 ± 0.6
	GM	-1.4 ± 0.9	-2.9 ± 0.6	2.1 ± 0.7	1.5 ± 0.4
	PGM/MA _(3eq)	3.3 ± 1.4	-0.1 ± 1.0	7.1 ± 3.6	2.6 ± 0.2
	GM/MA _(2eq)	3.4 ± 0.9	1.5 ± 0.5	6.4 ± 1.3	1.6 ± 1.0
	MA	-4.3 ± 0.5	-7.7 ± 0.6	-0.5 ± 2.2	3.7 ± 0.7
	None	-2.5 ± 0.4	-4.2 ± 0.3	-1.7 ± 0.6	1.7 ± 0.1
220	PG-MA	-3.1 ± 1.2	-5.3 ± 1.2	2.9 ± 1.0	2.4 ± 0.6
	Gly-MA	-5.6 ± 1.2	-8.9 ± 1.1	2.8 ± 1.7	3.6 ± 0.4
	PGM	-4.0 ± 1.0	-5.9 ± 0.7	2.9 ± 2.6	1.9 ± 1.0
	GM	-7.2 ± 1.5	-8.6 ± 1.3	-2.6 ± 0.8	1.5 ± 0.7
	PGM/MA _(3eq)	-2.8 ± 1.0	-5.0 ± 0.6	3.1 ± 1.7	2.5 ± 1.0
	GM/MA _(2eq)	-2.1 ± 1.0	-4.6 ± 0.6	1.5 ± 0.5	2.6 ± 0.8
	MA	-9.9 ± 0.8	-13.8 ± 1.0	-2.5 ± 1.2	4.2 ± 1.3
	None	-10.5 ± 1.1	-11.6 ± 1.0	-6.4 ± 0.7	1.2 ± 0.3

Value was the average of ^a96 replicates at 103°C and 24 replicates at @150; 200; 220°C, ^b6 replicates, ^c5 replicates

In terms of thermal stability, MA-treated wood was the lowest one (observed intensively at 200 and 220°C curing conditions). The similar result also corroborated research from Bodirlau *et al.* (2008) quoted that MA-treated wood has low thermal stability at high temperature (>200°C). Further, the acidic property of MA-based additives was also believed as the cause of an accelerated thermal-induced degradation. At the highest thermal process (220°C), both additive-treated wood and wood control degraded intensively, where wood control reached mass loss about 10%.

After leaching process, Δm after leaching values of additive-treated wood increased for treatments at 150°C curing condition, indicating that almost all impregnated additives have already polymerized (for certain additives) or fixed in wood at this temperature. This better fixation can also be observed to their lower mass loss due to leaching process (WL_L) compared to the curing process at 103°C. Among all the impregnated additives, PGM/MA_(3eq) and GM/MA_(2eq)-based additives made better fixation in wood than others. A possible three-dimensional composite system of both three compositions of additives was the cause for their better resistance against leaching process. On the other hand, at higher thermal process, at 200 and 220°C, an intensive decrease in Δm values for both before and after leaching of additive-treated wood due to the thermal degradation made reduction in their WL_L values, especially at 200°C curing temperature. However, due to the extensive thermal degradation at 220°C, WL_L values of most maleic anhydride-treated wood (MA, PG-MA, Gly-MA, PGM/MA_(3eq), and GM/MA_(2eq)-treated wood) slightly increased at which some of the degradation products were presumably leached out during leaching process.

3.2 Wettability

According to the contact angle values (Figure 1), in most cases, wettability of additive-treated wood and wood control decreased as the curing temperature increased. These results also confirmed some previous research reported that thermal treated wood have more surface hydrophobic characteristic (less wettability/higher contact angle values) than untreated wood (Pétrissans *et al.* 2003; Hakkou *et al.* 2005).

Among the additive-treated wood, methacrylate-based additive (PGM, GM, PGM/MA_(3eq), and GM/MA_(2eq)) treated wood had higher wettability property than maleic anhydride-based additive (PG-MA, Gly-MA, and MA) treated wood particularly at 103 and 150°C curing conditions. The incomplete polymerization of PGM/MA_(3eq) and GM/MA_(2eq)-based additives and the less reactive properties of PGM and GM-based additives in wood as well as a glycidol as a by-product during synthesis of PGM and GM were believed as the main factors for their higher wettability properties (lower contact angle values) compared to others, especially at this lower curing conditions. In contrast, MA-treated wood had the highest contact angle values than others at 103°C. The existence of the double bonds and cyclic structure of the unreacted MA at this temperature was presumably as the cause for their lowest wettability than others. All of these phenomena were the result of the difference in polarity and reactivity of each additive in wood. At 150°C curing condition, PGM/MA_(3eq) had higher contact angle values than GM/MA_(2eq) indicating that polyglycerol reacted faster than glycerol at this formulation. On the other hand, the formation of mono-esterified product (leaving the carboxylic acid group in another hand) in MA-treated wood was believed as the cause for its lower contact angle values at this lower thermal process.

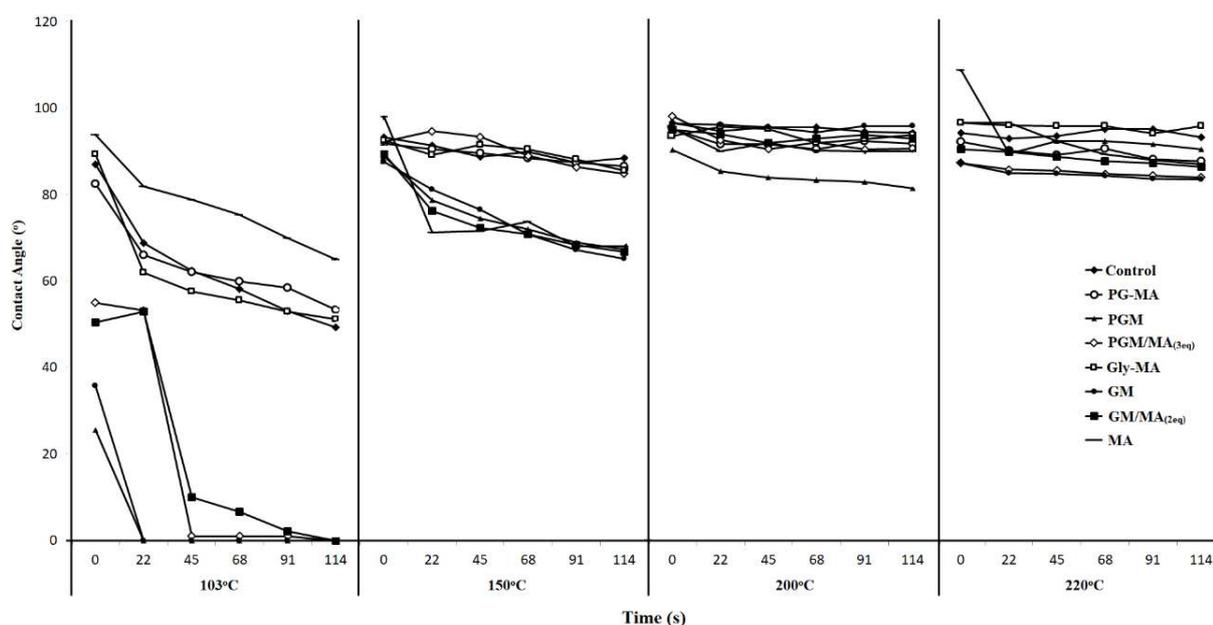


Figure 1: Contact angle values of additive-treated wood and wood control from different curing temperatures

At higher thermal condition (200°C), almost all additive-treated wood and wood control have similar wettability properties. A higher amount of hydroxyl groups of polyglycerol in PGM than hydroxyl groups of glycerol in GM-based additive made PGM-treated wood still have higher wettability (lower contact angle values) than GM-treated wood or others. At 220°C, due to the intensive thermal degradation, each additive-treated wood had different thermal stability properties triggering the different wettability properties one and each other at which their thermal-degradation products presumably contributed on its properties.

3.3 Dimensional stability

Dimensional stability measured as ASE after three leaching cycles of drying-soaking system in the Table 2 shows that in general, ASE values of both additive-treated wood and wood control increased as the curing temperature increased, and additive-treated wood had higher ASE values than wood control at each temperature. This condition was probably caused by two possible factors, chemically [the formation of the new chemical bonds between additive and wood components, degradation of hemicellulose of wood, and/or cross-linking in lignin (Esteves and Pereira 2009)] and physically (reduction of moisture absorption as the response of the new chemical bonds and an anchoring system between additive-wood). In addition, the results also confirmed some previous research reporting that thermal treated wood (wood control at 150, 200, 220°C in this case) had better dimensional stability compared to untreated wood (Stamm *et al.* 1946; Tjeerdma *et al.* 1998; Militz 2002; Esteves and Pereira 2009; Rowell *et al.* 2009). A steep increase in ASE values happened at 200°C curing temperature indicating that thermal-induced dimensional stability was started at this curing temperature according to this experimental condition. Among the additive-treated wood, all maleic anhydride-based additives treated wood (PG-MA, Gly-MA, PGM/MA_(3eq)) and GM/MA_(2eq), and MA-treated wood) had better in dimensional stability than PGM and GM-treated wood. A relatively low ASE values of PGM and GM-treated wood was probably caused by the low reactivity of the additives (only occupied by the hydroxyl and methacrylate group) to fix better to the wood compared to the others (carboxylic acid group) even at higher curing

temperature. The results also emphasized some previous studies reported that maleic anhydride treated wood had ASE values > 40% (Iwamoto and Itoh 2005; Liu et al. 2012; Essoua et al. 2015). The existence of the double bonds, the higher portion of the cis-conformation of the molecule, and the reactive carboxylic acid group from MA based additives was the possible factors for its high dimensional stability of its modified wood. At the highest thermal process (220°C), the difference of ASE values between additive-treated wood and control became imminent due to the extensive thermal degradation during process.

3.4 Modulus of Elasticity (MOE) and Modulus of Rupture (MOR)

Table 2: Data of dimensional stability (ASE) and mechanical properties as Modulus of Elasticity (MOE) and Modulus of Rupture (MOR)

T(°C)	Additive	ASE ^d (%)	MOE ^e (N/mm ²)	MOR ^e (N/mm ²)
103	PG-MA	46.1 ± 2.0	9479 ± 1088	96 ± 18
	Gly-MA	46.5 ± 4.9	9205 ± 876	89 ± 11
	PG-GM	32.1 ± 2.2	9837 ± 1009	119 ± 15
	Gly-GM	32.4 ± 1.7	9827 ± 1174	112 ± 14
	PGM/MA _(3eq)	46.1 ± 3.4	10834 ± 509	106 ± 19
	GM/MA _(2eq)	43.5 ± 2.4	10444 ± 975	99 ± 12
	MA	41.0 ± 2.8	10070 ± 971	81 ± 16
	None	13.9 ± 8.0	12459 ± 1389	132 ± 17
150	PG-MA	48.1 ± 4.6	10723 ± 748	88 ± 11
	Gly-MA	55.0 ± 4.5	10392 ± 946	85 ± 14
	PG-GM	34.3 ± 7.6	10480 ± 915	116 ± 18
	Gly-GM	23.6 ± 7.8	10395 ± 816	112 ± 15
	PGM/MA _(3eq)	48.4 ± 6.6	10641 ± 1212	79 ± 23
	GM/MA _(2eq)	51.8 ± 9.8	11123 ± 860	87 ± 14
	MA	47.7 ± 3.3	10916 ± 850	75 ± 8
	None	21.6 ± 6.3	12801 ± 1243	134 ± 17
200	PG-MA	61.7 ± 3.2	10328 ± 960	75 ± 9
	Gly-MA	69.0 ± 4.6	9283 ± 1381	63 ± 12
	PG-GM	51.6 ± 7.1	9904 ± 827	84 ± 15
	Gly-GM	54.3 ± 2.2	10584 ± 1253	86 ± 16
	PGM/MA _(3eq)	66.3 ± 5.4	10159 ± 1182	69 ± 11
	GM/MA _(2eq)	63.8 ± 6.5	10965 ± 962	73 ± 15
	MA	66.8 ± 9.0	9761 ± 1663	62 ± 15
	None	49.4 ± 2.5	12933 ± 2046	102 ± 19
220	PG-MA	74.7 ± 4.4	9254 ± 1048	53 ± 12
	Gly-MA	78.2 ± 1.9	9318 ± 1523	54 ± 27
	PG-GM	73.0 ± 4.2	8902 ± 959	51 ± 7
	Gly-GM	75.6 ± 6.7	8888 ± 969	48 ± 11
	PGM/MA _(3eq)	77.9 ± 0.9	8984 ± 1645	53 ± 10
	GM/MA _(2eq)	73.1 ± 3.5	9193 ± 1153	48 ± 5
	MA	66.7 ± 2.2	9701 ± 1025	54 ± 10
	None	63.5 ± 2.3	9441 ± 3761	52 ± 21

^d4 replicates at 3rd cycle of ASE, and ^e10 replicates

Mechanical properties measured as three-point bending test of MOE and MOR in Table 2 revealed that in most cases MOE and MOR values of both additive-treated wood and wood control decreased as the curing temperature increased. Moreover, MOE/MOR of the additive-treated wood were lower than control at each curing condition, indicating that there has been an intensive modification of wood with the addition of the additives particularly for maleic anhydride-modified wood at higher thermal process.

At low curing temperature (103°C), acidic-induced mechanical degradation was presumably the main reason for the low MOE/MOR values of additive-treated wood in general, whereas level of the additive-induced modification was still low. At 150°C curing condition, MOE values of almost all additive-treated wood and wood control increased. Compared to 103°C curing condition, a higher difference of those increment for additive-treated wood at 150°C compared to its control was assumed not only by the increase of additive fixation in wood (the higher Δm after leaching value) but also the increase of wood mechanical properties its self (wood control) at 150°C. The increase in MOE values for wood control was assumed as the increase of wood crystallinity, whereas level of thermal-induced degradation was still low (had low mass loss due to thermal treatment in Table 1). This result appears in parallel with research from Yildiz and Gümüşkaya (2007) reporting that beech wood can reach the maximum crystallinity at certain elevated temperature condition then decrease after that at higher elevated temperature condition.

Among all additive-treated wood, PGM/MA_(3eq) and GM/MA_(2eq)-treated wood show slightly higher MOE values than others. A three-dimensional composite system in these additives was probably as the reason for this case. However, in terms of MOR values, almost all maleic anhydride-based additive treated wood had lower MOR values than PGM and GM-based additive treated wood. An acidic property of maleic anhydride-based additives was believed as the main element in this case. At 200°C curing temperature, thermal-induced degradation emerged obviously, where MOR value of wood control decreased by 22%. However, this decrease was slightly happened in almost all additive treated wood. This condition was assumed that the mechanical properties of the additive-treated wood had been degraded faster at lower temperature (103°C) in comparison to wood control. Therefore, the difference in MOR values of additive-treated wood at 103, 150, and 200°C curing condition was lower than control at 150 and 200°C curing condition. At the highest thermal process, because of the intensive thermal degradation in this condition, the mechanical properties of both additive-treated wood and wood control degraded considerably.

3.5 Decay resistance

According to the decay durability test against white-rot fungi, *Coriolus versicolor*, mass loss values due to decay for both additive-treated wood and wood control before and after leaching decreased (resistance to decay increased) as the curing temperature increased (Table 3). A high decrease in mass loss was observed at 200°C, particularly for maleic anhydride-based additive treated wood (PG-MA, Gly-MA, PGM/MA_(3eq) and GM/MA_(2eq)) showing very low mass loss values than others. This condition was probably caused by two possible factors, chemically [the formation of the new chemical bonds between additive and wood components or wood degradation products, the generation of toxic compounds during heating, the heat induced-chemical modification of wood components, and degradation intensively of hemicellulose (Hakkou *et al.* 2005)] and physically (reduction of moisture absorption as the result of the new chemical bond, an anchoring system between additive-wood, and reduction of hydroxyl group of polysaccharide due to chemical reaction).

Table 3: Data of decay resistance against *Coriolus versicolor* of samples before and after leaching and termite resistance against *Reticulitermes flavipes* of samples after leaching

T (°C)	Additive	Decay resistance		Termite resistance	
		ML (%) before leaching ^a	ML (%) after leaching ^b	ML _t ^c (%) after leaching	Survival Rate ^c (%)
103	PG-MA	7.6 ± 1.1	24.1 ± 5.2	3.9 ± 0.6	3 ± 3
	Gly-MA	7.85 ± 0.6	29.3 ± 6.0	3.6 ± 0.8	0 ± 0
	PGM	7.8 ± 1.3	45.3 ± 5.5	6.7 ± 3.5	61 ± 15
	GM	6.8 ± 0.6	45.0 ± 9.7	7.0 ± 1.5	67 ± 10
	PGM/MA _(3eq)	7.5 ± 0.3	9.0 ± 6.0	3.4 ± 0.2	27 ± 5
	GM/MA _(2eq)	8.2 ± 0.9	37.7 ± 9.1	3.7 ± 0.9	54 ± 7
	MA	9.5 ± 0.9	6.6 ± 0.6	3.7 ± 0.7	11 ± 1
	None	24.2 ± 2.6	42.4 ± 7.3	9.7 ± 3.2	65 ± 7
150	PG-MA	5.3 ± 3.1	32.7 ± 3.2	5.4 ± 1.0	51 ± 15
	Gly-MA	3.5 ± 0.4	21.4 ± 1.9	4.5 ± 0.7	34 ± 3
	PGM	11.3 ± 5.8	36.2 ± 2.4	3.2 ± 1.1	29 ± 22
	GM	5.9 ± 1.0	30.9 ± 2.3	6.9 ± 0.9	77 ± 15
	PGM/MA _(3eq)	2.8 ± 0.8	25.5 ± 6.3	4.2 ± 0.9	65 ± 1
	GM/MA _(2eq)	3.8 ± 0.9	23.2 ± 1.8	4.5 ± 0.9	55 ± 2
	MA	7.7 ± 0.8	6.2 ± 0.5	4.0 ± 0.3	15 ± 10
	None	21.2 ± 1.4	41.8 ± 7.5	5.1 ± 1.2	57 ± 6
200	PG-MA	0.9 ± 0.5	3.1 ± 3.0	7.7 ± 1.2	64 ± 12
	Gly-MA	0.3 ± 0.3	0.7 ± 0.8	4.0 ± 1.5	46 ± 7
	PGM	3.6 ± 2.1	15.1 ± 2.3	4.8 ± 1.4	47 ± 2
	GM	2.7 ± 2.3	13.7 ± 7.4	5.8 ± 1.2	63 ± 5
	PGM/MA _(3eq)	0.0 ± 0.2	3.1 ± 1.8	3.3 ± 0.9	54 ± 4
	GM/MA _(2eq)	0.4 ± 0.6	1.4 ± 1.2	3.4 ± 0.7	43 ± 6
	MA	0.1 ± 0.4	0.8 ± 0.3	4.3 ± 0.3	55 ± 1
	None	14.0 ± 2.4	21.3 ± 2.6	9.7 ± 0.9	74 ± 2
220	PG-MA	0.0 ± 0.2	-0.4 ± 0.2	3.8 ± 0.7	40 ± 7
	Gly-MA	-0.3 ± 0.2	-0.2 ± 0.2	2.8 ± 1.8	41 ± 20
	PGM	0.2 ± 0.3	3.3 ± 1.0	2.0 ± 0.5	29 ± 30
	GM	0.2 ± 0.2	0.6 ± 1.0	5.7 ± 1.5	62 ± 12
	PGM/MA _(3eq)	-0.0 ± 0.1	-0.2 ± 0.2	2.1 ± 0.3	45 ± 3
	GM/MA _(2eq)	-0.3 ± 0.1	-0.2 ± 0.1	2.2 ± 0.5	58 ± 6
	MA	-0.5 ± 0.1	0.4 ± 0.2	2.1 ± 0.6	27 ± 15
	None	1.7 ± 1.2	1.6 ± 0.9	8.6 ± 2.2	55 ± 13
Virulence	29.7 ± 1.3	51.2 ± 3.5	8.0 ± 1.0	81 ± 9	

Value was the average of ^a6 replicates with five weeks incubation period, ^b5 replicates with twelve weeks incubation period, and ^c3 replicates

On the other hand, the less reactive of PGM and GM-based additives in wood was believed as the cause for their far higher mass loss values than maleic anhydride-based additive treated wood. In the same temperature (200°C), mass loss value of wood control decreased for about 50% compared to control at 103°C, indicating that thermally treated wood at 200°C was not enough to fully protect wood against decay. In other words, the existence of the additive in wood, especially for maleic anhydride-based additive, was really important and worked synergistically at this temperature. These results also had similarity with research from Iwamoto

and Itoh (2005) reporting that maleic anhydride-based wood cured at 180°C had better decay resistance than cured at 150°C. However, due to the highest thermal degradation happened at 220°C curing condition, all wood samples had the lowest mass loss values. At this temperature, mass loss value of wood control decreased to less than 2%, confirming a common characteristic of the thermally treated wood for their good decay resistance properties.

3.5 Termite resistance

Durability against termite, evaluated by a non-choice screening test for all wood samples after leaching process, revealed that in general the existence of the additives in wood can increase the resistance of the treated wood to the termite attacks compared to control without additives (Table 3). At 103°C curing condition, it appears that maleic anhydride-based additive treated wood had higher resistance against termites (lower mass loss) than others. The more acidic properties of the maleic anhydride-based additives were the main possible factor in this point. However, some of them made lower survival rate of the termites. On the other hand, the less reactive of the PGM and GM-based additives to the wood influenced their less resistance (higher mass loss) against termites, however the survival rate of the termites at this condition was as high as control. At 150°C curing condition, even though most of the additives had reacted more intense to the wood (had higher Δm after leaching values in Table 1) proven by a higher survival rate number of the termites, the protection against termite was still low. On the other hand, at this temperature, wood control had higher resistance against termite (had lower mass loss values) than at 103, 200, or 220°C curing temperature. The similar result was also happened in the work of Salman *et al.* (2017), where mass loss values of wood control due to the same termite attacks (*Reticulitermes flavipes*) at 150°C were lower than at 103, 200, and 220°C. Other similar results were also reported by Unsal *et al.* (2009) quoting that pine wood treated at 150°C had significantly lower mass loss (higher resistance) against termite *Reticulitermes flavipes* Kollar than at 120°C-treated and untreated wood. In this research, the increase of wood control resistance against termite at 150°C could be connected to an increase in wood crystallinity and a cross-linking in lignin (Esteves and Pereira 2009) at which thermal-induced wood degradation was still low. At higher thermal process, at 200 and 220°C, wood control had higher mass loss values as at 103°C. This condition could be due to a decrease of the hemicellulose content as the effect of the thermal degradation. As had been reported by Bignell *et al.* (2010) that diminution of the hemicellulose content could trigger the degradation effectively of the cellulose by the termites. In contrast, it worked different for additive-treated wood, where almost all additive-treated wood had lower mass loss values, particularly at 220°C. This condition means that the existence of the additives in wood could work synergistically with the thermal process, permitting to a high protection of the modified wood against termite attacks.

4. CONCLUSION

This study has revealed and convinced that the addition of low concentration additives into beech wood followed with certain thermal treatments can improve not only dimensional stability and decay durability properties but also termite resistance of the modified wood. Further, the research also has disclosed this synergic effect between thermal and chemical modification of the additive-treated wood, which observed at 200 and 220°C at this additive concentration. Moreover, the new additive formulations based on vinylic derivatives of glycerol instead of polyglycerol also gave similar properties on their modified woods as vinylicpolyglycerol-treated wood, especially as maleic anhydride-based additive treated woods (PG-MA, Gly-MA, PGM/MA_(3eq), GM/MA_(2eq)). Among the additive treated wood, maleic anhydride-based treated woods (PG-MA, Gly-MA, PGM/MA_(3eq), GM/MA_(2eq), and MA-treated wood) show considerable increase in dimensional stability, decay resistance against *Corioulus verisicolor*, and

termite resistance against *Reticulitermes flavipes* compared to the others. However, due to acidic property of the additives, the mechanical properties of the additive-treated wood decreased faster than wood without additive.

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Appendix 3: Acidity of the aqueous additive solution

10% w/w Additive Solution	pH
PG-MA	1.41
Gly-MA	1.32
PG-GM	5.56
Gly-GM	5.78
PGM/MA _(3eq)	1.60
GM/MA _(2eq)	1.51
MA	1.10

Appendix 4: Solution up-take and retention values of the impregnated additive

Additive	Solution Up-take (%)	Retention (Kg/m ³)
PG-MA	119 ± 8	73.92 ± 3.69
Gly-MA	116 ± 5	72.27 ± 3.45
PG-GM	121 ± 7	75.54 ± 2.32
Gly-GM	114 ± 11	74.45 ± 2.56
PGM/MA _(3eq)	114 ± 9	72.44 ± 4.83
GM/MA _(2eq)	108 ± 11	72.12 ± 2.32
MA	127 ± 6	79.31 ± 1.88

Each value was based on the average of 20 samples

Appendix 5: Weight percent gain at 103°C (WPG), mass changes (WPG at higher curing temperature / Δm), and weight loss due to curing temperature (WL_{TT}).

Additives	103°C*		150°C*		200°C*		220°C*	
	10%	WPG (%)	Δm (%)	WL _{TT} (%)	Δm (%)	WL _{TT} (%)	Δm (%)	WL _{TT} (%)
PG-MA		10.33 ± 1.20	8.79 ± 1.03	1.10 ± 0.22	3.79 ± 1.65	5.92 ± 1.15	-3.15 ± 1.22	12.5 ± 0.62
Gly-MA		10.02 ± 0.89	8.57 ± 0.80	1.58 ± 0.25	1.10 ± 0.99	8.05 ± 0.74	-5.66 ± 1.15	14.27 ± 1.11
PG-GM		10.65 ± 0.88	10.44 ± 1.61	0.39 ± 1.20	5.16 ± 0.80	5.09 ± 0.57	-3.93 ± 1.37	12.83 ± 0.97
Gly-GM		8.04 ± 0.69	7.13 ± 0.52	0.84 ± 0.22	-0.67 ± 1.27	8.09 ± 1.13	-6.11 ± 1.78	13.17 ± 1.72
PGM/MA _(3eq)		11.12 ± 1.25	9.81 ± 0.99	1.25 ± 0.17	3.27 ± 1.37	7.24 ± 1.18	-2.81 ± 1.05	12.59 ± 0.40
GM/MA _(2eq)		11.17 ± 0.90	10.24 ± 0.59	1.11 ± 0.16	3.39 ± 0.91	6.70 ± 0.33	-2.08 ± 1.02	11.97 ± 0.45
MA		9.31 ± 0.74	7.17 ± 0.78	1.78 ± 0.36	-4.31 ± 0.51	12.29 ± 0.46	-9.86 ± 0.77	17.53 ± 0.61
Control		0	-0.13 ± 0.17	0.13 ± 0.17	-2.60 ± 0.46	2.60 ± 0.46	-10.47 ± 0.79	10.47 ± 0.79

*Each value was based on the average of 96 samples at 103°C and 24 samples for each thermal treatment (150; 200; 220°C)

Appendix 6: Bulking (B) or dimensional changes (ΔV) and swelling in the water (St) of the modified wood at different curing temperatures

Additives 10%	103°C*		150°C*		200°C*		220°C*	
	B (%)	S ₁ (%)	ΔV (%)	S ₁ (%)	ΔV (%)	S ₁ (%)	ΔV (%)	S ₁ (%)
PG-MA	9.94 ± 1.74	11.73 ± 1.59	8.94 ± 1.52	13.02 ± 1.27	7.35 ± 0.57	9.81 ± 0.97	2.86 ± 0.95	6.04 ± 1.56
Gly-MA	11.48 ± 1.74	13.89 ± 4.27	11.00 ± 1.26	11.49 ± 1.59	6.32 ± 0.68	7.56 ± 2.01	2.76 ± 1.67	5.16 ± 0.44
PG-GM	10.44 ± 1.42	15.42 ± 1.40	11.48 ± 1.38	16.64 ± 1.77	8.94 ± 0.5	11.80 ± 1.70	2.91 ± 2.58	8.76 ± 1.67
Gly-GM	4.68 ± 2.33	19.17 ± 0.99	5.40 ± 2.32	20.00 ± 1.85	2.14 ± 0.73	12.82 ± 1.35	-2.62 ± 0.83	6.86 ± 1.79
PGM/MA _(3eq)	10.03 ± 2.42	12.56 ± 0.32	10.08 ± 2.32	13.41 ± 1.52	7.07 ± 3.75	9.17 ± 0.91	3.13 ± 1.68	6.22 ± 0.66
GM/MA _(2eq)	8.84 ± 2.97	13.4 ± 0.93	11.39 ± 3.07	12.53 ± 2.54	6.39 ± 1.27	8.58 ± 1.56	1.53 ± 0.51	6.24 ± 0.90
MA	6.94 ± 3.19	12.26 ± 0.99	6.66 ± 2.98	10.85 ± 1.00	-0.50 ± 2.24	7.23 ± 0.71	-2.46 ± 1.20	6.65 ± 0.21
Control	0.00	26.04 ± 3.34	0.52 ± 0.24	24.25 ± 1.45	-1.69 ± 0.56	12.76 ± 0.63	-6.44 ± 0.69	8.47 ± 0.61

*Each value was based on the average of five samples

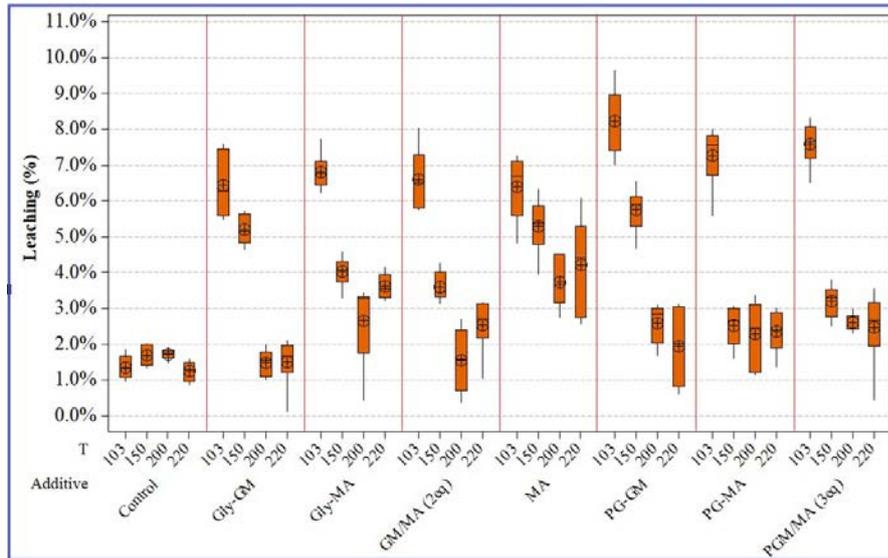
Appendix 7: Density and density changes of additive-treated wood and wood control

Additives 10%	Density (g/cm ³) and Density Changes (%)*						
	d 103°C	d 150°C	Δd 105°C	d 200°C	Δd 200°C	d 220°C	Δd 220°C
PG-MA	0.623 ± 0.03	0.620 ± 0.010	-1.04 ± 0.47	0.596 ± 0.010	-3.18 ± 0.86	0.568 ± 0.013	-6.14 ± 0.69
Gly-MA	0.614 ± 0.021	0.606 ± 0.012	-0.89 ± 0.24	0.603 ± 0.029	-3.60 ± 0.58	0.562 ± 0.027	-6.49 ± 0.75
PG-GM	0.624 ± 0.026	0.604 ± 0.016	-1.47 ± 0.46	0.585 ± 0.011	-4.35 ± 0.98	0.597 ± 0.024	-7.33 ± 0.78
Gly-GM	0.675 ± 0.053	0.661 ± 0.051	-1.11 ± 0.17	0.645 ± 0.033	-4.72 ± 1.22	0.627 ± 0.014	-7.09 ± 1.25
PGM/MA _(3eq)	0.641 ± 0.029	0.627 ± 0.028	-1.59 ± 0.21	0.608 ± 0.025	-3.48 ± 0.54	0.596 ± 0.029	-6.39 ± 0.61
GM/MA _(2eq)	0.679 ± 0.060	0.630 ± 0.052	-1.58 ± 0.52	0.634 ± 0.047	-3.51 ± 0.42	0.624 ± 0.048	-5.75 ± 0.93
MA	0.637 ± 0.022	0.622 ± 0.024	-1.15 ± 0.69	0.612 ± 0.018	-5.65 ± 0.62	0.578 ± 0.031	-8.46 ± 0.83
Control	0.644 ± 0.049	0.620 ± 0.033	-0.55 ± 0.34	0.661 ± 0.056	-1.50 ± 0.19	0.608 ± 0.046	-4.56 ± 0.20

*Each value was based on the average of five samples

Boxplots data of various parameter analysis in the Paper 5 based on two-way ANOVA ($\alpha = 0.05$).

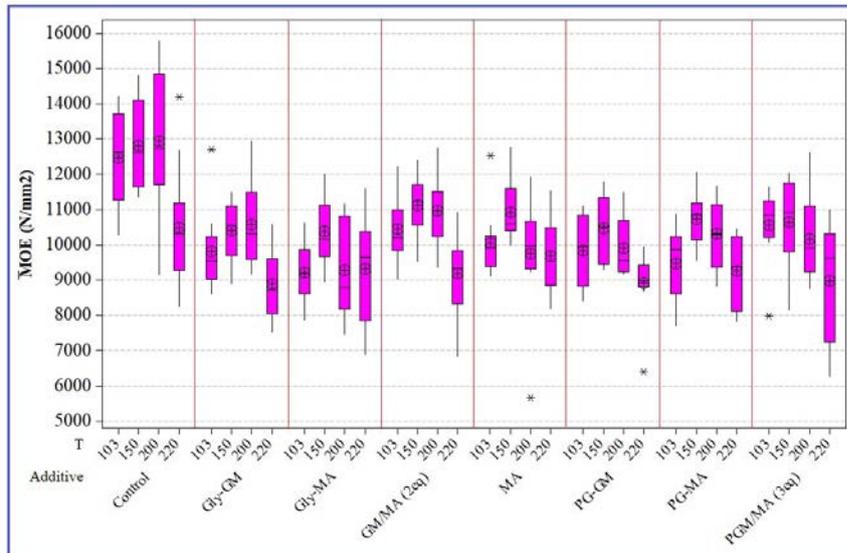
Appendix 8: Leaching properties of additive-treated wood and wood control at different curing temperature



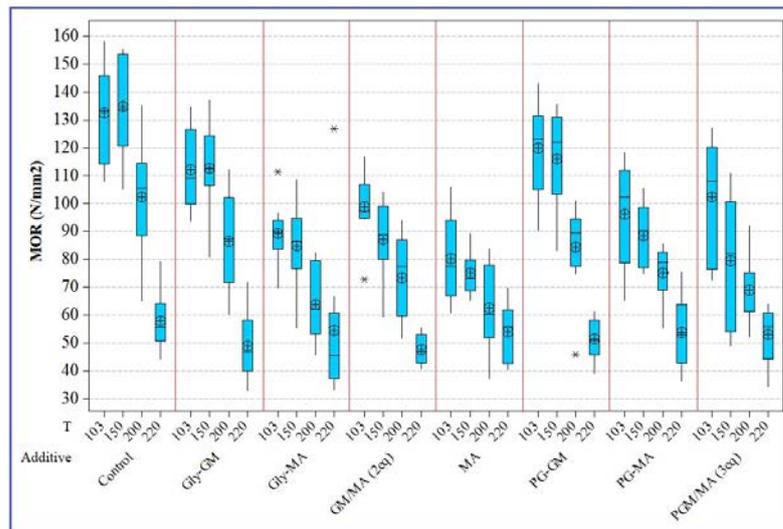
Appendix 9: Anti-swelling efficiency properties of additive-treated wood and wood control at different curing temperature



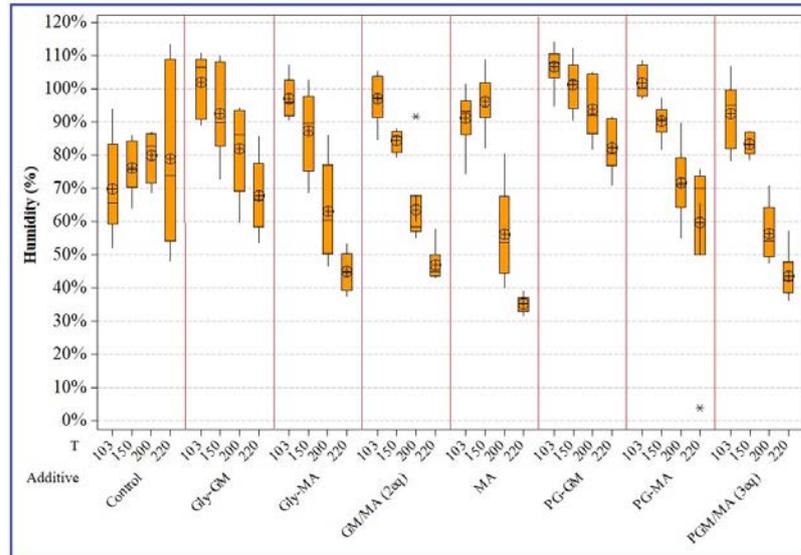
Appendix 10: Modulus of elasticity of additive-treated wood and wood control at different curing temperature



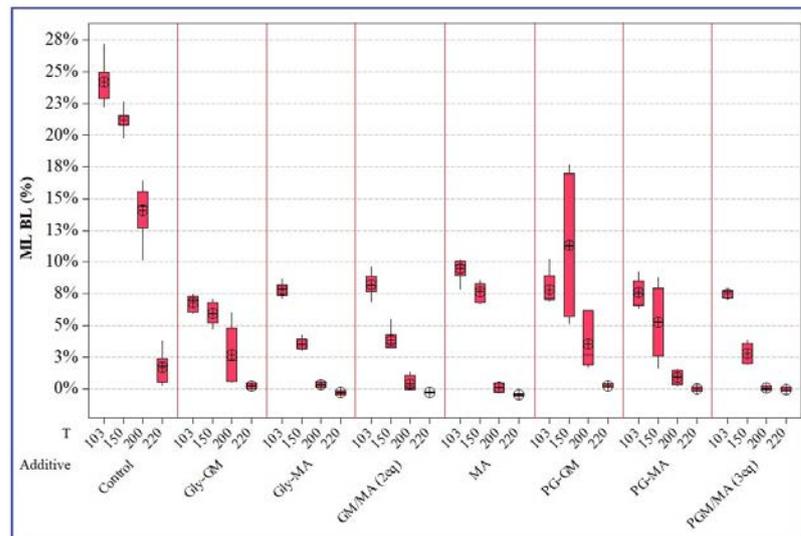
Appendix 11: Modulus of rupture of additive-treated wood and wood control at different curing temperature



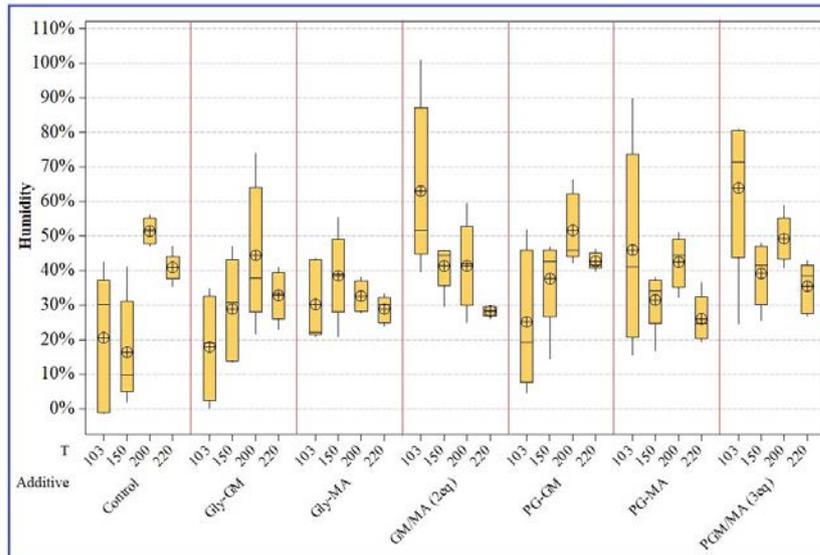
Appendix 12: Humidity of wood samples before leaching due to decay CV



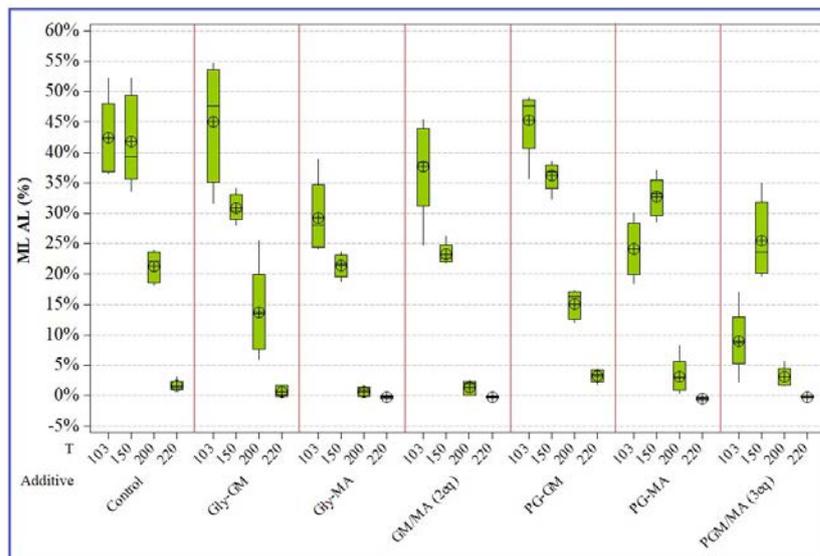
Appendix 13: Mass losses of wood samples before leaching due to decay CV



Appendix 14: Humidity of wood samples after leaching due to decay CV



Appendix 15: Mass losses of wood samples after leaching due to decay CV



Appendix 16: Weight losses of wood sample after leaching due to termite attacks



Appendix 17: Survival rate of termites during attacking wood sample after leaching



Appendix 18: TGA data of additive components, pure additives, untreated beech, and additive-treated beech

Samples	Mass loss TGA (%)								
	Actual			Estimation			Differences		
	103-220°C (8 min)	220°C (2 h)	Total 103-220°C	103-220°C (8 min)	220°C (2 h)	Total 103-220°C	103-220°C (8 min)	220°C (2 h)	Total 103-220°C
PG-MA pure	4.91	7.29	12.20	-	-	-	-	-	-
Beech-PG-MA	3.88	10.92	14.80	1.41	9.92	11.33	2.47	1.00	3.47
Gly-MA pure	6.49	14.47	20.96	-	-	-	-	-	-
Beech-Gly-MA	4.74	13.13	17.87	1.60	10.64	12.24	3.14	2.49	5.63
PG-GM pure	1.22	7.91	9.13	-	-	-	-	-	-
Beech-PG-GM	2.37	9.42	11.79	1.06	9.96	11.02	1.31	-0.54	0.77
Gly-GM pure	3.47	19.90	23.37	-	-	-	-	-	-
Beech-Gly-GM	4.23	10.54	14.77	1.24	10.99	12.23	2.99	-0.45	2.54
PGM/MA _(3eq) pure	2.73	6.27	9.00	-	-	-	-	-	-
Beech- PGM/MA _(3eq)	3.81	12.15	15.96	1.22	9.79	11.01	2.59	2.36	4.95
GM/MA _(2eq) pure	4.22	6.44	10.66	-	-	-	-	-	-
Beech- GM/MA _(2eq)	5.59	10.32	15.91	1.33	9.85	11.19	4.26	0.47	4.72
MA pure	43.35	73.29	100.00	-	-	-	-	-	-
Beech-MA	8.25	15.45	23.70	4.47	15.32	18.44	3.77	0.13	5.26
Beech wood pure	1.04	10.20	11.24	-	-	-	-	-	-
PG pure	0.66	7.91	8.57	-	-	-	-	-	-
Gly pure	56.90	94.19	100.00	-	-	-	-	-	-

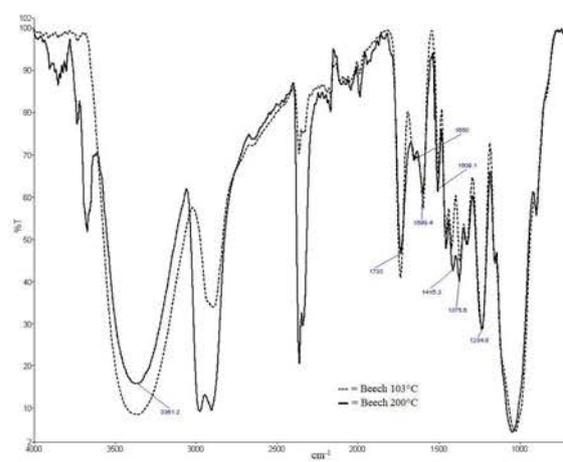
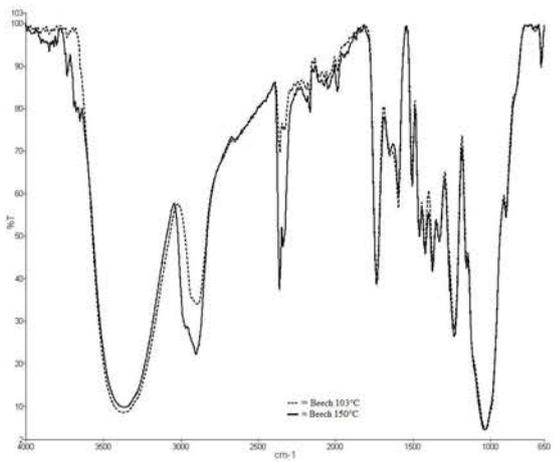
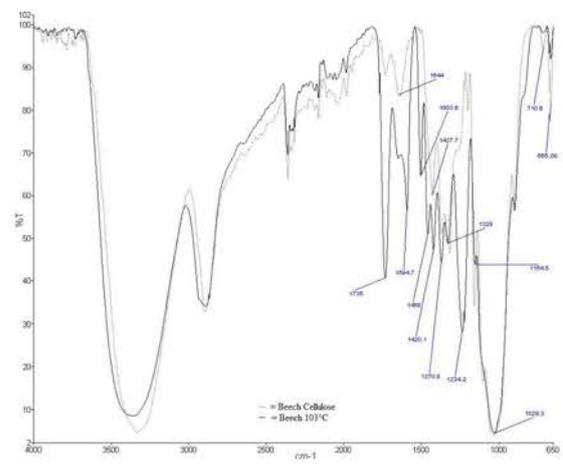
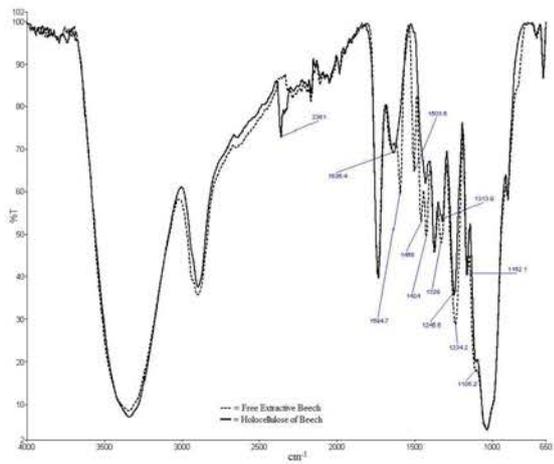
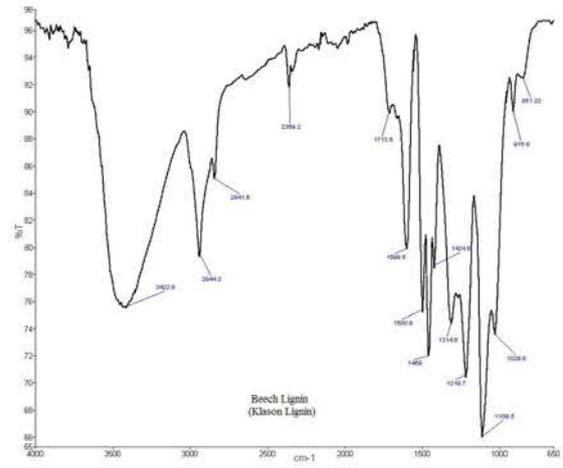
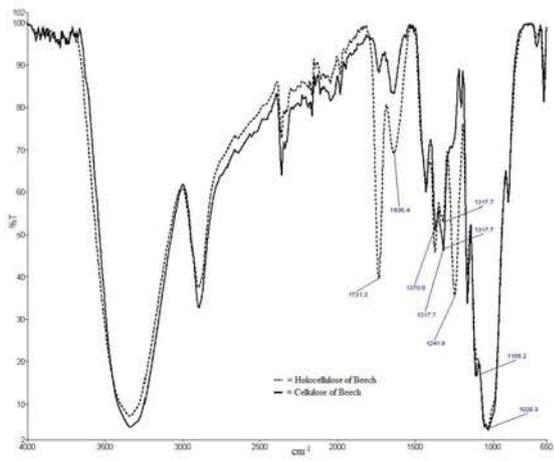
Appendix 19: Organic chemical compositions of European beech

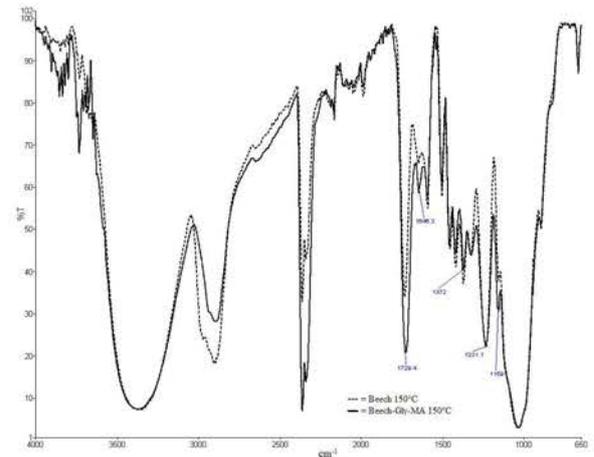
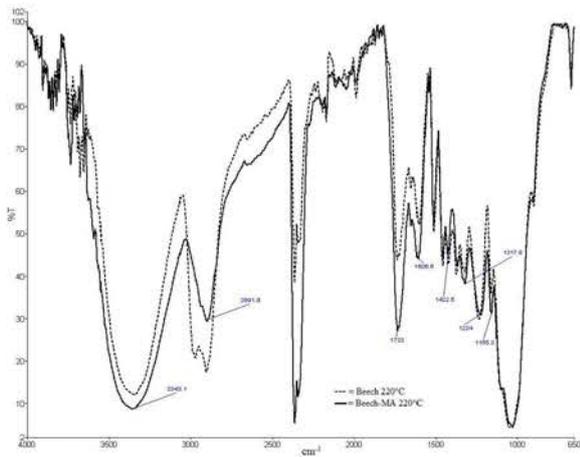
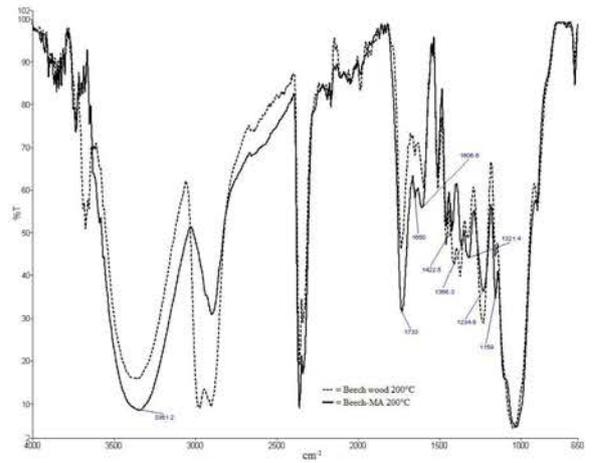
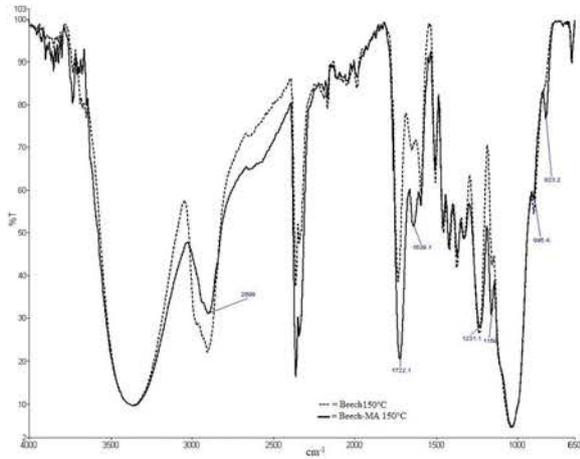
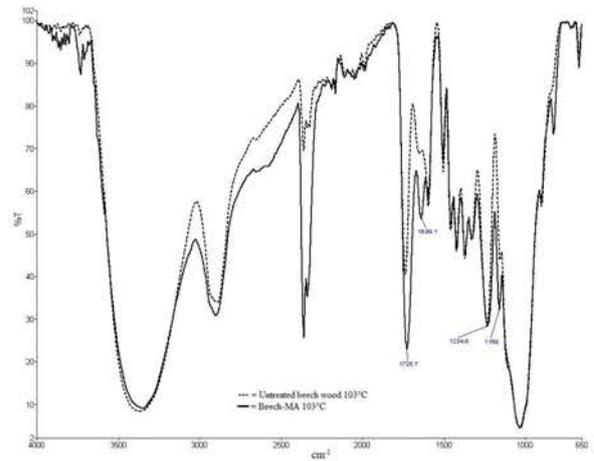
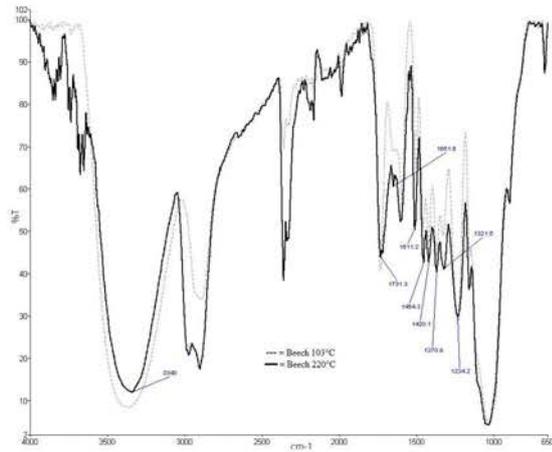
Index	Percentage to dry matter
Holocellulose content (Rowell 2012) *	73.76 ± 1.51
Cellulose content (Kurschner and Hoffner method)*	41.64 ± 0.84
Lignin (Klason lignin) TAPPI (1988)*	23.04 ± 0.67
Substance extracted by ethanol-toluene = (1:1)**	2.28 ± 0.68
Substance extracted by ethanol**	0.31 ± 0.05
Substance extracted by water **	1.76 ± 0.26

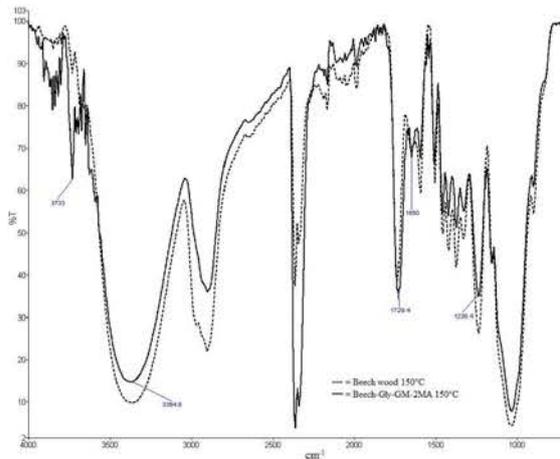
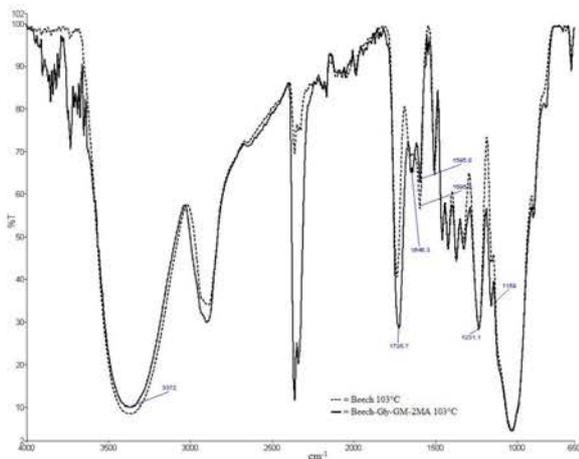
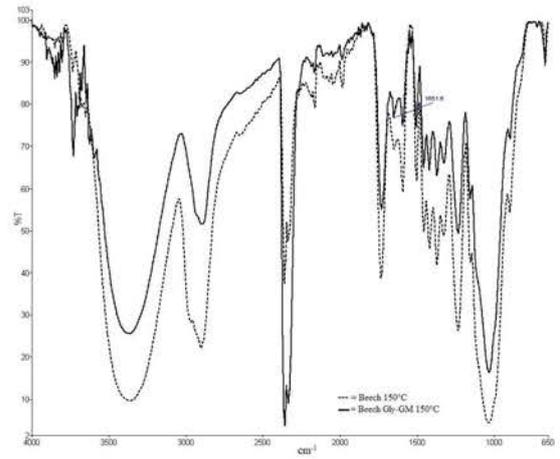
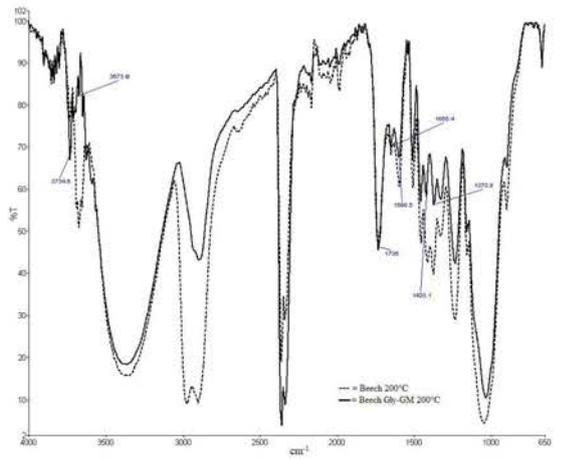
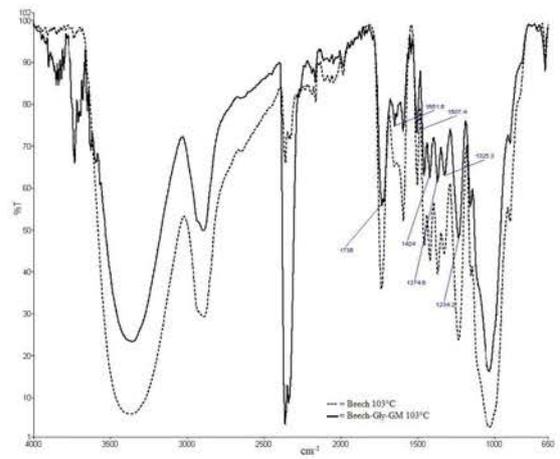
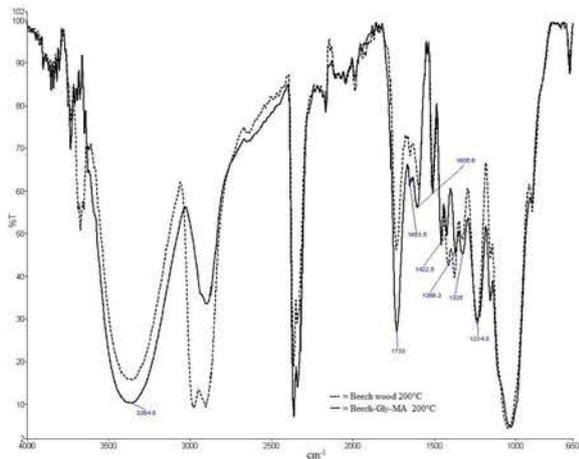
* Each value was the average of six measurements of three replicates of dry wood samples

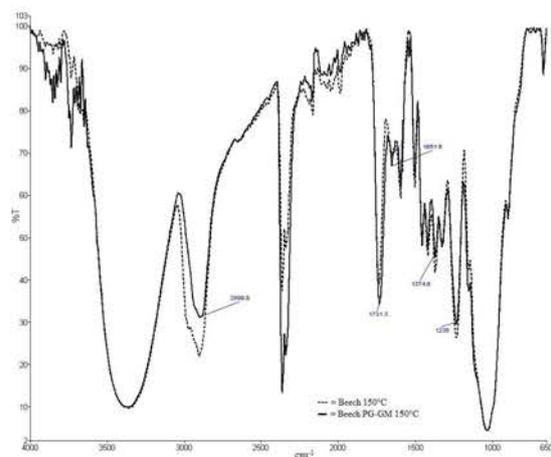
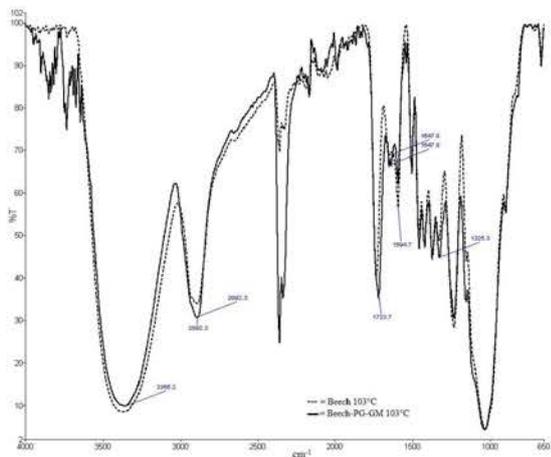
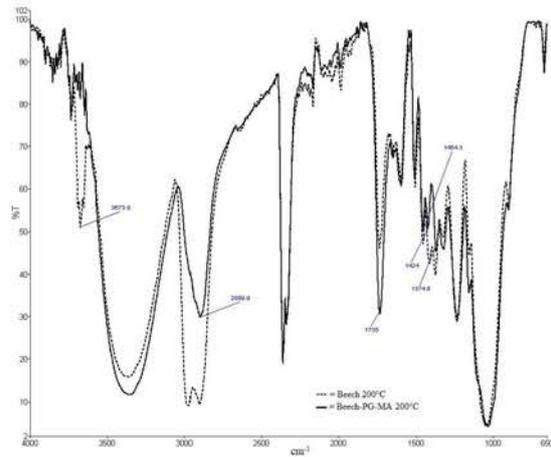
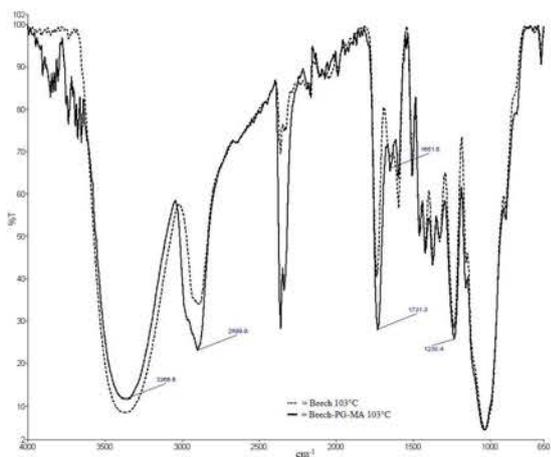
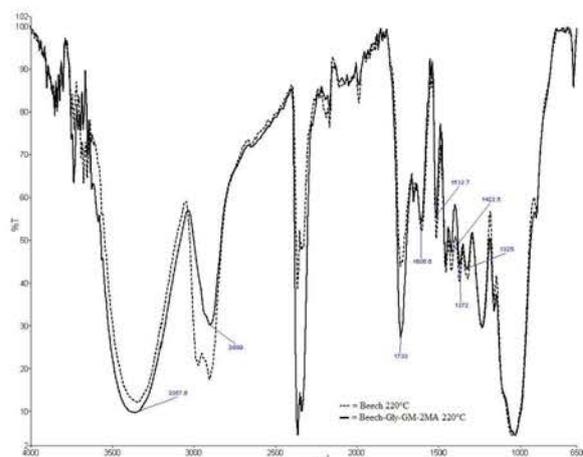
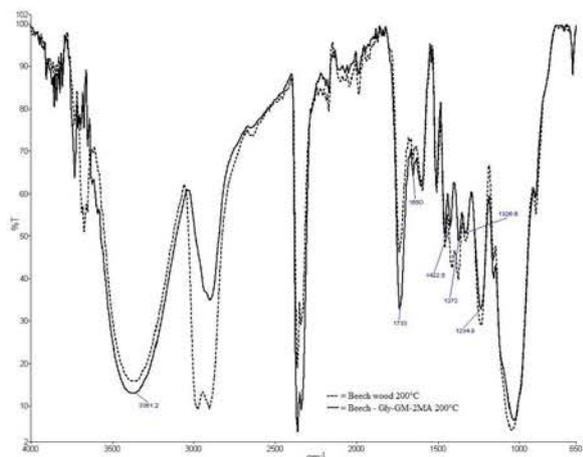
**Each value was the average of three measurements of three replicates of dry wood samples

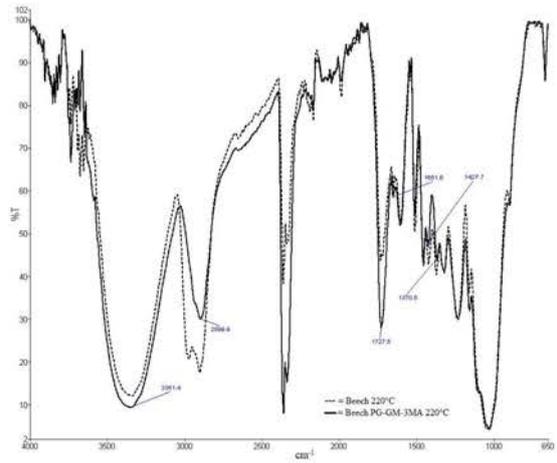
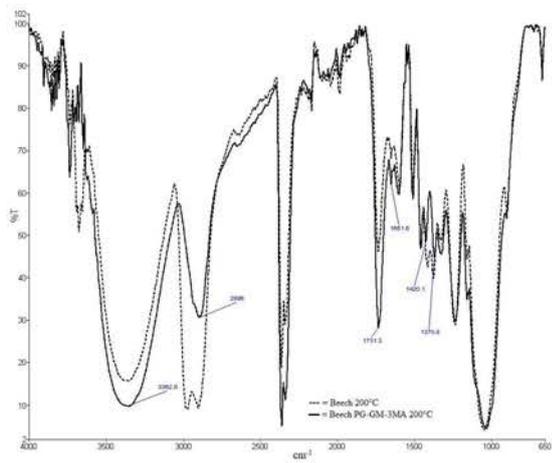
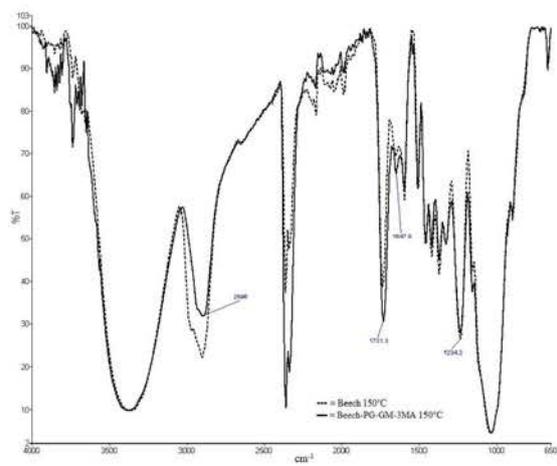
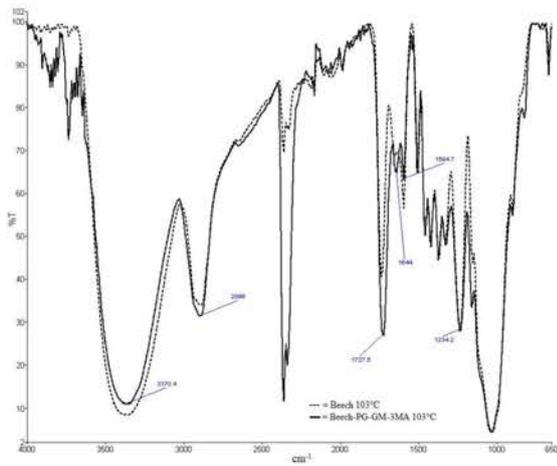
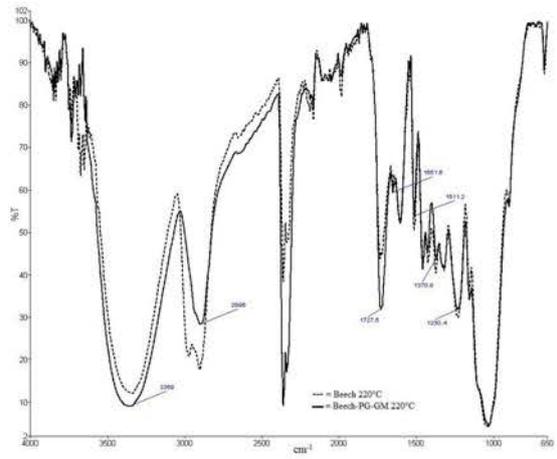
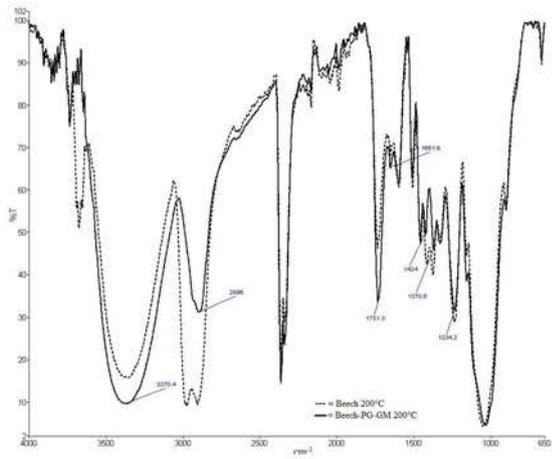
Appendix 20: FTIR analysis











Abstract

In this study, improvement of physical and biological durability properties of European beech (*Fagus sylvatica*) has been performed through different bulking impregnation treatments. The first modification was based on the impregnation of vinylic derivatives of glycerol or polyglycerol as additive followed with different thermal modification conditions in the opened system (OHT) or in the closed system (HPS). The second modification was based on the *in-situ* polyesterification of sorbitol and citric acid at different concentrations and curing temperatures in the opened system. Various physical, chemical, mechanical, and biological durability properties of the modified woods were evaluated, including certain properties during modification. The results have disclosed that certain treatments can improve significantly physical and biological durability properties of wood against decay (white rot, brown rot, and soft rot fungi) and termites attacks in comparison to untreated wood or thermally modified woods.

Keywords: biological durability, citric acid, *Fagus sylvatica*, glycerol, maleic anhydride, mechanical properties, polyesterification, polyglycerol, sorbitol, termite, thermal modification, wood rotting

Résumé

Dans cette étude, l'amélioration des propriétés physiques et de sa durabilité aux agents de dégradation biologique du hêtre européen (*Fagus sylvatica*) a été réalisée au moyen de différents traitements. Les premiers types de traitements sont basés sur l'imprégnation de dérivés vinyliques de glycérol ou de polyglycérol en tant qu'additif suivi d'une étape de modification thermique réalisée dans un réacteur ouvert (OHT) ou fermé (HPS). Le deuxième type de traitement repose sur la poly-estérification *in situ* du sorbitol et de l'acide citrique à différentes concentrations et températures de durcissement en système ouvert. Diverses propriétés de durabilité physique, chimique, mécanique et biologique des bois modifiés ont été évaluées. Les résultats montrent que certains traitements peuvent améliorer de manière significative les propriétés de durabilité physique et biologique du bois contre les agents de pourriture blanche, brune et molle et surtout vis-à-vis de l'attaque des termites comparativement au bois non traité ou modifié thermiquement uniquement.

Mots-clés: acide citrique, anhydride maléique, durabilité, *Fagus sylvatica*, glycérol, modification thermique, polyestérification, polyglycérol, propriétés mécaniques, pourriture, termites, sorbitol