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Marie-Christine Lagel

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# THÈSE

DOCTEUR DE L'UNIVERSITÉ DE LORRAINE

École Doctorale RP2E

Spécialité : Sciences du Bois et des Fibres

Par

Marie-Christine LAGEL

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## DÉVELOPPEMENT DE NOUVEAUX MATÉRIAUX A BASE DE POLYMÈRES NATURELS ET LEURS APPLICATIONS

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Sous la responsabilité des Professeurs Antonio PIZZI & Alain CELZARD

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**Président du jury :**

Dr. Jean-Michel Leban

**Rapporteurs :**

Pr. Bertrand Charrier

Pr. Frédéric Pichelin

**Examineurs :**

Dr. Jean-Michel Leban

Pr. Marie-Pierre Laborie

Pr. Antonio Pizzi

Pr. Alain Celzard

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*« Ils peuvent parce qu'ils pensent qu'ils peuvent. »  
Virgile*

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## BREVET

Pizzi A., **Lagel M.C.**, Redl A.. Colles à bois pour la préparation de panneaux de particules. Brevet PCT/IB2014/065129. 7 Octobre 2013.

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## 1. INTRODUCTION

Depuis plusieurs années avec la raréfaction des énergies fossiles et l'augmentation du prix du pétrole, différentes équipes de recherche travaillent sur l'utilisation de ressources naturelles en substitution des produits issus de l'industrie pétrochimique. Ainsi, l'utilisation de matières premières biosourcées a été intégrée dans de diverses et nombreuses applications. En effet, le charbon, le pétrole et le gaz sont les trois principales ressources primaires utilisées depuis des décennies. Cette consommation d'énergie mondiale provient à plus de 80 % de ressources fossiles, ressources fossiles qui sont loin d'être inépuisables. Le secteur le plus consommateur d'énergie est celui du bâtiment, juste devant celui des transports. Ainsi, les matériaux d'isolation se doivent d'être de nos jours de plus en plus performants afin de limiter les consommations d'énergie. Ils doivent également nous garantir un certain confort et surtout limiter les pertes d'énergies inutiles.

L'industrie pétrochimique est présente partout dans notre environnement quotidien, bien évidemment, afin de nous fournir de l'énergie et dans le secteur des transports. Mais elle est également présente dans les produits manufacturés que nous utilisons chaque jour. Ainsi, l'économie mondiale repose sur ce qui est communément appelé le « prix du baril ». Ceci que ce soit dans les domaines économiques, sociaux mais également politiques. De même, une volonté politique a permis le développement des énergies renouvelables et des produits biosourcés et plus respectueux de l'environnement. La protection et la préservation de l'environnement sont devenues des enjeux primordiaux pour de nombreux pays et donc pour de nombreux grands groupes internationaux qui développent leurs démarches écoresponsables.

La valorisation de la biomasse est ainsi de plus en plus étudiée. Celle-ci permettant l'utilisation des ressources naturelles qui sont abondantes sur notre planète afin de pouvoir supplanter les produits pétrochimiques. La biomasse peut être utilisée dans divers domaines industriels : l'énergie, la construction et les matériaux, etc... La biomasse représente la part la plus importante de la production d'énergies renouvelables avec plus de 60 %. Son utilisation est une solution compétitive face à l'épuisement des ressources fossiles mais également face aux risques écologiques ou toxiques (comme pour certains matériaux, la réduction ou même l'élimination des émissions de composés organiques volatils). En effet, l'épuisement des ressources fossiles est annoncé d'ici trente à cinquante ans. Ce délai est donné par rapport aux ressources actuellement connues et par rapport aux techniques d'extraction actuellement utilisées. Il ne prend pas en compte les nouveaux gisements qui pourraient être découverts d'ici là et l'évolution des

techniques d'extraction. Mais il faut avoir à l'esprit que ce délai se compte en dizaine d'années et non pas en centaine d'années...

La source d'énergie originelle utilisée par l'homme est le bois. Il constitue de nos jours encore un combustible pour chauffage individuel utilisé en France, mais son utilisation reste minoritaire par rapport au gaz et à l'électricité. Du point de vue de sa composition, le bois est une ressource très riche. En effet, il est constitué de polymères comme la cellulose, les hémicelluloses et la lignine. De plus, il contient également des composés extractibles de nature polyphénolique qui sont très réactifs comme les tanins. Ceux-ci sont majoritairement présents dans l'écorce de l'arbre, ainsi contrairement à leur situation antérieure : les écorces deviennent source de composés chimiques à forte valeur ajoutée.

L'industrie du bois et de ses dérivés s'est ainsi tournée vers la production de panneaux de bois biosourcés et plus respectueux de l'environnement. En effet, les tanins ont été utilisés industriellement dans le développement de colles biosourcées pour matériaux lignocellulosiques, en particulier en Afrique, en Amérique du Sud et au Japon ; ainsi ils sont agrisourcés et biodégradables. En conséquence, l'intégration de ressources naturelles dans des procédés industriels est parfaitement réalisable. Ainsi, l'objectif de diminuer voire même de remplacer totalement les colles synthétiques dérivées de la pétrochimie par des produits d'origine naturelle et renouvelable est atteint. Tout cela bien évidemment en garantissant les performances des panneaux en comparaison avec des panneaux non-biosourcés. En effet, initialement les colles synthétiques ont été optimisées afin de réduire leurs coûts tout en conservant les performances mécaniques. Mais de nos jours ces colles sont optimisées afin de réduire leurs impacts sur l'environnement et sur la santé humaine, ceci donc en intégrant des ressources naturelles et renouvelables. Il y a un autre domaine dans lequel les mutations ont été liées aux mêmes enjeux : celui des bioplastiques. Ils sont depuis de nombreuses années commercialisés et possèdent leur propre part de marché et dans certaines applications ils ont remplacé leurs homologues pétrochimiques.

Ainsi, la recherche dans ce domaine de développement des matériaux plus respectueux de l'environnement voire totalement biosourcés est en pleine expansion. Néanmoins, les applications et utilisations industrielles de ces matériaux verts restent rares en comparaison avec leurs réels potentiels. En effet, très souvent ils ont du mal à se mesurer aux matériaux pétrochimiques dont les coûts restent extrêmement compétitifs.

Les objectifs des travaux de recherche réalisés tout au long de cette thèse s'inscrivent dans cette démarche.



Cette thèse s'organise de la manière suivante :

- Une première partie « Etude bibliographique » présentant les différents adhésifs employés avec les matériaux lignocellulosiques, les protéines de blé utilisées dans les adhésifs, les généralités sur la production de panneaux de particules, les généralités sur les tanins, et sur les mousses solides et enfin sur les abrasifs.

- Une seconde partie « Travaux de recherche » présentant les résultats obtenus au cours de cette thèse, sous forme de publications parues et/ou acceptées dans différents journaux scientifiques.

- Une dernière partie présentant les conclusions générales et les perspectives qui en découlent.

## 2. ETUDE BIBLIOGRAPHIQUE

### 2.1. Les adhésifs

Les adhésifs sont classés selon leur composition chimique, leur type de solvant et encore selon les applications auxquelles ils sont destinés.

Les adhésifs destinés aux produits lignocellulosiques sont généralement assez visqueux et le solvant utilisé est l'eau. Une fois mis en œuvre, ces adhésifs, ne peuvent être retirés que par une action mécanique.

#### 2.1.1. Les adhésifs synthétiques

Ces adhésifs sont utilisés majoritairement en comparaison aux adhésifs naturels. On les utilise généralement dans un contexte industriel de par leur structure qui est le plus souvent en réseaux et en chaînes, ce qui leur confère une durabilité et une résistance importante.

- Résines thermoplastiques des colles semi-synthétiques : colles cellulosiques, colles au caoutchouc chloré, colles de contact.

- Résines thermodurcissables.

##### ➤ *Phénol – formaldéhyde*

Ces résines totalement synthétiques ont été les premières à être commercialisées à partir du début du XX<sup>ème</sup> siècle. Elles sont le fruit d'une polycondensation entre le formaldéhyde et le phénol. Cette polycondensation peut être réalisée soit en condition acide (résine novolaque), soit basique (résine résol). Le formaldéhyde pouvant réagir avec les positions ortho ou para du phénol, de très nombreux isomères peuvent être formés (Pizzi 2003a). Ces résines possèdent de très bonnes résistances à l'humidité et au feu. Un point que l'on pourrait qualifier de négatif est leur couleur sombre lorsqu'elles sont mises en œuvre.

##### ➤ *Urée – formaldéhyde*

Alors que l'urée fut découverte par Wöhler en 1824, la première résine urée-formaldéhyde (UF) n'a été fabriquée qu'en 1920 aux Etats-Unis. Le premier choc pétrolier qui induit une pénurie des colles d'origine végétale et animale, entraîna un important développement de ces colles aminoplastes. Ce sont d'ailleurs toujours les colles les plus répandues sur le marché mondial dans l'industrie du bois. Leur utilisation confère aux panneaux de bonnes propriétés mécaniques et thermiques (Pizzi 2003b). De plus, elles présentent une bonne résistance au feu et elles sont incolores lorsqu'elles sont mises en œuvre (souci esthétique). Mais leur faible tenue en milieu

humide ainsi que le dégagement de formaldéhyde limitent leur emploi. Des résines urée-formaldéhyde-glyoxal et urée-glyoxal ont également été développées afin de réduire les émissions en composés organiques volatils des matériaux finis (Deng et al. 2013 ; Deng et al. 2014a ; 2014b ; 2014c).

➤ *Mélatamine – urée – formaldéhyde*

Les résines mélamine-urée-formaldéhyde (MUF) sont parmi celles les plus utilisées pour des panneaux lignocellulosiques en utilisation en milieu extérieur. En effet, le coût élevé de la mélamine a induit une optimisation des ratios mélamine/urée/formaldéhyde, les résistances au feu et à l'humidité sont donc meilleures que celles des résines UF (Pizzi 2003c) et de même les MUF sont incolores une fois durcies.

➤ *Isocyanates*

L'emploi des colles isocyanates dans l'industrie du bois est assez récent. Même si, le 4,4'-diisocyanate de diphenylméthylène (MDI) est l'un des éléments de base pour la production des mousses polyuréthanes. Mais début des années 1970, Frazier (2003) a montré qu'il était possible de les utiliser pour la production de panneaux de particules. De nos jours, les colles isocyanates sont principalement utilisées pour la production de panneau à copeaux orientés (Oriented Strand Board : OSB). Ces résines sont très résistantes mécaniquement et permettent des assemblages mixtes. De plus, elles sont très résistantes vis-à-vis de l'humidité et donc sont largement utilisées en extérieur. Elles sont incolores une fois durcies et ne dégagent pas de formaldéhyde. Néanmoins, lors du pressage, les groupements  $-N=C=O$  libres sont dangereux pour la santé.

Dans l'industrie des panneaux de bois la plupart des colles synthétiques contiennent du formaldéhyde. Cependant, le classement du formaldéhyde en tant qu'agent cancérigène, mutagène ou toxique pour la reproduction (CMR) évolue. Jusqu'à maintenant il était classé comme cancérigène de catégorie 2 : « substances suspectées d'être cancérigènes pour l'être humain », il est désormais classé dans la catégorie 1B : « substances dont le potentiel cancérigène pour l'être humain est supposé par des données animales ». Ce changement a eu lieu le 1er avril 2015. Ces panneaux de bois ont tendance à libérer du formaldéhyde. Les acteurs de la recherche d'aujourd'hui se doivent de développer de nouveaux adhésifs plus respectueux de l'environnement et de la santé humaine.

### 2.1.2. Les adhésifs organiques

- *D'origine minérale*, comme les silicates : généralement silicate de soude. Ces adhésifs sont utilisés dans l'industrie du carton.
- *D'origine animale* : gélatines, albumines et globulines du sang, caséine, collagène,... L'albumine est utilisée dans l'industrie du contreplaqué. Le collagène (présent dans les colles de poisson), la caséine, les protéines du lait, sont employés dans le collage du bois et dans les peintures.
- *D'origine végétale* : tanins, lignine, fécules, amidon, cellulose, gommages naturelles, protéines de blé, protéines de soja,... L'amidon et la cellulose sont généralement utilisés dans le collage des papiers, des textiles, des cartons et des revêtements muraux. Les gommages humidifiées permettent de faire adhérer deux produits (expl : timbre et enveloppe).

L'utilisation industrielle des adhésifs organiques dérivés des produits de l'agriculture a débuté dès les années 1920. Mais après la première guerre mondiale et le premier choc pétrolier elles ont été délaissées au profit des adhésifs dérivant des produits pétrochimiques (Sun 2005). De nos jours, la plupart des adhésifs organiques industriels sont des bioplastiques fabriqués à partir de protéines, d'huiles, de sucres,...

## 2.2. Les protéines de blé

### 2.2.1. La biologie des protéines de blé

La protéine (ou protide) est une macromolécule composée d'une chaîne d'acides aminés liés entre eux par des liaisons peptidiques (Figure 1). Cette chaîne est généralement appelée protéine dès qu'elle contient plus de cinquante acides aminés (El Atyqy 2013).

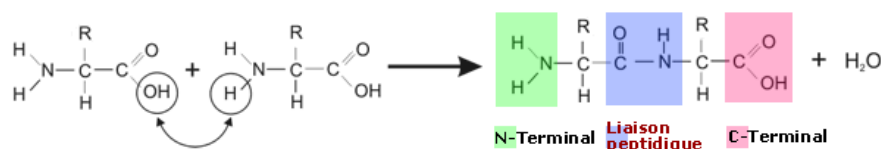


Figure 1 : Liaison peptidique entre deux acides aminés (El Atyqy 2013)

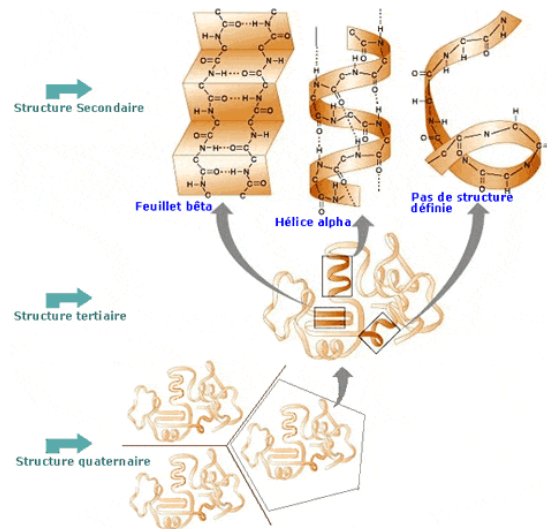
### 2.2.1.1. *La classification des protéines*

Les protéines sont classées selon plusieurs caractéristiques : leur composition chimique, leur rôle biologique et leur solubilité.

- Concernant leur composition chimique, il y a deux classes :
  - Les holoprotéines (ou protéines simples) qui contiennent exclusivement des acides aminés. Les protéines de blé et le gluten sont classés dans ce groupe.
  - Les hétéroprotéines qui contiennent en plus des acides aminés, une partie non protéique qui joue un rôle important dans la fonction de la protéine.
  
- Concernant leur rôle biologique, on distingue également deux classes :
  - Les protéines fibreuses qui se trouvent dans les tissus (muscles, os, peau...), elles ont un rôle structurel.
  - Les protéines globulaires, comme le collagène et la kératine, jouent un rôle entre autre dans le métabolisme. Par exemple, les hormones et les enzymes font partie de ce groupe.
  
- Concernant leur solubilité, certaines protéines sont solubles et d'autres insolubles. Les protéines solubles sont divisées en deux groupes : les protéines solubles dans l'eau pure (comme l'albumine) et les protéines qui ne se dissolvent qu'en présence de sels neutres ou dans un milieu légèrement acide ou faiblement alcalin (comme les globulines). Quant aux protéines insolubles, elles le sont dans tout milieu aqueux.

### 2.2.1.2. *La structure des protéines*

Chaque protéine est formée d'une séquence linéaire de plusieurs acides aminés, qui représente la structure primaire de la protéine. La protéine possède également une structure secondaire (hélice ou feuillet), ceci étant dû aux liaisons hydrogènes, à l'attraction entre les charges positives et négatives et entre les radicaux hydrophobes ou hydrophiles. Les protéines sont encore plus compactes lorsqu'elles possèdent une structure tertiaire. Lorsqu'une protéine est constituée de plus d'une chaîne polypeptidique, elle a une structure quaternaire (Figure 2) (El Atyqy 2013).



**Figure 2 : Structure des protéines (El Atyqy 2013)**

La polymérisation covalente des acides aminés par une liaison peptidique entraîne la formation des chaînes peptidiques. La différence entre protéine et peptide est définie par le nombre, la nature et l'ordre des acides aminés. Soit le nombre d'acides aminés est inférieur à cinquante, dans ce cas ce sont des peptides (et des polypeptides lorsque leur nombre est supérieur à dix). Soit le nombre d'acides aminés est supérieur à cinquante et là ce sont des protéines. Les acides aminés sont donc les éléments constitutifs des protéines.

### 2.2.1.3. *Le gluten*

Le gluten est un complexe protéique extractible et insoluble dans l'eau que l'on trouve en majorité dans le blé mais également dans l'orge, l'avoine et le seigle. Le gluten peut être séparé des autres constituants végétaux par lavage humide prolongé.

Le taux de protéines et donc de gluten change d'une variété à l'autre et dépend également des conditions agronomiques et climatiques.

Concernant la composition du gluten, il contient de 70 à 80 % de protéines (comme les gliadines et les gluténines qui sont insolubles dans l'eau). Les propriétés adhésives et l'élasticité du gluten sont dues à la gliadine qui est poisseuse et soluble dans l'alcool. On trouve également un peu de leucosine et de globuline, solubles en solution saline.

Les propriétés d'extensibilité, d'élasticité et de ténacité des pâtes à pain sont dues au gluten. Cependant, certaines personnes sont allergiques à ces protéines (Novak 2004).

### ***2.2.2. La composition chimique des protéines de blé***

Les vingt-cinq acides aminés qui constituent les protéines sont appelés alpha acides aminés. Ces acides aminés contiennent un groupe amino  $-NH_2$  et un groupe carboxyle  $-COOH$ . Cela signifie que le groupe  $-NH_2$  est fixé à l'atome de carbone adjacent au groupe  $-COOH$  (Vidal et al. 2010).

Concernant le gluten, les groupes amides des liaisons peptidiques au niveau des protéines sont capables de réagir avec des aldéhydes de la même manière que les autres amides, comme l'urée. Ces réactivités peuvent être similaires à celles avec la mélamine et avec les phénols (Lei et al. 2010).

Les protéines contiennent des chaînes latérales où se trouvent des groupes réactifs d'acides aminés qui ont également le potentiel de réagir avec des adhésifs phénoliques ou autres adhésifs (Lei 2009).

## **2.3. Les protéines de blé hydrolysées dans les résines**

### ***2.3.1. L'hydrolyse des protéines de blé***

L'hydrolyse des protéines consiste en la rupture des liaisons peptidiques qui sont assez stables, cette hydrolyse n'est donc pas spontanée. Elle peut être chimique ou biochimique.

➤ L'hydrolyse chimique, elle est réalisée avec des acides ou des bases. Après une hydrolyse complète des protéines, sont obtenus les acides aminés qui les constituent. Mais il n'est pas rare que cette hydrolyse provoque une déstructuration d'une grande partie des acides aminés (encore appelée désamination). Celle-ci concerne généralement le tryptophane. De plus, certains réactifs hydrolysent la liaison peptidique avec une spécificité sur un des acides aminés de cette liaison. Généralement, pour réaliser cette hydrolyse, on fait bouillir les protéines pendant plusieurs heures, au minimum 24 heures, avec de l'acide sulfurique à 25 % ou avec de l'acide chlorhydrique ou encore avec de l'acide fluorhydrique.

Les hydrolyses acides sont moins destructrices que les hydrolyses basiques, mais elles provoquent une décomposition d'une partie des acides aminés avec production d'ammoniac. Des réactions secondaires entre les acides aminés et les glucides provoquent la formation d'autres produits mal définis.

Les paramètres jouant sur l'avancement de l'hydrolyse sont la température et la quantité d'acide ou de base (Boury 1960).

➤ L'hydrolyse biochimique, les catalyseurs provenant de la matière vivante sont plus généralement appelés enzymes. Ceux qui accélèrent les réactions hydrolytiques sont des hydrolases. Pour l'hydrolyse des protéines, les enzymes protéolytiques sont utilisées elles provoquent la rupture de la liaison peptidique. Il y a deux sous-groupes qui diffèrent selon leur spécificité : les exopeptidases (qui n'hydrolysent que la première ou la dernière liaison peptidique) et les endopeptidases (qui hydrolysent les liaisons peptidiques internes entre deux aminoacides se suivant) (El Atyqy 2013).

En résumé, une protéine sous l'action des protéases va se comporter selon le schéma suivant : Protéine → Polypeptide → Peptide → Acides aminés.

Pour chaque molécule, il est possible de définir un nombre total de liaisons peptidiques ( $h_{\text{total}}$ ) qui est équivalent au nombre total des acides aminés moins une unité. Ce nombre peut être défini après une hydrolyse acide totale et une détermination des acides aminés après séparation par chromatographie en phase inverse.

Le nombre de liaisons peptidiques hydrolysées ( $h$ ) peut être défini par dosage volumétrique, ou encore en suivant le taux d'azote soluble en fonction du temps (Bouquelet 2008).

Le taux d'hydrolyse s'exprime de cette manière :  $\Delta H (\%) = \frac{h}{h_{\text{total}}} \times 100$ .

Dans un respect de l'environnement de plus en plus important, l'université de l'Etat d'Iowa, a développé durant les années 2000 une approche enzymatique de l'hydrolyse des protéines afin de fabriquer des hydrolysats de soja qui pouvaient ensuite être utilisés avec des résines phénol-formaldéhyde pour des applications dans le collage du bois. Cette nouvelle approche est plus respectueuse de l'environnement et moins coûteuse en comparaison à l'utilisation d'un milieu basique ou acide, de hautes températures et pressions. Et l'ajout de soja a démontré une meilleure adhérence sur une grande variété de substrats.

### ***2.3.2. Les voies de valorisation des protéines extraites de la biomasse : synthèse de résines et leurs propriétés***

Jusque dans les années 1960, les adhésifs à base de ressources animales et végétales ont dominé le marché. Ces ressources étaient le sang animal, la caséine et les protéines de soja. Mais lors du développement de la pétrochimie dans les années 1970, ces adhésifs à base naturelle ont été de moins en moins utilisés. En effet, des adhésifs avec des propriétés spécifiques, une qualité constante et de moindres coûts étaient maintenant réalisables... Néanmoins avec la



diminution des ressources fossiles, la recherche se tourne vers l'utilisation de la biomasse afin de remplacer les produits provenant de la pétrochimie. Ainsi, les groupes de recherche se sont intéressés aux résines phénoliques. En effet, elles sont utilisées principalement pour produire des panneaux de bois pouvant être utilisés en milieu extérieur. Les résines phénoliques sont les colles à bois les plus utilisées, juste après les résines aminoplastes.

Le groupe de recherche Chimar Hellas a étudié l'utilisation de divers matériaux naturels (tanins, lignine, cellulose, protéines de soja, amidon...) dans la formulation d'adhésifs. Tous ces matériaux ont été utilisés seuls ou en combinaison avec d'autres produits pétrochimiques dans les adhésifs pour les panneaux de bois. Le but était de réduire la consommation de ressources fossiles et de développer l'utilisation de la biomasse en tant que matière première. Mais également d'obtenir des résines avec les mêmes qualités ou même avec des qualités améliorées par rapport aux résines plus classiques. Les recherches parrainées par l'United Soybean Board (Chesterfield, Etats-Unis) ont pour but l'optimisation des résines synthétiques-protéines de soja dans les produits adhésifs phénoliques. Ainsi, les résines UF pourraient être remplacées à terme par des résines à base de soja afin d'éliminer complètement les émissions de formaldéhyde provenant des colles dans les applications intérieures. Cependant, l'utilisation d'adhésif à base de protéines n'est pas nouvelle. Le premier brevet datant de 1923, démontre que le soja pouvait être utilisé comme adhésif (Otis 1923).

Cette résine de soja, de couleur plus claire qu'une simple résine PF peut être utilisée en tant que résine liquide servant à la préparation de panneaux de fibres et de panneaux de particules, réalisés à base de sous-produits agricoles (Lei 2009). Mais il est important de trouver des matières premières alternatives aux produits pétrochimiques qui ne rentrent pas en concurrence avec les ressources nécessaires à la nutrition des hommes et des animaux. En outre, le coût des résines phénol-formaldéhyde (PF) est élevé et est dépendant des fluctuations du prix du pétrole. De plus, les composants des résines phénoliques sont considérés comme des polluants de l'air intérieur et comme étant des composés nocifs pour la santé humaine. L'enjeu des recherches est donc crucial pour pouvoir remplacer ces produits pétroliers par de la biomasse (Papadopoulou et al. 2008).

Lors d'une réaction de polycondensation, le formaldéhyde relie les groupes aminés de la protéine avec le phénol, ce qui forme ainsi un polymère. Mais généralement, les protéines sont ajoutées en faibles proportions dans les résines PF car les amines ne réagissent pas très bien dans des conditions basiques mais également car la réaction du formaldéhyde avec des acides aminés donne des structures cycliques, ce qui empêche les acides aminés d'être incorporés dans le squelette du polymère.

Concernant les protéines de soja déjà utilisées dans la formulation de résines PF, on trouve de la farine de soja dénaturée par une solution aqueuse caustique ou des isolats de protéines de soja hydrolysés. La solution caustique de protéines dénaturées possède une viscosité élevée à cause du poids moléculaire important des fractions protéiques. Ces solutions sont donc à utiliser à des extraits secs relativement faibles, de telle sorte que l'adhésif peut être par la suite facilement appliqué sur le substrat. Cette viscosité peut être abaissée par l'hydrolyse des fractions protéiques, mais cela conduit aussi à des forces de liaisons moins importantes, ce qui peut engendrer des conséquences sur les propriétés des résines. Au vu de la petitesse des fragments peptidiques, les protéines hydrolysées doivent normalement être mises à réagir avec des quantités importantes de composés phénoliques et de formaldéhyde, dans le but de former un solide réseau. D'après Charles R. Frihart et James M. Wescott (2004), il faut veiller à stabiliser les solutions de protéines dénaturées, car si elles ne le sont pas, la résine PF préparée sera très instable et sa viscosité augmentera très rapidement. L'ajout de formaldéhyde stabilise ces solutions de protéines dénaturées et leur confère une bonne stabilité au stockage. En effet, le formaldéhyde stabilise les protéines contre une hydrolyse plus importante et les active également pour la réaction avec les résines PF. Le formaldéhyde possède quatre fonctions. Tout d'abord, il modifie les groupes fonctionnels des protéines afin qu'il n'y ait pas d'associations intermoléculaires. Ensuite, il stabilise la farine de soja vis-à-vis de la dégradation biologique. Il protège également les protéines d'une réaction supplémentaire avec le phénol. Et enfin, il permet des mélanges plus stables avec les résines PF.

La teneur en formaldéhyde est fixée par la quantité qui réagit facilement avec les protéines : l'excès de formaldéhyde est donc évité, en effet, les produits doivent avoir des teneurs en formaldéhyde libre les plus faibles possibles. Tout d'abord, les protéines sont attaquées par la soude et puis le formaldéhyde réagit avec ces protéines (Figure 3) (Frihart et Wescott 2004). Ensuite, le phénol réagit avec les protéines.

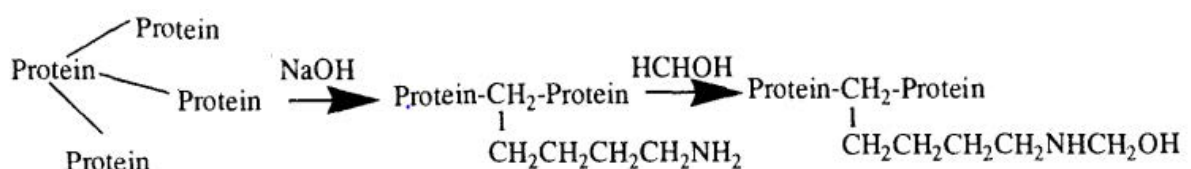


Figure 3 : Schéma de la réaction du formaldéhyde avec la protéine (Frihart et Wescott 2004)

Jusqu'à présent, les résines à base de protéines naturelles ne possèdent pas une résistance significative à l'humidité. Ce point est à améliorer pour que les résines PF à base de protéines soient utilisées dans de nouveaux domaines, comme le collage du bois. Les temps de pressage des adhésifs PF contenant un faible taux de protéines sont comparables à ceux mis en œuvre pour des

résines PF commerciales. Mais lors de l'utilisation de pourcentages de protéines soja plus élevés, il faut veiller à utiliser des temps de pressage plus longs (Frihart et Wescott 2004).

Ces adhésifs sont capables de proposer une qualité d'adhérence très intéressante, tandis que les émissions de formaldéhyde provenant des panneaux à base de bois produits avec ces adhésifs sont similaires à ceux des résines commerciales ou même inférieures (Papadopoulou et al. 2008).

Une résine PF-protéines de soja comprenant 70 % de farine de soja et 30 % de résine PF a été développée et a donné des performances honorables (Kuo et al. 2001). Une résine PF similaire à base de soja a également été mise au point et a été utilisée pour la production de panneaux à copeaux orientés (OSB) (Hse et al. 2001). La farine de soja est tout d'abord traitée et additionnée au phénol (ratios testés : phénol/farine de soja : 4/4 ; 3/4 ; 2/4 ; 1/4) et avec l'hydroxyde de sodium. Le mélange est chauffé sous agitation, puis le formaldéhyde est ajouté dans le système. Les performances de l'OSB produit ainsi en laboratoire sont identiques à celles données pour un OSB produit avec une résine PF pure.

Les contreplaqués de résineux représentaient une grande part du marché des panneaux à base de bois, mais depuis l'introduction de l'OSB ils ont fortement décliné. La résine PF est l'adhésif le plus utilisé pour les contreplaqués ou pour les panneaux MDF, ou encore les panneaux pour utilisation en extérieur.

Les protéines de soja hydrolysées ajoutées en faible proportion aux résines PF induit une réduction des coûts sans dégradation des performances de celles-ci (United Soybean Board 2010). De plus, selon la fiche d'information d'United Soybean Board concernant l'environnement et les adhésifs pour le bois à base de protéines de soja, la protéine de soja n'est pas volatile et n'est pas un polluant atmosphérique dangereux. Concernant les produits de dégradation de la protéine de soja, ils ne sont pas différents des produits qui résultent de la dégradation de la farine de soja (Brown 2005).

Des recherches ont également été menées sur les résines mélamine-urée-formaldéhyde (MUF). L'addition de soja leur confère une meilleure résistance à l'eau, de moindres émissions de formaldéhyde et un coût inférieur à celui d'une résine MUF classique (Lei 2009).

Des nouveaux marchés s'ouvrent pour ces adhésifs innovants, comme des applications en construction et dans les marchés d'étanchéité. Des adhésifs uréthanes contenant du soja ont été utilisés pour remplacer les polyols provenant de la pétrochimie par la société américaine Bondaflex.

Un autre nouveau marché pour les adhésifs résistants à la chaleur à base de soja pourrait être leur utilisation dans les matériaux composites à base naturelle. En effet, à des températures élevées les performances des résines à base de protéines sont intéressantes. Ainsi, leurs utilisations dans des produits structuraux comme dans les poutres en I ou dans les poutres aboutées sont donc envisageables. Ces adhésifs ont démontré une résistance thermique supérieure, prolongeant la résistance de la structure ossature bois lors d'un incendie (United Soybean Board 2010).

Les adhésifs à base de protéines, combinés avec des résines phénol-résorcinol-formaldéhyde sont même utilisés dans la fabrication de produits de bois vert aboutés. De plus, les adhésifs de protéines de soja nécessitent moins de temps et utilisent moins d'énergie pour durcir (Brown 2005).

Certaines recherches ont également été menées en utilisant des protéines de blé, qui en Europe sont plus abondantes que les protéines de soja. Outre l'utilisation alimentaire (boulangerie et pâtisserie) du gluten, de nombreuses études ont été menées sur des adhésifs bois à base de protéines de blé (Lei et al. 2010). Le gluten est un allergène humain assez répandu, il est donc parfois retiré des produits de consommation et peut ainsi constituer une ressource disponible et abondante pour les industries des adhésifs. De plus, les boues papetières, qui représentent une quantité importante de résidus de biomasse, sont des matières premières idéales pour les protéines utilisées dans les applications des composites à base de bois (Pervaiz et Sain 2011).

Ainsi, des recherches de développement sont en cours afin d'utiliser les protéines dans la mise en œuvre de panneaux renouvelables à base de fibres naturelles. Ces composites pourraient être commercialisés à des prix compétitifs, tout en étant une solution sans formaldéhyde pour des panneaux de particules et de fibres de moyenne densité (United Soybean Board 2010).

## **2.4. Les panneaux de particules**

### ***2.4.1. Présentation des panneaux de particules***

A l'aide de broyeurs, les particules sont fabriquées avec des bois ronds ou alors avec des produits connexes provenant d'autres industries du bois. Aucune direction n'est privilégiée lors de la mise en œuvre des panneaux. Les trois caractéristiques qui les définissent sont : une isotropie dans le plan, des caractéristiques mécaniques inférieures à celles du bois massif et un gonflement en épaisseur sous l'action de l'eau ou de l'humidité. Ces panneaux de particules sont très utilisés

dans le monde (plus de 50 millions de mètres cubes produits chaque année, dont 35 millions en France en 2010).

Les panneaux de particules sont composés d'une ou plusieurs couches de particules de bois. Généralement, il y a trois couches : les couches extérieures sont composées de particules fines et la couche du milieu est composée quant à elle de particules plus grosses. Les taux d'encollage y sont également différents (Figure 4). Le taux d'encollage correspond à la quantité de résine utilisée par rapport à la quantité de particules. C'est donc le pourcentage de résine solide sur la masse particules anhydres.



**Figure 4 : Profil d'un panneau de particules**

La quantité de résine utilisée dépend du type de résine et des caractéristiques des particules (taille, quantité, humidité...). Un excès de résine n'est pas intéressant au point de vue économique mais également car lors du pressage à chaud des problèmes de pression de vapeur trop élevées seront induits.

## ***2.4.2. Caractérisation des panneaux de particules***

### *2.4.2.1. Classification des panneaux de particules*

Les panneaux de particules sont définis par la norme NF EN 309 :

- Type P1 : Exigences pour panneaux pour usage général utilisés en milieu sec
- Type P2 : Exigences pour panneaux pour agencements intérieurs (y compris les meubles) utilisés en milieu sec
- Type P3 : Exigences pour panneaux non travaillants utilisés en milieu humide
- Type P4 : Exigences pour panneaux travaillants utilisés en milieu sec
- Type P5 : Exigences pour panneaux travaillants utilisés en milieu humide
- Type P6 : Exigences pour panneaux travaillants sous contrainte élevée utilisés en milieu sec

- Type P7 : Exigences pour panneaux travaillants sous contrainte élevée utilisés en milieu humide

En France, deux marques de qualité existent : le panneau de particules CTB-S pour usage en milieu sec en construction répondant au moins au type P4, et le panneau de particules CTB-H répondant au moins au type P5.

Leurs exigences sont données dans la norme NF EN 312.

On peut remarquer que les performances mécaniques des panneaux de particules sont inférieures à celles des contreplaqués. Mais les variations dimensionnelles qui ne sont que d'environ 1 à 2 mm par mètre linéaire font des panneaux de particules un produit dérivé du bois possédant des variations dimensionnelles très faibles. En effet, la moyenne pour le MDF M1 est de 5 mm par mètre linéaire. Cependant, il faut tout de même en tenir compte lors de la mise en œuvre de ces panneaux.

#### 2.4.2.2. *Les exigences de cohésion interne*

La cohésion interne d'un panneau est sa résistance lorsqu'on applique une traction perpendiculaire à son plan. Cette valeur obtenue selon la norme (NF EN 319), généralement exprimée en N/mm<sup>2</sup>, définit si le panneau satisfait aux exigences requises pour une application en tant que panneau travaillant en milieu sec ou humide.

La résistance à la traction perpendiculaire au plan de panneau de chaque éprouvette  $f_t$  est calculée selon la formule suivante :

$$f_t = \frac{F_{max}}{a \times b}$$

où :

$F_{max}$  est la contrainte de rupture, en newton.

a, b sont la longueur et la largeur de l'éprouvette, en millimètre.

Pour un panneau travaillant en milieu sec (type P4), la valeur de cohésion interne doit être comprise entre 0,20 et 0,45 N/mm<sup>2</sup> et entre 0,25 et 0,50 N/mm<sup>2</sup> en milieu humide (type P5).

#### 2.4.2.3. *Les exigences en gonflement*

Le gonflement des panneaux de particules peut être mesuré, après 24 h d'immersion dans l'eau, mais encore après 2 h d'immersion dans de l'eau bouillante. Ce dernier essai est plus

particulièrement destiné à tester les panneaux qui sont utilisés en milieu humide. Selon la norme NF EN 317, le gonflement après 24 h d'immersion doit être compris entre 13 et 19 % pour les panneaux travaillant en milieu sec (type P4) et de 9 à 13 % en milieu humide (type P5).

#### 2.4.2.4. Les exigences des principales certifications concernant les émissions de formaldéhyde

Le formaldéhyde est une substance irritante pour le nez et les voies respiratoires émise notamment par certains matériaux de construction, le mobilier, certaines colles, et donc par les panneaux de particules ayant été fabriqués avec un adhésif contenant du formaldéhyde. Dès 1980, les allemands fixent une valeur guide à 120 µg de formaldéhyde par mètre cube d'air, ce qui correspond à des panneaux de classe E1. Les panneaux de classes E2 et E3 doivent être recouverts (avec de la mélamine par exemple) pour satisfaire à cette valeur guide. Depuis 2002, une norme française (NF EN 312) classe les panneaux selon deux classes : E1 et E2. La classe E1 impose une valeur inférieure ou égale à 8 mg de formaldéhyde pour 100 g de panneau sec, cette valeur a récemment été revue à la baisse à 6,5 mg. De nos jours, la grande majorité des panneaux proposés sont de classe E1.

##### 2.4.2.4.1. La marque NF Environnement

C'est une certification française écologique qui est officielle, mais elle concerne uniquement les colles destinées à la papeterie, aux revêtements de sols, aux revêtements plastiques en lés. Concernant les composés organiques volatils (COV), l'exigence est que les pertes totales en COV doivent être inférieures ou égales à 2 % de la masse de COV mise en œuvre (NF Environnement 2002 ; Prioriterre 2010).

##### 2.4.2.4.2. L'étiquetage français sur les émissions de COV

Depuis le décret du 13 mai 2011, l'étiquetage des produits de construction ou de revêtement de mur ou de sol et des peintures et vernis utilisés à l'intérieur de bâtiments est obligatoire (Figure 5).

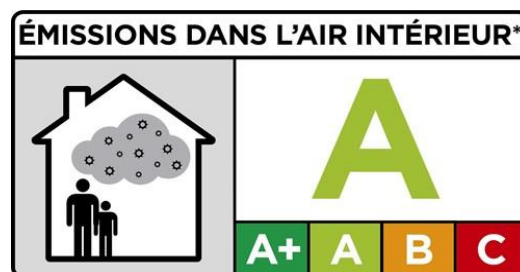


Figure 5 : Etiquetage français

Il y a différentes classes proposées par ce décret (Tableau 1).

	<i>Classes</i>			
	<i>A+</i>	<i>A</i>	<i>B</i>	<i>C</i>
<b><i>COV Totaux (<math>\mu\text{g}/\text{m}^3</math>)</i></b>	< 1000	< 1500	< 2000	> 2000
<b><i>Formaldéhyde (<math>\mu\text{g}/\text{m}^3</math>)</i></b>	< 10	< 60	< 120	> 120

**Tableau 1 : Classes du décret du 11 mai 2011**

Cet étiquetage a pour but d'informer les consommateurs sur tous les produits qu'ils peuvent trouver disponibles à la vente (Ministère de l'Ecologie, du Développement Durable et de l'Energie 2012).

#### .2.4.2.4.3. Le label Emicode

Il s'agit d'une certification allemande qui porte sur les émissions des colles mais aussi des revêtements de sols. Cette certification garantit aux consommateurs l'absence de substances cancérigènes et elle évalue le niveau d'émissions de composés organiques volatils comme le formaldéhyde, qui est présent dans les colles utilisées pour les panneaux à base de bois. Il y a trois classes d'émission, celles-ci ont été revues en Mai 2010 (Tableau 2). On remarque que les différentes classes sont essentiellement départagées par les concentrations en COV totales (Emicode 2010 ; Prioriterre 2010).

	<i>Classes</i>		
	<i>EC1 Plus</i>	<i>EC1</i>	<i>EC2</i>
<b><i>COV Totaux après 3 jours (<math>\mu\text{g}/\text{m}^3</math>)</i></b>	< 750	< 1000	< 3000
<b><i>Formaldéhyde après 3 jours (<math>\mu\text{g}/\text{m}^3</math>)</i></b>	< 50	< 50	< 50

**Tableau 2 : Classes du label Emicode**

#### .2.4.2.4.4. CARB phase 2

CARB 2 est la deuxième phase du règlement, qui est entré en vigueur le 1<sup>er</sup> Janvier 2011. Ces normes d'émissions sont établies par le California Air Resources Board. La valeur d'émission limite concernant le formaldéhyde est de 0,09 ppm selon la norme ASTM E1333 (CARB 2011).

Ainsi, les utilisations des matières naturelles dans les adhésifs constituent un réel enjeu pour les prochaines années, d'un point de vue économique mais également écologique. Ceci est encouragé par la réglementation qui se fait de plus en plus stricte vis-à-vis des composés organiques volatils, mais également par la volonté de diminuer l'utilisation des ressources fossiles.



## 2.5. Les tanins

Les tanins sont des composés polyphénoliques qui sont présents naturellement dans les plantes. Chez les arbres, les tanins se trouvent en plus grandes proportions dans l'écorce, mais cela dépend des essences. Après la cellulose, les hémicelluloses et la lignine, les tanins sont le quatrième composant de la biomasse (Hernes et Hedges 2000). Les tanins sont difficilement assimilables par les champignons et les insectes, ceci leur confère un rôle d'armes chimiques défensives pour les arbres vis-à-vis des attaques biologiques extérieures (Robbins et al. 1987).

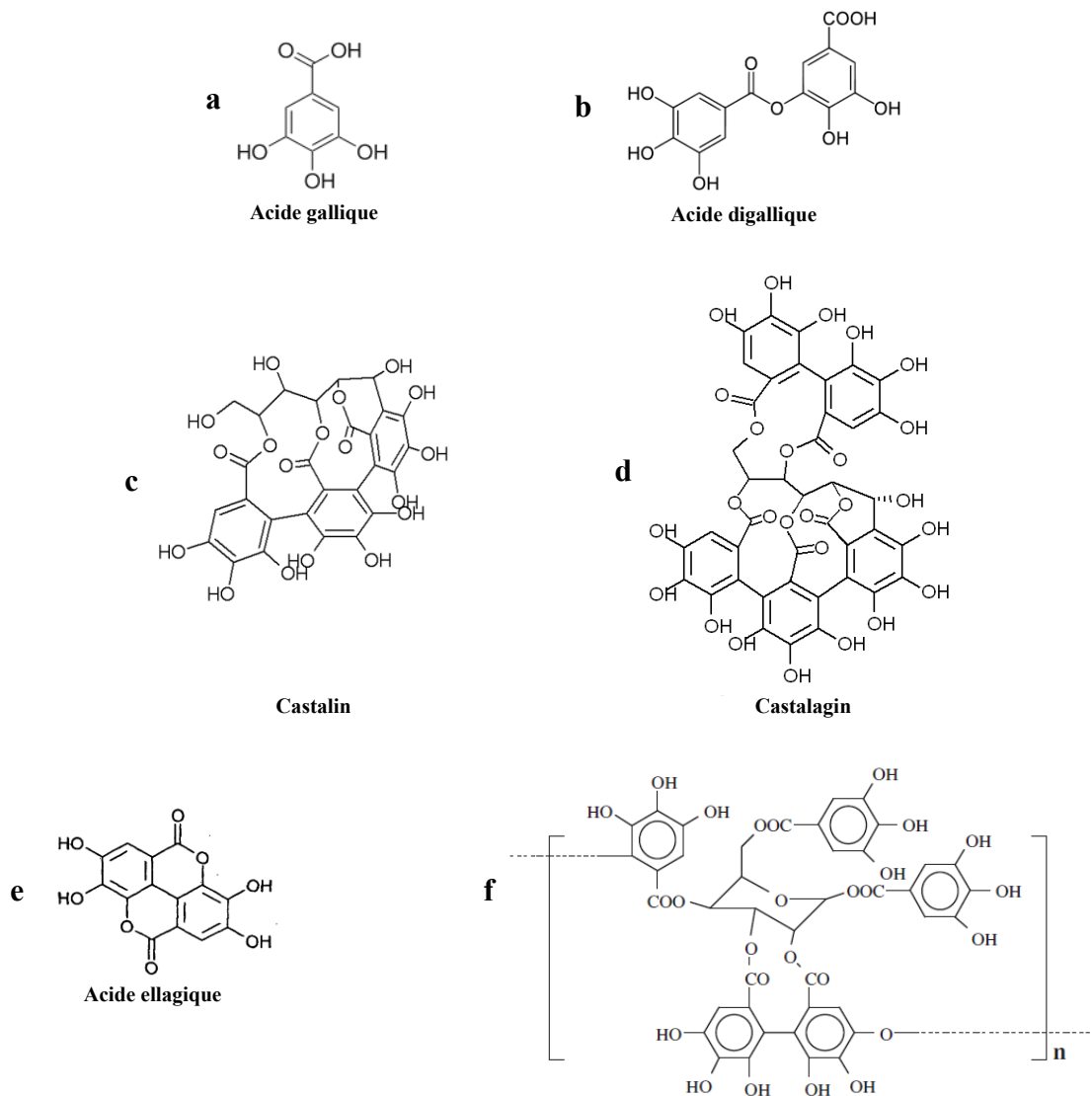
La plupart des tanins commerciaux sont extraits industriellement par une simple extraction à l'eau chaude, de copeaux de bois, d'écorce, de galle ou encore d'autres matières végétales.

### 2.5.1. Classification

Les tanins sont des molécules polyphénoliques que l'on trouve dans la plupart des végétaux. Leur structure chimique étant très importante, c'est celle-ci qui détermine la catégorie dans laquelle les tanins sont classés. Il existe deux classes : les tanins hydrolysables et les tanins condensés. Les tanins sont de manière générale extraits à l'aide de solvants polaires comme l'eau, les alcools ou encore l'acétone.

#### 2.5.1.1. *Tanins hydrolysables*

Les tanins hydrolysables sont constitués en majorité d'oligomères polyphénoliques de pentagalloyl glucose. Il existe deux types de tanins hydrolysables, comme le châtaignier (qui est le plus abondant (Pizzi et al. 2009a)), le tara, les noix de galle du chêne, le chêne, etc... Ce premier type est composé d'un mélange de sucres avec des oligomères de phénols simples comme les acides gallique (Figure 6a), digallique (Figure 6b) ; le castalin (Figure 6c) et le castalagin (Figure 6d) (Radebe et al. 2013 ; Giovando et al. 2013). Le second type est composé d'ellagitanins qui sont des esters de sucre, notamment du glucose, avec des acides gallique et digallique, et également avec des structures plus complexes contenant de l'acide ellagique (Figure 6e & 6f).



**Figure 6 : Principaux composants des tanins hydrolysables**

Le nom de ces tanins hydrolysables provient du fait que leurs liaisons sont facilement hydrolysées par des acides ou des bases (Carretero 2000 ; Pizzi 2003d).

La faible réactivité qu'ils possèdent limite leur utilisation industrielle au tannage du cuir. Les tanins les plus utilisés industriellement pour le tannage du cuir sont ceux de châtaignier et de tara.

Ce n'est que depuis quelques années que des recherches ont permis de les utiliser pour la préparation de copolymères de phénol, de formaldéhyde et de tanins hydrolysables. Ces résines ont été utilisées pour la préparation de colles à bois phénoliques (Spina et al. 2013a ; 2013b). De plus, ils ont été utilisés dans la fabrication de mousses polyuréthanes (Thébault et al. 2014) ou encore de résines époxy (Aouf et al. 2014).

### 2.5.1.2. Tanins condensés

De par leur forte réactivité, les tanins condensés sont largement exploités commercialement. Voici les espèces majoritairement commercialisées : *Acacia* (Mimosa) ; *Schinopsis* (Quebracho) ; *Tsuga* (Hemlock) ; *Rhus* (Sumac) et *Pin Radiata* (Pizzi 2003d).

Les tanins condensés sont des polyflavonoïdes : des polymères de plusieurs dizaines d'unités flavonoïdes (Figure 7) liées par des liaisons C-C ; ainsi ces molécules ne sont pas facilement hydrolysables.

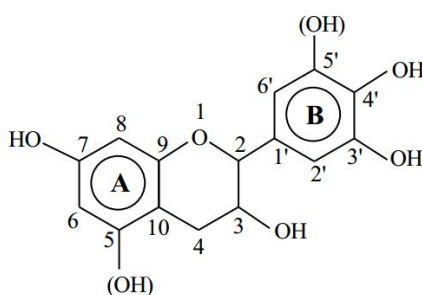
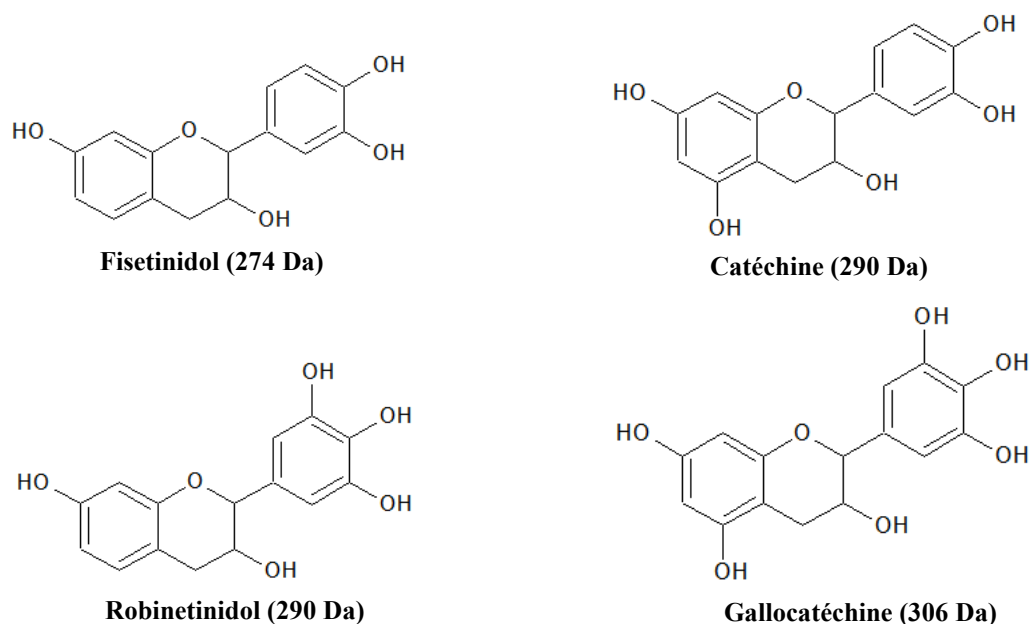


Figure 7 : Représentation d'une unité flavonoïde et de sa numérotation

L'anneau A est appelé anneau résorcinol s'il ne possède qu'un seul groupe -OH et anneau phloroglucinol s'il en possède deux. L'anneau B est appelé anneau catéchol s'il ne possède que deux groupes -OH et anneau pyrogallol s'il possède un groupe -OH supplémentaire en position 5'.

Les tanins sont composés d'un mélange de quatre monoflavonoïdes (Figure 8).



**Figure 8 : Quatre types de monoflavonoïdes**

Une nomenclature des polyflavonoïdes a été définie à partir de ces différents types d'anneaux (Porter 1988) (Tableau 3) :

<i>Type de l'anneau A</i>	<i>Type de l'anneau B</i>	<i>Flavonoïde</i>	<i>Polyflavonoïde</i>
Phloroglucinol	Pyrogallol	Gallocatéchine	Prodelphinidine
Phloroglucinol	Catéchol	Catéchine	Procyanidine
Résorcinol	Pyrogallol	Robinetinidol	Prorobinetinidine
Résorcinol	Catéchol	Fisetinidol	Profisetinidine

**Tableau 3 : Nomenclature des flavonoïdes**

Suivant l'espèce de tanins considérée, les monoflavonoïdes sont présents en différentes proportions. Il y a également une petite fraction de composés non-tanins comme les carbohydrates, les gommes hydrocolloïdes et quelques acides aminés et iminés. De plus, les gommes hydrocolloïdes qui représentent encore 3 et 6 % de la masse des tanins ont un rôle primordial dans la viscosité des solutions de tanins (Pizzi 2003d).

Le degré de polymérisation des tanins et la nature même de celle-ci (linéaire ou ramifiée) dépendent également de l'espèce.

Les polyflavonoïdes de tanins de mimosa sont constitués de 2 à 11 monoflavonoïdes, avec une moyenne de 4 à 5 de degré de polymérisation. Pour les tanins de pin, il y a jusqu'à 30 monomères pour un degré de polymérisation moyen compris entre 4 et 5. Pour les tanins de quebracho le degré de polymérisation est compris entre 6 et 7.

Les compositions respectives des tanins de quebracho et de mimosa, qui sont très proches chimiquement, sont de 20 à 30 % de robinetinidol et de 70 à 80 % de fisetinidol ; de 50 à 70 % de robinetinidol et de 15 à 25 % de fisetinidol. Les tanins de quebracho sont donc des polyflavonoïdes de type profisetinidine et les tanins de mimosa sont de type prorobinetinidine (Pizzi 2003d ; Pasch et al. 2001).

## ***2.5.2. Réactivité***

### *2.5.2.1. Autocondensation des tanins*

Selon Roux et al. (1975), les tanins condensés sont formés uniquement de flavonoïdes de type flavan-3-ol et flavan-3,4-diols. En effet, les autres types de flavonoïdes possèdent un groupe carboxyle en position 4, ceci limitant le caractère nucléophile et occupant une des positions possibles de condensation. De plus, la substitution en position méta de l'anneau A de type résorcinol des flavonoïdes de type flavan-3,4-diols par les groupements hydroxyles et l'oxygène de l'hétérocycle implique une très importante nucléophilie sur les positions C6 et C8. Les polyflavonoïdes des tanins condensés sont donc principalement liés via des liaisons C4-C6 et C4-C8. La toute première réaction d'autocondensation des flavonoïdes mène à la formation de proanthocyanidines également appelés biflavonoïdes. Lorsque les polyflavonoïdes sont formés par 3 à 8 monomères, il s'agit alors de tanins condensés à proprement parler (Roux 1972 ; Roux et al. 1975 ; Roux et al. 1976 ; Pizzi 1980).

En présence de bases ou d'acides faibles de Lewis, les polyflavonoïdes sont capables de s'autocondenser via des réactions radicalaires. Ces réactions conduisent à la formation d'un réseau d'enchevêtrement et à son durcissement (Meikleham et al. 1994 ; Pizzi et al. 1995a ; Pizzi et Meikleham 1995 ; Merlin et Pizzi 1996 ; Masson et al. 1996a ; 1996b ; Masson et al. 1997). Ce réseau d'enchevêtrement a pu être quantifié en réalisant des analyses thermomécaniques en flexion trois points. Ainsi, le nombre moyen de degré de liberté des segments de polymères au cours de l'autocondensation des tanins a pu être déterminé (Garcia et Pizzi 1998a ; 1998b). La conclusion a été qu'au début, un polymère linéaire se forme jusqu'à un seuil critique à partir duquel un réseau enchevêtré se met en place.

En présence d'acides minéraux forts et avec un apport de chaleur, les tanins peuvent réagir de deux façons différentes. La première étant la dégradation des polymères et la formation de catéchine et d'anthocyanidines (Figure 9).

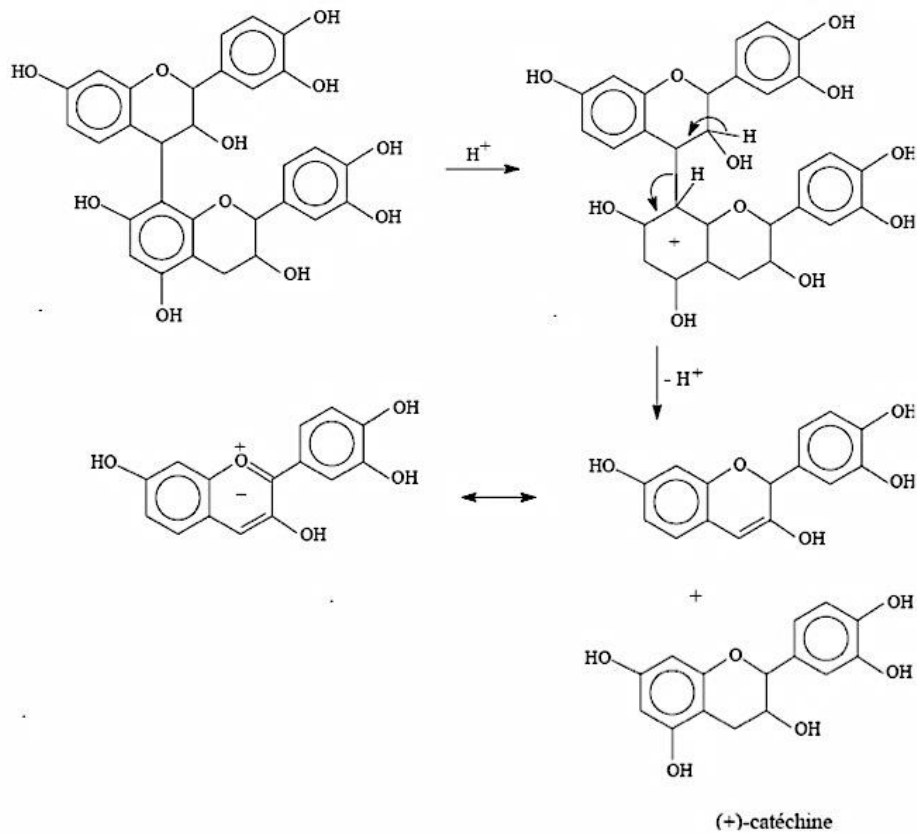


Figure 9 : Dégradation des tanins en catéchine et anthocyanidine (Pizzi 1983)

La seconde réaction est une condensation découlant de l'hydrolyse des hétérocycles (liaisons p-hydroxybenzyl éther). En effet, il y a rupture de la liaison O1-C2 de l'hétérocycle ce qui donne lieu à la formation d'un carbocation en C2. Les ions p-hydroxybenzyl carbonium (Figure 10) ainsi formés, condensent via les sites nucléophiles C6 ou C8 d'autres polyflavonoïdes afin de former les phlobaphènes (Roux et al. 1975 ; Meikleham et al. 1994 ; Pizzi et Meikleham 1995).

En milieu basique, les tanins peuvent également réagir de deux façons différentes. La première réaction est la rupture de la liaison interflavanoïde C4-C8. Cette réaction est particulièrement présente chez les tanins de pin et de noix de pécan, mais beaucoup plus rarement chez les tanins de mimosa. Ainsi, cette rupture de liaison mène à la formation d'un carbocation en C4 qui peut ensuite entraîner une recondensation basique en C6 ou C8 (Figure 11).

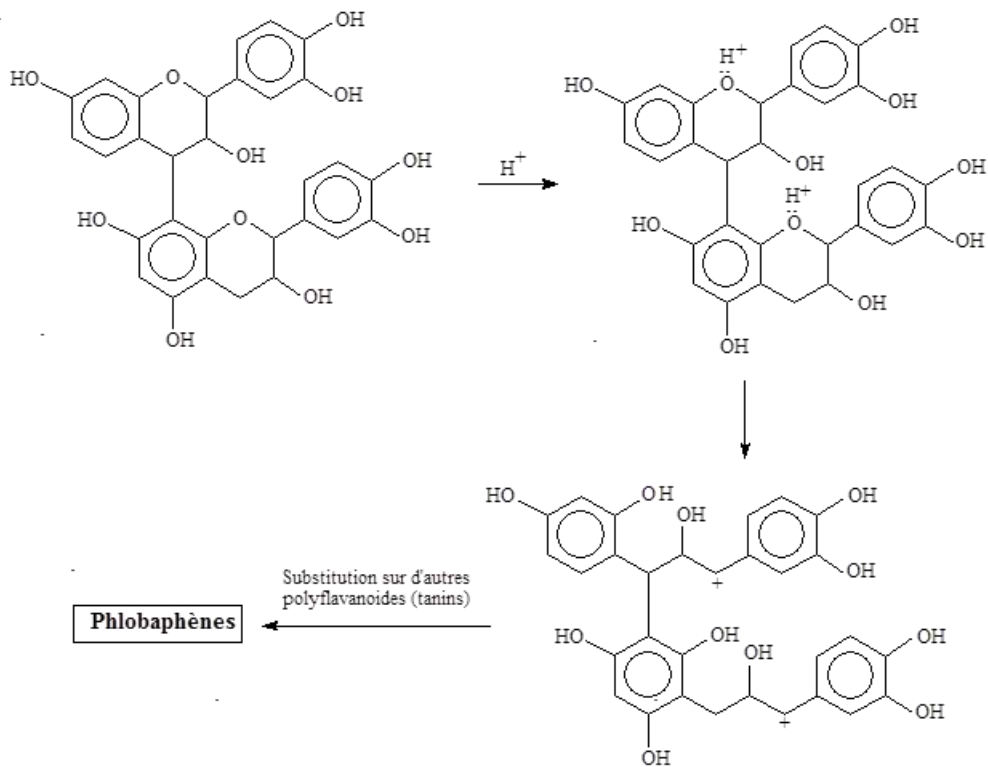


Figure 10 : Autocondensation acide des polyflavonoïdes et ouverture des hétérocycles (Pizzi 1983)

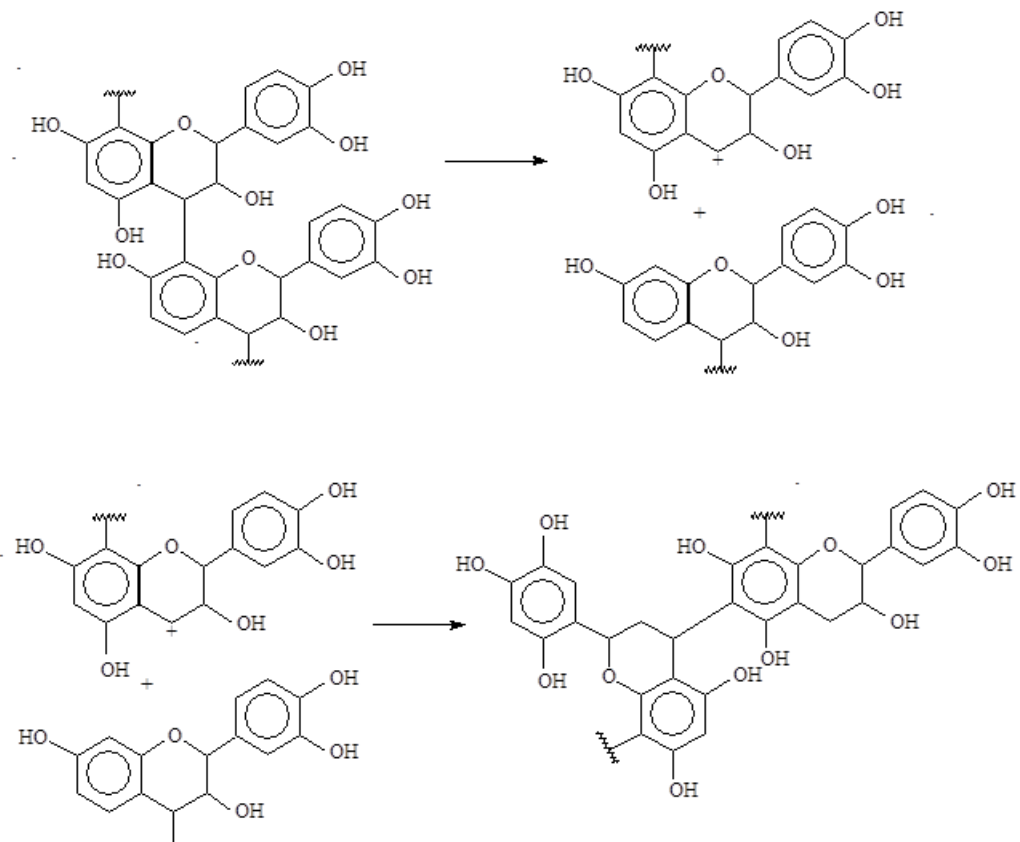


Figure 11 : Autocondensation basique : rupture des liaisons inter flavonoïdes puis autocondensation, (Tanins de pin et de noix de pécan) (Pizzi 1983)

La seconde réaction (Figure 12) est une autocondensation partielle. Cette autocondensation est due à l'augmentation de réactivité liée à l'ouverture de l'hétérocycle (Navarrete 2011). Ceci étant très nettement visible lors des études menées sur la catéchine monomère.

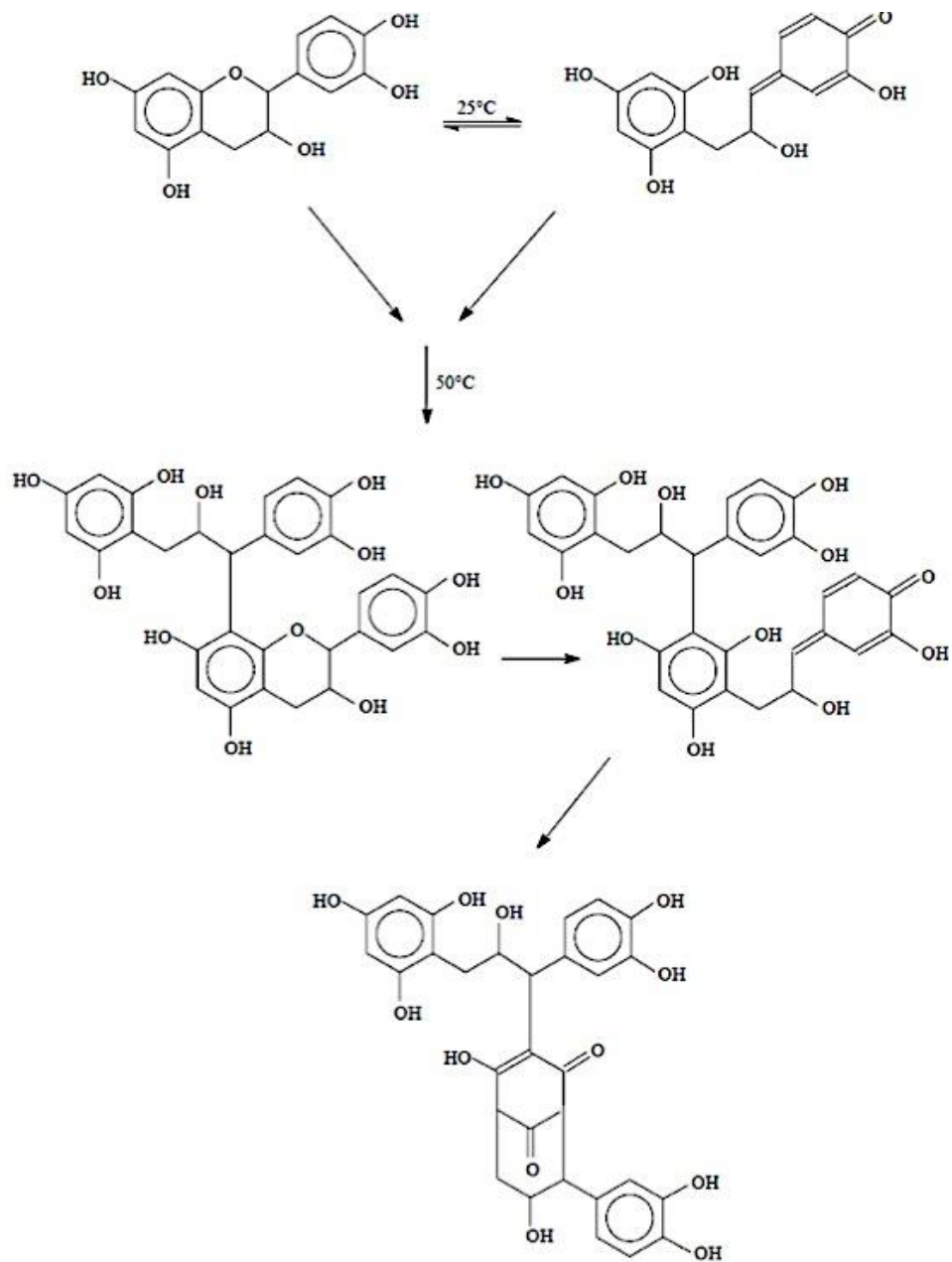


Figure 12 : Réarrangement catéchinique (Navarrete 2011)

Ces réactions d'autocondensation des tanins polyflavonoïdes ont été utilisées pour la fabrication de panneaux de particules et ceci sans emploi d'aldéhydes comme durcisseurs (Meikleham et al. 1994 ; Pizzi et al. 1995b). L'ajout de certains durcisseurs peut même perturber les réactions d'autocondensation (Garcia et al. 1997). De plus, les cinétiques de réaction dépendent des types



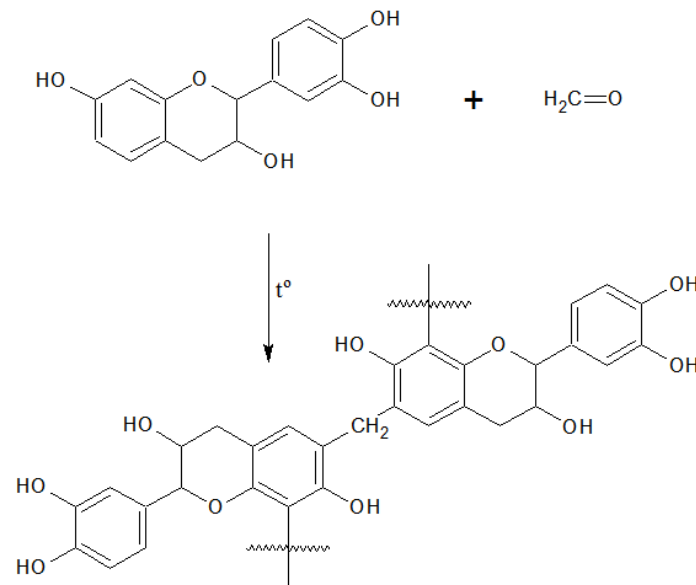
de tanins (Masson et al. 1997). L'autocondensation des tanins induit une augmentation de la viscosité de la résine mais il n'y a pas de gélification (Pizzi et Stephanou 1993) sauf s'il y a addition de silice ou présence de matériaux lignocellulosiques (Pizzi 1994). Quelques coréactifs comme le para-formaldéhyde renforcent l'autocondensation des polyflavonoïdes en intervenant dans la réticulation finale (Garcia et Pizzi 1998a). De même, l'hexaméthylène tétramine intervient dans la formation du réseau d'enchevêtrement final en combinant les deux mécanismes d'autocondensation dans ce cas les tanins réagissent relativement lentement. Les tanins de type procyanidine comme les tanins de pin réagissent plus rapidement et l'hexaméthylène tétramine ne montre pas d'effet particulièrement bénéfique.

#### 2.5.2.2. Réactivité avec les aldéhydes

Les polyflavonoïdes qui sont des molécules polyphénoliques, réagissent de la même manière que le phénol. Ces réactions peuvent bien évidemment avoir lieu en milieu acide ou basique. Lorsque le pH est plus basique, la nucléophilie du phénol est plus importante. Tout particulièrement vers pH 8 où des ions phénates sont formés. Concernant les réactivités des noyaux A et B, les sites nucléophiles du noyau A sont plus réactifs que ceux du noyau B. Ceci est valable pour n'importe quel type de tanins. L'explication réside dans la présence de groupements hydroxyles vicinaux, ceci provoquant l'activation de la totalité du noyau B sans localisation particulière comme c'est le cas pour le noyau A. Les tanins condensations sont constitués d'un mélange des quatre types de polyflavonoïde (Prodelphinidine, procyanidine, prorobinetidine et profisetidine). Et concernant l'anneau A, la proportion de phloroglucinol par rapport à celle de résorcinol permet de prédire la réactivité des tanins avec les aldéhydes et donc d'imaginer la qualité du réseau tridimensionnel. Pour l'anneau B, la proportion de pyrogallol par rapport à celle de catéchol joue un rôle dans l'ouverture de l'hétérocycle pyranique et ainsi détermine le type de réarrangement possible pour la structure (ceci en fonction du pH) (Pizzi et Stephanou 1994a ; 1994b).

Lors de la préparation de résine à base de tanins, le formaldéhyde est l'aldéhyde le plus souvent utilisé (Pizzi 2003d). Il est utilisé sous deux formes : le para-formaldéhyde (polymère solide de 8 à 100 unités) ou le formalin (solution aqueuse à 37 %). Le formaldéhyde en solution réagit plus rapidement car il est déjà sous forme fractionnée, alors que le para-formaldéhyde ne pourra être totalement réactif seulement après avoir été dépolymérisé par mise en solution et/ou chauffage.

Chez les tanins condensés, il n'y a qu'un seul site très réactif. En effet, le second étant utilisé pour une liaison interflavonoïde. Le formaldéhyde réagit avec les tanins afin de former des ponts méthylène entre les différents sites réactifs en C6 et C8 (Figure 13).



**Figure 13 : Réaction entre les flavonoïdes et le formaldéhyde**

Les tanins qui ont un noyau A de type résorcinol possèdent une réactivité vis-à-vis du formaldéhyde qui est comparable, quoique légèrement inférieure, à celle du résorcinol (Pizzi et Roux 1978a ; Rossouw et al. 1980 ; Pizzi et Stephanou 1994a). Les noyaux B de type pyrogallol ou catéchol ne sont donc pas réactifs. Ils sont uniquement réactifs lorsqu'il y a formation d'anions à des pH très élevés (environ pH 10) (Roux et al. 1975). Les noyaux B de type catéchol sont également réactifs à température élevée, mais la réactivité des noyaux A vis-à-vis du formaldéhyde est alors tellement importante que la durée de conservation des résines est alors extrêmement faible et non viable industriellement (Pizzi 1978 ; Osman et Pizzi 2002).

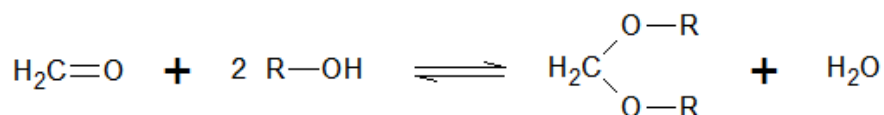
Ainsi, ce sont uniquement les noyaux A qui interviennent dans la formation du réseau d'enchevêtrement. Mais certaines recherches ont montré qu'en milieu légèrement acide ou basique et avec un excès de résorcinol, les noyaux B de type pyrogallol peuvent réagir avec le formaldéhyde (Pizzi 1977). A température ambiante, des molécules modèles ont été étudiées et les formations de dimères pyrogallol-formaldéhyde mais également des dimères et des trimères résorcinol-formaldéhyde ont été démontrées. Les noyaux B participent donc à la formation du réseau tridimensionnel tanins-formaldéhyde mais ceci est très limité et ce réseau est donc très faible. Ainsi, des agents de réticulation comme des résines phénoliques ou aminoplastes peuvent être utilisés. Elles rendent possible les liaisons entre des sites qui sont trop distants afin d'être

reliés par un pont méthylène (Pizzi et Scharfetter 1978 ; Pizzi et Roux 1978a). De même, l'addition d'une petite quantité d'acétate de zinc (5 à 10 % par rapport à la résine solide) et en travaillant à pH inférieur à 10 (plus précisément entre 4,5 et 5,5) (Hillis et Urbach 1959) induit la réaction entre les noyaux B de type catéchol et le formaldéhyde). Ceci permettant un haut degré de réticulation mais qui malheureusement ne confère pas au réseau des propriétés comparables à celles observées lors de l'addition de résines synthétiques (Osman et Pizzi 2002).

Concernant le pH utilisé, il a été trouvé que la réaction entre les tanins et le formaldéhyde est plus lente entre 4,0 et 4,5 pour les tanins de mimosa. Dans ce domaine de pH la quantité de formaldéhyde qui réagit avec les tanins est donc la plus faible (Plomley 1966). A pH neutre, le formaldéhyde réagit rapidement avec les flavonoïdes, en position C6 et C8. Mais aussi, même si c'est de manière plus lente, en position C2' et C6' du noyau B de type catéchol ou pyrogallol.

Il y a deux réactions compétitives qui existent entre les tanins et le formaldéhyde. En effet, il y a la consommation d'aldéhydes par réaction du formaldéhyde avec les tanins et/ou avec les condensats polyflavonoïdes-aldéhydes déjà formés. Mais il y a également la libération d'aldéhydes qui sont à nouveau disponibles pour réagir. Cette réaction peut être expliquée par la transformation des ponts éther instables qui ont été formés initialement, en ponts méthylène. Il y a même une troisième réaction mais uniquement dans le cas des tanins de quebracho, l'hydrolyse des liaisons interflavonoïdes : celle-ci provoque une dépolymérisation et donc un ralentissement de la réticulation. Ceci est expliqué par la structure des tanins de quebracho qui est pratiquement linéaire, ce qui n'est pas le cas pour les tanins de mimosa qui sont très ramifiés. Les liaisons interflavonoïdes sont ainsi plus sensibles à l'hydrolyse à cause de cette linéarité (Pizzi 2003d).

En outre, le formaldéhyde possède une réactivité élevée et il est possible de la contrôler en utilisant des alcools. Cela induit la formation d'hémiacétals (Figure 14).



**Figure 14 : Réaction entre le formaldéhyde et un alcool : formation d'un hémiacétal**

Ainsi, la libération du formaldéhyde a lieu quand l'alcool s'évapore lors de la phase de polymérisation de la résine (à haute température). Cette libération se fait progressivement lors de l'augmentation de la température, la réaction entre les tanins et le formaldéhyde se fait alors plus

lentement (Pizzi 2003d). Ceci a pour principal but d'allonger la durée de vie en pot des résines qui utilisent du formaldéhyde comme durcisseur, mais uniquement à température ambiante.

Comme il a été démontré, les sites réactifs peuvent quelques fois être trop éloignés les uns des autres afin de former des ponts méthylène et donc créer un réseau tridimensionnel encore plus performant. En effet, le formaldéhyde est une molécule de petite taille et donc les ponts méthylène sont courts. Par exemple dans le cas des tanins de mimosa, les flavonoïdes sont reliés par des liaisons C4-C8 : les sites en position C6 présents sur les flavonoïdes qui sont en milieu de chaîne ne sont pas aussi facilement atteignables par le formaldéhyde que sur un monoflavonoïde. Ainsi, d'autres aldéhydes bifonctionnels peuvent être employés en complément ou en remplacement du formaldéhyde. De plus se pose la question de la toxicité, car certes le formaldéhyde est très réactif avec les tanins mais il est fortement toxique et cancérigène.

Le premier aldéhyde bifonctionnel qui peut être utilisé est le glyoxal. Il est préparé via deux manières : soit par oxydation en phase gazeuse de l'éthylène glycol ; soit par oxydation en phase liquide de l'éthanal. Le glyoxal est un intermédiaire de réaction couramment utilisé en chimie et il est disponible en grande quantité dans le monde. En effet, il possède plusieurs avantages : il est très peu nocif, il ne présente que peu de risques pour l'homme et est classé parmi les composés non-toxiques par les organismes de santé. Il est biodégradable car il peut être assimilé et transformé par les champignons ou des bactéries. De plus, il n'est également pas volatil. Ainsi, il peut très facilement être utilisé industriellement. Et cela élimine le risque d'émissions de COV toxiques pendant la durée de vie du produit. Son principal défaut est sa réactivité moindre par rapport au formaldéhyde avec les composés phénoliques. Mais les travaux de Ballerini et al. (2005) ont montré que des résines à base de tanins de pin radiata peuvent être réalisées en utilisant le glyoxal comme durcisseur à la place du formaldéhyde. Les panneaux de bois mis au point avec cette résine possèdent une cohésion interne plus faible que les panneaux dit standards, mais ont des rejets en formaldéhyde nuls.

Un second aldéhyde bifonctionnel qui est utilisé est le glutaraldéhyde. Il est produit par oxydation du cyclopentène ou par réaction de Diels-Alder entre le méthyl vinyl éther et l'acroléine suivie d'une hydrolyse. Il est généralement utilisé comme désinfectant et donc à la différence du glyoxal, c'est un composé toxique extrêmement irritant. Même s'il réagit dans une moindre mesure que le formaldéhyde avec les tanins, il a été utilisé pour la fabrication de colles tanins-résorcine-glutaraldéhyde qui ont été étudiées par spectrométrie de masse (MALDI-ToF) (Sauget et al. 2014a).

Enfin, le troisième aldéhyde bifonctionnel qui est souvent utilisé, est le furfural. Il s'agit cette fois-ci d'une molécule hétérocyclique obtenue par déshydratation de sucres à cinq carbones qui sont issus de l'hydrolyse acide des hémicelluloses, en particulier le xylose (Figure 15).

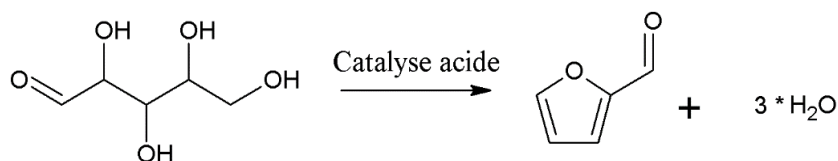


Figure 15 : Synthèse du furfural à partir du xylose

Cet intermédiaire de réaction est produit en très grande quantité dans le monde, principalement en Chine. Même s'il réagit lentement avec les composés phénoliques (Plomley 1966), c'est pourtant un agent de réticulation plus qu'efficace et c'est un excellent plastifiant lors de son utilisation dans les adhésifs à base de tanins (Pizzi 1978). Cependant, ce composé est toxique et irritant. Mais, il possède une réactivité importante quasiment identique à celle du formaldéhyde avec les flavonoïdes qui possèdent un anneau A de type résorcinol. Pour les tanins possédant un anneau A de type phloroglucinol, l'encombrement stérique induit par le groupement hydroxyle en position C5 rend le site réactif en position C6 beaucoup moins accessible que celui en position C8 (Rossouw et al. 1980).

Les cinétiques de réaction de plusieurs aldéhydes avec les tanins condensés de type résorcinol et phloroglucinol ont été étudiées (Rossouw 1979). Ces tests ont été réalisés avec le formaldéhyde, l'acétaldéhyde, le propionaldéhyde, l'iso-butyraldéhyde et le furfural. Des différences majeures ont été observées dans les vitesses de réaction des tanins de type résorcinol et phloroglucinol avec ces différents aldéhydes. Le classement des vitesses de réaction pour les tanins de type phloroglucinol est représenté sur la Figure 16.

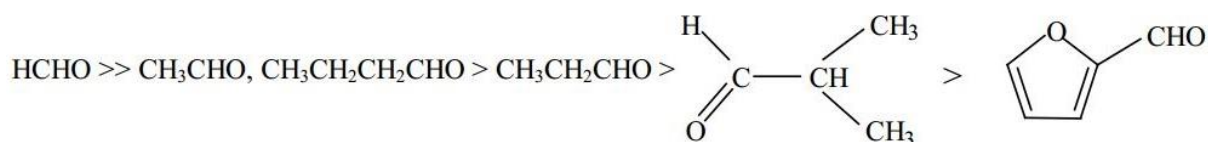


Figure 16 : Vitesses de réaction pour les tanins de type phloroglucinol

Pour les tanins de type résorcinol, l'échelle de réactivité est représenté sur la Figure 17. Figure 17

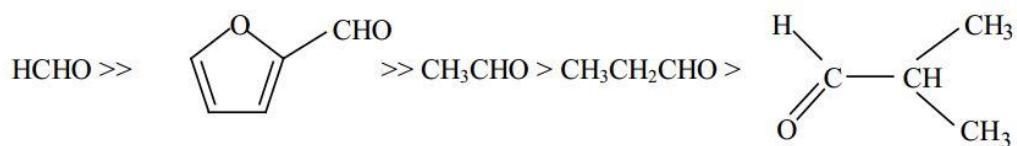


Figure 17 : Vitesses de réaction pour les tanins de type résorcinol

La différence de réactivité la plus importante est la position du furfural. Si sa réactivité vis-à-vis des composés phénoliques et des flavonoïdes possédant un anneau A de type résorcinol est importante, elle est fortement limitée par des problèmes d'encombrement stérique dans le cas des flavonoïdes ayant un anneau A de type phloroglucinol (Rossouw 1979). Dans le cas des flavonoïdes de type résorcinol, l'attaque de l'aldéhyde a lieu en position C8, site étant considérablement moins encombré stériquement que le site C6 des flavonoïdes de type phloroglucinol.

#### 2.5.2.3. Réactivité avec l'alcool furfurylique

L'alcool furfurylique est un liquide polaire à température ambiante. Il est de couleur jaune orangé clair, il est soluble dans l'eau, dans les alcools de bas poids moléculaires et dans la plupart des solvants organiques. Il possède une réactivité chimique importante dans le cadre des réactions d'oxydation et de polymérisation. Sa formule est  $\text{C}_5\text{H}_6\text{O}_2$ , il est composé d'un cycle furane sur lequel un groupe hydroxy méthyl est fixé en C1 (Figure 18). Ce composé organique présente des caractéristiques aromatiques et alcooliques.

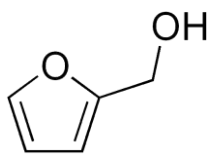


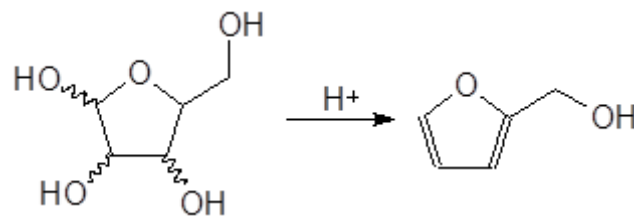
Figure 18 : Alcool furfurylique

Bien qu'il soit considéré nocif par inhalation, ingestion et contact avec la peau selon la directive européenne n°2001-60 du 7 août 2001, il est très souvent utilisé dans la production de résines, de vernis (car il leur confère une bonne résistance vis-à-vis de la corrosion), de matériaux synthétiques et principalement dans les fonderies. En effet, il est utilisé dans l'agglomération des sables de fonderie à l'aide de résines sans cuisson. Ces résines ont été introduites sur le marché en 1958. Une très petite quantité d'alcool furfurylique (0,5 à 5 %) est additionnée à de l'acide

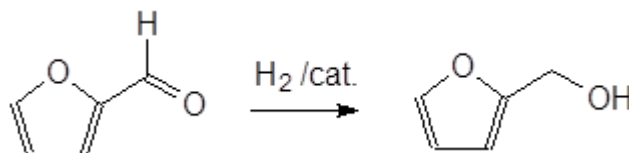
phosphorique afin d'avoir une catalyse acide rapide. Ainsi, l'alcool furfurylique polymérise à température ambiante et sans cuisson, d'où le nom de cette résine. Cette méthode permet donc de mettre en œuvre des moules plus facilement et rapidement qu'avec des méthodes classiques. La résistance thermique du polymère ainsi créé est suffisante pour garantir la cohésion du sable formant le moule juste le temps de couler le métal. Le moule se désagrège ensuite afin de pouvoir récupérer la pièce moulée mais également le sable. Ainsi, le démoulage est facile et la récupération de la matière première est simplifiée (Carey et Lott 1995).

L'alcool furfurylique est fabriqué industriellement par réduction d'un aldéhyde. Il est produit à partir de matières agricoles comme le blé, le maïs ou encore la sciure. Il est donc considéré comme étant un produit d'origine naturelle. Dans la littérature sont invoqués plusieurs procédés et produits de départ concernant la production du furfural (Sproull et al. 1986 ; Pessoa Jr. et al. 1997).

L'alcool furfurylique d'origine agricole est obtenu principalement à partir de deux réactions. La première étant l'hydrolyse des pentosanes des hémicelluloses (Figure 19) et la deuxième étant l'hydrogénation catalytique à haute pression du furfural (Figure 20).



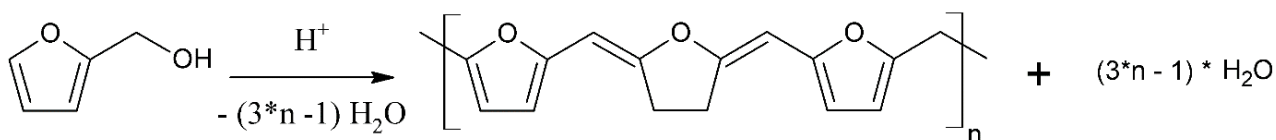
**Figure 19 : Hydrolyse des pentosanes des hémicelluloses**



**Figure 20 : Hydrogénation du furfural**

Les catalyseurs utilisés sont généralement des métaux. Il y a un peu plus d'une dizaine d'années des études ont démontré l'efficacité de deux mélanges : Molybdène (Mo), cobalt (Co) et bore (B) (Chen et al. 2002) ; cuivre (Cu) et oxyde de magnésium (MgO) (Nagaraja et al. 2003).

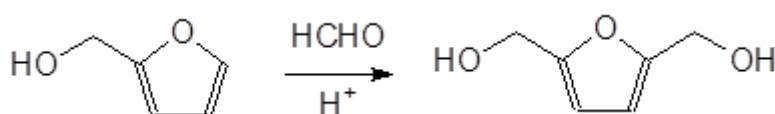
De plus, l'alcool furfurylique est bien connu de par sa réaction d'autocondensation en milieu acide, réaction qui est très exothermique formant l'alcool polyfurfurylique (Figure 21). Cette réaction est suffisamment exothermique puisqu'elle s'auto-entretient même après que l'énergie d'activation initiale ait été atteinte. Des recherches menées ces dernières années ont conduit à la fabrication de plastiques thermodurcis biosourcés ayant une excellente résistance mécanique (Li et al. 2013a).



**Figure 21 : Autocondensation de l'alcool furfurylique en milieu acide**

Afin de comprendre le mécanisme de polymérisation de l'alcool furfurylique, des études par spectrométries UV, FTIR et RMN ont été menées sur des polymères furaniques préparés dans un solvant et sous atmosphère d'azote (Choura et al. 1996 ; Gonzalez et al. 2002a ; 2002b ; Oliva-Teles et al. 2005 ; Bertarione et al. 2008 ; Bertarione et al. 2009). Ainsi, les réactions de polycondensation conduisent à des polymères linéaires, ramifiés et même à des structures tridimensionnelles selon les conditions de catalyse utilisées. Une croissance linéaire des chaînes est tout d'abord observée et ensuite ces chaînes réticulent.

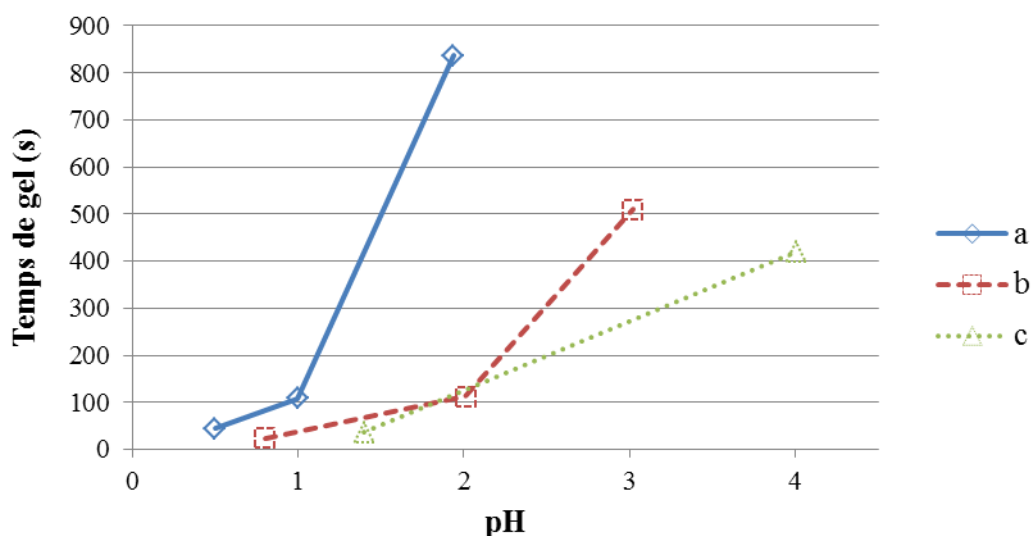
L'alcool furfurylique peut réagir avec le formaldéhyde en milieu acide et être transformé en 2,5-furandiméthanol (Figure 22) (Gandini et Belgacem 1997).



**Figure 22 : Réaction de l'alcool furfurylique avec le formaldéhyde**

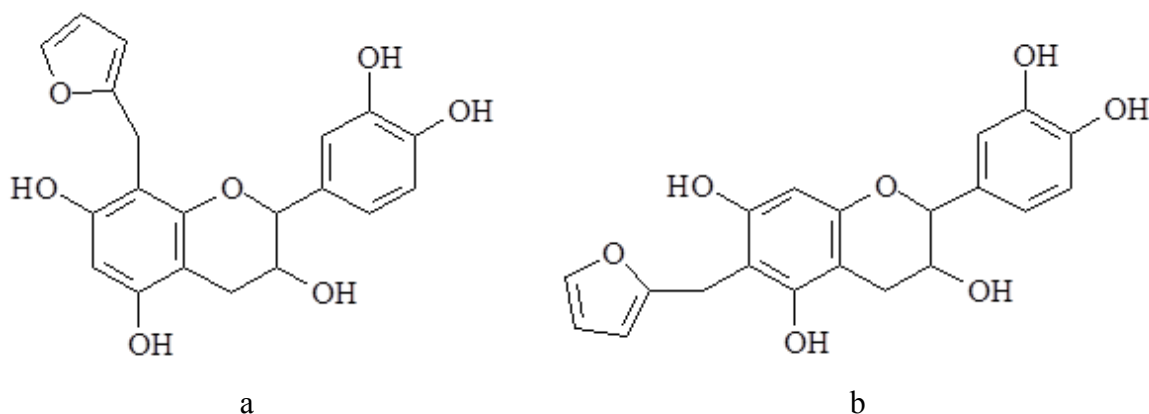
Le composé ainsi formé peut être un intermédiaire de réaction très efficace dans la synthèse de résines alcool furfurylique-formaldéhyde-tanins. Tanins qui réagissent eux-mêmes très bien avec cet aldéhyde. Les temps de gel de la résine varient alors en fonction de la combinaison de ces trois molécules (Figure 23).





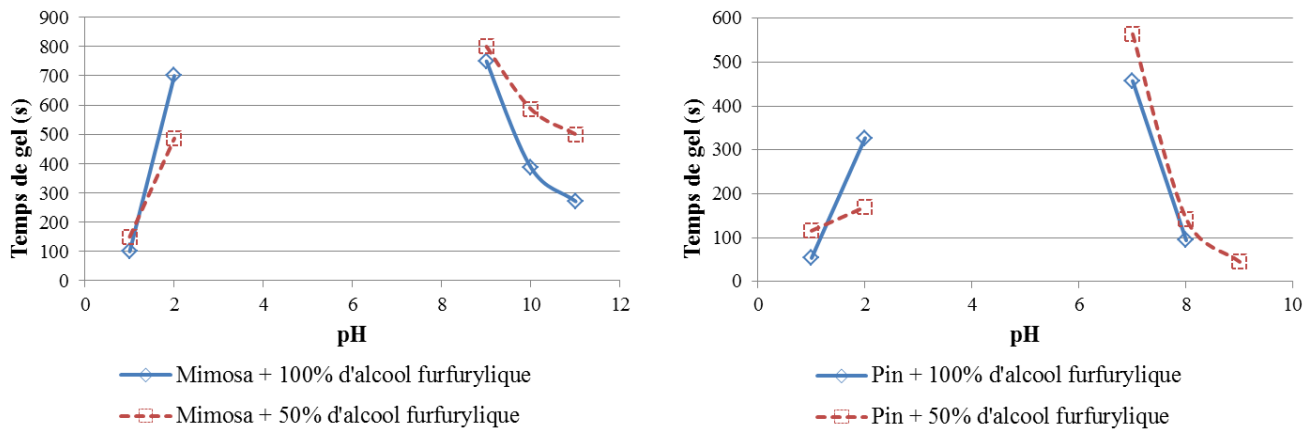
**Figure 23 : Temps de gel en fonction du pH des résines tanins-alcool furfurylique (1), tanins-alcool furfurylique-formaldéhyde (2) et tanins-formaldéhyde (3) (Tondi 2009)**

De cette façon, la réactivité des tanins avec l'alcool furfurylique a été étudiée en considérant dans un premier temps les unités flavonoïdes pures, comme la catéchine (Foo et Hemingway 1985). Ainsi, la catéchine et l'alcool furfurylique ont été placés dans des conditions favorables à leur réaction : à pH très acide (utilisation d'acide acétique) et à une température de 100°C. Après séparation et purification par chromatographie en phase liquide à haute performance (HPLC), la présence de deux flavonoïdes ayant des groupements furanyles en position C6 et C8 a été observée. Le premier avec un rendement de 4 % (Figure 24a) et le second avec un rendement de 1,5 % (Figure 24b).



**Figure 24 : Produits de la réaction de l'alcool furfurylique sur la catéchine**

Des travaux de recherches plus récents ayant pour but de mettre en œuvre des résines tanins-alcool furfurylique pour la fabrication de panneaux de particules de bois ont montré que leur utilisation en milieu basique est également possible (Abdullah et Pizzi 2013). L'augmentation du pH de la résine permet de diminuer le temps de gel de celle-ci (Figure 25).



**Figure 25 : Temps de gel en fonction du pH des résines alcool furfurylique-tanins de mimosa et alcool furfurylique-tanins de pin (Abdullah et Pizzi 2013)**

Il y a donc une diminution de la réactivité de l'alcool furfurylique, mais dans un même temps une augmentation de celle des tanins. Ainsi, la réticulation de ces deux molécules est observée.

### 2.5.3. Applications des tanins

#### 2.5.3.1. Le tannage du cuir

Le tannage du cuir est une application pour laquelle les tanins sont particulièrement prisés, et ceci depuis de très nombreuses années, en raison de leur couleur claire et surtout de leurs propriétés d'astringence envers les protéines (Pizzi 1994). Ce procédé chimique, consiste à traiter les peaux pour les rendre imputrescibles et plus souples. En effet, les protéines contenues dans la peau (principalement le collagène) sont stabilisées et deviennent insolubles grâce à la fixation de produits chimiques. Ainsi, les peaux sont plus résistantes vis-à-vis des attaques biologiques (Pizzi et al. 2004). Cette durabilité et la couleur finale du cuir sont directement liées au type de tanins utilisés. Plusieurs tanins sont utilisés dans l'industrie du tannage : châtaignier, mimosa, quebracho...

#### 2.5.3.2. Utilisations pharmaceutiques

Au sein même du corps humain ont lieu des réactions d'oxydation dues aux radicaux libres, ceci étant totalement normal. Mais dès lors qu'il y a un excès de radicaux libres, qui sont généralement

produits suite à des polluants externes comme par exemple la pollution atmosphérique, la fumée de cigarette, les aldéhydes, etc., à ce moment-là des problèmes de santé peuvent apparaître. Or les polyflavonoïdes font partis de la catégorie des polyphénols : molécules naturelles antioxydantes qui sont présentes en grande quantité dans notre régime alimentaire. Les polyphénols sont présents dans les boissons (café, thé, vin, jus de fruits...) ou encore dans certains aliments (fruits, légumes, céréales, chocolat...). Le rôle des polyphénols dans la prévention de nombreuses maladies dégénératives comme les cancers et les maladies cardiovasculaires n'est plus à démontrer (Duthie et al. 2000). En outre, ils sont utilisés comme antiradicalaires ou antioxydants (Hagerman et al. 1998) mais également dans la fabrication de nourriture animale (Jerez et al. 2006).

L'étude du « paradoxe français », terme donné par les diététiciens, est un bon exemple : les français sont les plus gros consommateurs de vins au monde tandis que la santé publique française est l'une des meilleures en Europe en matière de maladie cardiovasculaire ou de cancer. Certains chercheurs comme Corder et al. (2006) attribuent aux tanins la responsabilité de cela, tout en démontrant les effets bénéfiques de ceux-ci sur ces maladies.

En effet, les polyphénols sont composés de nombreux noyaux aromatiques avec des groupements hydroxyles. Ainsi, ils sont capables de donner ou d'accepter des atomes d'hydrogène ou encore des électrons et aussi de recevoir des radicaux libres (Manach et al. 2005 ; Scalbert et al. 2005). Leurs effets antioxydants proviennent principalement des catéchines et des proanthocyanidines qui sont présents dans la majeure partie des flavonoïdes.

Les tanins sont également utilisés dans d'autres applications pharmacologiques. En effet, ils peuvent être administrés par voie interne ; ils possèdent des effets antiseptiques lorsqu'ils précipitent les enzymes étant responsables des infections. Ils peuvent donc traiter des infections vasculaires comme les varices, ou encore être utilisés comme antidiarrhéiques. En utilisation externe, les tanins sont utilisés dans des cosmétiques visant à traiter les problèmes de peau (propriétés astringentes), dans les autobronzants, ou utilisés en tant qu'antimicrobiens, antiinflammatoires ou encore antiallergiques.

#### 2.5.3.3. *Préservation du bois*

La préservation du bois est parfois nécessaire et elle est généralement réalisée à l'aide de produits chimiques afin de prévenir l'attaque d'organismes xylophages. Un produit de préservation optimal doit posséder ces caractéristiques : être un fongicide et un bactéricide efficace ; être facilement mis en œuvre ; doit être difficilement dégradable et résistant au lessivage

et enfin doit être respectueux de l'environnement. Ces produits de préservations sont présents sur le marché sous quatre principaux formats.

Tout d'abord les produits de préservation à base d'huile. Ils sont le plus généralement issus de la distillation fractionnée de goudrons de charbon ou de bois. Ils ont principalement été utilisés dans la deuxième partie du vingtième siècle, sous forme de créosote. En effet, l'action antifongique est alors due au phénol et l'hydrophobie que procure cette substance huileuse réduit de manière non négligeable le lessivage de ce produit de préservation. Mais depuis 1994, une directive du Parlement Européen (94/60/CE) interdit leurs utilisations au vu de leur toxicité et de leur cancérogénicité.

Ensuite, il y a les composés synthétiques utilisés dans des solvants organiques. Ces produits sont les plus récents des produits de préservation. Les principes actifs (généralement des naphthénates de zinc ou de cuivre), les phénols halogénés ou encore les composés organiques d'étain et de cuivre sont tous insolubles dans l'eau (Kirkpatrick et Barnes 2006) donc une fois le solvant organique évaporé : ils sont ainsi difficilement lessivables et sont donc de très bons produits de préservation.

De plus, il y a les solutions aqueuses de sels minéraux. Ceux-ci présentent plusieurs avantages, en effet, ils sont disponibles sur le marché et leurs coûts sont peu élevés alors qu'ils pénètrent facilement dans le bois. Toutefois, l'utilisation de l'eau peut provoquer des variations dimensionnelles du bois et ainsi créer des gonflements et retraites successifs du bois qui impliquent la formation de fissures. En plus de cela, comme ces produits sont appliqués à l'aide de solution aqueuse, ils sont également plus facilement lessivables. Les sels les plus utilisés sont les ACQ (Cuivre et Ammonium Quaternaire) et dans le passé, les ACC (Arsenic, Cuivre, Chrome) ont été utilisés de façon massive (Radivojevic et Cooper 2010). Mais ils sont maintenant interdits par la directive du Parlement Européen datant de 2003 (2003/2/CE), sauf pour le traitement de préservation du bois de construction. Ainsi, d'autres produits plus respectueux de l'environnement comme le bore peuvent aussi être utilisés avec des résultats tout à fait honorables (Thevenon et al. 1998 ; Thevenon et al. 2009 ; Thevenon et al. 2010).

Enfin, se développent depuis quelques années des technologies alternatives. Ce sont d'autres moyens de protéger le bois sans pour autant utiliser les substances chimiques et les sels minéraux cités ci-dessus. Ainsi, l'acétylation du bois consiste à substituer les hydroxyles libres par des groupements acétyles qui sont quant à eux beaucoup moins digestes par les insectes (Brelid et al. 2000). Et également, le traitement thermique du bois par autoclave (180 à 230°C) peut être utilisé comme technique de préservation de celui-ci. En effet, cela dégrade suffisamment les fibres du

bois afin de les rendre moins sensibles aux attaques des insectes (Kamdem et al. 2002). Ces deux procédés restent encore onéreux mais ils préservent la stabilité dimensionnelle du bois.

Les tanins sont des fongicides naturels dont leur efficacité pour la préservation du bois est connue depuis plusieurs dizaines d'années (Zucker 1983). En effet, les tanins sont des extractibles qui proviennent du duramen de la plante et possèdent des propriétés antioxydantes et fongicides (Schultz et al. 1995 ; Schultz et Nicholas 2000 ; Schultz et Nicholas 2002). Les bois traités à l'aide de polyflavonoïdes ont une résistance vis-à-vis des champignons au minimum doublée par rapport à des bois non traités (Conradie et Pizzi 1986). Les tanins jouent un rôle de protection pour les plantes contre les attaques de nombreux agents pathogènes comme les bactéries et les champignons. En effet, ces agents pathogènes attaquent le bois en sécrétant des enzymes extracellulaires (cellulase et lignase) afin de dégrader les composants des fibres de bois (cellulose, lignine, hémicellulose...), d'où l'action des tanins qui inhibent ces enzymes en complexant avec elles, ceci permettant de neutraliser leurs attaques contre le bois (Laks et al. 1988). Les tanins comme produits de préservation du bois possèdent certains avantages, comme leur application facilitée en solution aqueuse ; leur compatibilité importante avec les molécules composant le bois (des réticulations sont possibles) et enfin leur très grande capacité à complexer ce qui réduit leur lessivage de manière plus qu'importante. Toutefois, ils sont moins efficaces que les métaux (cuivre ou arsenic) mais ils possèdent tout de même des performances suffisantes. Il est également possible de les utiliser en les combinant avec d'autres principes actifs comme l'acide borique (Pizzi et Baecker 1996) ou encore le cuivre (Scalbert et al. 1998 ; Yamaguchi et Okuda 1998) afin d'obtenir de meilleurs résultats. Durant ces dernières années, Tondi a développé des formulations à base de tanins et d'hexaméthylène tétramine utilisant de l'acide borique. Ces résines ont servi à imprégner le bois et ont été laissées pour réticulation à plus de 100°C pendant une douzaine d'heures. Les propriétés mécaniques et la résistance au feu des échantillons de bois traités ont été améliorées (Tondi et al. 2012).

#### 2.5.3.4. *Collage du bois*

Les tanins ont été très largement étudiés afin d'être utilisés dans les colles à bois (Zhou et al. 2013 ; Sauget et al. 2014b). Ceci étant une utilisation industrielle différente de leur application traditionnelle qui est le tannage du cuir. Les tanins condensés représentent 90 % des tanins commercialisés. Et ils ont été utilisés avec un réel succès dans le développement de colles à bois, colles pour le carton ou encore dans les différents types de panneaux à base de bois (Pizzi 1994 ; Yazaki et Collins 1994 ; Pizzi 2006 ; Pizzi 2009 ; Navarrete et al. 2013).

Lors de l'utilisation des tanins dans les colles à bois, ils peuvent être utilisés seuls ou alors comme copolymères dans des résines phénoliques ou aminoplastes. La polymérisation des résines à base de tanins seuls est le plus souvent assurée par le formaldéhyde. Comme les tanins sont de nature polyphénolique, il y a tout de même quelques émissions de composés organiques volatils mais en faibles quantités. Mais l'addition de tanins dans les résines synthétiques reste encore leur principale utilisation dans le domaine des colles à bois.

Lors de ces dernières années, des panneaux de particules ont été réalisés industriellement avec une colle à base de tanins de mimosa (Afrique du Sud). Dans ce pays, la totalité des panneaux utilisés en milieu extérieur sont fabriqués avec des colles à base de tanins. Les caractéristiques de ces panneaux sont largement comparables à celles des panneaux de particules fabriqués avec des résines phénoliques classiques. De plus, ils sont plus écologiques et plus économiques. Ces colles semblent donc être les remplaçantes des colles synthétiques lorsque les produits pétroliers ne seront plus disponibles en quantité nécessaires ou seront devenus trop chers (Pizzi et al. 1981). Des panneaux de bois pour utilisation extérieure ont même été mis au point avec un durcissement sans émission d'aldéhyde (Trosa et Pizzi 2001).

Les colles à base de tanins n'ont pas seulement été utilisées avec le bois mais également avec d'autre biomasse et ceci en ayant des propriétés mécaniques tout à fait honorables : la paille de blé (Tabarsa et al. 2011) ; les balles de riz et de café (Bisanda et al. 2003 ; Ndazi et al. 2006). Toujours en utilisation extérieure, il a été montré que l'utilisation de catalyseurs d'ions métalliques bivalents tels que l'acétate de zinc dans les adhésifs à base de tanins de mimosa peut diminuer la température de pressage du panneau et également réduire la quantité de résine utilisée (Pizzi et Cameron 1981).

Plus récemment des recherches ont été menées sur la substitution partielle du phénol par les tanins de châtaignier lors de la synthèse de résines phénoliques. Les tanins de châtaignier étant des tanins hydrolysables, sont réputés comme ayant une faible réactivité chimique, mais ici a été démontrée leur possibilité de réagir avec le phénol et le formaldéhyde (Spina et al. 2013a ; 2013b).

De plus, des contreplaqués ont aussi été réalisés avec des colles à base de tanins. Ceux-ci sont également plus économiques et écologiques que ceux produits avec des résines synthétiques et ils demandent une faible quantité de colle ceci étant dû à un double encollage (Pizzi et Roux 1978b ; Pizzi et Scharfetter 1978 ; Pizzi 1979 ; Vazquez et al. 2002). Pour la fabrication de contreplaqués peuvent être utilisés de la fécule de maïs et différents types de tanins : quebracho, pin, mimosa (Vazquez et al. 1992 ; Moubarik et al. 2009). Pour la préparation de contreplaqués, les tanins

peuvent être utilisés seuls ou en copolymères avec des résines synthétiques (Vazquez et al. 1993 ; Zhao et al. 1994 ; Hoong et al. 2009).

Depuis plusieurs dizaines d'années des adhésifs à base de tanins de mimosa durcissant à température ambiante sont utilisés pour l'aboutage de bois et la fabrication de stratifiés (Pizzi et Daling 1980 ; Pizzi et al. 1983). Ce type de résine est utilisé industriellement en Afrique du Sud. De plus, au Chili ce sont les tanins de pin qui sont utilisés industriellement dans la fabrication de colle pour aboutage. Ces adhésifs sont utilisés en milieu extérieur et satisfont totalement aux standards (Leyser et Pizzi 1990). Un autre procédé de synthèse a permis d'optimiser les formulations et d'utiliser 5 % de résorcinol au lieu des 14 à 20 % utilisés auparavant. Le durcissement est toujours optimal et a toujours lieu à température ambiante (Pizzi et al. 1988).

Kim (2009) a même développé des colles pour planchers en mélangeant les tanins au polyacétate de vinyle. Ceci a permis de réduire les émissions de formaldéhyde.

Enfin, plus récemment les tanins ont été utilisés dans la mise au point de biocomposites. Des panneaux de haute/moyenne et faible densité ont été développés avec des tanins de mimosa et de quebracho. Plusieurs fibres naturelles ont été utilisées : du lin et du chanvre. Ces panneaux sont très performants mécaniquement parlant et sont très économiques. Typiquement leurs applications cibles sont les panneaux de renfort de portières automobiles (Pizzi et al. 2009b ; Nicollin et al. 2012 ; Sauget et al. 2013 ; Sauget et al. 2014b).

## **2.6. Les mousses solides à base de tanins**

Par définition, une mousse est un milieu complexe constitué d'un matériau solide ou liquide intimement mêlé à du gaz. On parle donc respectivement de mousses solides ou de mousses liquides.

Lors de la fabrication des mousses solides, beaucoup de paramètres sont à prendre en compte. Comme évidemment la gravité, les conditions atmosphériques (température, pression, humidité de l'air ambiant), les énergies d'activation, mais aussi en rapport avec les moules utilisés : la conductivité thermique ou même la rugosité des parois de ceux-ci.

Afin de pouvoir obtenir une mousse solide, il doit y avoir un optimum entre l'expansion et le durcissement.

Toute la difficulté réside dans le réglage des cinétiques du dégazage et de la polymérisation afin d'obtenir cet optimum. Si le gaz s'évapore trop vite, la structure collapse avant de durcir. En revanche, si le durcissement est trop rapide, il n'y a pas de formation de cellules et on obtient une résine solide. Lors de la formation d'une mousse solide, trois grandes étapes interviennent : l'expansion, la polymérisation et le durcissement de celle-ci.

Après quelques instants (le temps d'induction), le seuil d'activation est atteint et le gaz libéré implique l'expansion verticale de la mousse. La résine est alors encore liquide. Ensuite, les chaînes macromoléculaires réticulent afin de former un réseau tridimensionnel. Cette réticulation est cruciale pour la formation de la mousse solide. Si elle a lieu prématurément, les cellules n'ont pas le temps de se former correctement et une résine solidifiée contenant quelques bulles est obtenue. Et si la réticulation a lieu trop tard, le collapse de la mousse formée est observé. Il est donc nécessaire d'atteindre un optimum pour la formation d'une mousse solide. Enfin, une fois la mousse formée, le point de gélification de la résine est passé mais la polymérisation n'est pas totalement finie. Le gaz d'expansion va continuer de s'échapper à travers la mousse et celle-ci va sécher. Parfois le mûrissement d'Oswald est observé lors de cette dernière étape : plusieurs petites cellules vont fusionner afin de former une seule et même grosse cellule.

Les premières mousses de tanins ont été développées dans les années 1990 (Meikleham et Pizzi 1994) à l'aide d'une résine tanins-alcool furfurylique-formaldéhyde. Ainsi, l'autocondensation exothermique de l'alcool furfurylique permet l'évaporation de l'éther diéthylique qui est un solvant ayant une température d'ébullition basse (34,6 °C). Suite à ces premières recherches, les mousses à base de tanins ont été et sont toujours un sujet de recherche intéressant d'un point de vue écologique (Tondi et Pizzi 2009 ; Lacoste et al. 2014a ; 2014b). En effet, ces mousses naturelles sont de sérieuses concurrentes aux mousses synthétiques.

Les mousses à base de tanins sont généralement développées à l'aide d'un moussage physique. Concernant les réactions qui rentrent en jeu, il y a l'autocondensation exothermique de l'alcool furfurylique qui implique à l'évaporation de l'agent moussant ; il y a également l'autocondensation des tanins qui intervient dans la réaction entre les tanins et l'alcool furfurylique. Lors des premières formulations le formaldéhyde a été utilisé afin de permettre un meilleur durcissement de la mousse formée et ainsi d'obtenir une meilleure résistance mécanique de celle-ci.

Depuis de nouveaux types de moussage ont été utilisés pour la fabrication de mousse de tanins, comme le moussage chimique avec la réaction d'isocyanates avec l'eau (Basso et al. 2013a) ou encore à l'aide d'une forte agitation mécanique avec un tensioactif non ionique (Szcurek et al.



2013a ; 2013b ; Szczurek et al. 2014). D'ailleurs ces tensioactifs ont une influence sur les propriétés de mousses de tanins (Basso et al. 2013b).

De manière générale les mousses à base de tanins sont formées en milieu acide, mais il a été possible d'en mettre en œuvre en milieu basique (Meikleham et Pizzi 1994 ; Basso et al. 2014a). D'autres formulations ont été développées afin d'obtenir des mousses de différentes propriétés mécaniques, elles peuvent être renforcées par addition de polymère de 4,4'-diisocyanate de diphenylméthylène (pMDI) (Li et al. 2012a), de nanotubes (Li et al. 2013b), ou encore avec des polymères hyperbranchés (Li et al. 2012b), ou alors au contraire afin d'obtenir des mousses flexibles (Li et al. 2012c ; Basso et al. 2014b).

Les mousses de tanins sont d'excellents isolants thermiques au même titre que le liège ou la laine de verre (0,040 W/m/K environ (Molle et Patry 2011)). En effet, leur conductivité thermique dépend bien évidemment des formulations mais peut descendre de 0,035 à 0,040 W/m/K (Li et al. 2013c ; Lacoste et al. 2013). De plus, leurs bonnes performances acoustiques les placent comme des potentiels absorbants acoustiques biosourcés, comparables à ceux disponibles actuellement sur le marché (Lacoste et al. 2015). Ainsi, les possibilités d'applications sont multiples et la densité finale de la mousse et donc sa résistance mécanique, doit être adaptée en fonction des applications visées.

Ces mousses à base de tanins, peuvent être employées directement en tant qu'isolant : à l'intérieur de panneaux en bois. Et ceci sans que leur acidité n'affecte significativement le bois (Tondi et al. 2008).

En comparaison aux mousses d'origines synthétiques, les mousses à base de tanins possèdent des conductivités thermiques comparables, tout en ayant de bonnes propriétés mécaniques. En effet, la conductivité thermique de la mousse de polyuréthane rigide est de 0,025 W/m/K ; de la mousse phénolique est comprise entre 0,018 et 0,035 W/m/K et celle du polystyrène expansé est de 0,036 W/m/K.

Un matériau d'isolation prêt à l'emploi a été mis au point (Zhou et al. 2013) : un panneau sandwich de mousses à base de tanins de mimosa (Figure 26). Des contreplaqués ou des panneaux à base de fibres de lin ont été collés sur une mousse de tanins à l'aide d'une colle tanins-résorcinol-formaldéhyde (TRF). Les propriétés mécaniques des panneaux sandwich dépendent essentiellement et directement des propriétés mécaniques de la mousse de tanins.



Figure 26 : Panneaux sandwich de mousses de tanins (Zhou et al. 2013)

En outre, les mousses à base de tanins peuvent être utilisées afin de dépolluer les eaux usées car ce sont des matériaux poreux qui sont capables d'adsorber des ions métalliques (Cu ou Pb). De plus, le type de tanins utilisés semble peu influencer la capacité d'adsorption mais la structure cellulaire quant à elle varie significativement (Tondi et al. 2009a). Ces mousses à base de tanins ont une grande capacité d'adsorption des polluants anioniques et cationiques ; comme le bleu de méthylène ou encore les produits pharmaceutiques. Ceci tout en ayant des propriétés comparables aux absorbants commerciaux (Sanchez-Martín et al. 2009 ; Sanchez-Martín et al. 2011a ; 2011b ; Sanchez-Martín et al. 2013a ; 2013b).

De plus, les mousses de tanins et de manière générale les mousses phénoliques possèdent une très bonne affinité avec l'eau et les solvants polaires (Figure 27) (Tondi et al. 2009b).

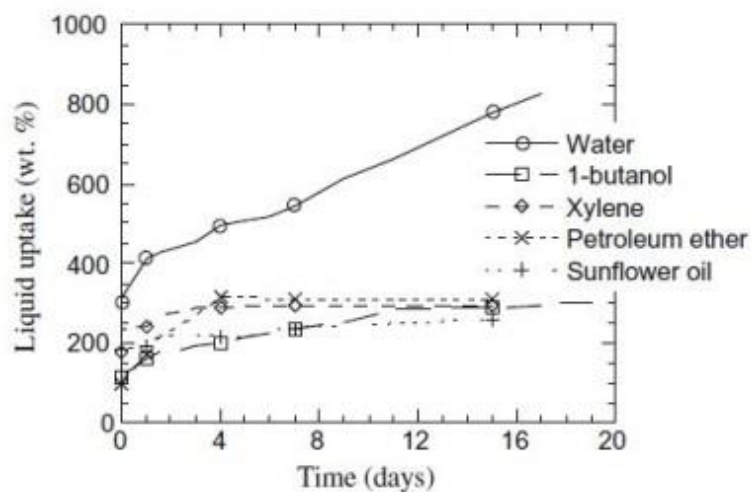


Figure 27 : Absorption de différents liquides par des mousses de tanins de mimosa (Tondi et al. 2009b)

Ainsi, une application s'est révélée pour les mousses à base de tanins : remplacer les mousses florales synthétiques, qui sont généralement phénoliques.



**Figure 28 : Mousses florales à base de tanins (Basso et al. 2013a)**

De plus, il est possible de réaliser des mousses sans solvant, sans formaldéhyde, à porosité complètement ouverte (ceci afin d'augmenter leur absorption de liquide) et en utilisant des catalyseurs alcalins : ceci afin de réaliser des mousses florales (Figure 28) (Basso et al. 2013a). En effet, il faut prêter attention au pH des mousses pour qu'elles ne soient pas trop acides afin que les fleurs piquées ne fanent pas trop rapidement.

## **2.7. Les abrasifs**

Un abrasif est une matière qui, par le biais d'un frottement, use un autre matériau qui possède une dureté inférieure à celle-ci.

Les abrasifs ou médias abrasifs (abrasifs agglomérés à des résines phénoliques) sont utilisés en polissage mécano-chimique. Il en existe de très nombreuses formes, des disques (à arêtes droites ou en biais), des billes, des cônes, des pyramides... La mécanisation des opérations d'ébavurage ou de polissage à l'aide des médias abrasifs, permet d'obtenir un traitement constant et très uniforme. Les abrasifs peuvent être utilisés dans des vibrateurs (circulaires ou linéaires) ou alors dans des centrifugeuses satellitaires à axe oblique). Les abrasifs peuvent être également projetés à grande vitesse sur la pièce à traiter. Ceci étant du sablage lorsque les grains d'abrasif sont angulaires, ou du microbillage lorsque les grains sont circulaires.

Les abrasifs sont caractérisés par deux principaux paramètres : la dureté des grains et la granulométrie de ceux-ci, qui influent sur l'état de surface final de la pièce à traiter.

Idéalement, le grain doit présenter une résistance maximum à l'usure des pointes et doit se casser avant d'être trop émoussé.

Concernant la nature même des abrasifs, les plus utilisés sont l'oxyde d'aluminium, le carbure de silicium, l'émeri, la poussière de diamant... La majorité des meules commerciales à liant vitreux utilisent soit des particules d'oxyde d'aluminium ou encore de carbure de silicium, ceci en fonction des applications (Rue 1985 ; Narayanan et al. 1988 ; Hay et al. 1990 ; Lee et Rue 1992 ; Jackson et al. 2001 ; Webster et Tricard 2004).

Les applications sont d'ailleurs diverses et variées : tronçonnage des métaux, préparation de surface, ébavurage, arasage, ponçage, polissage, décapage ou encore finition.

L'oxyde d'aluminium est résistant et totalement adapté à l'ébarbage des matériaux de haute ductilité comme les aciers, le bronze dur et les bois durs. Dans le cas des abrasifs appliqués, le carbure de silicium est le plus résistant et le plus angulaire des grains abrasifs utilisés. De plus, il ne nécessite seulement qu'une pression légère afin d'avoir une bonne coupe. Il représente donc l'abrasif idéal pour le ponçage des métaux non ferreux (aluminium, laiton, bronze...), le caoutchouc, les plastiques et autres matériaux tendres. Pour un ébarbage grossier des métaux avec une quantité importante de matière à enlever, l'alumine de zirconium est plutôt utilisé. En effet, il possède une caractéristique d'auto-affûtage. Ceci lui confère donc une grande longévité dans le temps. Pour un polissage, l'émeri est principalement utilisé. C'est un abrasif naturel composé de corindon et d'oxyde de fer (Norton 2015).

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## 4. TRAVAUX DE RECHERCHE

### 4.1. Prologue

Les travaux de recherche réalisés pendant cette thèse peuvent être classés en quatre parties :

- Adhésifs pour matériaux lignocellulosiques
- Mousses phénoliques avec substitution partielle du phénol par des tanins
- Mousses solides biosourcées à base de tanins
- Matériaux abrasifs et de friction biosourcés.

Tout d'abord, des travaux ont été menés dans l'optique de développer des adhésifs pouvant être utilisés dans l'industrie du bois et étant de plus en plus respectueux de l'environnement et de moins en moins toxiques. Ainsi, des colles mélamine-glyoxal pour la fabrication de contreplaqués ont été préparées et celles-ci ont été analysées chimiquement. Un autre type de colle a été développé : des colles phénoliques avec une substitution partielle du phénol par des hydrolysats de protéines de blé. De même, une analyse chimique des colles a été réalisée. Des panneaux de particules ont été préparés et caractérisés.

Dans un second temps, des résines phénoliques ont synthétisées en substituant partiellement le phénol par des tanins. Cette fois-ci des mousses solides ont été réalisées. Les résines et les mousses ont été caractérisées. Ceci donnant des mousses partiellement biosourcées mais ayant des caractéristiques comparables aux mousses synthétiques.

Ensuite, des travaux ont été menés afin de développer des matériaux quasiment totalement biosourcés. Premièrement, en développant des mousses à base de tanins de quebracho. Initialement, les mousses à base de tanins ont été mises au point avec les tanins de mimosa mais les recherches actuelles se tournent plutôt vers les tanins de quebracho. Ces mousses naturelles peuvent être uniquement tanniques ou encore tanins-furaniques. Ce premier type permet d'obtenir des mousses moins acides pour pouvoir être directement appliquées sur le bois dans la fabrication de produits d'isolation, ou encore être utilisées dans l'art floral. Enfin, la conception des mousses tanins-furaniques dépend intégralement des formulations de celles-ci. Ainsi, une étude sur leurs

différents composants a été menée afin de montrer leurs effets sur la structure même des mousses mais également sur leurs propriétés.

Dans un dernier temps, comme la résine tanins-furanique des mousses s'est révélée être une résine de haute résistance mécanique, l'idée est venue de l'utiliser pour d'autres produits que les mousses. Ainsi, des matériaux abrasifs et de friction à matrice biosourcée ont été développés. Les faisabilités de mettre en œuvre : des roues abrasives naturelles ; des disques abrasifs naturels pouvant être utilisés avec une meuleuse d'angle (11 000 tours/min), en tronçonnage ou en meulage ; mais également des plaquettes de frein automobile utilisées et testées en conditions réelles, ont totalement été démontrées.

## 4.2. Adhésifs pour matériaux lignocellulosiques

### 4.2.1. Adhésifs à bois : phénol-protéines de blé-formaldéhyde

# « *Phenol-wheat protein-formaldehyde thermoset wood adhesives* »

Auteurs : M.C. Lagel<sup>1</sup>, A. Pizzi<sup>1,2</sup>, A. Redl<sup>3</sup> et F. M. Al-Marzouki<sup>2</sup>.

<sup>1</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>2</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

<sup>3</sup>Tereos Syral, Zoning Industriel Portuaire, Marckolsheim, France

#### Résumé :

Les résines phénol-formaldéhyde (PF) ont été préparées avec des taux de substitution de 10, 20 et 30 % en masse du phénol par trois types d'hydrolysats de protéines de blé. Ces hydrolysats ayant des caractéristiques différentes : (1) des hydrolysats enzymatiques, (2) des hydrolysats enzymatiques de masses moléculaires inférieures, et (3) des hydrolysats acides de masses moléculaires intermédiaires. Toutes ces résines ont été caractérisées par leur pH, leur viscosité et par analyse thermomécanique. La distribution des espèces mixtes protéines-oligomères phénoliques formées dans la préparation de ces résines a été identifiée par spectrométrie de masse couplant une source d'ionisation laser assistée par une matrice et un analyseur à temps de vol (MALDI-ToF).

# Phenol-wheat protein-formaldehyde thermoset wood adhesives

M. C. Lagel<sup>1</sup> · A. Pizzi<sup>1,2</sup> · A. Redl<sup>3</sup> · F. M. Al-Marzouki<sup>2</sup>

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**Abstract** Phenol–formaldehyde (PF) resins were prepared with a level of 10, 20 and 30 % substitution of the phenol in the resin by three types of wheat gluten protein hydrolysates having different characteristics, namely (1) an enzymatic hydrolysate, (2) a lower molecular weight enzymatic hydrolysate, and (3) a middle sized molecular weight acid hydrolysate. All these resins were characterized by their pH, their viscosities and by thermo mechanical analysis. The mixed protein–phenolic oligomer species distribution formed in the preparation of these resins were identified by matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry.

## 1 Introduction

Exterior and marine grade particleboard and other panels of the same type for construction use phenol–formaldehyde (PF) binders for their durability, particularly in North America. Although the emission of formaldehyde from PF bonded panels is relatively low, reduction of formaldehyde emission and at least a partial substitution of the oil-derived phenol with natural resources are still a topic. Literature on both, the reduction of formaldehyde and in particular on the partial substitution of phenol itself with natural

materials exists. Partial or total substitution of phenol with condensed tannins (Pizzi 1983), with hydrolysable tannins (Spina et al. 2012, 2013), with soy protein hydrolysates (Kaichang and Yuan 2007), or combinations of soy protein or flours with isocyanates (Amaral-Labat et al. 2008) have been attempted, some with a fair degree of success. Some studies were even conducted on the feasibility to use gluten in wood-panels adhesives (Lei 2009; Lei et al. 2010; Krug 2003; Krug and Tobisch 2010). It must be kept in mind that just in Europe alone there are more than half a million tons/year of wheat gluten that is extracted from wheat to produce starch and starch derivatives. 75 % of the extracted gluten is added to bakery products in order to fortify wheat flour and a significant amount is used for animal feed (~20 %) but there is still a significant potential of use in industrial applications.

This article is about the feasibility of replacing and capture formaldehyde in wood adhesives by natural components like wheat gluten hydrolysates proteins.

## 2 Materials and methods

Three types of wheat protein hydrolysates having different characteristics were tested (Fig. 1; Table 1): (1) *Solpro 508* (enzymatic hydrolysates); (2) *LMW Protein* (smaller enzymatic hydrolysates), and (3) *Solpro 050* (middle sized acid hydrolysates). All proteins were provided by Tereos Syral (Marckolsheim, France). Hydrolysates were prepared by proprietary process under mild process conditions. Wheat proteins are extracted from wheat flour by an aqueous extraction process yielding a concentration in proteins from approximately 10 % protein in wheat flour to 75–80 % protein in vital wheat gluten. Remaining components are mainly residual starch and lipids. Here wheat

✉ M. C. Lagel  
lagel.mc@gmail.com

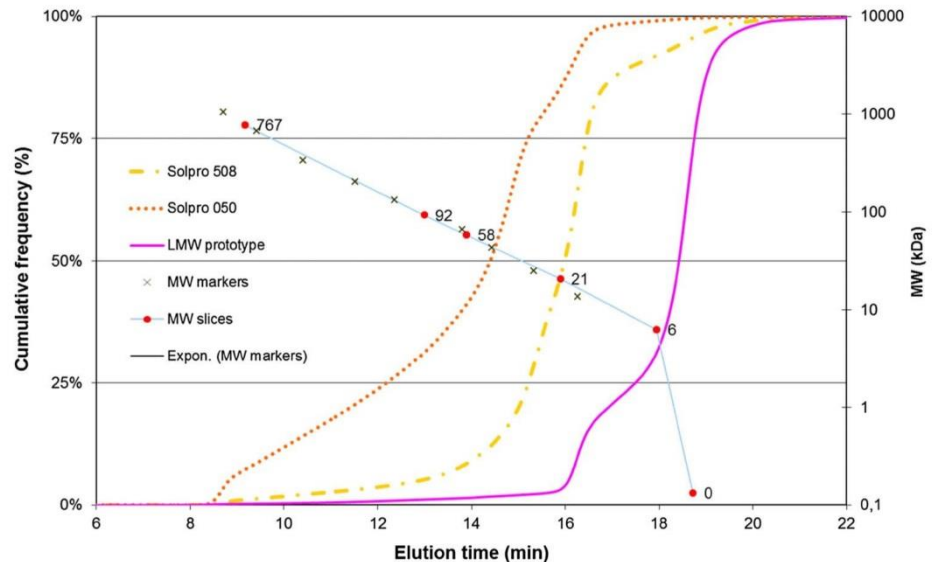
<sup>1</sup> LERMAB, University of Lorraine, 27 rue Philippe Seguin, 88051 Epinal, France

<sup>2</sup> Department of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

<sup>3</sup> Tereos Syral, Zoning Industriel Portuaire, 67390 Marckolsheim, France



**Fig. 1** Cumulative molecular weight distribution of wheat protein hydrolysates (LMW Protein, Solpro 508 Solpro 050) and calibration curve for the used column set



gluten was used as substrate for the hydrolysates, the other proteins present in wheat (albumins and globulins) are only found in traces.

Wheat protein hydrolysates are a yellow light powder. Solpro 508 and LMW protein have solubility (pH 6.2) of 65 %; they have target values of crude protein of 80 %, crude ash of 1 % and of crude fat of 6 %.

Solpro 050 has solubility (pH 6.2) of 65 %; it has target values of crude protein of 82 %, of crude ash of 4 % and of crude fat of 8.5 %

The cumulative chromatograms of wheat protein hydrolysates (LMW Protein, Solpro 508 Solpro 050) and the calibration curve are shown in Fig. 1. The molar mass distribution is pictured like in a mirror when transferring the elution volume scale to a molar mass scale using the shown calibration curve. These data are obtained by a Size-Exclusion Chromatography (SEC) including size exclusion High Performance Liquid Chromatography (HPLC) analysis done by Tereos Syral. The SE-HPLC apparatus was a Waters model (Alliance) controlled by Millenium software (Waters). A TSK G4000-SWXL (Tosoh Biosep) size exclusion analytical column (7.8 mm 300 mm) was used with a TSK SWXL (Tosoh Biosep) guard column (6 mm 40 mm). The columns were eluted at ambient temperature with 0.1 M sodium phosphate buffer (pH 6.9) containing 0.1 % SDS. The flow rate was 0.7 mL/min, and proteins were recorded at 214 nm.

## 2.1 Synthesis of thermoset adhesives

### 2.1.1 Phenol formaldehyde resin

The PF control resin (molar ratio F/P = 1.7) was synthesized as follows: 1 mol of phenol as a 80 % phenol,

0.35 mol of sodium hydroxide as a 30 % water solution, and 1.7 mol of formaldehyde as a 37 % aqueous solution were used according to a preparation procedure already reported earlier by Zhao et al. (2000).

The mixture is slowly brought to reflux at 94 °C under continuous stirring within about 30 min. Once this temperature is reached, the mixture is left to react for 30 min.

In a second step, 0.5 mol of formaldehyde is added. The reaction is performed until a viscosity of 500–800 mPa.s at 25 °C is reached. The pH of the resulting resin is approximately 11.

### 2.1.2 Phenol formaldehyde resin with wheat protein hydrolysates

Three degrees of mass substitution of 80 % phenol by the three types of protein hydrolysates were tested: 10, 20, and 30 % in mass, based on the same formulation and procedure outlined above. The same amounts of sodium hydroxide and of formaldehyde were added. This type of resin has an original molar ratio F/P = 1.7 (Pizzi et al. 2013).

A second type of resin containing proteins was synthesized with protein hydrolysates of low molecular weight (LMW protein), with substitution rates of 10 and 20 %. In this case no second addition of formaldehyde was performed. This type of resin had an original molar ratio F/P = 1.5 (also called type 2 resin).

The mentioned molar ratios only refer to phenol, but in reality amino acids present in amino groups in hydrolysates proteins are capable to react also with the formaldehyde and thus the real molar ratios are even lower. On the basis of glycine equivalent of the protein, thus considering only

the skeletal amino groups of the protein, thus not taking into account the amino groups of the side chains of some of the constituent amino acids, the final molar ratio is of 1:1.96 molar maximum for a 30 % substitution rate. If the amino groups of glutamine are also taken into account the molar ratio falls to a value of around 1:1.8–1.85.

As the resin was prepared under alkaline conditions two reactions predominate: (1) the reaction of phenolic ortho and para free sites with the methylol groups on the PF resin and with any free formaldehyde present, and (2) the initial addition reaction of the formaldehyde both as such and in the form of methylol groups on the PF resin with the amide groups of the protein and with the scarcer amino groups of some amino acids. As the initial addition (not condensation) of formaldehyde with amides in alkaline environment in the presence of a PF resin is competitive with the phenol–formaldehyde reaction itself (Pizzi 1994; Pizzi et al. 1993), this leads to the formation of methylene bridges between different sites, namely, phenol to phenol, and phenol to amide group of the protein.

## 2.2 Test on thermoset adhesives

### 2.2.1 pH, viscosity and solid content

The viscosity of the resins was determined by a Brookfield viscometer at 25 °C, with a speed of 50 rpm.

The solids content of the resins was determined according to the European Norm NF EN ISO 3251 (AFNOR 2008) by drying in an oven at 103 °C until the mass of residue is stable, generally it takes one day (Table 2).

### 2.2.2 MALDI-TOF analysis

**MALDI-TOF-MS** The spectra were recorded on a AXIMA Performance MALDI instrument (Shimadzu, Manchester, UK). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

**MALDI-TOF sample preparation** The samples were dissolved in acetone (4 mg/mL). The sample solutions were mixed with an acetone solution (10 mg/mL acetone) of the matrix. As matrix 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation NaCl was added to the matrix. The solutions of the sample and the matrix were mixed in equal amounts and 0.5–1 µL of the resulting solution was placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer.

**Table 1** Standards used for the SEC-HPLC analysis of wheat protein hydrolysates

Standards	MW (Da)
Thyroglobulin	1050,000
Thyroglobulin	670,000
Thyroglobulin	335,000
Bovine albumin	204,000
Bovine albumin	132,000
Bovine albumin	66,000
Ovalbumin	43,000
Chymotripsinogen A	25,000
Ribonuclease A	13,700
Blue dextran = Vo	2,000,000
Asparagine = Vt	132.1

### 2.2.3 Thermo mechanical analysis (TMA)

TMA (Mettler Toledo TMA 40, Switzerland) was used to perform the analyses. The samples for this test were composed of two pieces of beech veneer ( $0.5 \times 5 \times 21 \text{ mm}^3$ ) with an amount of 30 mg resin evenly spread on this area (15 mg on each piece), they were immediately put in contact and tested. All resins were tested with and without triacetin.

For TMA, a three-point bending force of 0.1–0.5 N was applied and relaxed with a period of 6/6 s causing periodical deflection of the sample and enabling calculation of the modulus of elasticity (MOE) of the joint sample as a function of the increasing temperature (ramp 10 °C/min).

The maximum of the elasticity modulus is achieved for the maximum of the polymerization temperature; indeed at this temperature all chains are fixed. At this time, the polymerization is over and if the temperature is still increasing, the degradation of the resin begins and there are no further reactions.

## 3 Results and discussion

### 3.1 pH, viscosity, and solid content of thermoset adhesives

Generally, the viscosities are between 500 and 800 mPa.s (Table 2). The aim was to get a viscosity at 25 °C between 500 and 800 mPa.s, so all resins don't have exactly the same reaction time, and no link between viscosities and types of hydrolysates protein can be done.

The pH values are in the range of 10.3–11.7 and are all lower than for the PF control even if the amount of NaOH was the same for every synthesized resin. It is due to the pH of protein which is about 6 (Table 2).



**Table 2** pH, viscosity, and solid content of all PF resins tested

Resins	pH	Viscosity (mPa.s)	Solid content (%)
PF	12.3	695	46.9
PF-10 % LMW	10.3	642	45.2
PF-20 % LMW	11.2	715	49.5
PF-30 % LMW	11.3	850	48.4
PF-10 % LMW (Type 2)	11.4	950	49.1
PF-20 % LMW (Type 2)	11.1	462	50.6
PF-10 % Solpro 508	11.3	850	45.6
PF-20 % Solpro 508	11.7	895	45.8
PF-30 % Solpro 508	11.4	875	48.0
PF-10 % Solpro 050	11.4	550	47.8
PF-20 % Solpro 050	11.5	795	48.4

The high viscosity of solutions of the hydrolysates of gluten proteins at concentrations of 50 % where possible or otherwise 25 % in water (Table 3) indicate that (1) the viscosity obtained for PF-protein cocondensates shown in Table 2 are indeed not too high, as indicated by the experimental values obtained, and (2) that it is rather likely that higher molecular weight fractions of the proteins exist in the hydrolysates higher than what is determinable by MALDI-TOF spectrometry. Moreover the SEC-HPLC curves in Fig. 1 show that very high molecular weight fractions are present in the hydrolysates. As traces of carbohydrates are not detected in the MALDI-TOF analysis, it must be assumed that these higher molecular weight fractions are due to the protein material too, and the viscosity does not increase consequently. The higher molecular masses observed by SEC-HPLC are most probably aggregates, the existence of which has already been observed for formaldehyde-based resins (Lei et al. 2006).

The solids are near 50 %, as stipulated in the experimental procedure adopted (Zhao et al. 2000) (Table 2). As the liquid 80 % phenol was replaced by solid hydrolysates protein, the higher the substitution of phenol with the protein hydrolysate, the higher the solid contents are, except in the case of the resin with LMW protein with an original molar ratio F/P = 1.7. At low replacement rate the solid contents are partly still lower than the PF control, as in the case for the LMW and the Solpro 508. Maybe in the other cases, some reaction takes place during the determination of the solid content and yield to the formation of water which then also is evaporated, so solids contents are higher.

### 3.2 MALDI-TOF analysis of thermoset adhesives

Three formulations were tested: PF-(10 and 20 %) Solpro 050 and PF-20 % LMW (type 2).

**Table 3** Viscosity of all wheat protein hydrolysates tested

Proteins	Viscosity (mPa.s)
LMW protein (50 % in water)	20,100
Solpro 508 (50 % in water)	38,330
Solpro 050 (25 % in water)	62,580

According to the literature (Finney et al. 1982; Belderok et al. 2000) gluten is the main component in wheat protein and the main amino acids in gluten are at 31.9 % Glutamine (MW 146.2), at 14.1 % Proline (MW 115.1), at 7.2 % Leucine (MW 131.2), at 5.7 % Serine (MW 105.1) and at 5.4 %: Glycine (MW 75.1) (Rombouts et al. 2009).

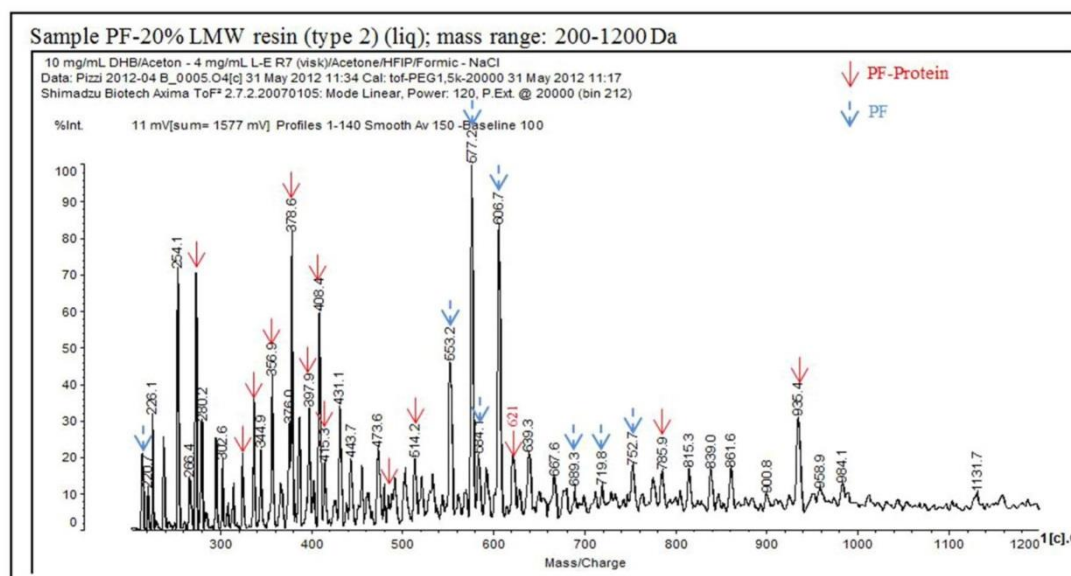
As we are dealing with gluten protein hydrolysates, thus with heavily modified materials, it was necessary to control their composition relative to gluten itself as shown in the literature. For this reason MALDI-TOF mass spectrometry was used to determine the composition of the materials used.

In reality there is a variation in the composition between the gluten hydrolysates used and the relative amino acids distribution in gluten itself. Thus, while in these materials the amino acids Glutamine, Proline, Leucine, Serine and Glycine predominate in gluten itself (Rombouts et al. 2009) the distribution is rather Glutamine, Leucine, Phenylalanine, Tyrosine, and Alanine.

As control PF resins were synthesized by alkaline catalysis as polycondensation of phenol and formaldehyde, phenol units are linked in order to form a polymer via methylene bridges. Each ortho or para position of phenolic rings may react with formaldehyde (Schrod et al. 2003). It is not possible to define from MALDI-TOF analysis the predominance of ortho–ortho, ortho–para or para–para linkages. In reality, classical phenol–formaldehyde reaction theory indicates that while the reactivity of the para sites is slightly higher than the ortho one, the presence of two ortho sites and only one para site give distributions that are often not very different (Megson 1958).

Reactions between phenol and formaldehyde give  $-\text{CH}_2-$ ,  $-\text{CH}_2^+$ , or  $-\text{CH}_2\text{OH}$  attached to phenol.

The focus in this paper here is on the reactions of the amino acids present in the protein hydrolysates with formaldehyde or with already formed PF groups during the resin preparation. Figure 2 shows as an example the MALDI-TOF spectrum of the PF resin modified with 20 % LMW and without second addition of formaldehyde (type 2 reaction). Peaks representing the reactions which involve various PF resin groups and protein hydrolysates are marked with arrows in solid lines. Peaks only resulting from the reaction between phenol and formaldehyde are indicated by dotted arrows. It may be supposed that there are reactions between PF resin groups and the amino acids



**Fig. 2** MALDI-TOF spectrum of the liquid resin PF-20 % LMW (type 2) for a range from 200 to 1200 Da

of the protein, because as previously found, PF resin spectrum give peaks until 800 Da and here it is quite the same range but with a number of peaks more important (Lagel et al. 2014).

Table 4 summarizes the molecules which can be assigned to the various molecular weights according to the reactions between (1) phenol and formaldehyde as well as (2) between the amino acids of the protein and PF resin groups. It was calculated by adding the molecular weight of amino acid with PF resin groups and the molecular weight of Na. The possibility that amino group of the amino acids reacts directly with formaldehyde is excluded in this paper because the spectra always begin solely at 200 Da.

The results in Tables 4 and 5 show that glutamine is the amino acid most implicated in reactions with phenol and formaldehyde, leading to molecular weights of 379, 274, and 408 Da in order of predominance. It could be explained by the fact that this amino acid is more reactive due to the presence of two amino groups. Indeed the other amino acids contain only one amino group.

Because of the important number of peaks, this analysis is focused on the resin containing LMW protein hydrolysates (protein hydrolysates of smaller size relative to the others). Thus, there is an important number of different molecules formed even if molecular weights of such molecules are quite similar (up to 1132 Da). Thus, LMW and Solpro 050 protein hydrolysates where the last molecule is at 1047 Da are in the range of this analysis. Thus, due to their similarities in molecular weight one cannot see an influence of the molecular weight of the hydrolysates on the rate of the reaction with phenol and formaldehyde. Not a

lot of peaks are seen for the analysis of the resin with protein hydrolysates Solpro 050. It can be presumed that it is because amino acids reacted with PF resin groups have precipitated. It would be for this reason why they do not appear in the spectra. It may then be because Solpro 050 is an acid hydrolysate. Thus there are not so many different molecules that have been formed during the reaction. Analyses of dry samples do not provide additional information.

The main reactions between PF resin groups and key amino acids of gluten in the three formulations which were analyzed by MALDI-TOF are summarized in Table 5.

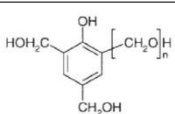
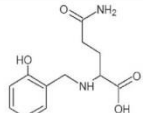
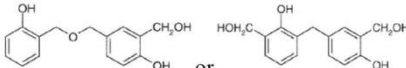
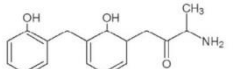
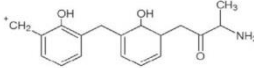
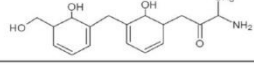
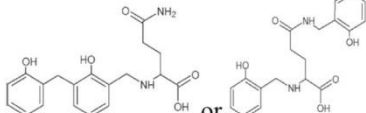
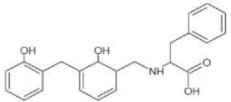
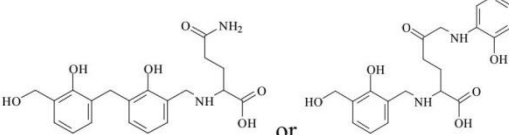
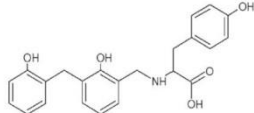
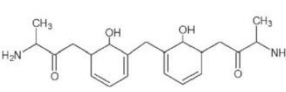
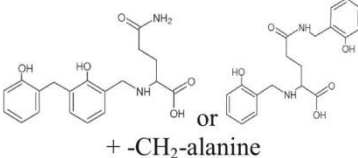
The peak intensities are given in relation to the most important peak of each spectrum for each resin tested. In PF-20 % LMW (type 2) resin the most intense peak involving coreaction between phenol formaldehyde and protein is at 379 Da and has an intensity of 82 %. In contrast, in the PF-10 % Solpro 050 resin this peak only shows a very low intensity of 2 %, which is the lowest one. The highest peak is at 577 Da and corresponds to a PF resin group alone.

In the PF-20 % Solpro 050 resin the most important peak (associated with 100 % intensity) occurs at 408 Da involving glutamine. The peak with the second highest intensity at 379 Da also involved glutamine.

Evaluating all three spectra the most important reactions yield the peaks at 379 and 408 Da involving glutamine.

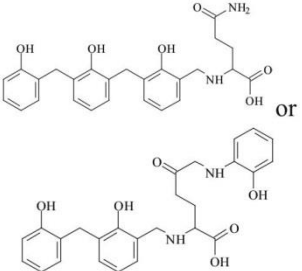
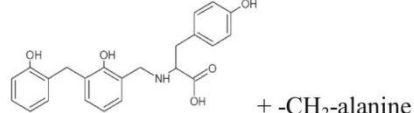
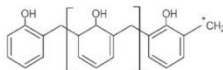
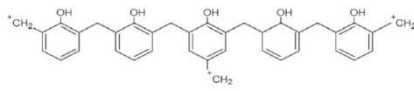
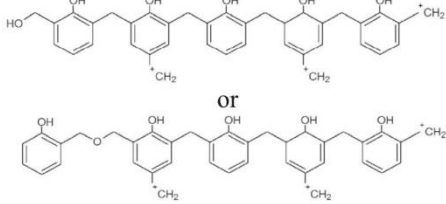
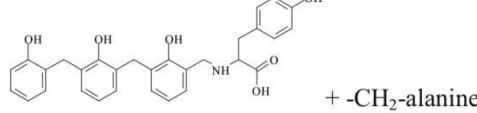
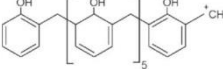
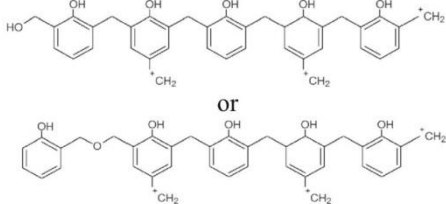
In MALDI-TOF experiences the methylene linkages between the phenols of the PF resin are stable (Schrod et al. 2003; Pizzi et al. 2004), thus one does not experience decomposition or rearrangements on this part of the product. However, some instability may exist in the case of the

**Table 4** Peaks corresponding (1) to PF resin groups with different molecular weight and (2) to structures resulting from reactions between PF resin groups and key amino acids of gluten in PF-20 % LMW resin (type 2, without second formaldehyde addition)

<i>Molecular weight with Na<sup>+</sup> (Da)</i>	<i>Theoretical molecular weight with Na<sup>+</sup> (Da)</i>	<i>Molecules</i>	<i>Amino acid</i>
238.4	237	 n=2	PF resin group
274.2	274		Glutamine
284.7	283		PF resin group
324.5	324		Alanine
336.6	336		Alanine
356.9	356		Alanine
378.6	379		Glutamine
397.9	398		Phenylalanine
408.4	408		Glutamine
415.3	414		Tyrosine
425.6	425		Alanine
480.1	480	 + -CH <sub>2</sub> -alanine	Alanine and glutamine



**Table 4** continued

485	485		Glutamine
514.2	515	 + -CH <sub>2</sub> -alanine	Alanine and tyrosine
553.2	553		PF resin group
577.2	577		PF resin group
606.7	606	 or	PF resin group
621	621	 + -CH <sub>2</sub> -alanine	Alanine and tyrosine
752.7	754		PF resin group
785.9	786	 or	Tyrosine
935.4	934	786 + Glutamine attached to -CH <sub>2</sub>	Tyrosine and glutamine

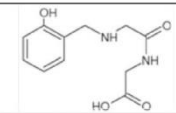
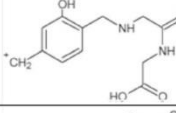
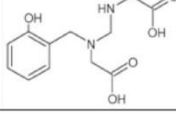
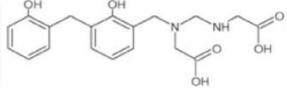
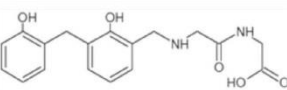
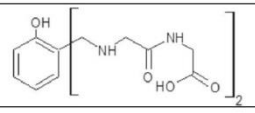
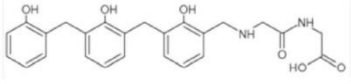
methylene linkages between the PF resin groups and amino groups, and between amino groups (Despres et al. 2007) hence of the protein. In effect some rearrangements of the

hydrolysates protein might occur, as indeed shown by the peaks at 274, 291, and 471 Da (in order of predominance) (Fig. 3; Table 6).

**Table 5** Peaks corresponding to the molecular weight of main reactions between phenol and formaldehyde as well as the amino acids alanine, glutamine, and tyrosine

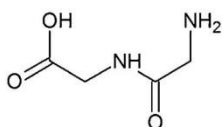
Theoretical molecular weight with Na <sup>+</sup> (Da)	Amino acid involved	PF-20 % LMW (type 2)		PF-10 % Solpro 050		PF-20 % Solpro 050	
		Molecular weight with Na <sup>+</sup> (Da)	Peak intensity (%)	Molecular weight with Na <sup>+</sup> (Da)	Peak intensity (%)	Molecular weight with Na <sup>+</sup> (Da)	Peak intensity (%)
274	Glutamine	274.2	71	273.1	4	272.3	1
324	Alanine	324.5	22	325.3	4	326.1	4
336	Alanine	336.6	36	–	–	336.2	2
356	Alanine	356.9	42	–	–	357.2	1
379	Glutamine	378.6	82	378.2	2	378.6	30
408	Glutamine	408.4	60	407.5	4	408.6	100
480	Alanine and glutamine	480.1	13	–	–	480.3	3
786	Tyrosine	785.9	17	–	–	786.0	4

**Table 6** Reactions between glycines and PF resin groups as well as formaldehyde in PF-20 % LMW (type 2) resin

<i>Molecular weight with Na<sup>+</sup> (Da)</i>	<i>Theoretical molecular weight with Na<sup>+</sup> (Da)</i>	<i>Molecules</i>
262	261	
274.2	274	
293.9	291	
308.5	309	
366.5	366	
402.6	404	
473.6	471	

**Table 7** Thermo mechanical analysis results

Formulation	Temperature (°C)		Elasticity modulus (MPa)	
	Without triacetin	With triacetin	Without triacetin	With triacetin
PF	165	151	3752	4267
PF-10 % LMW	154	159	5029	5219
PF-20 % LMW	153	156	6519	5891
PF-30 % LMW	163	168	7183	8476
PF-10 % LMW (Type 2)	164	157	5254	4899
PF-20 % LMW (Type 2)	165	161	5809	9920
PF-10 % Solpro 508	158	145	5364	3732
PF-20 % Solpro 508	152	171	4981	5469
PF-30 % Solpro 508	154	171	5637	6710
PF-10 % Solpro 050	160	162	5779	10,253
PF-20 % Solpro 050	157	146	4823	7507

**Fig. 3** Two glycines (MW 132)

### 3.3 Thermo mechanical analysis (TMA) of thermoset adhesives

Concerning the resins containing 20 % of LMW (Type 2) and 20 % Solpro 050, the use of triacetin had a positive effect on the properties. A diminution of the maximum temperature of polymerization and also an augmentation of the maximum of elasticity modulus are noticed (Table 7). Compared to PF resin, without triacetin, PF-hydrolysates proteins have lower maximum temperature of polymerization and higher elasticity modulus. With triacetin, PF-hydrolysates proteins have higher maximum temperature of polymerization (except for PF-10 % Solpro 508 and PF-20 % Solpro 050) but higher elasticity modulus (except for PF-10 % Solpro 508) in comparison to PF resin (Table 7).

Looking at the elasticity modulus for the same substitution rate, the best performing protein hydrolysates can be evaluated. For a substitution rate of 10 %, the best protein is Solpro 050, because the elasticity modulus is about twice that with triacetin. In addition, for substitution rates of 20 and 30 %, the best protein is LMW, because with triacetin they have the highest elasticity modulus.

## 4 Conclusion

This study was performed to compare the performances of phenolic resins containing wheat protein hydrolysates with conventional phenolic resins. The aim in the coming years

is to develop the use of wheat proteins and more generally natural resources in wood adhesives while retaining the properties of the standard panels. The addition of triacetin to phenolic resins containing wheat proteins improves the performance of these thermoset adhesives. It would be interesting to synthesize resins with a higher degree of substitution (30 % or even higher), in using LMW protein and Solpro 050. The results of this study on the addition of wheat protein hydrolysates in phenolic resins seem to be encouraging, and are a further step toward the development of bio-based adhesives.

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*4.2.2. Adhésif phénol-formaldéhyde-protéines de blé pour fabrication de panneaux de particules*

**« Phenol-Wheat protein-Formaldehyde adhesives for wood-based panels »**

Auteurs : M.C. Lagel<sup>1</sup>, A. Pizzi<sup>1,2</sup> et A. Redl<sup>3</sup>.

<sup>1</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>2</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

<sup>3</sup>Tereos Syral, Zoning Industriel Portuaire, Marckolsheim, France

Résumé :

Les résines phénol-formaldéhyde (PF) ont été préparées avec un niveau de 10 %, 20 % et 30 % de substitution du phénol dans la résine par trois types d'hydrolysats de protéines de blé ayant des caractéristiques différentes, à savoir (i) un hydrolysate enzymatique, (ii) un poids moléculaire hydrolysate enzymatique inférieur, et (iii) une taille de l'hydrolysate acide de poids moléculaire intermédiaire. La distribution des espèces de protéine oligomère phénolique mixte formée dans la préparation de ces résines a été identifiée par spectrométrie de masse couplant une source d'ionisation laser assistée par une matrice et un analyseur à temps de vol (MALDI-ToF).

Mots-clés : Colles biosourcées, Colles phénol-formaldéhyde, Protéines de blé, Colles à bois.

## PHENOL - WHEAT PROTEIN - FORMALDEHYDE ADHESIVES FOR WOOD - BASED PANELS

**Marie-Christine LAGEL**

M.Sc. - University of Lorraine

Address: LERMAB, 27 rue Philippe Seguin, 88051 Epinal, France

E-mail: [marie-christine.lagel@univ-lorraine.fr](mailto:marie-christine.lagel@univ-lorraine.fr)

**Antonio PIZZI**

Dr.Chem., Ph.D., D.Sc - University of Lorraine<sup>1</sup> & King Abdulaziz University<sup>2</sup>

Address: 1. LERMAB, 27 rue Philippe Seguin, 88051 Epinal, France

2. Dept. of Physics, Jeddah, Saudi Arabia

E-mail: [antonio.pizzi@univ-lorraine.fr](mailto:antonio.pizzi@univ-lorraine.fr)

**Andreas REDL**

Dr. - Tereos Syral

Address: Zoning Industriel Portuaire, 67390 Marckolsheim, France

E-mail: [andreas.redl@tereos.com](mailto:andreas.redl@tereos.com)

### **Abstract:**

*Phenol-formaldehyde (PF) resins were prepared with a level of 10%, 20% and 30% substitution of the phenol in the resin by three types of wheat gluten protein hydrolysates having different characteristics, namely (i) an enzymatic hydrolysate, (ii) a lower molecular weight enzymatic hydrolysate, and (iii) a middle sized molecular weight acid hydrolysate. The mixed protein-phenolic oligomer species distribution formed in the preparation of these resins were identified by matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry.*

**Key words:** *biobased resins; phenol formaldehyde resins; wheat gluten proteins; wood adhesives.*

### **INTRODUCTION**

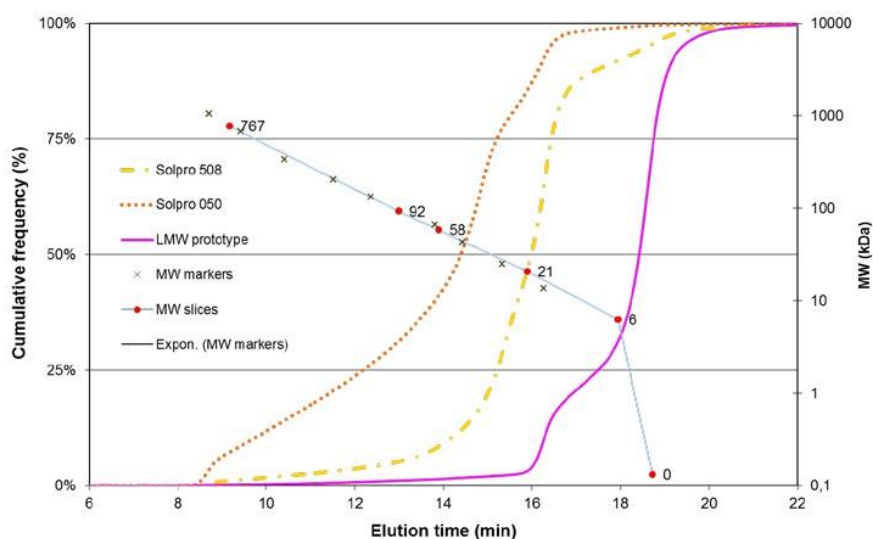
Exterior and marine grade particleboard and other panels of the same type for construction use phenol-formaldehyde (PF) binders for their durability, particularly in North America. Although the emission of formaldehyde from PF bonded panels is relatively low reduction of formaldehyde emission and at least a partial substitution of the oil-derived phenol with natural material are still a topic. Literature on both, the reduction of formaldehyde and in particular on the partial substitution of phenol itself with natural materials exists. Partial or total substitution of phenol with condensed tannins (Pizzi 1983), with hydrolysable tannins (Spina *et al.* 2012, 2013), with soy protein hydrolysates (Kaichang *et al.* 2007), or combinations of soy protein or flours with isocyanates (Amaral-Labat *et al.* 2008) have been tried, some with a fair degree of success. Some studies were even conducted on the feasibility to use gluten in wood-panels adhesives (Lei *et al.* 2009, 2010; Krug 2003; Krug *et al.* 2010). It must be kept in mind that just in Europe alone there are more than half a million tons/year of wheat gluten that is extracted from wheat to produce starch and starch derivatives. Main part (75%) of the extracted gluten is added to bakery products in order to fortify wheat flour and a significant amount is used for animal feed (~20%) but there is still a significant potential of use in industrial applications.

### **OBJECTIVE**

This article is about the feasibility of replacing and capturing formaldehyde in wood adhesives by natural components like wheat gluten proteins.

### **METHOD**

Three types of wheat protein hydrolysates having different characteristics have been tested (Fig. 1): (i) *Solpro 508* (enzymatic hydrolysates); (ii) *LMW Protein* (smaller enzymatic hydrolysates), and (iii) *Solpro 050* (middle sized acid hydrolysates).



**Fig. 1.**

**Title: Cumulative molecular weight distribution of wheat protein hydrolysates (LMW Protein, Solpro 508 Solpro 050) and calibration curve for the used column set.**

All proteins have been provided by Tereos Syral (Marckolsheim, France). Hydrolysates have been prepared by proprietary process in mild process conditions. Wheat proteins are extracted from wheat flour by an aqueous extraction process yielding a concentration in proteins from approximately 10% protein in wheat flour to 75-80% protein in vital wheat gluten. Remaining components are mainly residual starch and lipids. Here wheat gluten has been used as substrate for the hydrolysates, the other proteins present in wheat (albumins and globulins) are only present in traces.

Wheat protein hydrolysates are a yellow light powder. Solpro 508 and LMW protein have solubility (pH 6.2) of 65%; they have target values of crude protein of 80%, of crude ash of 1% and of crude fat of 6%. Solpro 050 has solubility (pH 6.2) of 65%; they have target values of crude protein of 82%, of crude ash of 4% and of crude fat of 8.5%.

Cumulative molecular weight distribution of wheat protein hydrolysates (LMW Protein, Solpro 508 Solpro 050) and calibration curve are shown in Fig. 1 (The molar mass distribution is shown like in a mirror). These data are obtained by a Size-Exclusion Chromatography (SEC) including size exclusion High Performance Liquid Chromatography (HPLC) analysis (Table 1).

Table 1

**Standards used for the SEC-HPLC analysis of wheat protein hydrolysates**

Standards	MW (Da)
Thyroglobulin	1,050,000
	670
	335
Bovine albumin	204
	132
	66
Ovalbumin	43
Chymotripsinogen A	25
Ribonuclease A	13,7
Blue Dextran = Vo	2,000,000
Asparagine = Vt	132



## **1.1. Synthesis of phenolic resins and particle boards**

### **1.1.1. Phenol formaldehyde resin**

The PF control resin (molar ratio F/P = 1.7) was synthesized as follows: 1 mole of phenol as a 80% phenol, 0.35 mole of sodium hydroxide as a 30% water solution, and 1.7 mole of formaldehyde as a 37% aqueous solution were used according to a preparation procedure already reported earlier (Zhao *et al.* 2000).

The mixture is slowly brought in about 30 minutes to reflux at 94°C under continuous stirring. Once this temperature is reached, the mixture is left to react for 30 minutes.

In a second step, 0.5 mole of formaldehyde is added. The reaction is continued until a viscosity of 500 to 800mPa.s at 25°C is reached. The pH of the resulting resin is approximately 11.

### **1.1.2. Phenol formaldehyde resin with wheat protein hydrolysates**

Three degrees of mass substitution of 80% phenol by the three types of protein hydrolysates are tested: 10, 20, and 30% in mass, based on the same formulation and procedure outlined above. The same amounts of sodium hydroxide and of formaldehyde were added. This type of resin has an original molar ratio F/P = 1.7 (Pizzi *et al.* 2013).

A second type of resin containing proteins was synthesized with protein hydrolysates of low molecular weight (LMW protein), with substitutions rates of 10 and 20%. In this case no second addition of formaldehyde was performed. This type of resin had an original molar ratio F/P = 1.5 (also called type 2 resin).

These mentioned molar ratios only refer to phenol, but in reality amino acids present in amino groups in hydrolysates proteins are capable to react also with the formaldehyde and thus the real molar ratios are even lower.

As the resin was done under alkaline conditions two reactions predominate: (i) the reaction of phenolic ortho and para free sites with the methylol groups on the PF resin and with any free formaldehyde present, and (ii) the initial addition reaction of the formaldehyde both as such, as well as in the form of methylol groups on the PF resin with the amide groups of the protein and with the scarcer amino groups of some amino acids. As the initial addition (not condensation) of formaldehyde with amides in alkaline environment in presence of a PF resin is competitive with the phenol-formaldehyde reaction itself (Pizzi 1994 & Pizzi *et al.* 1993). This leads to the formation of methylene bridges between different sites, namely, phenol top phenol, and phenol to amide group of the protein.

### **1.1.3. Preparation of particleboards**

Triplicate, one layer laboratory particleboards of dimensions 350x300x14mm with target density of 700kg/m<sup>3</sup> were prepared. The panel was sanded in order to have a final thickness of 13mm. The pressing cycle was of 7.5 minutes (first step at 28kg/cm<sup>2</sup> during 3min; second step at 12kg/cm<sup>2</sup> and 2min and last step at 5.8kg/cm<sup>2</sup> and 2.5min). The long press time used is standard in this laboratory as the press cannot give a temperature higher than 180°C against a present factory working temperature of 220°-230°C. Under these conditions we are able to compare different adhesives performance in relation to what would be expected on a factory line. The NF EN 312 standard does not specify length of pressing time, but only IB strength, thus one can compare results to the standard whatever the press time used. Wood chips moisture content before adhesive application was 2.5%. The resin solids content on dry wood was 10%. For each formulation two different types of boards were made: one with the resin alone and another with 7% triacetin on dry weight of resin as an accelerator of PF resin curing (Zhao *et al.* 1999, 2000; Pizzi *et al.* 1994, 1997).

## **1.2. Test on adhesive resins**

### **1.2.1. pH, viscosity and solid content**

The pH was 11 at 20°C.

The end of the condensation reaction was fixed by the viscosity of resin, determined by Brookfield viscometer measurement at 25°C, with a speed of 50rpm.

The solids content of the resins was determined according to the European Norm NF EN ISO 3251 (AFNOR 2008), by drying in an oven at 103°C, until that the mass of residue is stable, generally it takes 1 day.

### **1.2.2. MALDI-TOF analysis**

**MALDI-TOF-MS:** The spectra were recorded on a AXIMA Performance MALDI instrument (Shimadzu, Manchester, UK). The irradiation source was a pulsed nitrogen laser with a wavelength of 337nm. The length of one laser pulse was 3ns. The measurements were carried out using the following conditions: polarity-



positive, flight path-linear, mass-high (20kV acceleration voltage), 100-150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200-800ns.

**MALDI-TOF Sample Preparation:** The samples were dissolved in acetone (4mg/mL). The sample solutions were mixed with an acetone solution (10mg/mL acetone) of the matrix. As the matrix 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation NaCl was added to the matrix. The solutions of the sample and the matrix were mixed in equal amounts and 0.5 to 1 $\mu$ L of the resulting solution were placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer.

### **1.2.3. Thermo Mechanical Analysis (TMA)**

TMA (Mettler Toledo TMA 40, Switzerland) was used to perform the analyses. The samples for this test were composed of two pieces of beech veneer (0.5x5x21mm) with an amount of 30mg resin evenly spread on this area (15mg on each piece), they are immediately placed in contact and tested. All resins were tested with and without triacetin.

For TMA, a three-point bending force of 0.1 to 0.5N applied and relaxed with a period of 6s/6s causes periodical deflection of the sample and enables calculation of the modulus of elasticity (MOE) of the joint sample as function of the increasing temperature (ramp 10°C/min).

The maximum of the elasticity modulus is achieved for the maximum of the polymerization temperature; indeed at this temperature all chains are fixed. At this time, the polymerization is over and if the temperature is still increasing, the degradation of the resin begins and there are no further reactions.

### **1.3. Tests of the prepared lab particleboards**

Density profiles of the particleboards samples were determined by X-rays densitometry (Grecon DAX 5000, Germany).

The difference between the density of the panel at its surface and at its core is expressed by using a ratio: (Density at the core of the panel) / (Density at the surface of the panel).

The panels were tested according to NF B51-262 (AFNOR 1972) for two hours boiling water swelling. This test consists in immersing the samples (50x50mm) during two hours in boiling water. After they are placed in an oven at 103°C and dried during 24 hours.

The internal bond strength was measured according to NF EN 319, (AFNOR 1993) with an Instron 4467 (UK) universal testing machine at a rate of 2mm/min.

The tests for subsequent formaldehyde emission are performed according to NF EN 717-3 (Flask method). A calibration curve is made using spectrophotometric analysis of dilution series of formaldehyde solution (whose concentration was determined using an iodometric titration).

Approximately 20 grams of a panel are inserted into the jar, in which there is 50mL distilled water, and then the jar is placed for 180 minutes in an oven at 40°C. The solution obtained is then reacted with a solution of ammonium acetate and a solution of acetylacetone and is then placed in a water bath at 40°C during 15 minutes.

After one hour rest away from light, solutions can be measured using the spectrophotometer. The detected value of absorbance provides the formaldehyde concentration (mg/mL) using the calibration curve and then we can calculate the formaldehyde emission of the panel (mg/100g dry panel). The time between cutting and the test does not exceed 72 hours as specified in the standard.

## **RESULTS & DISCUSSION**

### **2.1. Test on adhesive resins**

#### **2.1.1. pH, viscosity, and solid content**

Generally, the viscosities are between 500 and 800mPa.s (Table 2).

The target was to have a viscosity at 25°C, between 500 to 800mPa.s, so all resins don't have exactly the same reaction time, and we cannot do a link between viscosities and types of protein.

The pH values are in the range of 10.3 to 11.7 and are all lower than for the PF control and this even if the amount of NaOH was the same for every prepared resin. It is due to the pH of protein which is around 6 (Table 2).

The high viscosity of solutions of the hydrolysates of gluten proteins at concentrations of 50% where possible or otherwise of 25% in water (Table 3) indicate that (i) the viscosity obtained for PF-protein cocondensates shown in Table 2 are indeed possible, and (ii) that is rather likely that higher molecular weight fractions of the proteins exist in the hydrolysates higher than what determinable by MALDI-TOF spectrometry.

Table 2

**pH, viscosity, and solid content of all PF resins tested**

Resins	pH	Viscosity (mPa.s)	Solid content (%)
PF	12.3	695	46.9
PF-10% LMW	10.3	642	45.2
PF-20% LMW	11.2	715	49.5
PF-30% LMW	11.3	850	48.4
PF-10% LMW (Type 2)	11.4	950	49.1
PF-20% LMW (Type 2)	11.1	462	50.6
PF-10% Solpro 508	11.3	850	45.6
PF-20% Solpro 508	11.7	895	45.8
PF-30% Solpro 508	11.4	875	48.0
PF-10% Solpro 050	11.4	550	47.8
PF-20% Solpro 050	11.5	795	48.4

Table 3

**Viscosity of all wheat protein hydrolysates tested**

Proteins	Viscosity (mPa.s)
LMW protein (50% in water)	20,100
Solpro 508 (50% in water)	38,330
Solpro 050 (25% in water)	62,580

Moreover the SEC-HPLC curves in Fig. 1 show that very high molecular weight fractions are present in the hydrolysates. As traces of carbohydrates are not detected in the MALDI-TOF analysis it must be considered that this higher molecular weight fractions are due to protein material too.

The solids are near 50%, as stipulated in the experimental procedure adopted (Zhao *et al.* 2000) (Table 2). As the liquid 80% phenol was replaced by solid hydrolysates protein, the higher the substitution of phenol with the protein hydrolysate, the higher the solid contents are, except in the case of the resin with LMW protein with an original molar ratio F/P =1.7). At low replacement rate the solid contents are partly still lower than the PF control, as in the case for the LMW and the Solpro 508. Maybe in the other cases, some reaction takes place during the determination of the solid content and yield to the formation of water which then also is evaporated so solids contents are higher.

### 2.1.2. MALDI-TOF analysis

Three formulations were tested: PF- (10% and 20%) Solpro 050 and PF-20% LMW (type 2).

According to the literature (Finney *et al.* 1982 & Belderok *et al.* 2000) gluten is the main component in wheat protein and the main amino acids in gluten are at 31.9%: Glutamine (MW 146.2), at 14.1%: Proline (MW 115.1), at 7.2%: Leucine (MW 131.2), at 5.7%: Serine (MW 105.1) and at 5.4%: Glycine (MW 75,1) (Rombouts *et al.* 2009).

As we are dealing with gluten protein hydrolysates, thus with heavily modified materials, it was necessary to control their composition relative to gluten itself as shown in the literature. For this reason MALDI-TOF mass spectrometry was used to determine the composition of the materials we used.

In reality there is a variation of composition between the gluten hydrolysates we have used and the relative amino acids distribution in gluten itself. Thus, while in our materials the amino acids Glutamine, Proline, Leucine, Serine and Glycine predominate in gluten itself (Rombouts *et al.* 2009) the distribution is rather Glutamine, Leucine, Phenylalanine, Tyrosine, and Alanine.

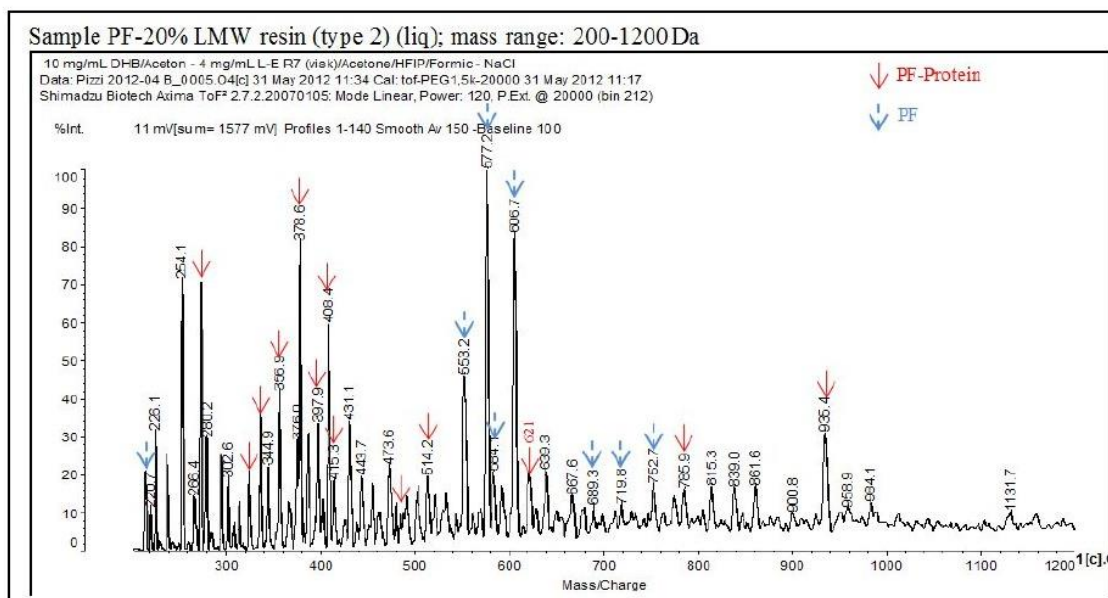
As control PF resins were synthesized by basic catalysis as polycondensation of phenol and formaldehyde. Phenol units are linked in order to form a polymer via methylene bridges. Each ortho or para position of phenolic rings may react with formaldehyde (Schrod *et al.* 2003). It is not possible to determine from MALDI-TOF analysis the predominance of ortho-ortho, ortho-para or para-para linkages. In reality classical phenol-formaldehyde reaction theory indicates that while the reactivity of the para sites is slightly



higher than the ortho one, the presence of two ortho sites and only one para site give distribution that are often not very different (Megson 1958).

Reactions between phenol and formaldehyde give  $-CH_2$ ;  $-CH_2^+$ , or  $-CH_2OH$  attached to phenol.

The focus in the paper here is on the reactions of the amino acids present in the protein hydrolysates with formaldehyde or with already formed PF groups during the resin preparation. Fig. 2 shows as one example the MALDI-TOF spectrum of the PF resin modified with 20% LMW and without second addition of formaldehyde (type 2 reaction).



**Fig. 2.**  
MALDI-TOF spectrum of the liquid resin PF-20% LMW (type 2) for a range from 200 to 1200 Da.

Peaks representing the reactions which involve various PF resin groups and protein hydrolysates are marked with arrows in solid lines. Peaks only resulting from the reaction between phenol and formaldehyde are indicated by dotted arrows. We can assume that there are reaction between PF resin groups and the amino acids of the protein, because as it was found previously, PF resin spectrum give peaks until 800Da and here it is quite the same range but with a number of peaks more important (Lagel *et al.* 2014).

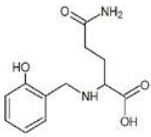
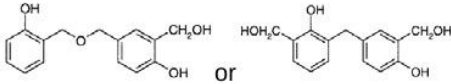
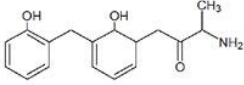
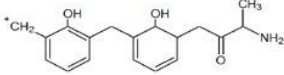
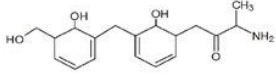
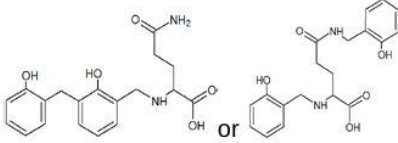
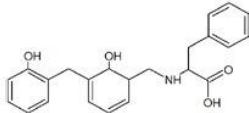
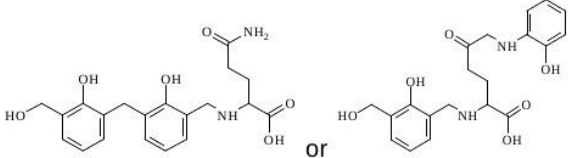
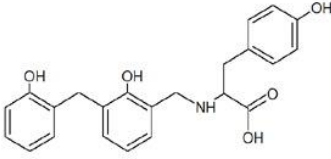
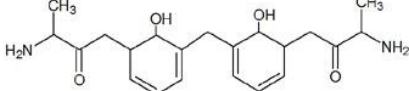
Table 4 summarizes the molecules which can be assigned to the various molecular weights according the reactions between (i) phenol and formaldehyde as well as (ii) between the amino acids of the protein and PF resin groups. It was calculating by adding the molecular weight of amino acid with PF resin groups and the molecular weight of Na. The possibility that amino group of the amino acids reacts directly with formaldehyde is excluded in this study because the spectra always begin solely at 200Da.

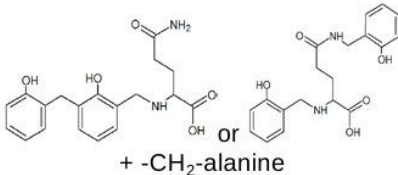
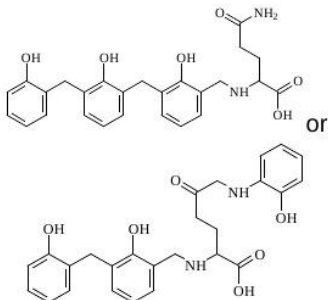
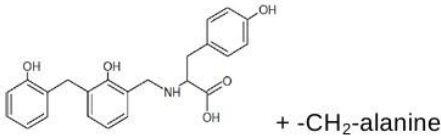
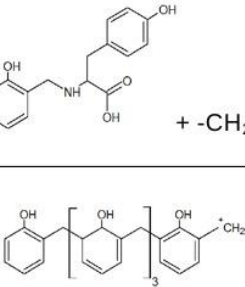
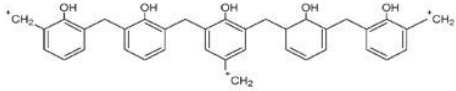
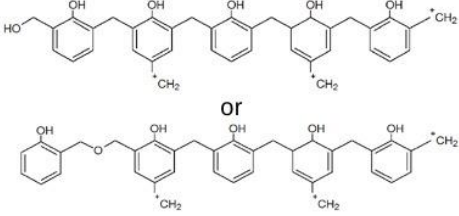
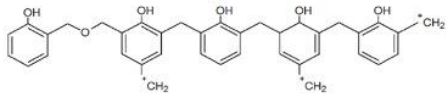
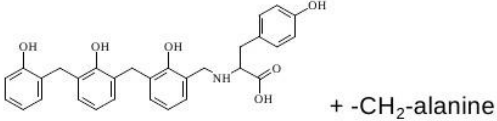
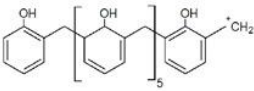
Table 4

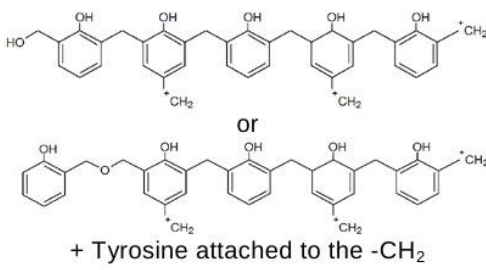
**Peaks corresponding (i) to PF resin groups with different molecular weight and (ii) to structures resulting from reactions between PF resin groups and key amino acids of gluten in PF-20% LMW resin (type 2, without second formaldehyde addition)**

Molecular weight with $Na^+$ (Da)	Theoretical molecular weight with $Na^+$ (Da)	Molecules	Amino acid
238.4	237	<p style="text-align: center;"><math>n=2</math></p>	PF resin group



274.2	274		Glutamine
284.7	283		PF resin group
324.5	324		Alanine
336.6	336		Alanine
356.9	356		Alanine
378.6	379		Glutamine
397.9	398		Phenylalanine
408.4	408		Glutamine
415.3	414		Tyrosine
425.6	425		Alanine

480.1	480	 <p>+ -CH<sub>2</sub>-alanine</p>	Alanine and glutamine
485	485	 <p>+ -CH<sub>2</sub>-alanine</p>	Glutamine
514.2	515	 <p>+ -CH<sub>2</sub>-alanine</p>	Alanine and tyrosine
553.2	553		PF resin group
577.2	577		PF resin group
606.7	606	 <p>OR</p> 	PF resin group
621	621	 <p>+ -CH<sub>2</sub>-alanine</p>	Alanine and tyrosine
752.7	754		PF resin group

785.9	786	 <p>+ Tyrosine attached to the -CH<sub>2</sub></p>	Tyrosine
935.4	934	786 + Glutamine attached to -CH <sub>2</sub>	Tyrosine and glutamine

The results in the Tables 4 and 5 shows, that glutamine is the amino acid most implicated in reactions with phenol and formaldehyde, leading to molecular weights of 379, 274, and 408Da in order of predominance. It could be explain be the fact that this amino acid is more reactive due to the presence of two amino groups, indeed the others amino acids contain only one amino group.

Because of the important number of peaks, this analysis is focused on the resin containing LMW protein hydrolysates (protein hydrolysates of smaller size relative to the others). So there is an important number of different created molecules and this even if molecular weights of the created molecules are quite the same (go until 1132Da) than protein hydrolysates Solpro 050 where the last molecule is at 1047Da in our range of analysis. So we cannot see an influence of the molecular weight of the hydrolysates on the speed of the reaction with phenol and formaldehyde. We can presume that if for the analysis of the resin with protein hydrolysates Solpro 050 we do not see a lot of peaks, it is because amino acids reacted with PF resin groups have rushed and it would be for this reason they do not appear in spectra. And so there are not so much different molecules that have been created during the reaction. Analyses of dry samples do not provide additional information.

Table 5 summarizes the main reactions between PF resin groups and key amino acids of gluten in the three formulations which were analyzed by MALDI-TOF.

Table 5

**Peaks corresponding to the molecular weight of main reactions between phenol and formaldehyde as well as the amino acids alanine, glutamine, and tyrosine**

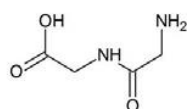
Theoretical molecular weight with Na <sup>+</sup> (Da)	Amino acid involved	PF-20% LMW (type 2)		PF-10% Solpro 050		PF-20% Solpro 050	
		Molecular weight with Na <sup>+</sup> (Da)	Peak intensity (%)	Molecular weight with Na <sup>+</sup> (Da)	Peak intensity (%)	Molecular weight with Na <sup>+</sup> (Da)	Peak intensity (%)
274	Glutamine	274.2	71	273.1	4	272.3	1
324	Alanine	324.5	22	325.3	4	326.1	4
336	Alanine	336.6	36	/	/	336.2	2
356	Alanine	356.9	42	/	/	357.2	1
379	Glutamine	378.6	82	378.2	2	378.6	30
408	Glutamine	408.4	60	407.5	4	408.6	100
480	Alanine and glutamine	480.1	13	/	/	480.3	3
786	Tyrosine	785.9	17	/	/	786.0	4

The peaks intensities are given in relation to the most important peak of each spectrum for each tested resin. In PF-20% LMW (type 2) resin the peak at 379Da is the most intense one at 82%; in contrast in the PF-10% Solpro 050 resin this peak only shows a very low intensity of 4%, which is the lowest one. The highest peak is at 577 Da and corresponds to a PF resin group alone.

In the PF-20% Solpro 050 resin the most important peak (associated with 100% intensity) occurs at 408 Da involving glutamine. Also the peak with the second highest intensity at 379Da involved glutamine.

Evaluating all three spectra the most important reactions yield the peaks at 379 and 408 Da involving glutamine.

In MALDI-TOF experiences the methylene linkages between the phenols of the PF resin are stable (Schrod *et al.* 2003 & Pizzi *et al.* 2004), thus one does not experience decomposition or rearrangements on this part of the product. However, some instability may exist in the case of the methylene linkages between the PF resin and amino groups, and between amino groups (Despres *et al.* 2007) hence of the protein. In effect some rearrangements of the protein hydrolysates might occur, as indeed shown by the peaks at 274, 291, and 471Da (in order of predominance) (Fig. 3 & Table 6).



**Fig. 3.**

**Title: Two glycines (MW 132).**

Table 6

**Reactions between glycines and PF resin groups as well as formaldehyde in PF-20% LMW (type 2) resin**

Molecular weight with Na <sup>+</sup> (Da)	Theoretical molecular weight with Na <sup>+</sup> (Da)	Molecules
262	261	
274.2	274	
293.9	291	
308.5	309	
366.5	366	
402.6	404	
473.6	471	

### 2.1.3. Thermo Mechanical Analysis (TMA)

Concerning the resins containing 20% of LMW (Type 2) and 20% Solpro 050, the use of triacetin had a positive effect on the properties. A diminution of the maximum temperature of polymerization and also an augmentation of the maximum of elasticity modulus are notice (Table 7).



Table 7

**Thermo mechanical analysis results tests**

Formulation	Temperature (°C)		Elasticity modulus (MPa)	
	Without triacetin	With triacetin	Without triacetin	With triacetin
PF	165	151	3752	4267
PF-10% LMW	154	159	5029	5219
PF-20% LMW	153	156	6519	5891
PF-30% LMW	163	168	7183	8476
PF-10% LMW (Type 2)	164	157	5254	4899
PF-20% LMW (Type 2)	165	161	5809	9920
PF-10% Solpro 508	158	145	5364	3732
PF-20% Solpro 508	152	171	4981	5469
PF-30% Solpro 508	154	171	5637	6710
PF-10% Solpro 050	160	162	5779	10253
PF-20% Solpro 050	157	146	4823	7507

In comparison to PF resin, without triacetin, PF-hydrolysates proteins have lower maximum temperature of polymerization and have higher elasticity modulus. With triacetin, PF-hydrolysates proteins have higher maximum temperature of polymerization (except for PF-10% Solpro 508 & PF-20% Solpro 050) but they have higher elasticity modulus (except for PF-10% Solpro 508) in comparison to PF resin.

Looking at the elasticity modulus for the same substitution rate, the best performing protein hydrolysates are summarized in Table 8.

For a substitution rate of 10%, the best protein is Solpro 050, because the elasticity modulus is about twice with triacetin. And for substitution rates of 20 and 30%, the best protein is LMW, because with triacetin they have the highest elasticity modulus.

By correlating the results of thermo mechanical analysis and those of internal bond, the protein hydrolysates Solpro 050 gave satisfying internal bond and improved modulus of elasticity in the case of addition of triacetin. Indeed, it is the only one which for both substitution rates, the internal bond is improved.

**2.1. Tests on particle boards**

Despite of the panel's thickness after press and after sanding, there is a little variation in density between different samples. As the distribution of particles in the mold was made manually, it can lead to some difference in the final panel. Tests were done on samples having the densities the closest to the target density of 700kg/m<sup>3</sup>.

**2.1.1. Density profile**

The surface density of the boards is greater than at its center as measured by X-rays density profiler (Table 8), which is explain by the fact that surfaces are directly in contact with heat source and the surface is like glossy. The higher the density ratio is, the closer the densities of the surfaces and the center of the panel are.

Generally, panels containing protein hydrolysates have density ratios that are higher than panels done with PF resin. The use of protein hydrolysates appears to allow for a better heat diffusion, this being the case with and without triacetin. The protein hydrolysates which gave panels of higher density ratios are those for which the hydrolysate had been prepared by enzymatic hydrolysis (LMW and Solpro 508). As regards the density profile ratio this is acceptable for laboratory panels for which the conditions are rather different than in a plant or a pilot plant.

Table 8

Identification of best formulations

Formulation	Density ratio		Dry swelling after water immersion (%)		Elasticity modulus (MPa)		Before swelling				After swelling				Formaldehyde emission (mg/100g dry pane)	Total score for best substitutions	Total score for best hydrolysates
	Density ratio		Dry swelling after water immersion (%)		Elasticity modulus (MPa)		Density (kg/m <sup>3</sup> )		Internal bond (N/mm <sup>2</sup> )		Density (kg/m <sup>3</sup> )		Internal bond (N/mm <sup>2</sup> )				
	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin	Without triacetin	With triacetin			
PF	0.69	0.70	8.3	6.5	3752	4267	705	701	0.58	1.01	671	715	0.18	0.59	3.88	/	/
PF-10% LMW	0.73	0.73	19.3	7.0	5029	5219	680	711	0.26	0.94	663	708	0.01	0.27	4.32	3	
PF-20% LMW	0.71	0.72	14.8	6.8	6519	5891	599	707	0.23	0.60	600	625	0.01	0.17	6.10	1	4
PF-30% LMW	0.69	0.76	25.2	8.4	7183	8476	702	707	0.24	0.34	678	702	Break	0.19	4.90	2	
PF-10% LMW (Type 2)	0.71	0.73	18.3	4.5	5254	4899	594	598	0.28	0.60	589	594	Break	0.21	3.74	2	4
PF-20% LMW (Type 2)	0.73	0.78	Break	5.2	5809	9920	573	607	0.09	0.52	591	608	Break	0.22	4.52	2	
PF-10% Solpro 508	0.74	0.77	23.4	14.0	5364	3732	691	692	0.29	0.51	672	678	Break	0.03	6.01	1	
PF-20% Solpro 508	0.73	0.73	25.8	14.9	4981	5469	679	689	0.31	0.46	652	655	Break	0.03	5.25	1	1
PF-30% Solpro 508	0.72	0.72	31.3	15.0	5637	6710	682	676	0.18	0.56	664	607	0.04	0.06	4.62	0	
PF-10% Solpro 050	0.70	0.74	8.9	5.1	5779	10253	614	647	0.31	0.68	607	623	0.06	0.36	7.12	4	
PF-20% Solpro 050	0.70	0.70	9.8	4.6	4823	7507	701	6942	0.68	0.86	697	689	0.17	0.50	2.11	3	5



### **2.1.1. Swelling and internal bond tests**

The standard NF EN 312 requires for a 13mm non construction purpose panel in P3 quality a maximum thickness swelling after 24h of 14%. However this value is given to a panel made of industry which has three layers, with the density substantially greater in the face layers than in the core layer.

The panels used in this project are monolayers. Thus, as the densities of the different layers are not the same, the values of swelling of industrial panels made with the same formulations should correspond to 60%-70% of the values found here. Contrary to what generally falsely believed the swelling of surfaces and core is rather different due to the difference in penetrability by a liquid in solids of higher density. In general, all panels containing proteins and triacetin comply the requirements of the standard. Moreover, panels without triacetin made with 20% LMW, 10 and 20% Solpro 050, get swelling ratio less than or around 14% (Table 8).

The choice was made to identify the best panels for the nearest 700kg/m<sup>3</sup> density having significant internal bond. Panels of type P2, 13mm thick used in dry environments and non-construction purposes working, with higher internal bond than 0.35N/mm<sup>2</sup> are considered correct related to their internal bond (IB) strength (AFNOR 2010). None of the formulations containing proteins without triacetin yielded mechanically resistant panels, except in the case of protein hydrolysates Solpro 050 with a degree of substitution of 10% (Table 8).

All panels bonded with addition of triacetin to the adhesive have an internal bond (IB) strength higher than 0.35N/mm<sup>2</sup>, except for the resin containing LMW protein hydrolysates using a degree of substitution of 30%. In this case the effect of the addition of triacetin is not sufficient to obtain a panel of sufficient mechanical resistance. The results obtained (Table 8) show that the panels containing protein hydrolysates have lower IB strength than those without proteins but they still meet the requirements of the standard.

Moreover, the panel bonded with a resin PF-10% Solpro 050 with triacetin has an internal bond comparable with those of the panel with 20% Solpro 050 without triacetin while it has a much lower density; this formulation is also worthwhile to note. For resins containing protein hydrolysates Solpro 508, the best formulation is 30% protein with triacetin. This yields a panel with better internal bond than others even if its density is slightly lower than 700kg/m<sup>3</sup>. Protein hydrolysates Solpro 050, gives the most suitable formulation, this being the one using a substitution rate of 20% with or without triacetin.

Comparing the results with those obtained for panels bonded with a PF resin (Table 8), one finds that the IB strength of the PF panels without and with triacetin are respectively 0.18 and 0.59N/mm<sup>2</sup>. Thus, all the panels which have been subjected to swelling test and containing protein hydrolysates, (with or without triacetin) have lower IB strength than those of made with the pure PF resin. The only formulation which is closest to the results of panels made with PF resin is: PF-20% Solpro 050. Moreover, it is noteworthy that panels bonded with a resin PF-10% Solpro 050 with triacetin has a higher internal bond of those obtained for the panel containing 10% LMW with triacetin at a much lower density.

### **2.1.2. Formaldehyde emissions**

Only the panels containing triacetin were tested. These panels gave IB strength values higher than the 0.35N/mm<sup>2</sup> required by the EN 312 (except for the formulation PF-30% LMW with triacetin, which gave internal bond of 0.34N/mm<sup>2</sup>).

According to the standard NF EN 312 (AFNOR 2010), the formaldehyde concentration should be less than 6.5mg/100g of dry board to be a panel of class E1. The tests done herewith were according to standard NF EN 717-3. Even if effectively standard NF EN 717-3 does not require a limit in panel's formaldehyde emissions.

Panels tested have a moisture content of about 5.9%.

By comparing panels bonded with PF-protein resins and panels with just PF resin, formulations PF-10% LMW (type 2) and PF-20% Solpro 050 are the only one which gave panels containing less formaldehyde. For LMW protein hydrolysates, whatever the P/F ratio, panels containing less formaldehyde are those with a substitution rate of 10%. Conversely, for protein hydrolysates Solpro 508 and 050, the panels presenting lower emission are those with the highest rates of substitutions (20% Solpro 050 and 30% for Solpro 508). As they have a bigger size, there is more sites and more place in order to fix the formaldehyde and do not let it release.

## **2.2. Comparison of different tests**

In Table 8 are reported the best formulations for each tests.

Considering results of the tests lead with addition of triacetin, resins and panels which have the best properties for five out of six criteria are those which contain 10% Solpro 050. Resins with 10% LMW protein and 20% Solpro 050 with four out of six criteria being satisfied. Protein hydrolysates Solpro 050 are better for five out of six tests. Next comes the LMW protein hydrolysates that are interesting for four out of six tests,



and whatever the P/F ratio. In a nutshell, when using triacetin, protein hydrolysates Solpro 050 and LMW protein appear to have good properties as phenol-substitution additives for PF resins.

## CONCLUSIONS

This study was conducted to compare the performances of phenolic resins containing wheat protein hydrolysates with conventional phenolic resins. The aim in the coming years is to develop the use of wheat proteins and more generally biomass in wood adhesives while retaining the properties of the standard panels.

The addition of triacetin to phenolic resins containing wheat proteins improves the performance of wood panels bonded with these resins. The most successful protein hydrolysates used appear to be the LMW and Solpro 050 protein hydrolysates.

It would be interesting to synthesize resins with higher a degree of substitution (30% or even higher), in using LMW protein and Solpro 050.

The results of this study on the addition of wheat protein hydrolysates in phenolic resins seem to be encouraging, and it's a further step toward the development of bio-based adhesives.

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#### *4.2.3. Caractérisation d'extrait de tanin d'Aningré (Aningeria spp.) et performance en tant que résine adhésive*

### **« Aningre (Aningeria spp.) tannin extract characterization and performance as an adhesive resin »**

Auteurs : N. Konai, A. Pizzi, D. Raidandi, M.C. Lagel, C. L'Hostis, C. Saidou, A. Hamido, S. Abdalla, F. Bahabri, A. Ganash.

<sup>1</sup>Laboratoire de Mécanique des matériaux, structures et de fabrication intégrée, Ecole Nationale Supérieure Polytechnique, Université de Yaoundé 1, Cameroun

<sup>2</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>3</sup>Laboratoire de génie chimique et de l'environnement, Université de Ngaoundéré, Cameroun

<sup>4</sup>Institut de la matière condensée et des nanosciences (IMCN), Université Catholique de Louvain, Belgique

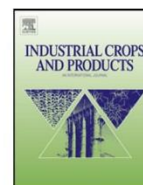
<sup>5</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

<sup>6</sup>Département de Chimie, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

#### Résumé :

Les espèces d'arbres Aningré sont très abondantes en Afrique centrale, ont une croissance rapide et possèdent un rendement très élevé de tanin. Ainsi, l'extrait de tanin d'Aningré a été caractérisé en utilisant le moyen infrarouge (ATR-FT MIR) avec des spectres allant de 1800 à 600 cm<sup>-1</sup> et par spectrométrie de masse couplant une source d'ionisation laser assistée par une matrice et un analyseur à temps de vol (MALDI-ToF). Ces deux méthodes de caractérisation ont démontré que le tanin d'Aningré est un procyanidine/prodelphinidine composé de catéchine, gallocatéchine, aussi bien des unités catéchine galloylatée ou gallocatéchine. En outre, des oligomères présentant une combinaison simultanée de groupes méthoxy et de glucose liées ont été observés, ceux-ci n'ont pas été observés auparavant dans des extraits de tanin d'écorce ou de bois. Deux formulations de résines ont été développées avec cet extrait. Le module d'élasticité (MOE) a été étudié par analyse thermomécanique et des panneaux de particules de bois ont été préparés avec ces résines.

Mots-clés : Aningre, Tanin, Caractérisation, ATR-FTIR, MALDI-ToF, Adhésif, TMA, Profil de densité, Cohésion interne.



## Aningre (*Aningeria* spp.) tannin extract characterization and performance as an adhesive resin

N. Konai<sup>a</sup>, A. Pizzi<sup>b,e,\*</sup>, D. Raidandi<sup>a</sup>, M.C. Lagel<sup>b</sup>, C. L'Hostis<sup>b</sup>, C. Saidou<sup>c</sup>, A. Hamido<sup>d</sup>, S. Abdalla<sup>e</sup>, F. Bahabri<sup>e</sup>, A. Ganash<sup>f</sup>

<sup>a</sup> Laboratory of Materials Mechanics, Structures and Integrated Manufacturing, National Advanced School of Engineering, Yaoundé 1 University, BP 8390 Yaoundé, Cameroon

<sup>b</sup> LERMAB, Nancy University, 27 rue du Merle Blanc, BP 1041, 88051 Epinal, France

<sup>c</sup> Laboratory of Chemical Engineering and environment, Ngaoundéré University, BP 455 Ensai, Ngaoundéré, Cameroon

<sup>d</sup> Institute of Condensed Matter and Nanosciences (IMCN), Université Catholique de Louvain, Bâtiment de Hemptinne, 2, Chemin du Cyclotron, B-1348 Louvain-la-Neuve, Belgium

<sup>e</sup> Dept. of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

<sup>f</sup> Dept. of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia

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### ABSTRACT

As aningre tree species are very abundant in central Africa, are rapid growing and have a very high percentage yield of tannin, aningre tannin extract was characterized using attenuated total reflectance Fourier transform (ATR-FT MIR) spectra in the 1800 and 600 cm<sup>-1</sup> range and Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-TOF) mass spectrometry. These two characterization methods have proven that aningre tannin is a procyanidin/prodelphinidin composed of catechin, gallogatechin as well as galloylated catechin and gallocatechin units. Moreover, oligomers presenting the simultaneous combination of methoxy groups and linked glucose have been observed, these not having been observed before in bark and wood extracted tannins. Two resin formulations were developed with this extract. The Modulus of Elasticity (MOE) was studied by thermomechanical analysis and wood particleboards were prepared bonded with these resins.

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### 1. Introduction

Nowadays, many countries have ratified the December 1997 Kyoto Protocol on Environmental Pollution to reduce greenhouse gases emissions. Against these environmental problems, uses of natural resins and biodegradable materials are one of the best solutions. Thus, their uses and particularly the use of green resins has increased (Pizzi, 2006). Many applications of tannins resins have been developed. Flavonoid tannins have been promoted as wood adhesive (Pizzi, 1983) and for other applications (Pizzi 2015).

One of the more severe problem in the use of present commercial tannins for industrial resins is their limited supply. This situation is aggravated by tannins having traditionally been used for leather manufacture, such an application being still their primary market. As the interest in the use of these materials for adhesives,

resins, foams, plastics and other applications is strongly growing the scarcity of the supply of the present commercial tannins has led to two different approaches to try to ease their supply problem: (i) the addition to commercial tannins of other natural materials (Navarrete et al., 2012) or the much older approach of its addition to synthetic resins, and (ii) the identification and testing for extraction and resin applicability of other fast growing, tannin-rich, widely diffuse tree species. In this latter context several alternative tannins have been characterized such as, among others, maritime pine industrial tannin (Navarrete et al., 2010); pomegranate peel tannins (Saad et al., 2012) and eucalyptus species bark tannins (Fechtal and Riedl, 1993). As the importance of tannin supply and applicability is often geographically localized the quest is on for tannin-yielding tree species that can satisfy demand in different parts of the world. It is in this context that the present paper responds to this approach in investigating the applicability of the tannin of a widely diffuse species in central Africa.

The new tannin tested is the aningre tannin. Aningre woods species (*Aningeria altissima*, *Aningeria robusta*, *Aningeria superba*, *Gambeyobotrys gigantea*) also called Abam in Cameroon are culti-

\* Corresponding author at: LERMAB, University of Lorraine, 27 rue Philippe Seguin, CS60036, 88026 Epinal, France. Fax: +33 329296138.

E-mail address: [antonio.pizzi@univ-lorraine.fr](mailto:antonio.pizzi@univ-lorraine.fr) (A. Pizzi).



vated in the West, Center, South and East Regions of the country. They exist and are widely diffuse in many african countries under various names: in Angola (Mukali), in the Congo (N'kali), in Ivory Coast Cote (Aningueri Blanca), in Kenya (Muna). The Aningre tree species are fast growing and very abundant and widely diffuse in central Africa. They present already an economical interest not only because the local populations use the timber but because bark and roots have pharmaceutical applications, and antioxydants and anti inflammatory properties. They present a very high percentage yield in tannin extraction. Its bark from which the extraction is carried out is a waste materials and the tannin extracted from it has thus a great economic potential in the central Africa wood industry as such resins will be manufactured locally.

Between tannin characterization methods, Karas et al. (1987) had introduced in 1987, Matrix-Assisted Laser Desorption/Ionization combined with time-of-flight (MALDI-TOF) mass spectrometry as a suitable analysis method (Pash et al., 2001; Danis et al., 1992); Fourier transform infrared (FT-IR) spectrometry is used to provide information about the surface chemistry and bulk properties of simple and functionalized polymers. Thermomechanical analysis (TMA) has already been used in resin characterization. In 2002, Garnier and Pizzi (2002) studied the rheology of polyflavonoid tannin using TMA, concluding that TMA takes into account the polymers interactions with the lignocellulose substrate and links experimental data with panels manufacturing. The gelling and hardening reactions of different commercial polyflavonoid tannins (quebracho, mimosa, pine, pecan) extract of prorobitenedin/profisetinidin, procyanidin and prodelphinidin types with formaldehyde were also studied using parallel plates rheometry.

The aims of this paper are firstly to extract and characterize aningre tannin using Attenuated Total Reflectance Fourier Transform Middle Infrared (ATR-FTMIR) and Matrix Assisted Laser Desorption/Ionization Time Of Flight (MALDI TOF) in order to identify and differentiate the structure of the oligomers present. Secondly, to develop adhesive resins, evaluate their bonding behaviour and performances using TMA characterization and determining the Internal Bond (IB) strength of the particleboards bonded with different adhesive formulations based on this tannin.

## 2. Materials and methods

### 2.1. Aningre tannin extraction

The Aningre ground bark was introduced in a water solution containing 2% sodium bisulfite and 0.5% sodium bicarbonate (water: bark ratio was 6:1). All solution was introduced in a bath water, under continuous stirring at 60 °C during 4h. Then, proceeded to separation and filtration to get a reddish black liquid and a solid residue. The recovered liquid fraction was then concentrated at 60 °C using a rotary evaporator, then it was frozen using liquid nitrogen and laboratory spray drier. A tannin powder, easier to use for analysis and storage was finally obtained (Sealy-Fisher and Pizzi, 1992).

### 2.2. Aningre tannin characterization

#### 2.2.1. ATR-FT MIR analysis

The aningre tannin extract were analyzed using the Perkin Elmer Frontier ATR device equipped with a diamond/ZnSe crystal. About 2 mg grinded powders were put on the crystal device and the contact was obtained applying a strength of about 150 N on the sample. Each spectrum was obtained with 32 scans with the resolution of 4 cm<sup>-1</sup> from 4000 to 600 cm<sup>-1</sup>. The sample was scanned five times

and the average of these spectra was studied in the finger print region between 1800 and 600 cm<sup>-1</sup>.

#### 2.2.2. MALDI-TOF analysis

The samples were dissolved in acetone (4 mg/ml). The sample solutions were mixed with an acetone solution (10 mg/ml acetone) of the matrix. 2,5-dihydroxybenzoic acid was used as matrix. For the enhancement of ion formation, the matrix was mixed with NaCl. The solutions of the sample and the matrix were mixed (50:50) and 0.5–1 µl of the resulting solution was placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer (Navarrete et al., 2010). The spectra were recorded in a KRATOS compact MALDI AXIMA PERFORMANCE TOF 2 instruments. The software Maldi-MS was used for the data treatment.

### 2.3. Resin development

#### 2.3.1. Two formulations of resins were developed

**Formulation 1:** a water solution containing 40% aningre tannin was mixed with 5.5% of paraformaldehyde powder and pH was adjusted to 12 adding sodium hydroxide solution (NaOH).

**Formulation 2:** water solution containing 40% aningre tannin was mixed with 12% of glyoxal predissolved in water and the pH was adjusted to 12 adding sodium hydroxide solution (NaOH).

All components weight are on solids tannin. The high pH was chosen as the hardener used performs best at such a pH (Hillis and Urbach, 1959; Pichelin et al., 2006).

In fact, it consisted to mix all components of a formulation in a beaker at 25 °C temperature, process was stopped when viscosity reached 750 mPa s. Brookfield viscosimeter RV. Spindle Nr, 27 at 25 °C was used.

#### 2.4. Bonding behaviour using thermomechanical analyzer

The Thermomechanical Analyzer METTLER TOLEDO TMA 40 was used to study the hardening reaction of single resin system and determine resin rigidity joint as a function temperature. The TOLEDO TMA40 was linked to a processor TC11 and a computer to register and interpret graphically the behaviour of the resin. The software used for data treatment was STARE 6.10.

#### 2.4.1. TMA sample preparation

About 22–25 mg of resin was put on beech wood plates (2 plates) of dimensions 17 × 5 × 1.1 mm and then, the beech wood were bonded and placed in the furnace of the Thermomechanical Analyzer to undergo tests. Samples were tested in bending in non-isothermal mode between 25 °C and 250 °C at a heating rate of 10 °C/min (Mansouri et al., 2011).

#### 2.4.2. Stiffness of resin/modulus of elasticity (MOE)

The maximal of the Modulus of Elasticity curve depending temperature represent the Modulus of Elasticity (MOE). The MOE of the wood joints bonded with different resin systems give a good indication of the final strength of the adhesive system tested and the possible performance of the adhesive system tested.

#### 2.4.3. Particleboards manufacturing and internal bond

**2.4.3.1. Particleboards manufacturing.** The particleboards were manufactured during 7 min 30 s pressing time divided in three steps: the first step with a pressure of 28 kg/cm<sup>2</sup> lasted 3 min, the second with a pressure of 12 kg/cm<sup>2</sup> lasted 2 min and the third with a pressure of 5.8 kg/cm<sup>2</sup>, 2 min 30 s. The two plates temperatures press were set at 220 °C. To ameliorate reactivity of particleboards manufactured with glyoxal hardener, others particleboards were manufactured during 10 min pressing (3 min, –2 min 30 s, –4 min

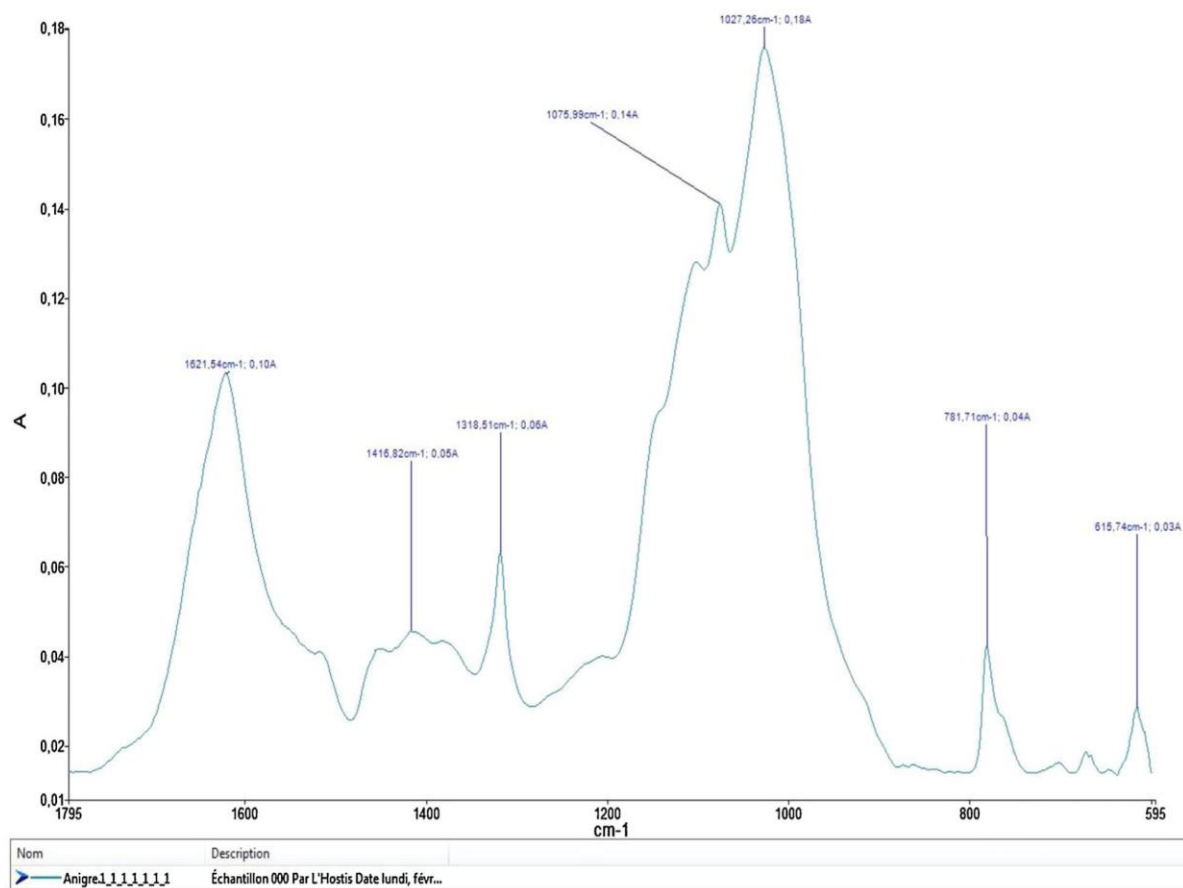


Fig. 1. ATR-FT MIR spectra of anigre tannin.

30 s) at 220 °C and with the same pressure than those manufactured during 7 min 30 s. The dimensions of particleboards manufactured were 350 × 300 × 14 mm; each particleboard weight was 1000 g. After manufacture, particleboards were cut into 50 × 50 × 13 mm samples for testing according to Norm EN312 (NF EN 312-2, 1996). The Particleboards were prepared adding 10% of total resin solids on dry wood particles and 2% as shaving humidity rate.

**2.4.3.2. Particleboard density profile.** A StenOgraph of GreCon X-ray device was used to study the density profile of the particleboards prepared. All specimens respect the international standard NF EN 326-1 (1994).

**2.4.3.3. Internal bond (IB) strength.** The Internal Bond of particleboards was determined according the International standard NF EN 312-2 (1996) using INSTRON 4467 universal testing machine. Dry IB test was done on 15 specimens and 15 others specimens were chosen to test IB after placed samples in boiling water during 2 h (NF B 51-262, 1972).

### 3. Results and discussion

#### 3.1. Tannin characterization

##### 3.1.1. Attenuated Total Reflectance Fourier Transform Middle Infrared (ATR-FTMIR) analysis

The examination of the anigre tannin ATR-FT spectrum (Fig. 1) in the range 1800–600  $\text{cm}^{-1}$  revealed various functional group which are typical for condensed and hydrolysable tannins.

Before discriminating the two families of tannin, typical bands for the various hydroxyl-aromatic molecules can be identified: the 1318 and 1027  $\text{cm}^{-1}$  peaks are considered as the most significant for the description of ring substituents. The former is attributed to bending aromatic group (Jensen et al., 2008) and the latter is also resulting from the combination of C–H aromatic bending, C–O stretching and C–OH deformations (Socrates, 2000; Colthup, 1964). The 1075  $\text{cm}^{-1}$  shouldering is associated to the C–H aromatic in-plane bending (Socrates, 2000; Fernandez and Agosin, 2007).

It is possible to discriminate the two mains families of tannin: The presence of condensed tannin in this extract is proved not only by the 1621  $\text{cm}^{-1}$  peak, typical indication of proanthocyanidins which are mainly occupied by vibrational motions of C=C groups in the aromatic rings (Socrates, 2000) but also by the C–O stretching modes present at 1076 and 1027  $\text{cm}^{-1}$  peaks representative of the symmetrical elongation of the C–O–C group in the pyran ring of condensed tannins (Ghica et al., 2009; Chen et al., 2010). A-Ring torsion and C–H aromatic bending at 781  $\text{cm}^{-1}$  are attributed to flavane, flavanol, pyrocatechol, resorcinol epicatechin or to OH waggings of aromatic and out-of-plane bending of aromatic CH (Socrates, 2000; Chen et al., 2010;).

The presence of some hydrolysable tannins can be suspected firstly by the symmetric stretching C–O of the ester group located at 1318  $\text{cm}^{-1}$  peak (Laghi et al., 2010). However, this ester group can also be attributed to gallic acid residues linked to catechin/epicatechin or epicatechin gallate shown to exist in procyanidins-type tannins (Navarrete et al., 2010). Secondly by the absorption at 781  $\text{cm}^{-1}$  representing the CH<sub>2</sub>–OH deformation (Senvaitiene et al., 2005) of the sugar fraction of an hydrolysable



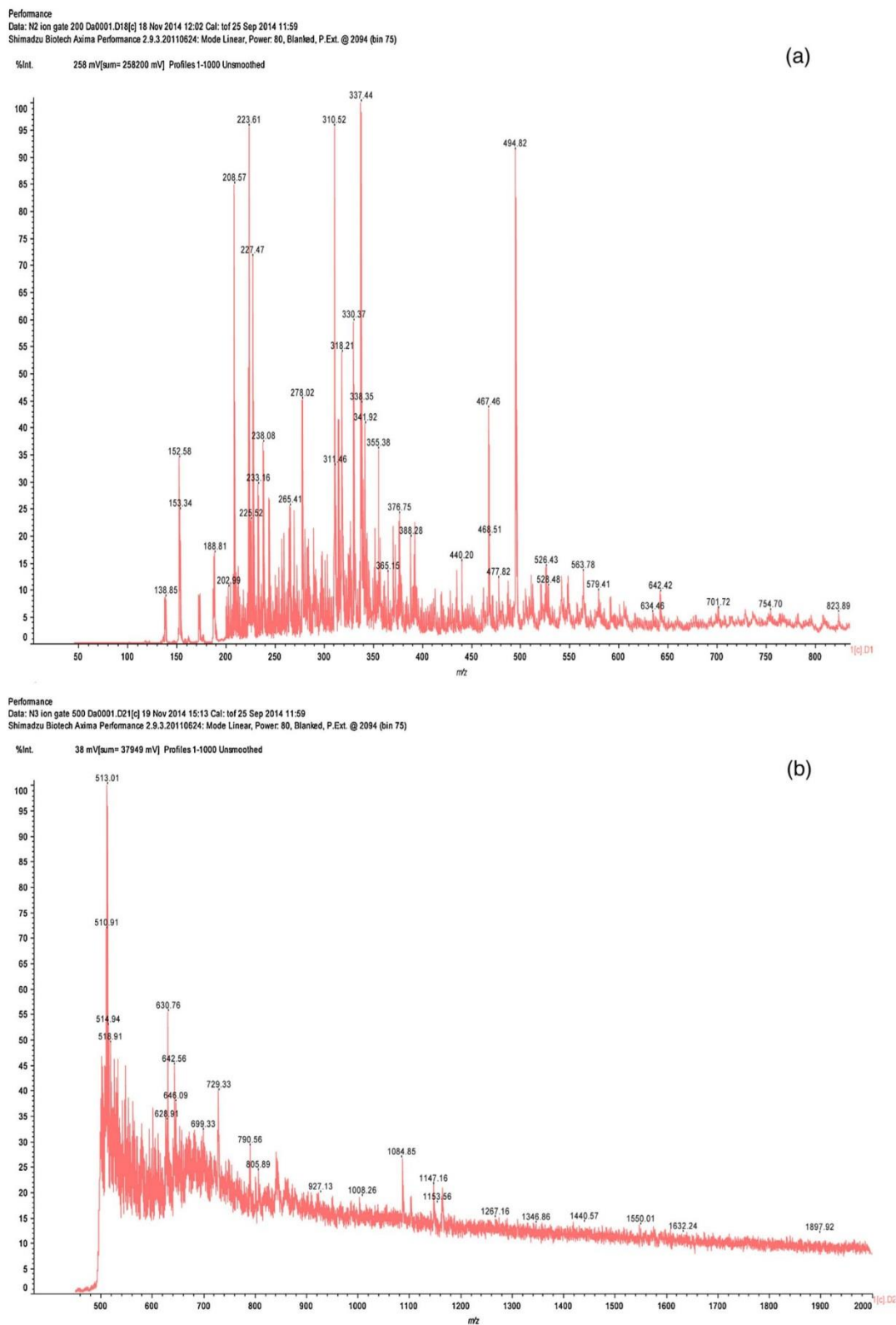


Fig. 2. MALDI-TOF of anigre tannin (a) in the 50–850 Da range, (b) in the 450–2000 Da range.

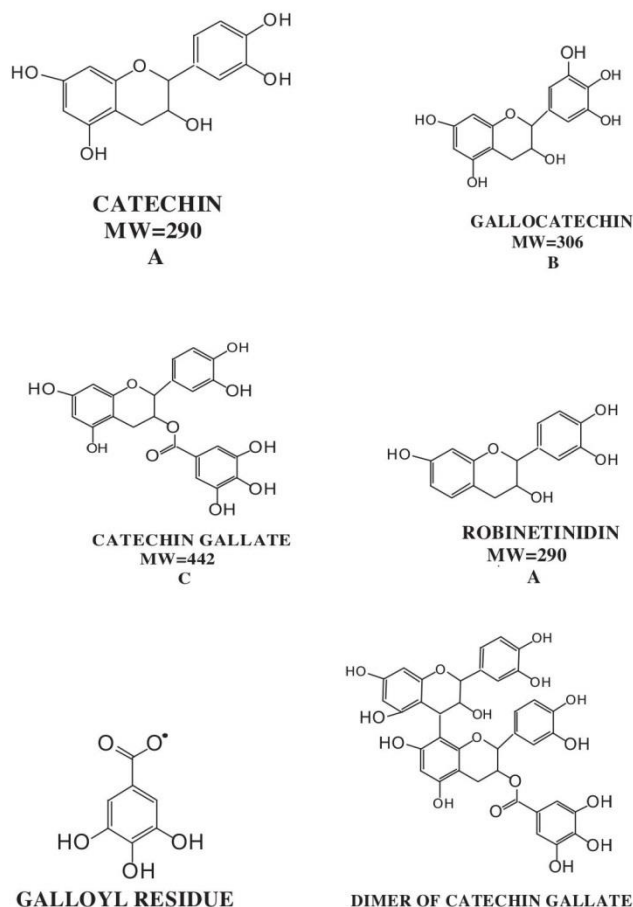


Fig. 3. Monomers and oligomers structures present in aningre tannin extract.

tannin. However, the peaks at 1415 and 615  $\text{cm}^{-1}$  are representing, respectively typical vibration frequencies of the symmetric stretching of methyl groups (Senvaitiene et al., 2005; Lei et al., 2008) and the presence of substituted aromatic ring (Kamal et al., 2010). The peak at 615  $\text{cm}^{-1}$  can be also attributed to C–O group of phenol and C–C stretching.

### 3.1.2. MALDI-TOF analysis

The MALDI-TOF Spectra in Fig. 2a and b show three monomers present in this tannin, their combination being somewhat unusual: in procyanidin-type tannins catechin is the monomer constituting the oligomers, with in some cases some galocatechin being present. In Aningre tannin instead catechin, galocatechin and catechin gallate are all present in the formation of the oligomers: A–C. To the mass A correspond two structures: catechin and robinetinidin which may both coexist, catechin being almost surely the only monomer representing this molecular weight in this tannin; B stands for galocatechin and C for catechin gallate. The molecular weight of all these three structures must be augmented of 23 Da to obtain the value of their characteristic peaks of the MALDI spectrum due to the  $\text{Na}^+$  matrix enhancer used. Galocatechin and catechin gallate appear to be protonated but catechin is not. Their real masses are: 290.3, 306.3 and 442.4, respectively for A–C. Their masses including  $\text{Na}^+$  one are: 311/312, 330 and 467 Da, respectively for catechin ( $+\text{Na}^+$ ), galocatechin protonated ( $+\text{Na}^+$ ) and catechin gallate protonated ( $+\text{Na}^+$ ). Catechin, galocatechin and catechin gallate structures are shown in Fig. 3. The MALDI-TOF

spectrum analysis shows the oligomer to be formed as shown in Table 1.

Two series of oligomers appears to compose this tannin: one is composed of flavonoid oligomers without the galloyl group and the other comprising the galloyl group linked to flavonoids oligomers, all in either in their protonated form or not with  $\text{Na}^+$  attached or not. Accordingly, to the former group (flavonoids oligomers without galloyl residue) belong the peaks at 311/312 Da; 330 Da; 567 Da; 634 Da; and 1440 Da (Table 1). To the second group (some galloyl group linked to flavonoids oligomers) belong the peaks at 467 Da; 755 Da; 790 Da; 1084 Da and 1550 Da (Table 1). The coupling of galloyl group and flavonoids is not new in tannin chemistry (Navarrete et al., 2010; Pizzi et al., 2009). However, what is new is the presence of methoxylated flavonoid oligomers in glucoside form such as in the case of the 567 Da peak, the simultaneous combination of methoxy groups and linked glucose not having been observed before in bark and wood extracted tannins but only in the tannins of *Vitis vinifera*.

It must be noticed that the protonated form and the loss of hydrogen to form oligomers must be taken into account if they are in the “body” of the oligomer (Saad et al., 2012). Many oligomers are in these forms: 330; 467; 755 and 1550 Da for protonated group and 310; 440 Da for those with loss of hydrogen. The dominant peak at 310 Da ( $+\text{Na}^+$ ) represents the catechin which lost one hydrogen during MALDI laser treatment; 440 Da represents catechin gallate which lost two hydrogens. Dimer of catechin gallate and galloyl residue structures are represented in Fig. 3.

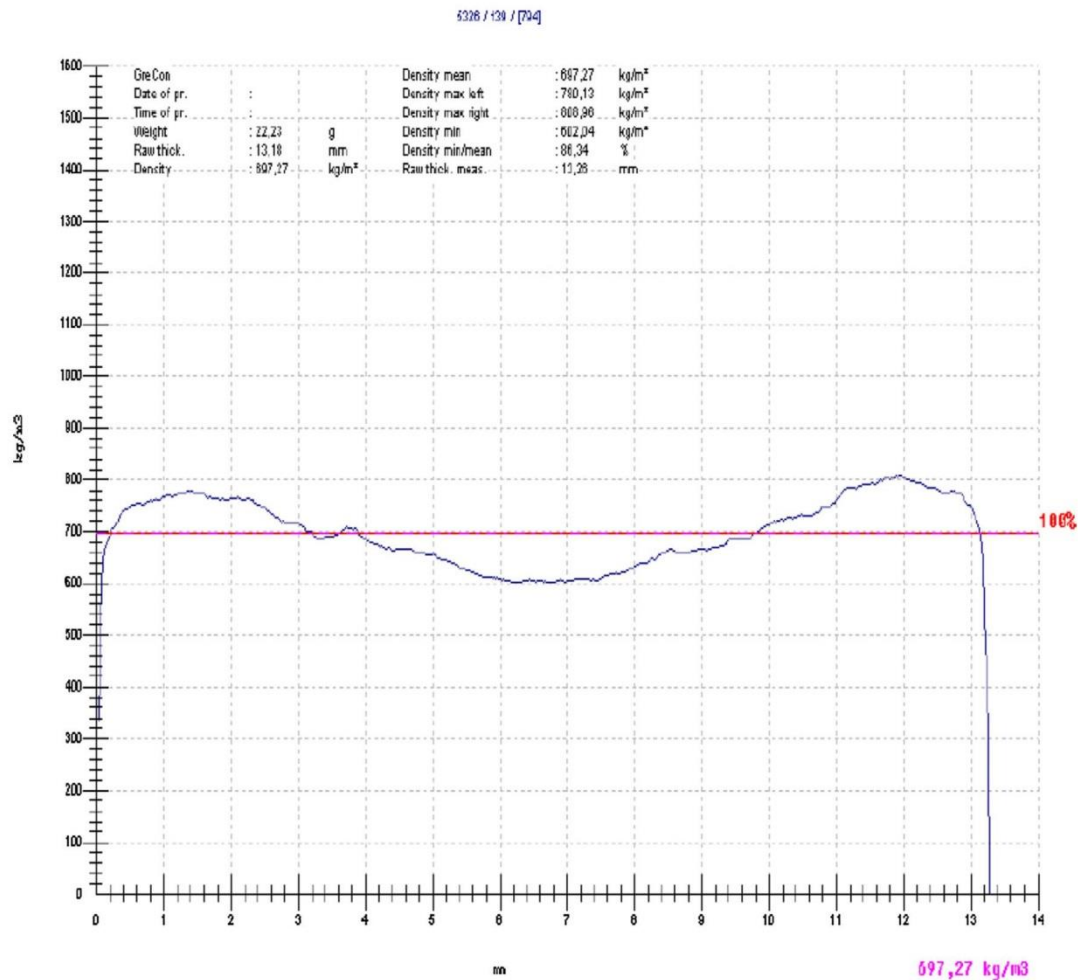


Fig. 4. Typical density profile of aningre tannin bonded particleboard.

**Table 1**

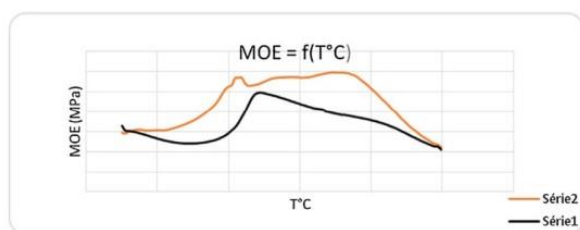
Monomers and oligomer structures present in aningre tannin extract as determined by MALDI ToF mass spectrometry.

M+Na <sup>+</sup> (exp.) Da	Species	Remark
311/312	Catechin or robinetinidin (+Na <sup>+</sup> )	Flavonoid monomer
330	Gallocatechin protonated (+Na <sup>+</sup> )	Flavonoid monomer
467	Catechin gallate protonated (+Na <sup>+</sup> )	Flavonoid monomer
567	Protonated catechin-fisetinidin dimer (without Na <sup>+</sup> ) OR dicationized (2 × Na <sup>+</sup> ) methoxylated hydroxyl flavonol glucoside	Flavonoid dimer
634	Gallocatechin dimer (thus = two gallocatechins) (+Na <sup>+</sup> )	Flavonoid dimer
755	Catechin-catechin gallate (Na <sup>+</sup> )	Flavonoid dimer
790	Dimer of gallocatechin with one galloyl residue attached (+Na <sup>+</sup> )	Flavonoid dimer
1084	Monogalloyl gallocatechin trimer (equal to three gallocatechins linked, one of which is galloylated) (+Na <sup>+</sup> )	Flavonoid trimer
1440	Catechin pentamer (without Na <sup>+</sup> )	Flavonoid pentamer
1550	Multiprotonated digalloyl gallocatechin tetramer (equal to four gallocatechins linked, two of which are galloylated) (+Na <sup>+</sup> ) OR gallocatechin pentamer (Na <sup>+</sup> )	Flavonoid tetramer or pentamer

All these oligomers obtained with MALDI-TOF confirmed the ATR-FT MIR interpretation indicating the presence of procyanidin/prodelphinidins type-tannin. With the presence of

gallocatechin units, we conclude that, aningre tannin is then a procyanidin with some segments in the form of prodelphinidins bound to the procyanidins.





**Fig. 5.** Resin behavior tested by TMA analysis. Variation of the Modulus of Elasticity (MOE) of aningre tannin bonded joints as a function of temperature. Serie 1: resin behavior of formulation 2; Serie 2: resin behaviour of formulation 1.

### 3.2. Resin development and particleboard manufacturing

#### 3.2.1. Density profile

For all samples, the density profile presents the same general shape with a maximum density for the surface layers and the minimum of density approximately in the center of the middle layer (Fig. 4). Average densities values respect international standard norms 630–700 kg/m<sup>3</sup>.

The constancy of the board core density indicates that these profiles allow good bending properties of the particleboards prepared and acceptable IB strength.

#### 3.2.2. TMA analysis and internal bond

The TMA analysis (Fig. 5) showed that the resin formulation containing 5.5% of paraformaldehyde powder as hardener had better rigidity than the formulation containing 12% glyoxal dissolved in water as hardener (1191 > 781 MPa). The results of the TMA tests were confirmed by preparing and testing laboratory particleboards. Particleboards manufactured with the formulation containing paraformaldehyde powder as hardener had the best IB strength. Result satisfied the dry IB strength requirement of the standard Norm NF EN 312-2 (1996). Dry IB strength of particleboards manufactured with glyoxal as hardener (formulation 2) at 220 °C during 7.5 min were less just slightly lower than 0.35 MPa (0.34 MPa). This means that the reactivity of formulation 2 was lower, ameliorating dry IB (0.41 > 0.34 MPa) value was obtained at 220 °C during 10 min. All wet IB were not significant, the higher value obtained was 0.04 MPa with formulation 1. They broke in the surfaces because “overcooked”, too high a temperature for too long a time, thus the wood was damaged.

## 4. Conclusion

ATR-FT MIR and MALDI-TOF characterization of aningre tannin have indicated that, aningre tannin is a procyanidin/prodelphinidins composed of catechin, gallogatechin as well as galloylated catechin and gallocatechin units. Furthermore the characteristics of particleboards bonded with aningre tannin adhesives give encouraging results.

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### 4.3. Mousses phénoliques avec substitution partielle du phénol par des tanins

#### *4.3.1. Développement et caractérisation de mousses phénoliques réalisées avec une résine phénol-formaldéhyde et des tanins de châtaignier*

## **« *Development and Characterisation of Phenolic Foams with Phenol-Formaldehyde-Chestnut Tanins Resin* »**

Auteurs : M.C. Lagel<sup>1</sup>, A. Pizzi<sup>1,2</sup>, S. Giovando<sup>3</sup> et A. Celzard<sup>4</sup>.

<sup>1</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>2</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

<sup>3</sup>Silva Chimica, San Michele Mondovi', Italie

<sup>4</sup>IJL, Université de Lorraine, Epinal, France

#### Résumé :

Avec l'épuisement des ressources fossiles, les extraits de tanins peuvent être une alternative naturelle à certains produits synthétiques. Les extraits de tanins hydrolysables de châtaignier ont été utilisés afin de remplacer partiellement le phénol dans les résines phénol-formaldéhyde (PF) pour la réalisation de mousses phénoliques rigides. Les mousses phénoliques phénol-formaldéhyde-tanins de châtaignier (PFT) ont été initialement synthétisées à partir de résines PFT copolymérisées avec différents rapports molaire. Les mousses PFT ainsi préparées ont été testées thermiquement, leur conductivité thermique étant légèrement moins bonne que celle des mousses phénoliques PF pure ; en résistance mécanique et en résistance vis-à-vis de l'eau, ces deux propriétés étant meilleures que celles des mousses phénoliques PF pures. En effet, les résines PF représentent une partie importante de résines synthétiques. Elles sont utilisées dans différents domaines d'application tels que des mousses phénoliques ou pour la préparation de panneaux de particules. Il est donc important de travailler sur la possibilité de développer des résines plus « vertes ».

Mots-clés : Biopolymères et polymères renouvelables, Cellulose et autres produits du bois, Mousses, Biomatériaux.



# Development and Characterisation of Phenolic Foams with Phenol-Formaldehyde-Chestnut Tannins Resin

M.C. Lagel<sup>1</sup>, A. Pizzi<sup>1,2</sup>, S. Giovando<sup>3</sup> and A. Celzard<sup>4</sup>

<sup>1</sup>LERMAB, University of Lorraine, 27 rue Philippe Seguin, 88051 Epinal, France

<sup>2</sup>Dept. of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

<sup>3</sup>Silva Chimica, via Torre 7, 12080 San Michele Mondovì, Italy

<sup>4</sup>IJL, University of Lorraine, 27 rue Philippe Seguin, 88051 Epinal, France

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**ABSTRACT:** With the depletion of fossil resources, tannin extracts can be a natural alternative to some synthetic products. Hydrolysable chestnut tannin extracts have been used to partially replace phenol in PF resins for phenolic rigid foams. Phenol-formaldehyde-chestnut tannin (PFT) phenolic foams were initially made from copolymerized PFT resins of different molar ratio. The PFT foams so prepared were tested for thermal conductivity, these being slightly worse than that of pure PF foams; and for mechanical and water absorption, these two properties being better than those of pure PF foams. Indeed, PF resins represent an important part of synthetic resins. They are used in different fields of application such as in phenolic foams or for the preparation of particleboard. So it is important to work on the possibility of going green with these resins.

**KEYWORDS:** Biopolymers and renewable polymers, cellulose and other wood products, foams, biomaterials

## 1 INTRODUCTION

During the last decades we have witnessed an important increase in oil prices. Consequently, considerable research has been carried out on the use of natural resources to replace petrochemicals. These developments have occurred in several diverse industrial sectors. Natural materials such as condensed polyflavonoid tannins have been used to develop new biobased materials such as, for example, biobased adhesive resins, insulation foams or floral foams [1–9]. Condensed polyflavonoid tannins are extracted from wood and/or bark after a simple hot water extraction. The tannins used up to now for the production of rigid foams are exclusively condensed polyflavonoid tannins.

However, another class of tannins exists, namely hydrolysable tannins, the main components of which are oligomers of pentagalloyl glucose. Some research work has already been done on the use of hydrolysable tannins (chestnut tannin extracts) in the development of phenol-formaldehyde (PF) adhesives for wood-based panels [10]. The PF adhesives are synthetic resins extensively used in the wood-based panel industry.

Thus, the substitution of phenol in some proportion with a renewable resource such as hydrolysable tannin in PF resins while maintaining the same performance would be of interest. In this article, the possibility of preparing phenol-hydrolysable-tannin formaldehyde copolymer resins and using them for the preparation of phenolic foams was studied. Chestnut wood tannin extract was the tannin chosen for this research as it is the most abundant hydrolysable tannin.

## 2 EXPERIMENTAL

### 2.1 Resins Synthesis

#### 2.1.1 Phenol-Formaldehyde Control Resin, P/F Ratio of 1/1.7

A PF resin (ratio P/F of 1/1.7) was synthesized according to systems already reported by coreacting 212.5 g of 80% phenol, 84.5 g of sodium hydroxide as a 30% water solution and 249.5 g of formaldehyde as a 37% aqueous solution [11].

The mixture is then slowly brought to reflux at 94°C under continuous mechanical stirring. Once a temperature of 90°C is reached, the mixture is left for 2 hours. The resin is then cooled and the pH is adjusted to 7 with a 45% solution of phenol sulfonic acid in ethylene

\*Corresponding author: lagel.mc@gmail.com

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glycol. The mixture is then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

### 2.1.2 Phenol-Chestnut Tannins-Formaldehyde Resin, P:T 70:30 and P/F Ratio of 1/2.5

The procedure for the synthesis of PFT resin was adapted from a previous work [10]. Spray-dried chestnut (*Castanea sativa*) wood tannin extract from Silva Chimica (San Michele Mondovi, Italy) was used.

For the PFT resin at P:T 70:30 and P/F ratio of 1/2.5, 30% of synthetic phenol by mass was replaced with spray-dried chestnut tannin extracts; and 148.75 g of 80% phenol, 99.48 g of 96% paraformaldehyde powder and 57.4 g of a 30% sodium hydroxide water solution were used.

First phenol and tannins (55 g) were dissolved in a water/methanol mixture (62.7 g of water/9.6 g of methanol). Paraformaldehyde was then added. This mixture was heated at 40°C for 30 minutes under reflux and continuous mechanical stirring. The temperature was then increased to 94°C, and 57.4 g of 30% sodium hydroxide water solution were added in four equal parts of 14.35 g each at regular intervals of 15 minutes.

After the last addition of sodium hydroxide, which occurred 45 minutes after the first addition, the mixture was further heated for 15 minutes to reach a total reaction time of 1 hour.

The resin was then cooled to room temperature and the pH adjusted to 6 with a 65% formic acid water solution. The mixture was then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

### 2.1.3 Phenol-Formaldehyde with Chestnut Tannins Resin, P:T 70:30 and P/F Ratio of 1/1.7

For PFT resin, P:T 70:30 and P/F ratio of 1/1.7, 30% of synthetic phenol by mass was replaced with spray-dried chestnut tannin extracts; and 148.75 g of 80% Phenol, 67.29 g of 96% paraformaldehyde powder and 57.4 g of a 30% sodium hydroxide water solution were used.

First phenol and tannins (55 g) were dissolved in a water/methanol mixture (62.7 g of water/9.6 g of methanol). Paraformaldehyde was then added. This mixture was heated at 40°C for 30 minutes under reflux and continuous mechanical stirring. The temperature was then increased to 94°C, and 57.4 g of 30% sodium hydroxide water solution were added in four equal parts of 14.35 g each at regular intervals of 15 minutes.

After the last addition of sodium hydroxide, which occurred at 45 minutes after the first addition, the

mixture was further heated for 1 hour and 15 minutes to reach a total reaction time of 2 hours.

The resin was then cooled to room temperature and the pH adjusted to 7 with a 45% solution of phenol sulfonic acid in ethylene glycol. The mixture was then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

## 2.2 Resins Characterisations

### 2.2.1 Exothermic Behaviour

The aim of this test was to measure the reactivity of the resin as a function of time. The test consists of adding a defined amount of catalyst in a defined amount of resin. This mixture is then stirred while the temperature is recorded. The peak of the maximum of temperature reached and the time at which it occurs were recorded. This test was performed on the day of the synthesis of the resin and then repeated weekly.

For the PF resin, 10 g of resin was added to 0.3 g of a 65% solution of phenol sulfonic acid in ethylene glycol. For the PF resin coreacted with chestnut tannin, 5 g of resin was added to 5 g of a 45% solution of phenol sulfonic acid in ethylene glycol. A large amount of resin was prepared at the beginning of the test and then one sample of resin was tested weekly.

### 2.2.2 Viscosity

Viscosities were determined with a Brookfield viscometer at 25°C.

## 2.3 Development of Foams

All foams were prepared equally using the same procedure and under the same set of conditions. Their characteristics were then determined.

Some surfactants were first added to the PF or PFT resin, like Cremophor ELP, which is a nonionic solubilizer, and DC 193, which is a silicone polyether copolymer. The amounts of surfactants were determined to optimise the appearance of the foams (homogeneity, no big holes...). After this, a blowing agent was added to the mix and then an acid catalyst was finally added.

For foaming, pentane was used as blowing agent (blowing point was at 36°C). The reaction between the PFT resin and the acid catalyst was exothermic. Foam hardening occurs at the end of foaming. A different foaming approach was also tried: thus, foaming was carried out with 4,4' diphenylmethane diisocyanate (pMDI), without pentane, if flammable reactive solvents are not wanted in the process. In this approach foaming was caused by the CO<sub>2</sub> released by reaction of the pMDI with water.



In the preparation of tannin foams 65% *para*-toluene sulfonic acid in water is generally used. However, this was found to be unsuitable for the PFT foams. Thus, different catalysts had to be tried.

The reagents were first mixed together to ensure homogeneity of the mixture. The mixture was then poured in a plastic beaker of 250 mL, in which the walls were covered with aluminum foil in order to easily remove the foam.

Different foams were prepared by changing the catalyst (65% solution of phenol sulfonic acid in ethylene glycol, 65% solution of phenol sulfonic acid in water

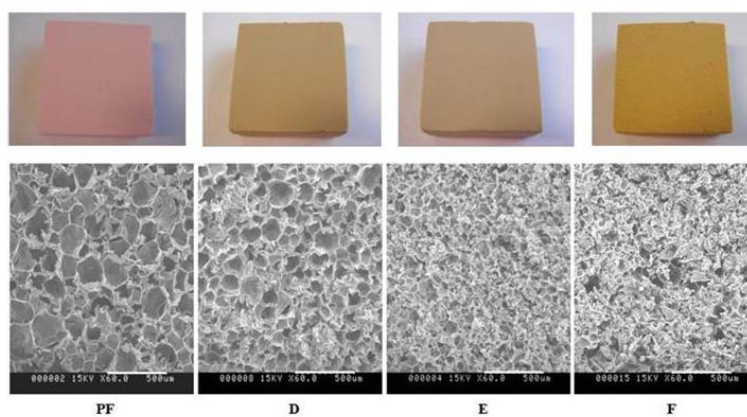
and 65% solution of phenol sulfonic/sulfuric acids [50/50] in ethylene glycol).

The foams were dried at room temperature for 24 hours and cut off at their core. The samples were stored at 20°C and 60% relative humidity for 3 weeks.

Foams were prepared with both types of PFT resins. At first a foaming temperature of 80°C was tried. Afterwards a lower temperature of 60°C was tried. Several foam types were prepared (Table 1 and Figure 1) with different catalysts and with different foaming agents (chemical and physical).

**Table 1** Procedures of foams.

Resin	PE.	PFT.			PFT.					
	P/F ratio of 1/1.7	P:T 70:30 and P/F ratio of 1/2.5			P:T 70:30 and P/F ratio of 1/1.7					
Foam	PF	1	2	3	A	B	C	D	E	F
	Mass (g)									
<i>Resin</i>	25	25	25	25	25	25	25	25	25	25
<i>Cremophor ELP</i>	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
<i>DC 193</i>	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45
<i>Pentane</i>	1.5	1.5	1.5	/	1.5	1.5	/	1.5	1.5	/
<i>Phenol sulfonic acid at 65% in ethylene glycol</i>	3.5	8.75	/	/	8.75	/	/	8.75	/	/
<i>Sulfuric/phenol sulfonic acids (50/50) at 65% in ethylene glycol</i>	/	/	8.75	/	/	8.75	/	/	8.75	/
<i>Phenol sulfonic acid at 65% in water</i>	/	/	/	8.75	/	/	8.75	/	/	8.75
<i>pMDI</i>	/	/	/	3	/	/	3	/	/	3
<i>Foaming temperature (°C)</i>	80	80	80	80	60	60	60	80	80	80
<i>Average density (kg/m<sup>3</sup>)</i>	0.0298	0.0463	0.0645	0.0746	0.1007	0.0944	0.1267	0.0925	0.0908	0.1169



**Figure 1**

**Table 2** Solid content and viscosities of resins.

Resin	PF, P/F ratio of 1/1.7	PFT, P:T 70:30 and P/F ratio of 1/2.5	PFT, P:T 70:30 and P/F ratio of 1/1.7
Solid content (%)	77	72.2	75.9
Viscosity at 25°C (mPa.s)	3700	3420	4755

## 2.4 Characterisation of Foams

Characterisation of the foams (appearance, density, mechanical resistance) is necessary to determine their applications.

Solid contents and viscosities of all resins used for making the foams are in the same range, around 75% and 3900 mPa.s (Table 2), in order that a meaningful comparison of the foams' characteristics be obtained.

### 2.4.1 Scanning Electron Microscopy (SEM)

The SEM observations were done with a Hitachi S-520 scanning electron microscope and with prior metallization of samples.

Foams were observed perpendicularly to their growth direction at x60 magnification. The samples tested had a density close to the average of the densities of the foam samples. The PF foam (P/F ratio of 1/1.7) and PFT (P:T 70:30 and P/F ratio of 1/1.7) foams prepared at 80°C were studied (Foams D, E and F).

### 2.4.2 Mechanical Resistance under Compression

The mechanical tests were performed in compression (NF EN 13166) by using an Instron 5944 universal testing machine equipped with a 2 kN head load cell. Compression was performed at a constant rate of 2.0 mm/min. The sample sizes were 1.5 x 3 x 3 cm<sup>3</sup> and they were tested in the axial direction of the foam growth. The two samples that were tested had a density close to the average of the densities of the foam samples.

### 2.4.3 Thermal Conductivity

Thermal conductivity was measured using the transient planar source method (NF EN 13166) with a thermal conductivity analyzer Hot Disk TPS 2500, with a power of 10 mW for 40 seconds and equipped with a sensor 5501 with a radius of 6.403 mm. These tests were performed at room temperature and controlled humidity. The sensor was placed between two samples of size 1.5 x 3 x 3 cm. Conditions of the laboratory air were: 22°C +/- 1°C, 50% +/- 2% relative humidity.

Two samples that have been tested have a density close to the average of the densities of the foam samples. Two samples are needed to do one test, and it was repeated one time.

### 2.4.4 Water Absorption

The water absorption test involved keeping foam samples immersed in water for an entire week. Then, samples were removed from the water and drained for fifteen minutes on a 30° inclined grid (Iram1861).

The absorption related to the initial volume of the sample was determined using the formula:  $\frac{\text{final mass} - \text{initial mass}}{\text{Initial volume}} \times 100$ . Masses are in grams and volumes in cm<sup>3</sup>. The samples that were tested had a density close to the average of the densities of the foam samples.

## 3 RESULTS AND DISCUSSION

### 3.1 Characterisations of Resins

#### 3.1.1 Exothermic Behaviour

Concerning the exothermic behaviour for the PF resin at P/F molar ratio 1/1.7, the maximum temperature seems to decrease over time, but the starting temperature also seems to influence the final reactivity of the resin (Table 3).

For the PFT resin at P:T 70:30 weight ratio and P/F molar ratio of 1/2.5, elapsed time to peak temperature globally increases with resin ageing, and the difference between highest and starting temperature increases with time. However, the peak temperature increases with resin ageing while the opposite would have been logically expected. This phenomenon could be explained by the increase of the starting temperature, which implies an augmentation of peak temperature. An alternative explanation is that the PFT resin reactivity increases over time. This appears so because the starting temperature only increases 2°C between the first and the last test, while the peak temperature increases to 4.5°C. The PFT resin at P:T 70:30 and P/F molar ratio of 1/2.5 seems to remain reactive for a rather long time after it has been synthesized (Table 3).

**Table 3** Exothermal behaviour of PF and PFT resins.

Resin	Days	Starting temperature (°C)	Maximal temperature (°C)	Difference between maximal and starting temperature (°C)	Elapsed time before the peak of temperature
PF, P/F ratio of 1/1.7	J	17.5	32.9	15.4	7 min 30 sec
	J + 7	19.2	29.2	10.0	7 min 30 sec
	J + 14	21.3	37.2	15.9	7 min 57 sec
	J + 28	21.7	37.4	15.7	7 min 50 sec
	J + 35	20.1	30.2	10.1	6 min 42 sec
PFT, P:T 70:30 and P/F ratio of 1/2.5	J	18.5	27.5	9.0	3 min 30 sec
	J + 7	19.3	29.5	10.2	2 min 30 sec
	J + 14	20.7	31.0	10.3	2 min 50 sec
	J + 28	20.4	32.0	11.6	3 min 03 sec
PFT, P:T 70:30 and P/F ratio of 1/1.7	J	19.2	29.1	9.9	1 min 56 sec
	J + 7	19.3	29.5	10.2	2 min 30 sec
	J + 14	20.7	32.2	11.5	4 min 15 sec
	J + 28	20.5	32.6	12.1	4 min 00 sec

**Table 4** Viscosities of PF resin (P/F ratio of 1/1.7) and PFT resin (P:T 70:30 and P/F of 1/2.5).

Resin	Storage	At room temperature		At 35°C	
	Days	Viscosity (cP)	% of increase	Viscosity (cP)	% of increase
PF, P/F ratio of 1/1.7	J	12607	/	13370	/
	J + 14	21125	67.57	69500	419.82
	J + 21	27050	114.57	Unmeasurable, too thick	/
	J + 28	29941	137.50	Unmeasurable, too thick	/
	J + 35	32579	158.42	Unmeasurable, too thick	/
PFT, P:T 70:30 and P/F ratio of 1/2.5	J	5191	/	5284	/
	J + 14	6530	25.80	Unmeasurable, gelled	/
	J + 21	10885	109.70	Unmeasurable, gelled	/
	J + 28	16041	209.04	Unmeasurable, gelled	/
	J + 35	21718	318.40	Unmeasurable, gelled	/

For the PFT at P:T 70:30 and P/F molar ratio of 1/1.7, the elapsed time to the peak of temperature increases with the ageing of the resin (Table 3). However, the maximum temperature also increases with the ageing of the resin; and the difference between maximal and starting temperature also increases with the time.

By comparing the PFT resins of different P/F molar ratio, we note that the maximum temperatures reached are substantially the same. However, for the P/F 1/2.5 resin, the times required to achieve the maximum temperature are longer and increase more rapidly with the ageing of the resin. Thus, the PFT resin with P/F ratio of 1/1.7 is the best one as regards this property.

### 3.1.2 Viscosity

The viscosity of the PFT resins and PF resin were compared after storing the resins at room temperature (around 20°C) and 35°C. The viscosities increase as a function of storage time. This test was conducted on a PF resin of molar ratio 1/1.7 and PFT resin P:T 70:30 and P/F molar ratio 1/2.5 (Table 4).

The viscosity of the PFT resin P:T 70:30 and P/F ratio of 1/2.5, only shows a small increase of 26% after 14 days of ageing. However, we can see that in the long term the PFT resins are not very heat resistant. This could be explained by the reactivity of these



resins, which are quite important, and because of the coreactions between PF resin groups and chestnut tannins oligomers which are favored by the temperature. Thus, the lengths of the chains are increasing, so therefore the viscosity is also increasing.

With the PFT resin, P:T 70:30 and P/F ratio of 1/1.7, after a week the resin sample almost gelled.

However, by reducing the initial viscosity to 3000 or 3500 cP, the resin remains reactive and usable for a longer time and the viscosity does not increase much over time. Thus, the foams have been prepared with a resin which was aged for one month. The starting viscosity is thus a crucial parameter for the storage and the use of such resins over time.

## 3.2 Characterisations of Foams

### 3.2.1 Macroscopic Observation

Foams cured at 80°C and prepared with pMDI were slightly denser. Foams with pentane as blowing agent when mixed acids are used as catalyst are denser than those catalyzed with only phenol sulfonic acid.

Foams with a PFT resin and phenol sulfonic acid as catalyst were beige coloured compared to those obtained with the control PF resin, which were pink. Foams made with PFT resin and with the mix of acids are slightly clearer and their pores are finer than for foams made with PFT resin and with only phenol sulfonic acid. The PFT foams obtained with pMDI are orange coloured.

Foams cured at 60°C have almost the same appearance as those obtained at 80°C. Foams prepared with pMDI are also slightly denser. On the other hand, with pentane foaming, the one with the acids mixture is of lower density than the one with only phenol sulfonic acid, whatever the foaming temperature used.

### 3.2.2 Scanning Electron Microscopy

The PF only foams present the greatest porosity. Coreacting chestnut tannins with the PF resin yields foams of finer porosity (Figure 1).

Foams with the mix of acids (phenol sulfonic and sulfuric acids [50/50] at 65% in ethylene glycol) as catalyst present a finer porosity than the one with just phenol sulfonic acid. They are also more resistant to cutting than the one with pMDI foaming and with phenol sulfonic acid at 65% in water as catalyst (Figure 1).

Foams with phenol sulfonic acid at 65% in ethylene glycol as catalyst, have a bigger porosity than those catalysed with either the mix of acids or with pMDI. These last two have similar porosity (Figure 1).

### 3.2.3 Mechanical Resistance

The PF foams with and without chestnut tannins have typical behaviour of cellular solids with open porosity. Their deformation under compression takes place in three phases: a linear elastic phase, a plateau stress phase and finally a densification phase (Table 5 and Figures 2 to 4).

As regards the PFT resin P:T 70:30 and P/F ratio of 1/2.5 (Table 5 and Figure 2):

- Mechanical resistances of foams are directly related to their densities.
- The foams prepared with pMDI are the densest and the strongest.
- The experimental foam made with the mix of acids is the one that is closest to PF control resin foam, P/F ratio of 1/1.7, while it is denser than the latter.
- Foams made with phenol sulfonic acid at 65% in ethylene glycol, the density of which is closer to the one of PF control resin foam, are slightly weaker.

Looking at the first part of the compression curve, PFT foams deform less than PF foams. The foaming temperature influences the characteristics of the PFT foams, P:T 70:30 and P/F ratio of 1/1.7 (Table 5 and Figures 3 and 4). Thus, for the compressive strength at 20% strain, for foams made with pMDI and the mix of acids, the strongest is the one prepared at 60°C. On the contrary, the temperature did not have a big influence on the formulation with phenol sulfonic acid at 65% in ethylene glycol. Foams made with pMDI which are denser are also the most mechanically resistant. This time foams resistances are not directly related to their densities. Indeed, foam B has a compressive strength at 20% strain higher than foam A, whereas the density of foam A is higher.

Foams made with 65% phenol sulfonic acid in ethylene glycol are those closest to the PF foam, while they are much denser than the latter.

When we are looking at the first part of the curve, phenolic foams with tannins deform less under compression than the pure PF foam. This phenomenon is more pronounced for a foaming temperature of 80°C.

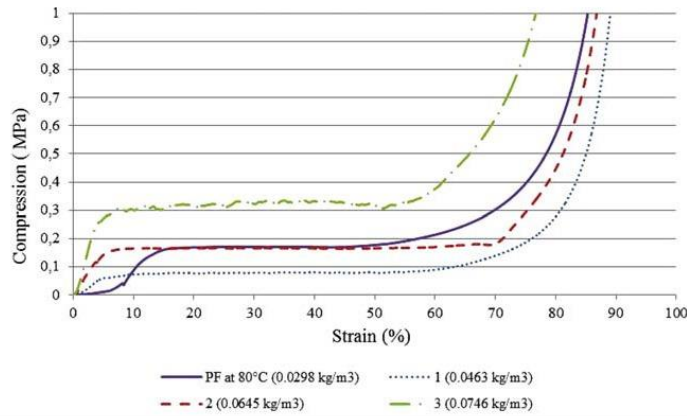
By comparing the foams produced with the two types of PFT resins catalysed with the mix of acids, at the same foaming temperature (80°C), almost the same mechanical properties are obtained. However, it can be said that the resin with a P/F molar ratio of 1/2.5 provides slightly more resistant foam.

Of the foams catalysed with the 65% phenol sulfonic acid in ethylene glycol, those made with 1/1.7 P/F molar ratio are the most resistant.

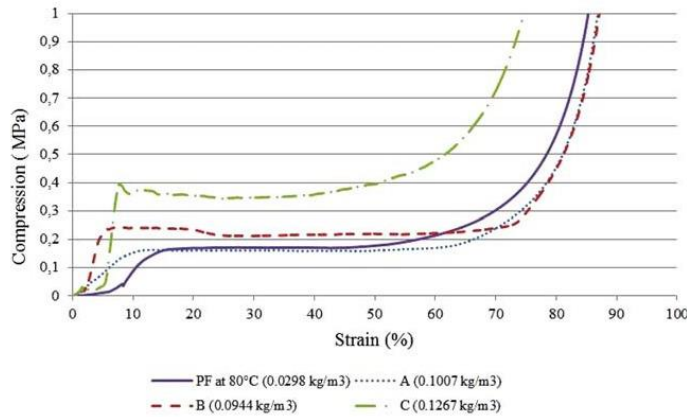


**Table 5** Mechanical test results of foams.

Resin	Formulation	Compressive strength at 20% strain (MPa)	Young's modulus (MPa)	Densification (%)	$\sigma_{pic}$ (MPa)	$\sigma_{plateau}$ (MPa)
PF, P/F ratio of 1/1.7	PF	0.1694	2.89	86.65	/	0.1779
	1	0.0771	1.72	74.64	/	0.0786
PFT, P:T 70:30 and P/F ratio of 1/2.5	2	0.1659	4.48	71.51	/	0.1970
	3	0.3128	8.63	76.22	/	0.3206
	A	0.1611	1.93	85.08	0.1636	0.1621
	B	0.2343	9.09	86.63	0.2421	0.2200
PFT, P:T 70:30 and P/F ratio of 1/1.7	C	0.3541	19.07	75.90	0.3956	0.3632
	D	0.1747	5.50	85.77	/	0.1844
	E	0.1617	5.31	83.30	/	0.1690
	F	0.2862	22.02	77.53	0.3441	0.3013



**Figure 2**



**Figure 3**

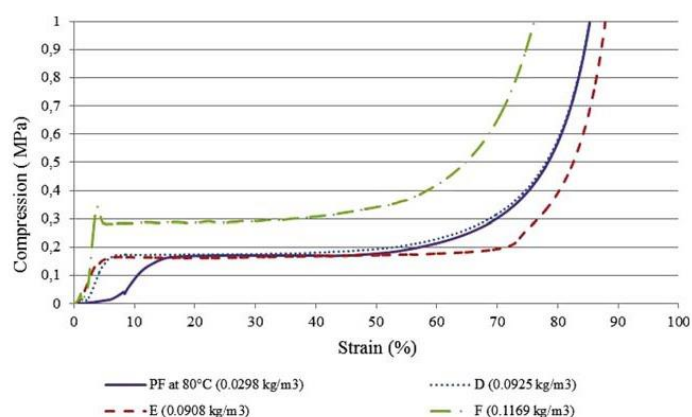


Figure 4

Foams prepared with pMDI have similar mechanical properties, although foams made with a P/F molar ratio of 1/2.5 are slightly stronger. The compression stress-strain curve of this foam has a peak before the plateau, which is not the case for the 1/1.7 P/F molar ratio foam.

### 3.2.4 Thermal Conductivity

As a reference, thermal conductivity of the control PF foam, P/F molar ratio 1/1.7, was measured. The value was 0.04350 W/(m.K), for a density of 0.0298 kg/m<sup>3</sup>.

When foaming at 80°C (Table 6), the more insulating PFT resin is the one with pMDI of finer porosity than the pure PF foam. The PFT foams are less insulating than pure PF foams. Foam 2, which has a density comparable to that of the PF foam, presents a thermal conductivity that is almost twice as high. The foam (with the mix of acids) having a fine porosity is the one which also has a higher thermal conductivity. If fine porosity is wanted, then pMDI addition gives a better level of insulation.

The PFT foams prepared at 60°C (Table 6) are slightly more insulating than those prepared at 80°C, but slightly denser. The most insulating foams are those made with pMDI.

The PFT foams are markedly less insulating than pure PF foams, which is most probably due to the higher proportion of polymeric carbohydrates present in hydrolysable tannins. In all these cases the thermal conductivity of these foams does not appear to be directly related to their densities.

By comparing foams produced with the two types of PFT resins at the same foaming temperature (80°C), foams made with phenol sulfonic acid at 65% in

Table 6 Thermal conductivity results of foams.

Resin	Formulation	Thermal conductivity (W/(m.K))	
PF, P/F ratio of 1/1.7	PF	0.04350	
	1	0.08397	
	PFT, P:T 70:30 and P/F ratio of 1/2.5	2	0.10435
		3	0.07373
		A	0.07908
		B	0.07607
PFT, P:T 70:30 and P/F ratio of 1/1.7	C	0.06052	
	D	0.08677	
	E	0.07671	
	F	0.07327	

ethylene glycol and with pMDI have almost the same thermal properties.

For foams catalysed with the mix of acids, the foam at P/F molar ratio of 1/1.7 is the most insulating one.

As regards the influence of the catalyst type with pentane foams, the most insulating foams are those exclusively prepared with 65% phenol sulfonic acid in ethylene glycol for the PFT resin at P:T 70:30 and P/F molar ratio of 1/2.5. Conversely, for the PFT resin at P:T 70:30 and P/F ratio of 1/1.7 the most insulating foam is the one prepared with the mix of acids.

The PFT foams with pMDI are the most insulating ones when compared to those foamed by pentane. However, they are denser and they have a finer

**Table 7** Water absorption results of foams.

Resin	Formulation	Percentage of absorbed water relative to the volume (%)
PF, P/F ratio of 1/1.7	PF	35.40
	1	23.79
PFT, P:T 70:30 and P/F ratio of 1/2.5	2	25.35
	3	30.34
	A	26.97
	B	25.13
PFT, P:T 70:30 and P/F ratio of 1/1.7	C	27.17
	D	27.56
	E	22.23
	F	34.22

porosity than other foams with tannins. They seem to present a fine closed-cell porosity.

### 3.2.5 Water Absorption

The PFT foams appear to be more water resistant than pure PF foams prepared with the PF control resin, P/F ratio of 1/1.7 (Table 7).

For the PFT resin, P:T 70:30 and P/F ratio of 1/2.5, the most water resistant foam is the one with pentane as blowing agent and 65% phenol sulfonic acid in ethylene glycol as catalyst.

For the PFT resin, P:T 70:30 and P/F ratio of 1/1.7, the most water-resistant foams are the one with pentane as blowing agent and the mix of acids as catalyst, whatever the foaming temperature used. In general the foams with pentane as blowing agent are more water resistant than the one with pMDI (for this type of foaming it is better to use a foaming temperature of 60°C for best water resistance). Concerning foams made with the mix of acids, the one which is slightly more water resistant is the one foamed at 80°C. The water absorptions of foams prepared with phenol sulfonic acid at 65% in ethylene glycol are similar.

Therefore, there is no general connection between the water absorption and the foaming temperature. Moreover, there appears to be an evident link between density and water absorption of such PFT foams; the less dense they are, the more water resistant they are.

## 4 CONCLUSIONS

The preparation of PFT resins with P/F molar ratio of 1/1.7 is possible. This is the same molar ratio as

commercial PF resins. Thus, the substitution of chestnut tannins for part of the phenol in such resins is possible. This approach is an alternative route to make value-added foams different from the condensed tannin/furanic foams already presented [3–7] by using a different raw material.

The study of the effect of the catalysts used shows that the use of sulfuric acid and phenol sulfonic acid yields less friable foams. The catalyst generally used for the preparation of tannin foams is *para*-toluene sulfonic acid at 65% in water, but this was found to be unsuitable for PFT foams. Moreover, foams obtained with the mix of sulfuric acid/phenol sulfonic acid are highly homogeneous and have very fine porosity. A further point of interest is that it is possible to replace pentane blowing agent with pMDI using the development of CO<sub>2</sub> of its reaction with water for foaming. As pentane is inflammable, explosive and has a low boiling point (36°C), one needs to take precautions to use and store it in a factory; the pMDI route is also a viable alternative.

Furthermore, the use of chestnut tannins in PF foams improves foam. Thus, PFT resin seems to remain reactive for rather a longer time than PF resins after its synthesis.

Concerning mechanical resistance, PFT foams deform less under compression and are more resistant than the pure PF control foam. In addition to that, PFT foams based on hydrolysable tannins appear to be more water resistant than PF foams.

Conversely, PFT foams have a thermal conductivity between 0.061 and 0.104 W/(m.K), which is higher than PF foam; this can be explained by the fact that they are also much denser.

The PFT foams which seem to be the most interesting are those which are more insulating and more mechanically resistant to water, which are those foamed at 60°C with a PFT resin at a P/F ratio of 1/1.7. These are also the ones of highest density.

This study shows that it is totally possible to replace an amount of petrochemicals by a natural resource such as chestnut tannins in the formulation of phenolic resins and phenolic foams.

## ACKNOWLEDGMENTS

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*4.3.2. Analyses de résines phénol-formaldéhyde et tanins de châtaignier à l'aide d'un spectromètre de masse couplant une source d'ionisation laser assistée par une matrice (MALDI) et un analyseur à temps de vol (ToF)*

## **« Matrix-Assisted Laser Desorption-Ionization Time of Flight (MALDI-ToF) Mass Spectrometry of Phenol-Formaldehyde-Chestnut Tannin Resins »**

Auteurs : M.C. Lagel<sup>1</sup>, A. Pizzi<sup>1,2</sup> et S. Giovando<sup>3</sup>.

<sup>1</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>2</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

<sup>3</sup>Silva Chimica, San Michele Mondovi', Italie

### Résumé :

Des extraits naturels de tanins hydrolysables de châtaignier ont été utilisés afin de remplacer partiellement le phénol dans les résines phénol-formaldéhyde (PF) pour les mousses rigides phénoliques. Ces résines ont été analysées par spectrométrie de masse couplant une source d'ionisation laser assistée par une matrice et un analyseur à temps de vol (MALDI-ToF). Les types et la distribution des copolymères phénol-formaldéhyde seuls ; des copolymères de tanins de châtaignier seuls et des copolymères de phénol-formaldéhyde-tanins de châtaignier ont été déterminés. Les analyses MALDI-ToF d'une résine de contrôle PF (avec le même rapport molaire) et des extraits de tanins châtaignier ont été effectuées afin d'identifier les pics des poids moléculaires correspondant aux copolymères de tanins de châtaignier avec le phénol et le formaldéhyde.

Mots-clés : Tanins de châtaignier, Copolymères de phénol-formaldéhyde et tanins de châtaignier, Analyses MALDI-ToF.

# Matrix-Assisted Laser Desorption-Ionization Time of Flight (MALDI-TOF) Mass Spectrometry of Phenol-Formaldehyde-Chestnut Tannin Resins

M.C. Lagel<sup>\*1</sup>, A. Pizzi<sup>1,2</sup> and S. Giovando<sup>3</sup>

<sup>1</sup>LERMAB, University of Lorraine, 27 rue Philippe Séguin, 88026 Epinal, France

<sup>2</sup>Dept. of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

<sup>3</sup>Silva Team, Silva Chimica, via Torre 7, 12080 San Michele Mondovì, Italy

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**ABSTRACT:** Natural hydrolysable chestnut tannin extracts used to partially substitute phenol in Phenol-Formaldehyde (PF) resins for phenolic rigid foams were analysed by matrix-assisted desorption ionization time of flight (MALDI-TOF) mass spectrometry. PF only, chestnut only and PF-chestnut copolymerised oligomer types and distribution were determined. MALDI-TOF analyses of a PF control resin (with the same molar ratio) and of chestnut tannin extracts were performed in order to identify the peaks of molecular weights corresponding to copolymers of chestnut tannins with phenol and formaldehyde.

**KEYWORDS:** Chestnut tannins, phenol-formaldehyde-chestnut tannins copolymers, MALDI-TOF analysis

## 1 INTRODUCTION

During the last decades a marked increase in oil prices has occurred. Consequently, considerable research has been carried out on the use of natural resources to replace petrochemicals. These developments have occurred in several diverse industrial sectors. Some research has concentrated on natural materials such as condensed polyflavonoid tannins to develop new biobased materials such as, for example, insulation foams or floral foams, biocomposites or biobased adhesive [1–6].

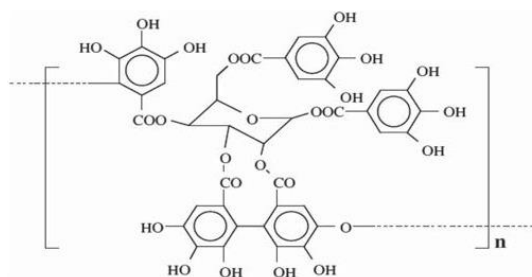
Most commercial tannins are industrially extracted by a simple water extraction from wood, bark, gall and other vegetable material. Two broad classes of tannins exist: in the first are the condensed polyflavonoid tannins. These have been extensively researched for adaptation to wood adhesives [5, 7], for fire-resistant tannin/furanic foams [8], and products/processes other than their traditional application for leather tanning.

The second class of tannins, namely hydrolysable tannins, are composed of polyphenolic oligomers of pentagalloyl glucose, and their lower reactivity has somewhat limited them to leather tanning, an application for which they are particularly prized due to their light color. Recently these tannins have been used to prepare phenol-hydrolysable-tannin-formaldehyde copolymer resins. These have been used for the preparation of phenolic wood adhesives [9, 10], and more recently for rigid fire-resistant foams [11].

There are two types of hydrolysable tannins such as chestnut, tara, turkey gall, oak, etc. The first type is composed of a mixture of sugars with oligomers of simple phenols such as gallic and digallic acids [12, 13], and the second type is composed of ellagitannins, which are esters of a sugar, mainly glucose, with gallic and digallic acids, and also with more complex structures containing ellagic acid (Formula 1).

\*Corresponding author: lagel.mc@gmail.com

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Formula 1

Chestnut wood tannin extract was the tannin chosen for this research being that it is the most abundant hydrolysable tannin [14]. The study presented here concentrates on the determination of the type and distribution of the oligomers formed in the reaction of phenol and chestnut tannin with formaldehyde to obtain phenol-hydrolysable-tannin-formaldehyde copolymer resins due to the results in fire-resistant phenol-formaldehyde-tannin foams recently developed [11]. This was done for continuity of the characterization of the resin developed in a previous work [9] to prepare rigid foams [11].

Since its introduction by Karas and Hillenkamp in 1987 [15], Matrix-Assisted Laser Desorption/Ionization (MALDI) mass spectrometry has greatly expanded the use of mass spectrometry towards large molecules, and has revealed itself to be a powerful method for the characterization of both synthetic and natural polymers [16–21]. Fragmentation of analyte molecules upon laser irradiation can be substantially reduced by embedding them in a light absorbing matrix. As a result, intact analyte molecules are desorbed and ionized along with the matrix and can be analysed in a mass spectrometer. This soft ionization technique is mostly combined with time-of-flight (TOF) mass analysers. This is because TOF-MS has the advantage of being capable of providing a complete mass spectrum per event for virtually an unlimited mass range, with only a small amount of analyte being necessary and relatively low cost of equipment. Its usefulness in the elucidation of the distribution of different oligomers in the case of polyflavonoid tannins in general has already been demonstrated [21–26]. In particular, its applicability for the identification of the oligomers distribution of hydrolysable tannins has also been demonstrated [14, 27, 28].

Thus, MALDI-TOF mass spectrometry has been used for this study, as it has already proven itself in the analysis of different types of tannins [12–14, 27, 29, 30]. For

this study, three investigations were carried out: (1) for chestnut tannin extract alone, (2) for PF resin alone, and (3) for PF-chestnut tannin resin. In this article the characteristics of just the raw chestnut tannin extract and the PF resin by itself are only briefly discussed to help the reader compare these with what was obtained for the PF-tannin copolymer. For a more comprehensive discussion of the oligomers distribution obtained by MALDI-TOF mass spectrometry for raw chestnut tannin extract and for the PF resin alone, the reader is directed to the relevant in-depth references [14, 27, 28, 31].

The importance of synthesising PF-hydrolysable tannin resins is multifold. Apart from the obvious, there is a need to increase the biosourced portion of oil-derived resins and thus decrease oil dependency. There are three other factors that play a role in this development. First, the present supply of condensed tannins is relatively limited, and thus other sources of reactive polyphenolic materials are looked at, in this case hydrolysable tannins. Second, there is the need to decrease or at least maintain resin costs within today's limits due to the continuous increase in cost of oil-derived materials. Lastly, the reactivity of hydrolysable tannins being similar to that of phenol allows the use of well-developed synthetic routes to more traditional PF resins, an approach that is not possible with the far more reactive condensed tannins.

The characteristics of the PF-chestnut tannins resin prepared are: P/F ratio of 1/1.7, P:T of 70:30. The MALDI-TOF analyses were performed in positive ion modes. This article will focus on chestnut tannins monomers and dimers, and it will be considered that the main PF groups will react with chestnut monomers and dimers.

## 2 MATERIALS AND METHODS

### 2.1 Chestnut Tannin Extracts

The chestnut tannin extract used for this study is Silvafeed ENC from the company Silva Team (San Michele Mondovì, Italy). It is extracted from mature chestnut wood (*Castanea sativa*) with a hot water extraction. The extract is a brown powder, which is soluble in water, has a pH (sol. 10%) of  $3.5 \pm 0.5$  and its relative density is between 0.5 and  $0.6 \text{ kg/dm}^3$ . This tannin contains less than 2% of fibers and more than 75% of polyphenols.

### 2.2 Other Materials and Their Sources

For the preparation of resins, phenol (Fisher Scientific, UK); sodium hydroxide (Carlo Erba Reagents, Italy); formaldehyde (Roth, Germany); para-formaldehyde



(Merck, Germany); methanol (VWR, Belgium) and phenolsulfonic acid at 65% weight in ethylene glycol (isomer mixture, Silvachimica Srl, Italy) were used.

For the MALDI-TOF analysis, acetone (Merck, supplied by VWR, France); 2,5-dihydroxy benzoic acid (LaserBio Labs, France); red phosphorous (LaserBio Labs, France) and sodium chloride (Carlo Erba Reagents - SdS, France) were used.

## 2.3 Resin Synthesis

### 2.3.1 Phenol-formaldehyde Control Resin, P/F Ratio of 1/1.7

A PF resin (ratio P/F of 1/1.7) was synthesised according to systems already reported by coreacting 1 mole of phenol, 0.35 mole of sodium hydroxide and 1.2 mole of formaldehyde [32]. Phenol at 80%, formaldehyde at 37% in water and sodium hydroxide at 30% in water were used.

The pH of the mixture was adjusted to 9 with 30% sodium hydroxide in water. The mixture was then slowly brought to 94°C with a water condenser and under continuous mechanical stirring. Once the temperature of 90°C was reached, the mixture was left for 2 hours. The resin was then cooled and the pH was adjusted to 7 with a 45% solution of phenolsulfonic acid in ethylene glycol. The mixture was then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

### 2.3.2 Phenol-formaldehyde with Chestnut Tannins Resin, P:T 70:30 and P/F Ratio of 1/1.7

For PFT resin, P:T 70:30 and P/F ratio of 1/1.7: 30% of synthetic phenol by mass was replaced with spray-dried chestnut tannin extract [11]. 148.75 g of 80% Phenol, 99.48 g of 96% paraformaldehyde powder and 45.2 g of a 30% sodium hydroxide water solution were used. First phenol and tannins (55 g) were dissolved in a water/methanol mixture (62.7 g of water/9.6 g of methanol). Paraformaldehyde was then added. This mixture was heated at 40°C for 30 minutes, with a water condenser and continuous mechanical stirring. The temperature was then increased to 94°C and 45.2 g of 30% sodium hydroxide water solution were added in four equal parts of 11.3 g each at regular intervals of 15 minutes.

After the last addition of sodium hydroxide, which occurred 45 minutes after the first addition, the mixture was further heated for 1 hour and 15 minutes to reach a total reaction time of 2 hours.

The resin was then cooled to room temperature and the pH adjusted to 7 with a 45% solution of phenolsulfonic acid in ethylene glycol. The mixture was then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

## 2.4 MALDI-TOF Analysis

**MALDI-TOF-MS:** The spectra were recorded on a SHIMADZU AXIMA Performance MALDI instrument (Manchester, UK). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity – positive, flight path – linear, mass – high (20 kV acceleration voltage), 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

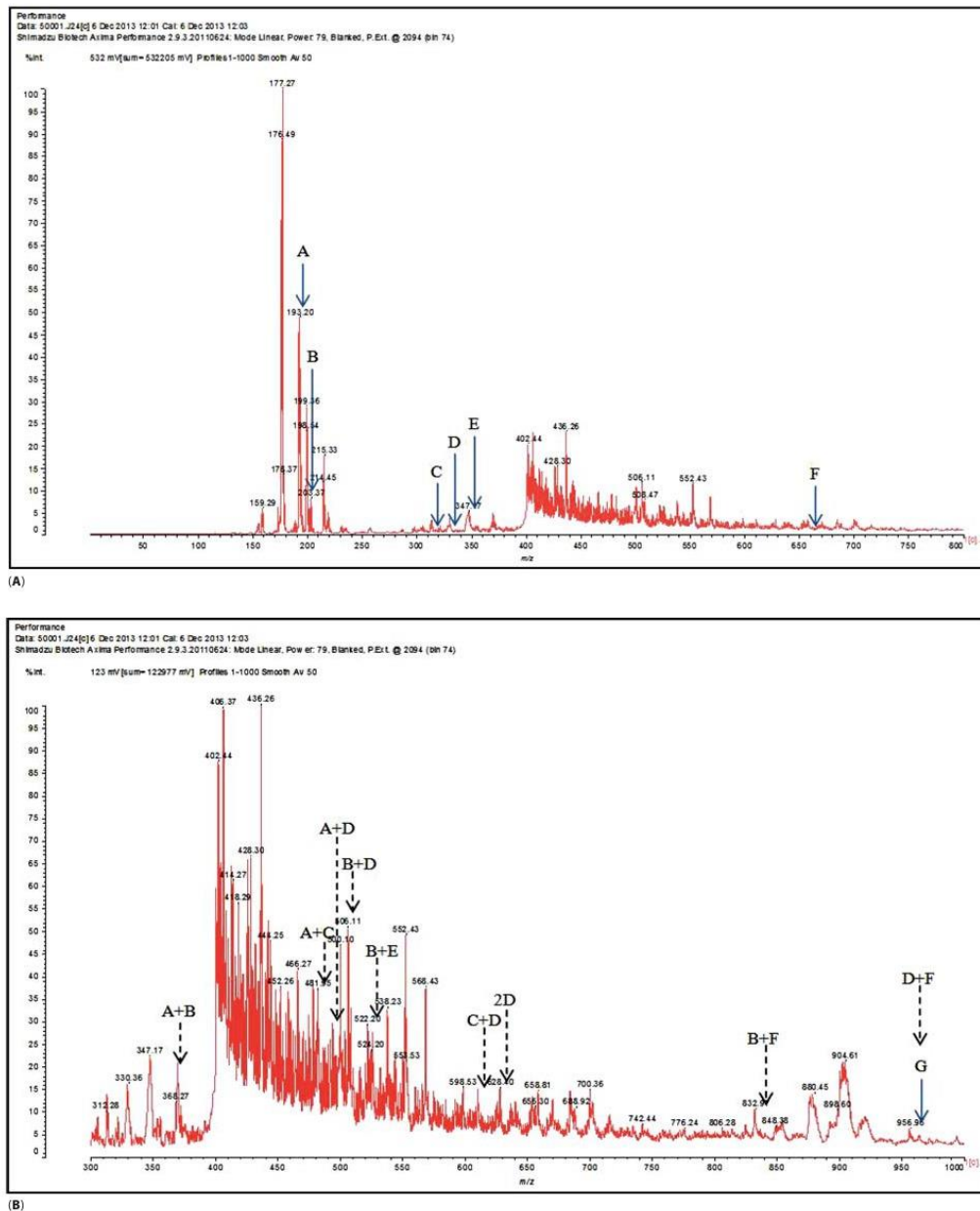
**MALDI-TOF Sample Preparation:** The samples were dissolved in acetone (4 mg/mL). The sample solutions were mixed with an acetone solution (10 mg/mL acetone) of the matrix. As the matrix, 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation, NaCl was added to the matrix (2 µL of NaCl at 0.1M in a mix of methanol:water of 2:1). The solutions of the sample and the matrix were mixed in equal amounts and 0.5 to 1 µL of the resulting solution were placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer.

## 3 RESULTS AND DISCUSSION

### 3.1 MALDI-TOF Analysis of Chestnut Tannin Extracts

By MALDI-TOF analysis, the main components found in the chestnut tannin extract used coincided with what was obtained by previous work [12, 13, 27, 33]. They are: gallic acid (A), glucose (B), catechin (C), ellagic acid (D), digallic acid (E), castalin (F) and castalagin (G). In this article they are identified with the letters from A to G for ease of understanding.

The peak corresponding to pure castalin is at 654 Da and the peak at 957 Da corresponds to pure castalagin. Pentagalloyl glucose (presents at 940 + 23 (Na<sup>+</sup>) = 963 Da) and castalagin are known to be the main constituents of chestnut extract [14, 27]. These, however, were not so predominant in the analysis of the extract used where only a monomer of pentagalloyl glucose was observed and no dimer or trimer. This indicates that either the extraction was



**Figure 1** (A) Main peaks corresponding to chestnut tannins monomers (from 0 to 800 Da). (B) Main peaks corresponding to chestnut tannins monomers and dimers (dashed) (from 300 to 1000Da).

done under more drastic conditions or the trees were much younger than those used in previous MALDI-TOF analyses. As the extraction used for the sample used here (Silvafeed ENC) was a hot water extraction without further purification, the young age of the

trees is the most likely cause. Considering all this, in the tannin extract used here the analysis showed that molecular masses were lower (Figures 1A and 1B). It was found that oligomers are linked galloyl residues with glucose [14, 27]. The peaks found were:



- 436 Da (1 galloyl residue + 2 stripped (-OHs) glucose residues);
- 506 Da (digalloylglucose = 23 (Na<sup>+</sup>) + 152x2 + 180 = 507 Da);
- 568 Da (1 galloyl residue + 3 stripped glucose residues);
- 659 Da (trigalloylglucose, 657 Da);
- 833 Da (1 galloyl residue + 5 stripped glucose residues);
- 962 Da (pentagalloyl glucose, 963 Da).

This analysis showed that the main constituents of the chestnut tannin extract used here were gallic acid (193 Da), digallic acid (345 Da), ellagic acid (325 Da) and glucose (203 Da).

Concerning the chestnut tannins dimers found in the spectrum of the chestnut tannins used, they were mainly (in order of predominance):

- Ellagic acid-glucose (506 Da);
- Gallic acid-catechin (482 Da);
- Digallic acid-glucose (526 Da);
- Gallic acid-ellagic acid (494 Da);
- Gallic acid-digallic acid (516 Da).

### 3.2 MALDI-TOF Analysis of PF Control Resin

The phenol-formaldehyde resin was synthesized by basic catalysis polycondensation of phenol and formaldehyde. Reactions between phenol and formaldehyde give -CH<sub>2</sub>, -CH<sub>2</sub><sup>+</sup> or -CH<sub>2</sub>OH groups on phenol, the main corresponding molecular weights found here are the same as those previously found and shown in Table 1 of Schrod *et al.* [31]. There are two repeating units; main peaks are spaced by 30 Da, or by 106 Da, which corresponds respectively to formaldehyde and Ph-CH<sub>2</sub><sup>+</sup>, where Ph = Phenol (Figure 2).

The main phenol-formaldehyde reaction products in the PF control resin spectrum are [31]: Ph-CH<sub>2</sub><sup>+</sup> (129 Da), dimethylolphenol (177 Da), trimethylolphenol (207 Da) and (HOCH<sub>2</sub>)<sub>2</sub>Ph-CH<sub>2</sub>OCH<sub>2</sub>OH (237 Da), the dimers PhCH<sub>2</sub>OCH<sub>2</sub>PhCH<sub>2</sub>OH (283 Da) and HOCH<sub>2</sub>PhCH<sub>2</sub>PhCH<sub>2</sub>OH (283 Da), PhCH<sub>2</sub>PhCH<sub>2</sub>PhCH<sub>2</sub>PhCH<sub>2</sub>PhCH<sub>2</sub><sup>+</sup> (554 Da), <sup>+</sup>H<sub>2</sub>CPhCH<sub>2</sub>PhCH<sub>2</sub>Ph(CH<sub>2</sub><sup>+</sup>)CH<sub>2</sub>PhCH<sub>2</sub>PhCH<sub>2</sub><sup>+</sup> (580 Da).

In this article, the main phenolic components that were found in the PF control resin spectrum were identified with the letters from H to O for ease of understanding: 129 Da (H), 177 Da (I), 207 Da (J), 237 Da (K), 283 Da (L & M), 554 Da (N), 580 Da (O).

### 3.3 MALDI-TOF Analysis of PF-Chestnut Tannins Resin

#### 3.3.1 Analysis in Considering Only Chestnut Tannins Monomers/Dimers and Only PF Control Resin Groups Alone

In Table 1 and Figure 3 are given the chestnut tannins monomers and dimers which can be found in the spectrum of the PF-chestnut tannins coreacted resin analysis. The main peaks corresponding to chestnut tannins monomers present in PF-chestnut tannins resin spectrum are: 313, 325 and 345 Da, which correspond respectively to catechin, ellagic acid and digallic acid.

Moreover, the main peaks corresponding to chestnut tannins dimers present in PF-chestnut tannins resin spectrum are: 363, 373 and 525 Da, which correspond respectively to 2xgallic acid, gallic acid-glucose and digallic acid-glucose. The main chestnut tannins monomers and dimers present in the chestnut tannin extracts spectrum are not the same as here, this indicates that there is a coreaction between phenol-formaldehyde-chestnut tannins; and even that there is no more pentagalloyl glucose.

Secondly, the presence of PF control resin groups in the spectrum of PF-chestnut tannins resin were studied; they are given in Table 1 and Figure 3. The main PF resin group present is that of dimethylolphenol at 177 Da. It is of interest that the dominant, purely PF oligomers present in the PF-chestnut coreacted resin are not the same as that for the pure PF resin; this also confirms that there is a definite coreaction between phenol, formaldehyde and chestnut tannin.

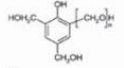
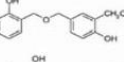
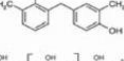
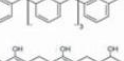
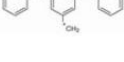
#### 3.3.2 Main Reactions between Chestnut Tannins Monomers/Dimers and PF Resin Groups

This MALDI-TOF analysis confirms the coreaction between chestnut tannins, phenol and formaldehyde. This analysis in positive mode and with hydrolysable tannins shows the reactions on the phenolic components of the resin. Thus, in Table 2 and in Figure 4 are shown the oligomers of coreaction which are formed by the phenolic components of the PF resin and the chestnut tannin monomers. Considering the number of these peaks, it appears there is extensive coreaction.

In Table 3 are given the main molecular weights corresponding to the main reactions between chestnut tannins monomers and PF resin oligomers.

The main coreaction products between chestnut tannins monomers and PF compounds observed in the spectrum of the PF-chestnut tannins resin analysis are, in order of predominance: catechin-[Ph-CH<sub>2</sub><sup>+</sup>] at 419

**Table 1** Peak analysis for chestnut tannin extracts and PF control resin groups in PF-chestnut tannins resin spectrum.

Molecules	Symbols	Theoretical molecular weight & Na <sup>+</sup> (Da)	Molecular weight & Na <sup>+</sup> (Da)	
Gallic acid	A	193	193.3	Chestnut tannins monomers
Glucose	B	203	203.53	
Catechin	C	313	313.6	
Ellagic acid	D	325	331.6	
Digallic acid	E	345	343.7	
Castalagin	G	957	956.0	
2 x Gallic acid	2A	363	361.7	Chestnut tannins dimers
Gallic acid-Glucose	A+B	373	371.7	
2 x Glucose	2B	383	381.7	
Gallic acid-Ellagic acid	A+D	495	495.7	
Glucose-Ellagic acid	B+D	505	507.8	
Glucose-Digallic acid	B+E	525	525.8	
2 x Catechin	2C	603	601.8	
Catechin-Ellagic acid	C+D	615	615.9	
2 x Digallic acid	2E	667	667.9	
Ellagic acid-Castalin	D+F	957	956.0	
Digallic acid-Castalin	E+F	977	980.0	
Gallic acid-Castalagin	A+G	1127	1129.1	
Catechin-Castalagin	C+G	1247	1247.7	
Ellagic acid-Castalagin	D+G	1259	1258.8	
Digallic acid-Castalagin	E+G	1279	1282.2	
2 x Castalin	2F	1287	1289.0	
Ph-CH <sub>2</sub> <sup>+</sup> (Ph = Phenol)	H	129	128.4	PF resin groups
Dimethylolphenol	I	177	177.5	
 where n=2	K	237	237.6	
	L	283	283.6	
	M	283	283.6	
	N	554	553.8	
	O	580	583.8	

Da, digallic acid-[Ph-CH<sub>2</sub><sup>+</sup>] at 451 Da and gallic acid-trimethylolphenol at 377 Da.

Furthermore, belonging to the coreacted mixed species between chestnut tannins monomers and PF compounds are the series of peaks at 299, 377, 387, 419, 451, 479, 527 and 539 Da.

Concerning digallic acid, ellagic acid and catechin, they were present in this order of predominance (from the most present to the least present molecule) in the chestnut tannin extracts spectrum; however, on the PF-chestnut tannins resin spectrum they are in the opposite order. So it can be said that digallic acid has coreacted more with phenol-formaldehyde compounds than ellagic acid and even much more than catechin. This can be explained by the lower proportion

of reactable sites of ellagic acid than digallic acid. But the hypothesis is not so evident because normally catechin is activated more by the OHs groups than digallic and ellagic acids. Maybe the molecules of catechin are blocked by the reactions of catechin with itself or with other chestnut tannins monomers, and that is why catechin does not react with phenol and formaldehyde.

The peak at 525 Da belongs to the reaction product between catechin and two molecules of Ph-CH<sub>2</sub><sup>+</sup>. There are two main possibilities by which the copolymerisation can take place. In the first one, one Ph-CH<sub>2</sub><sup>+</sup> attacks the site 6 of the aromatic ring A of catechin and the other Ph-CH<sub>2</sub><sup>+</sup> attacks the site 8 of the aromatic ring A. The second possibility is that both Ph-CH<sub>2</sub><sup>+</sup> molecules coreact together and then attack the site 6

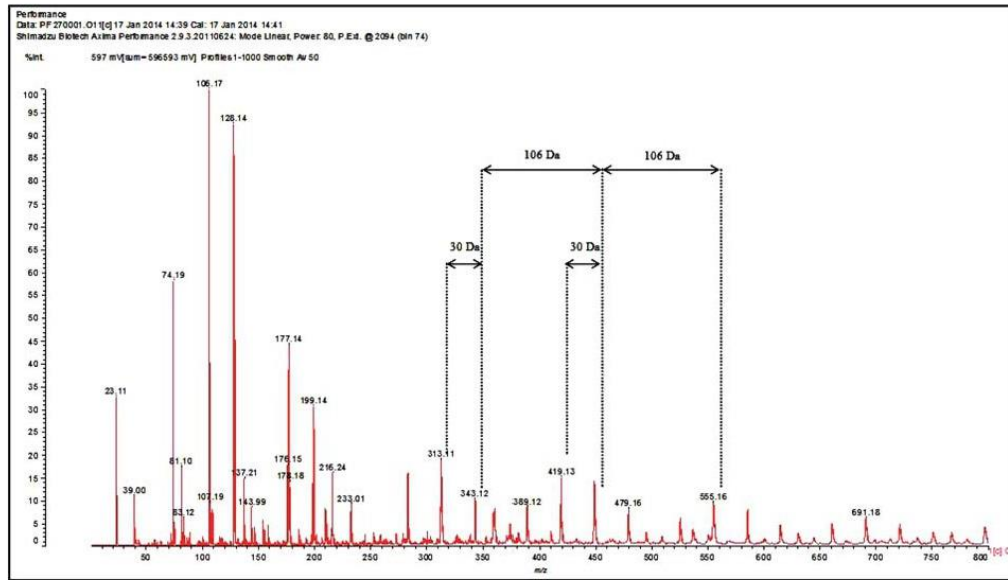


Figure 2 Spectrum of PF resin.

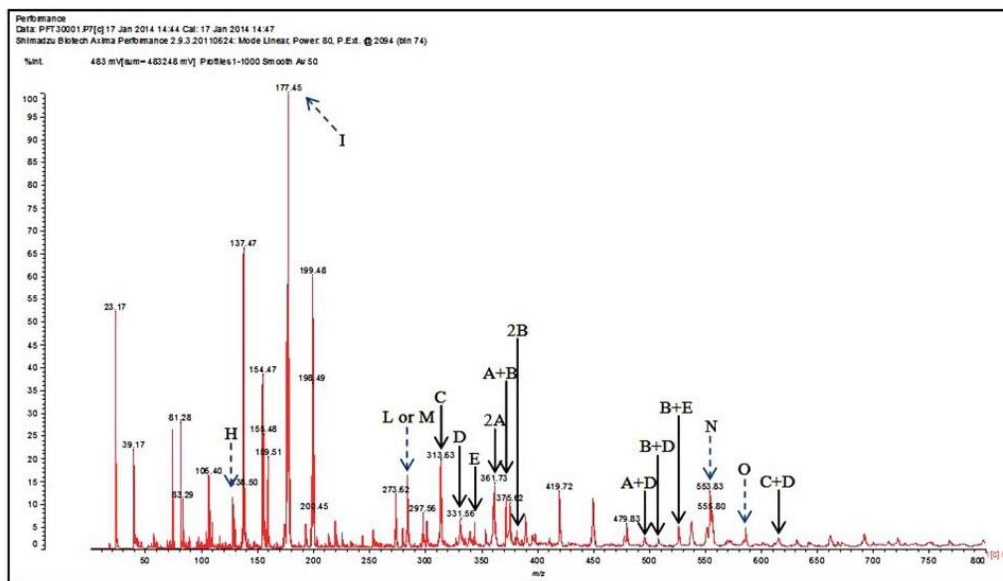
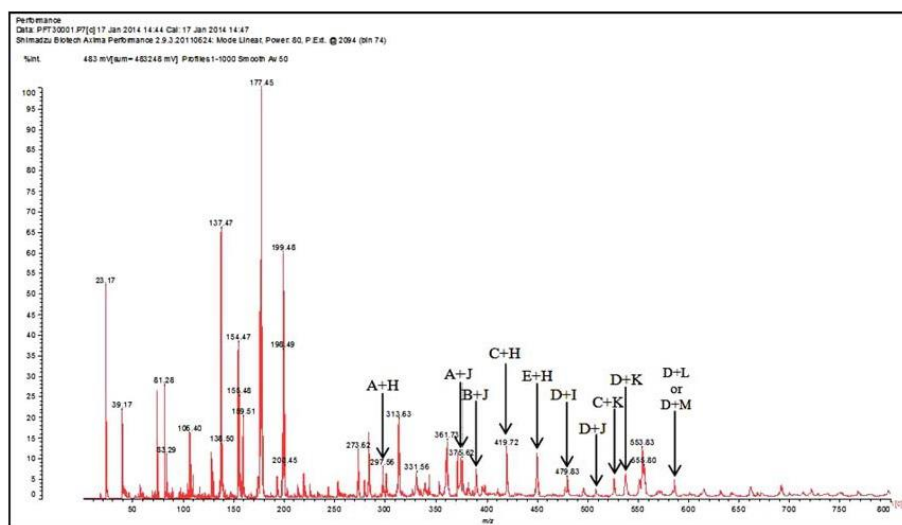


Figure 3 Main peaks corresponding to PF control resin groups alone (dashed) and key peaks corresponding to main chestnut tannins monomers and dimers alone in PF-chestnut tannins resin spectrum.

**Table 2** Copolymer peaks analysis for reactions between chestnut tannins monomers/dimers and PF resin groups in PF-chestnut tannins resin spectrum.

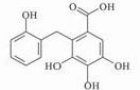
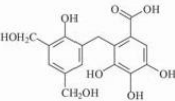
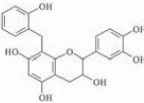
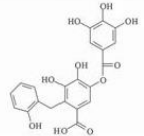
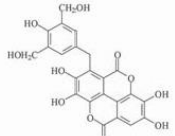
Copolymers of Chestnut tannins monomers and PF resin groups			Copolymers of Chestnut tannins dimers and PF resin groups		
Symbols	Theoretical molecular weight & Na <sup>+</sup> (Da)	Molecular weight & Na <sup>+</sup>	Symbols	Theoretical molecular weight & Na <sup>+</sup> (Da)	Molecular weight & Na <sup>+</sup>
A+H	299	297.6	H+(A+B)	479	479.8
B+H	357	357.6	I+(A+B)	527	525.8
A+J	377	375.6	I+2B	537	537.8
B+J	387	389.7	J+(A+B)	557	555.8
C+H	419	419.8	J+2B	567	569.7
D+H	431	431.7	K+(A+B)	587	585.9
E+H	451	449.8	H+(A+D)	601	601.8
D+I	479	479.8	H+(B+E)	631	631.9
C+J	497	495.7	L+2B	643	643.8
D+J	509	507.8	M+2B	643	643.8
C+K	527	525.8	I+(B+D)	659	661.9
D+K	539	537.8	J+(A+C)	667	667.9
C+L	573	571.7	I+(A+E)	669	671.9
C+M	573	571.7	J+(B+D)	689	692.0
D+L	585	585.9	J+(A+E)	699	699.8
D+M	585	585.9	H+(C+D)	721	721.9
A+N	724	721.9	I+(C+D)	769	768.0
A+O	750	749.9	J+(C+D)	799	797.9
E+N	876	875.3	K+(C+D)	829	828.0
E+O	902	904.0	L+(C+D)	875	875.3
G+H	1111	1110.0	M+(C+D)	875	875.3
F+N	1186	1184.2	N+(A+B)	904	904.0
F+O	1212	1213.9	H+(B+F)	941	941.8
G+L	1217	1219.3	J+(B+F)	1019	1021.8
G+M	1217	1219.3	N+(A+D)	1026	1027.7
			O+(A+C)	1040	1039.9
			O+(A+D)	1052	1051.8
			O+(A+E)	1072	1069.7
			H+(E+F)	1083	1085.8
			I+(D+F)	1111	1110.1
			N+(C+D)	1146	1145.9
			N+2D	1158	1157.5
			K+(D+F)	1171	1169.9
			O+2D	1184	1184.2
			N+2E	1198	1199.2
			L+(E+F)	1237	1236.0
			M+(E+F)	1237	1236.0
			I+(A+G)	1281	1282.2
			J+(A+G)	1311	1312.3
			K+(A+G)	1341	1341.8
			L+(A+G)	1387	1388.3
			M+(A+G)	1387	1388.3
			I+(C+G)	1401	1402.2
			J+(C+G)	1431	1431.2
			K+(C+G)	1461	1461.0
			L+(C+G)	1507	1507.5
			M+(C+G)	1507	1507.5
			O+(E+F)	1534	1535.3
			N+(C+G)	1778	1777.4





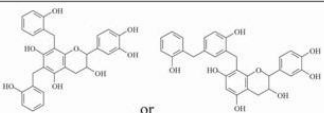
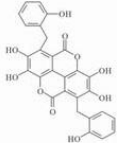
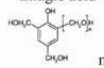
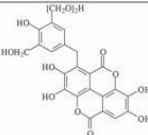
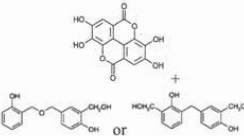
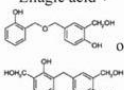
**Figure 4** Main peaks corresponding to reactions between chestnut tannins monomers and PF resin groups in PF-chestnut tannins resin spectrum.

**Table 3** Peaks corresponding to the molecular weights of main reactions between chestnut tannins and PF resin groups (Ph = Phenol) in PF-chestnut tannins resin spectrum.

Read molecular weight (Da)	Theoretical molecular weight (Da)	Molecules	Indications
297.6	299		Gallic acid + Ph-CH <sub>2</sub> <sup>+</sup>
375.6	377		Gallic acid + Trimethylolphenol
389.7	387	203 + 184	Glucose + Trimethylolphenol
419.7	419		Catechin + Ph-CH <sub>2</sub> <sup>+</sup>
449.8	451		Digallic acid + Ph-CH <sub>2</sub> <sup>+</sup>
479.8	479		Ellagic acid + Dimethylolphenol

(Continued)

Table 3 (cont.)

525.8	525		Catechin + 2 x Ph-CH <sub>2</sub> <sup>+</sup>
537.8	537		Ellagic acid + 2 x Ph-CH <sub>2</sub> <sup>+</sup>
537.8	539		Ellagic acid +  n=2
			
555.8	557	450 + Ph-CH <sub>2</sub> <sup>+</sup>	Digallic acid + 2 x Ph-CH <sub>2</sub> <sup>+</sup>
585.9	585		Ellagic acid +  OR
631.9	631	419 + 2 x Ph-CH <sub>2</sub> <sup>+</sup>	Catechin + 3 x Ph-CH <sub>2</sub> <sup>+</sup>
631.9	633	479 + Dimethylolphenol	Ellagic acid + 2 x Dimethylolphenol
661.9	663	451 + 2 x Ph-CH <sub>2</sub> <sup>+</sup>	Digallic acid + 3 x Ph-CH <sub>2</sub> <sup>+</sup>

of the aromatic ring A. So both isomers can be formed during the copolymerisation of chestnut tannins, phenol and formaldehyde.

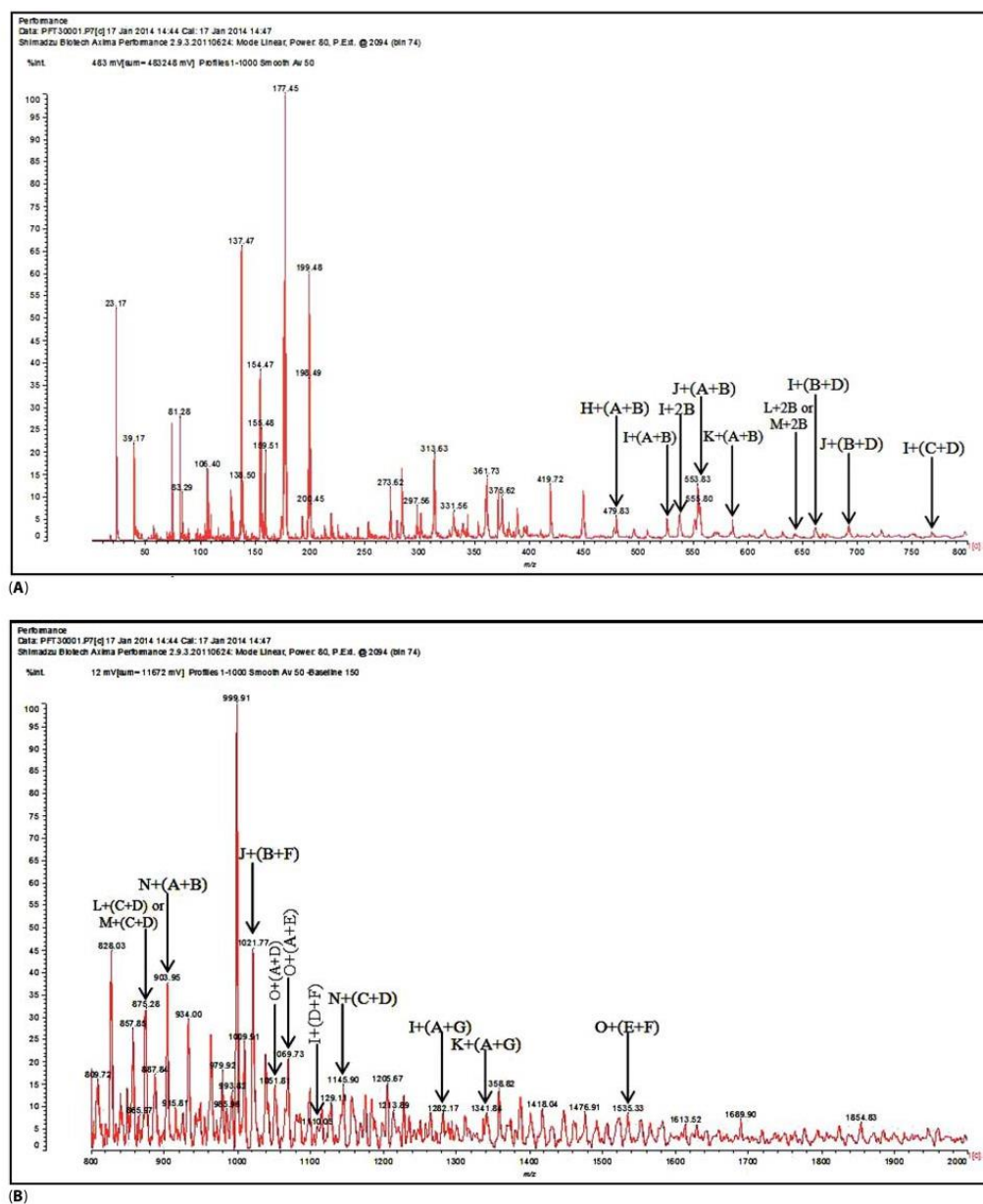
Concerning the reactions between chestnut tannin dimers and PF compounds, the molecular weights of these copolymers are shown in Table 2 and Figures 5A and 5B. It was chosen to only consider chestnut tannins dimers which are present in the spectrum of chestnut tannin extract. Indeed, the molecular weights present are quite low, with no more peaks above 930 Da.

The main reactions between chestnut tannins dimers and PF resin groups which can be found in the spectrum of PF-chestnut tannins resin analysis are given in Table 2. The products of coreaction are, in order of predominance: trimethylolphenol-(gallic acid-glucose) at 557 Da, dimethylolphenol-2xglucose

at 537 Da and dimethylolphenol-(gallic acid-glucose) at 527 Da. The series of peaks at 479, 527, 537, 557 and 587 Da belongs to the coreacted mixed species between chestnut tannins dimers and PF compounds.

Gallic acid, which is in practice the majority component in the analysis of chestnut tannin extract, is now almost depleted and its proportion is small. As it is also still present in the main coreactions between phenol, formaldehyde and chestnut tannin, it is clearly the main unit in the reactions of chestnut tannin with the PF compounds.

There are an important number of peaks in this MALDI-TOF analysis, and even if these are not so intense (even a few percent), they should not be disregarded. They show us that many coreactions take place between chestnut tannins, phenol and formaldehyde.



**Figure 5** (A) Main peaks corresponding to reactions between chestnut tannins dimers and PF resin groups in PF-chestnut tannins resin spectrum (from 0 to 800 Da). (B) Main peaks corresponding to reactions between chestnut tannins dimers and PF resin groups in PF-chestnut tannins resin spectrum (from 800 to 2000 Da).

## 4 CONCLUSIONS

MALDI-TOF analyses confirm previous knowledge about the structures involved in commercial chestnut gallo/ellagitannins, and for the first time, in complex tannins. The known rearrangements caused by the extraction clearly appear to occur as castalin, castalagin and pentagalloyl glucose are present, but in smaller proportions than expected, indicating strong hydrolysis during the extraction of the particular chestnut tannin extract used. The chestnut tannin extract used has been found to be composed mainly of gallic acid, digallic acid, ellagic acid and glucose.

Coreaction between PF oligomers and chestnut tannins occurs extensively and yields many possible combinations. Even for one molecular mass there can be different possibilities of reactions like, for example, for the peak at 479 Da.

Even if hydrolysable tannin aromatic rings are less reactive than the reactive sites of phenol, it has been shown that hydrolysable/complex chestnut tannins coreact with formaldehyde, forming methylene bridges linking phenol and the phenolic rings of tannins. These methylene bridges are formed between the ortho and para sites of the synthetic phenol and the meta sites of the gallic acid. As these meta sites are rather sterically hindered, it can be concluded that the main coreaction is between the methylol group formed on the PF oligomers and the aromatic rings in chestnut tannin.

Thus, hydrolysable/complex chestnut tannins are able to substitute a high proportion of synthetic phenol in PF resins for different applications, for example, foam wood particleboard adhesives or even foams.

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## 4.4. Mousses solides biosourcées à base de tanins

### 4.4.1. Mousses alcalines rigides à base de tanins

#### « *Alkaline tannin rigid foams* »

Auteurs : M.C. Basso<sup>1</sup>, S. Giovando<sup>3</sup>, A. Pizzi<sup>2,4</sup>, M.C. Lagel<sup>2</sup> et A. Celzard<sup>5</sup>.

<sup>1</sup>Indunor, Buenos Aires, Argentine

<sup>2</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>3</sup>Silva Chimica, San Michele Mondovi', Italie

<sup>4</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

<sup>5</sup>IJL, Université de Lorraine, Epinal, France

#### Résumé :

Les mousses de tanins condensés ont été obtenues dans des conditions alcalines. Cela a entraîné l'élimination de l'alcool furfurylique de ces formulations car dans des conditions alcalines la préparation de mousse ne peut pas compter sur la chaleur générée par l'autocondensation de l'alcool furfurylique qui se produit uniquement dans des conditions fortement acides. L'approche utilisée pour formuler la mousse alcaline est alors : (i) l'élimination totale de l'alcool furfurylique de la formulation, (ii) associée à l'utilisation d'un durcisseur différent du formaldéhyde (pour des raisons environnementales) et (iii) l'application d'une chaleur modérée afin de permettre le moussage. Ces mousses ne sont pas des mousses tanins-furaniques comme leurs homologues polymérisées en milieu acide, mais seulement des mousses tanniques. Les mousses à cellules ouvertes ont été évaluées de par leur densité apparente, leur résistance en compression, leur conductivité thermique et leur résistance au feu. Leurs caractéristiques sont similaires à celles des mousses tanins furaniques polymérisées en milieu acide.

Mots-clés : Mousses de tanins, Absence de furanes, Mousses alcalines.

# Alkaline Tannin Rigid Foams

M.C. Basso<sup>1,2</sup>, S. Giovando<sup>3</sup>, A. Pizzi<sup>\*2,4</sup>, M.C. Lagel<sup>2,3</sup> and A. Celzard<sup>5</sup>

<sup>1</sup>Indunor Group, Cerrito 1136, C1010AAX, Buenos Aires, Argentina

<sup>2</sup>LERMAB, University of Lorraine, 27 rue Philippe Seguin, CS60036, 88026, Epinal, France

<sup>3</sup>Silva Chimica, via Torre 7, S. Michele Mondovi (CN), Italy

<sup>4</sup>Dept. of Physics, King Abdulaziz University, Jeddah 22254, Saudi Arabia

<sup>5</sup>IJL, University of Lorraine, 27 rue Philippe Seguin, CS60036, 88026, Epinal, France

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**ABSTRACT:** Condensed flavonoid tannin foams were obtained under alkaline conditions. This entailed the elimination of furfuryl alcohol from these formulations, as under alkaline conditions, foam preparation could not rely on the heat generated by the self-condensation of furfuryl alcohol, which occurs only under strongly acidic conditions. The approach used to formulate the alkaline foam was: (i) the total elimination of furfuryl alcohol from the formulation, (ii) coupled with the use of an aldehyde hardener different from formaldehyde (for environmental reasons) and (iii) the application of moderate heat to allow foaming. These were not tannin/furanic foams as their acid-curing counterparts, but tannin only foams. The open cell foams were evaluated for bulk density, compressive strength, thermal conductivity and fire resistance. Their characteristics were similar to the acid-curing tannin/furanic foams.

**KEYWORDS:** Tannin foams, absence furanics, alkaline foams

## 1 INTRODUCTION

Polyflavonoid tannin-furanic rigid foams have been developed and tested for a number of different applications [1–4]. They are biosourced materials with excellent performance under a number of different conditions [5–13]. The formulation of appropriate combinations of materials to achieve the properties wanted for particular applications is a difficult undertaking and a number of different formulations have been developed in the last few years. Thus, formulations more environmentally acceptable such as those without formaldehyde [14] or formaldehyde and blowing agent [15], as well as formulations based on different flavonoid tannin types [12, 13], have been developed.

All these foam formulations, however, rely on the acid-catalyzed exothermal self-condensation reaction of furfuryl alcohol to provide blowing of the mixture to form the foam itself. They are all, then,

without exception, tannin/furanic foams. The catalyst of all these foams is invariably a strong acid such as para-toluene sulphonic acid; hence the foams themselves are strongly acidic due to the strong acid catalyst used. Such a strong acidity was necessary due to the need to generate the heat necessary for the blowing agent to foam the mixture, heat generated by the self-condensation reaction of furfuryl alcohol. Some self-neutralisation systems originating from other tannin technologies [16] have been successfully tested. However, the fact remains that at some important stage of the process the mix is strongly acidic and that acid can still be released in service. Such strong acidity, either permanent or transitory (as in self-neutralisation) can be rather damaging in some applications where the loose acid might seep through and damage materials with which the foam is in contact.

Thus, the need arose to develop formulations capable of curing under alkaline conditions and which

\*Corresponding author: antonio.pizzi@enstib.univ-lorraine.fr

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allowed the final foam to remain alkaline during its service life. This is no easy task as furfuryl alcohol does not give any exothermal self-condensation under alkaline conditions [17]. In the absence of the heat generated by the acid self-condensation of the furfuryl alcohol, the preparation of alkaline foams cannot be based on the same approach. Thus, previous formulations relying on this technology cannot be adapted to alkaline conditions. This limitation led to the investigation of a new approach to obtain tannin foams under alkaline conditions.

This approach has led to tannin only foams rather than tannin/furanic foams, as has been the case up to now for the acid-catalyzed variety.

## 2 EXPERIMENTAL

Commercial mildly sulphited quebracho (*Schinopsis lorentzii* and *Schinopsis balansae*) tannin (Tupan UP) ex Silva Chimica (San Michele Mondovi, Italy) was used for the preparation of all foams. The foams were prepared according to the mixture of components shown in Table 1. Five specimens for each case were prepared and the results of the tests are the average of the results obtained with the five specimens for each foam block prepared.

The foams were prepared by adding to the 50% solution of glutaraldehyde, the ethyleneglycol and

the surfactant. Added to this blend under continuous mechanical stirring were the quebracho tannin spray-dried powder and the hexamethylenetetramine (hexamine) water solution. Then the pentane (blowing agent) and the 33% NaOH water solution used as catalyst were added. The mixture was strongly stirred after the addition of each reagent to ensure homogenisation. Finally, the mixture was placed in a water bath at a constant temperature for 20 minutes to allow foam formation. After this the foams, but not yet the cured specimens, were placed overnight in an oven to ensure curing. Three types of foams were prepared, namely at 50°C, 70°C and 85°C (Table 1).

Blocks of foam with dimensions of 3 × 3 × 1.5 cm were weighed to obtain the bulk density. The cellular morphologies of the foams were obtained by scanning electron microscope (SEM Hitachi TM-3.000). Thermal conductivity of the foam samples with dimensions of 3 × 3 × 1.5 cm was measured by the transient plane source method (Hot Disk TPS 2500) at room temperature. The mechanical resistance to compression was investigated with an Instron 4206 universal testing machine at a load rate of 2.0 mm min<sup>-1</sup>. Flame resistance was tested by exposure to a flame at 1200°C. No significant differences in results were noticed within the specimens coming from the 5-repetition foams prepared for each case.

**Table 1** Formulations and results for an alkaline-curing tannin foam.

Formulation	50°	70°	85°
Quebracho tannin (flavonoid) (g)	30	30	30
Ethylene glycol (g)	1	1	1
Glutaraldehyde 50% water solution (g)	24	24	24
Hexamethylenetetramine 30% water solution (g)	1	1	1
Pentane (g)	4.5	4.5	4.5
Surfactant (polyalkylsiloxane/polyalkylene copolymer) (g)	0.5	0.5	0.5
NaOH 33% water solution (g)	10	10	10
Oven blowing temperature (°C)	50	70	85
Oven curing temperature (°C)	50	70	85
Foam density (g/cm <sup>3</sup> )	0.113	0.073	0.056
Thermal conductivity (W/mK)	0.067	0.050	0.050
Flame propagation rate (mm/s)	none*	none*	none*

\*Instantaneous self-extinction



### 3 RESULTS AND DISCUSSION

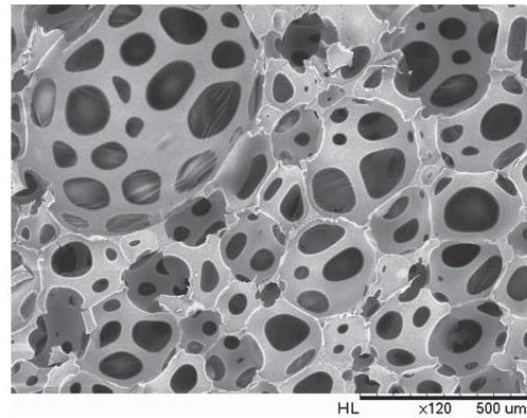
The approach investigated in this paper to prepare alkaline tannin foams was based on the total elimination of furfuryl alcohol from the formulation, coupled with the use of a non-volatile aldehyde hardener different from formaldehyde (for environmental reasons) and the application of moderate heat to allow foaming. This approach has led to tannin foams without any furfuryl alcohol, thus to tannin only foams rather than the tannin/furanic types characteristic of the acid-catalyzed type.

The formulation is shown in Table 1. It relies on the use of glutaraldehyde as hardener of the tannin in the absence of furfuryl alcohol. Such a formulation needs heating because lacking the heat generated by the acid-catalyzed furfuryl alcohol self-condensation that is characteristic of the acid foams approach, there is no heat at all self-generated in the formulation, and thus it needs heat for both foam expansion and its cure.

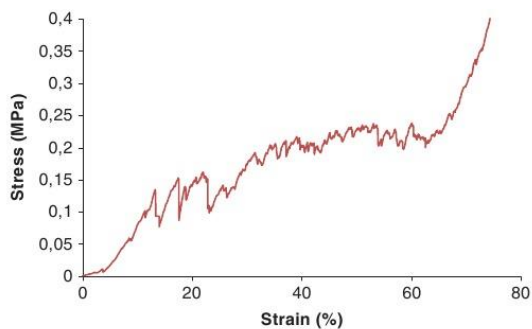
The results are shown in Table 1. The thermal conductivity of the alkaline foam formulation is good, but slightly worse than that obtainable for acid-curing foams. Self-extinction when exposed to a flame is instantaneous once the flame is removed from the sample, as for the equivalent acid-curing foams [18]. The foaming and curing temperature can affect the final characteristics of such foams. Thus, at 70°C the best results of density and thermal conductivity are obtained (Table 1). At a lower temperature the density is higher and the thermal conductivity is worse without any advantages in mechanical performance for the higher density, indicating a lower level of crosslinking. At a higher foaming and curing temperature foaming is too quick: again mechanical resistance is lower due to early immobilisation of the network [19, 20], the cells appearance is not regular and there are no advantages as regards thermal conductivity.

Figure 1 shows the cell structure configuration of this foam formulation, with evident anisotropy in the direction of foam growth. Individual non-interconnected pores or cells separate from one to another, and membranes between cells, also called cell walls, may be observed. Figure 2 shows the stress/strain curves obtained from compression tests of foams based on this formulation, indicating that the structure is fundamentally rigid. As for tannin/furanic foams, the stress-strain curves always show three distinct regions: linear elastic, collapse and densification [21]. The alkaline-cured formulation foam behaved as typical elastic fragile cellular solids. Mechanical strength at 20% deformation is about 0.14 MPa.

Alkaline-catalysed foams solve the problem that acid-catalysed foams have; when very acid foams are in contact with lignocellulosic materials extensive



**Figure 1** Scanning electron microscope image of alkaline-cured tannin foam prepared and hardened at 70°C.



**Figure 2** Stress vs strain diagram for compression of 70°C alkaline-cured tannin foam.

hydrolysis of cellulose and hemicelluloses ensues. This means that strongly acidic foams cannot be used as insulation in prolonged contact with wood panels or wood structures due to the weakening of the wood interface with the foam due to extensive hydrolysis of wood carbohydrate. The development of alkaline foams was then necessary for application to wood and wood products.

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#### *4.4.2. Développement et caractérisation de mousses à base de tanins de quebracho*

### **« *Development and characterization of quebracho tannins based foams* »**

Auteurs : M.C. Lagel<sup>1</sup>, A. Martinez de Yuso<sup>2</sup>, A. Pizzi<sup>1,3</sup>, A. Celzard<sup>2</sup> et V. Fierro<sup>2</sup>.

<sup>1</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>2</sup>IJL, Université de Lorraine, Epinal, France

<sup>3</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

#### Résumé :

Depuis quelques années maintenant de nouveaux matériaux à base de tanins ont été développés et étudiés. En particulier, les mousses de tanins qui peuvent être une alternative aux mousses synthétiques. Constituées à 90 % de produits biosourcés, elles présentent de bonnes caractéristiques thermiques et ne brûlent pas. Ce qui en fait potentiellement de très bonnes mousses utilisables dans l'isolation des bâtiments. Mais cette précédente étude était basée sur la formulation standard développée avec des tanins de mimosa (*Acacia Mearnsii*) par Tondi, et al. Ici, les tanins de quebracho (*Schinopsis Balansae*), qui sont également des tanins condensés, ont été utilisés. En effet, la production de tanins de mimosa a plafonné il y quelques années à 220 000 tonnes/an et est actuellement à 112 000 tonnes/an, alors que la production de tanins de quebracho est en constante augmentation et est actuellement à 80 000 tonnes/an.

Mots-clés : Matériaux biosourcés, Tanins de quebracho, Mousses, Isolation.

# Développement et caractérisation de mousses à base de tanins de Quebracho

M.C. Lagel<sup>1,2</sup>, A. Martínez de Yuso<sup>2</sup>, A. Pizzi<sup>1</sup>, A. Celzard<sup>2</sup> et V. Fierro<sup>2</sup>

Reçu le 27 janvier 2014, accepté le 10 mars 2014

**Résumé** – Depuis quelques années maintenant de nouveaux matériaux à base de tanins ont été développés et étudiés. En particulier, les mousses de tanins qui peuvent être une alternative aux mousses synthétiques. Constituées à 90 % de produits biosourcés, elles présentent de bonnes caractéristiques thermiques et ne brûlent pas. Ce qui en fait potentiellement de très bonnes mousses utilisables dans l'isolation des bâtiments. Mais cette précédente étude était basée sur la formulation standard développée avec des tanins de Mimosa (*Acacia Mearnsii*) par Tondi et al. Ici, les tanins de Quebracho (*Schinopsis Balansae*), qui sont également des tanins condensés, ont été utilisés. En effet, la production de tanins de Mimosa a plafonné il y a quelques années à 220 000 tonnes/an et est actuellement à 112 000 tonnes/an, alors que la production de tanins de Quebracho est en constante augmentation et est actuellement à 80 000 tonnes/an.

**Mots clés** : Matériaux biosourcés / tanins de Quebracho / mousses / isolation

**Abstract** – **Development and characterization of Quebracho tannins based foams.** Since many years new biobased materials has been developed. In particular tannins foams which can be an alternative to synthetic foams. These products are about 90% biobased. They have good thermal characteristics and they are fireproofed. So they are potentially very good foams for building insulation. However the previous study was based on the standard formulation developed with Mimosa tannins (*Acacia Mearnsii*) by Tondi et al. In this work, Quebracho tannins (*Schinopsis Balansae*) were used. Indeed, in the past the production of Mimosa tannins capped at 220 000 tonnes/year and now is at 112 000 tonnes/year while the production of Quebracho tannins is increasing and is currently at 80 000 tonnes/year.

**Key words**: Biobased materials / Quebracho tannins / foams / insulation

## 1 Introduction

### 1.1 Problématique

Depuis plusieurs années avec l'augmentation du prix du pétrole, différentes équipes de recherche travaillent sur l'utilisation de ressources naturelles en substitution des produits issus de la pétrochimie. Ainsi dans de diverses et nombreuses applications, a été intégrée l'utilisation de matières premières naturelles comme les tanins.

Ces tanins sont obtenus à partir de bois et/ou d'écorces après une simple extraction à l'eau. Les tanins principalement utilisés pour la réalisation de mousses naturelles sont les tanins condensés et leur unité de base est le flavonoïde (Fig. 1).

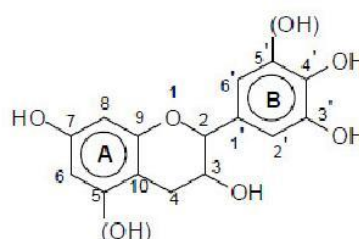


Fig. 1. Unité de base des tanins condensés : flavonoïde.

L'alcool furfurylique, qui est souvent utilisé lors de la préparation de mousses à base de tanins, est lui aussi d'origine naturelle, il est produit à partir de déchets agricoles comme par exemple la bagasse de canne à sucre (Fig. 2).

<sup>1</sup> LERMAB, Université de Lorraine, 27 rue Philippe Seguin, 88051 Epinal Cedex 9, France  
marie-christine.lagel@univ-lorraine.fr

<sup>2</sup> IJL, Université de Lorraine, 27 rue Philippe Seguin, 88051 Epinal Cedex 9, France

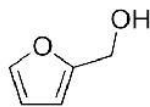


Fig. 2. Alcool furfurylique.

## 1.2 L'utilisation des tanins dans les mousses

Depuis de nombreuses années on observe l'utilisation de produits biosourcés dans des adhésifs organiques que l'on utilise dans notre vie de tous les jours. Par exemple, d'origine végétale pour les colles pour les timbres et les enveloppes; d'origine animale comme l'albumine qui est utilisée dans l'industrie du contreplaqué et enfin d'origine minérale qui sont utilisés dans l'industrie du carton.

Ainsi dans cette démarche d'utiliser de plus en plus de produits naturels, depuis plusieurs années de nombreux chercheurs se sont intéressés à la possibilité d'intégrer des tanins dans les résines afin que leur pourcentage en produit naturel et renouvelable soit augmenté.

En effet, nous pouvons citer la mise au point de colle à base de tanins, de résorcine et de formaldéhyde qui s'utilisent pour coller à froid des panneaux composites de mousses de tanins [1].

Il y a quelques années, des mousses phénoliques ont été mises au point à partir de tanins de Mimosa (*Acacia Mearnsii*) [2, 3]. Elles peuvent être utilisées en tant que matériaux absorbants de chocs, mousses florales, comme matériaux adsorbants de métaux dissous, ou encore comme mousses d'isolation thermique et phonique [4].

En effet pour cette dernière application, elles présentent une bonne résistance à la compression [5] et une faible conductivité thermique et de plus elles ne brûlent pas [6].

De plus, des milliers de combinaison sont possibles lors de la formulation de mousses, il est donc possible d'obtenir un très grand nombre de matériaux qui possèdent des caractéristiques différentes et qui pourront donc être utilisées dans de nombreux domaines.

## 2 Matériels et méthodes

### 2.1 Les tanins de Quebracho

De nombreuses études ont été menées sur la production de mousses à base de tanins de Mimosa. Ces tanins sont uniquement extraits de l'écorce de l'arbre.

Les tanins de Quebracho (*Schinopsis Balansae*) possèdent de grandes similitudes avec les tanins de Mimosa et ils sont de plus extraits de l'écorce de l'arbre mais également de tout le bois. Ces deux types de tanins sont des tanins condensés et présentent des enchaînements de type : 4-6 (Tab. 1).

Ainsi, il paraît très intéressant de continuer à développer des mousses à base de tanins de Quebracho, comme c'est déjà le cas depuis quelques années.

De plus, la production de tanins de Mimosa est en train de s'essouffler, il est donc judicieux de s'intéresser au tanin de Quebracho qui lui est en pleine expansion.

Les tanins de Quebracho en poudre sont fournis par l'entreprise Indunor en Argentine.

Tableau 1. Comparaison des tanins de Mimosa et de Quebracho.

Extraits	Type de flavonoïde	Unité de base
Mimosa	Prorobinetinidine	 Robinetinidol
Quebracho	Profisetinidine	 Fisetinidol

### 2.2 Densité de squelette

La densité de squelette des mousses est mesurée à l'aide d'un pycnomètre à l'hélium, l'AccuPyc II 1340 de Micromeritics, en réalisant 20 purges et 50 cycles de pression. La vitesse de mise en pression est de 0,050 psig/min et le maximum est de 19 500 psig.

### 2.3 Résistance mécanique

Les essais de résistance mécanique en compression sont réalisés sur la machine d'essai universelle Instron 5944, équipée d'un capteur de 2 kN. La compression est effectuée en utilisant une vitesse de compression constante de 2,0 mm/min. Les échantillons de taille : 1,5 cm × 3 cm × 3 cm sont testés dans la direction axiale de la montée de la mousse.

Les mousses ont un comportement de déformation en trois phases : une phase élastique linéaire, une phase de plateau en contrainte et enfin une phase de densification.

### 2.4 Conductivité thermique

La conductivité thermique est mesurée à l'aide de la méthode de la source plane en régime transitoire avec un analyseur de conductivité thermique Hot Disk TPS 2500, avec la sonde 5501 de rayon 6.403 mm et pour une puissance de 10 mW. Ceci à température ambiante et à humidité contrôlée. La sonde est placée entre deux échantillons de taille : 1,5 cm × 3 cm × 3 cm. Ces mesures ont été faites à 20 °C et 55 % d'humidité relative.

## 3 Étude de l'influence de l'agent moussant sur les mousses standard de Quebracho

### 3.1 Formulation de mousses de tanins

La composition de la mousse dite standard qui a été développée avec les tanins de Mimosa [2] est :

- Tanins et alcool furfurylique (résine de base).
- Formaldéhyde à 37 % dans l'eau (durcisseur).



- Ether diéthylique (DE),  $T_{\text{ébullition}} = 34,6 \text{ } ^\circ\text{C}$  (agent moussant).
- Acide para-toluène sulfonique à 65 % dans l'eau (catalyseur).

Lors de la formation de la mousse il y a tout d'abord la polymérisation des réactifs puis l'expansion de la mousse et enfin le durcissement de celle-ci.

Pour la préparation des mousses, l'alcool furfurylique est mélangé avec le formaldéhyde à 37 % en solution aqueuse, l'eau, ensuite les tanins. Une fois que le mélange est homogène on ajoute l'éther diéthylique et après mélange on ajoute enfin l'acide para-toluène sulfonique à 65 % dans l'eau.

L'étude porte sur la variation de la quantité de l'agent moussant, ainsi sept mousses différentes ont été réalisées avec la quantité standard d'éther diéthylique et de  $\pm 10\%$  à 30 % par rapport à la formulation standard (mousse n°4 dans le Tab. 2).

## 3.2 Résultats

### 3.2.1 Densités

Il existe une relation directe entre la quantité d'agent moussant utilisée dans la formulation et la densité de la mousse obtenue, que ce soit pour la densité apparente ou pour la densité de squelette. Ce qui corrobore ce qui avait été trouvé pour les mousses à base de tanins de Mimosa [7].

Pour les mousses de tanins de Quebracho on obtient des densités de squelette aux alentours de  $1,46 \text{ g/cm}^3$ , contre  $1,59 \text{ g/cm}^3$  pour les mousses Mimosa [3].

Ainsi, les densités de squelettes des mousses de tanins de Quebracho se rapprochent plus de celles des mousses Phénol-Formaldéhyde qui possèdent elles une densité de squelette de  $1,47 \text{ g/cm}^3$  (Tab. 3).

**Tableau 2.** Formulations des mousses de Quebracho.

Mousse n°	1	2	3	4	5	6	7
Tanins Quebracho	30	30	30	30	30	30	30
Alcool furfurylique	10,5	10,5	10,5	10,5	10,5	10,5	10,5
Formaldéhyde (37 % eau)	7,4	7,4	7,4	7,4	7,4	7,4	7,4
Eau	6	6	6	6	6	6	6
Ether diéthylique	2,1	2,4	2,7	3	3,3	3,6	3,9
pTSA (65 % eau)	11	11	11	11	11	11	11

**Tableau 3.** Densités apparentes et de squelette des mousses de Quebracho.

Mousses	Densité apparente ( $\text{g/cm}^3$ )	Densité de squelette ( $\text{g/cm}^3$ )
1	0,102	1,449
2	0,080	1,462
3	0,075	1,468
4	0,064	1,462
5	0,060	1,464
6	0,056	1,471
7	0,052	1,487

Plus la quantité d'agent gonflant est importante, plus la densité de la mousse obtenue est faible, ceci évolue de manière semblable qu'il s'agisse des tanins de Quebracho ou de Mimosa (Fig. 3).

### 3.2.2 Conductivité thermique

Pour des densités allant de  $0,05$  à  $0,10 \text{ g/cm}^3$ , on obtient entre  $0,047$  et  $0,050 \text{ W/(m.K)}$  pour les mousses Quebracho et entre  $0,045$  et  $0,055 \text{ W/(m.K)}$  pour les mousses Mimosa [7].

On remarque que la conductivité thermique des mousses augmente avec la densité apparente, ceci quels que soient les tanins utilisés. Donc plus la quantité d'agent moussant est importante, plus les mousses de tanins sont isolantes.

Les mousses à base de tanins de Quebracho semblent être plus isolantes que celles obtenues avec les tanins de Mimosa (Fig. 4).

### 3.2.3 Résistance mécanique

Les mousses ont un comportement de déformation en trois phases : une phase élastique linéaire, une phase de plateau en contrainte et enfin une phase de densification ; ceci quel que soient les tanins utilisés.

Les résistances en compression à 20 % de la déformation pour les mousses de Quebracho sont comprises entre  $0,24$  et  $0,70 \text{ MPa}$  et pour les mousses de Mimosa sont comprises entre  $0,10$  et  $0,25 \text{ MPa}$  [3].

Les mousses de Quebracho présentent des valeurs plus élevées que les mousses de Mimosa pour la résistance en compression (Fig. 5).

Et d'une manière générale, moins il y a d'agent moussant, plus la mousse est dense et donc plus elle est résistante, ceci quel que soient les tanins utilisés.

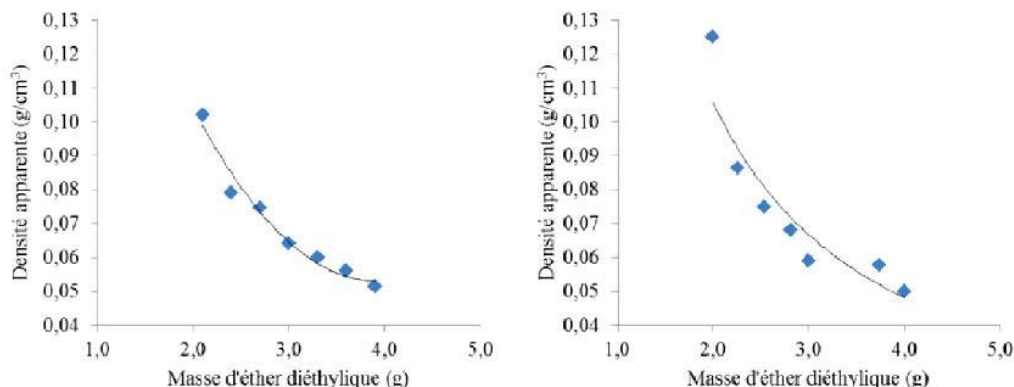


Fig. 3. Densités des mousses de tanins en fonction de la quantité d'agent moussant (à gauche, Quebracho et à droite, Mimosa).

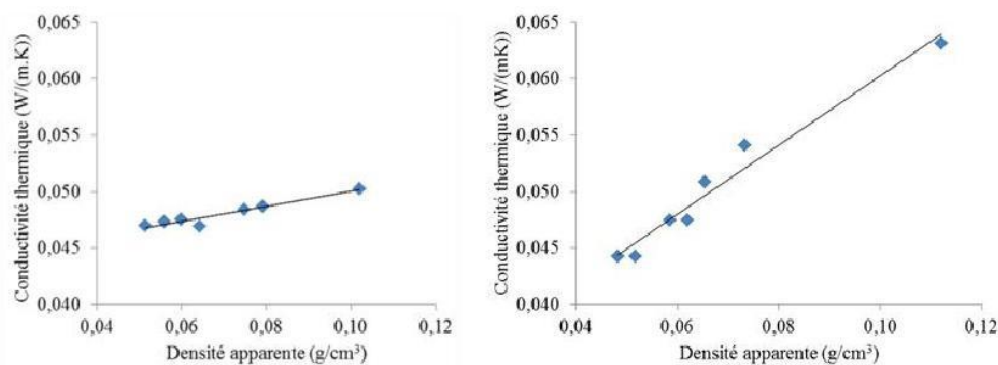


Fig. 4. Conductivité thermique en fonction de la densité des mousses de tanins (à gauche, Quebracho et à droite, Mimosa).

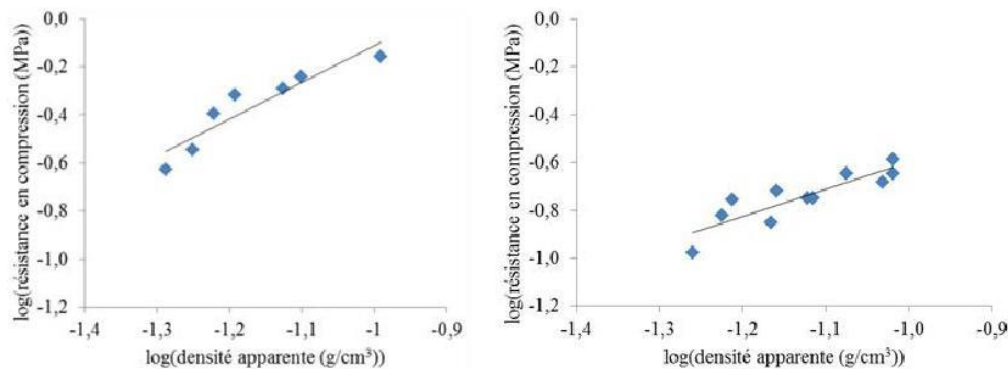


Fig. 5. Résistance en compression des mousses de tanins en fonction de sa densité (à gauche, Quebracho et à droite, Mimosa).

## 4 Conclusions

Bien que les tanins de Mimosa et Quebracho soient constitués de molécules de type robinidine/fisetidine en différentes proportions, ils ont une réactivité chimique similaire. Il est donc possible de substituer l'un par l'autre lors de la fabrication de mousses de tanins et ceci sans affecter significativement les performances de ces matériaux. Ceci étant d'autant plus intéressant que la

production des tanins de Quebracho est en augmentation contrairement à celle des tanins de Mimosa.

De manière générale, les mousses de tanins sont d'excellents isolants thermiques au même titre que le liège ou la laine de verre. De plus leurs résistances mécaniques sont également intéressantes.

Ainsi, les possibilités d'applications sont multiples et les caractéristiques finales de la mousse (sa densité apparente, sa conductivité thermique, sa résistance



mécanique...) doivent être adaptées en fonction de ses applications.

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#### *4.4.3. Structure et propriétés des mousses rigides à base de tanins de quebracho*

### **« Structure and properties of rigid foams derived from quebracho tannin »**

Auteurs : A. Martinez de Yuso<sup>1</sup>, M.C. Lagel<sup>1,2</sup>, A. Pizzi<sup>2,3</sup>, V. Fierro<sup>1</sup> et A. Celzard<sup>1</sup>.

<sup>1</sup>IJL, Université de Lorraine, Epinal, France

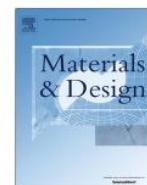
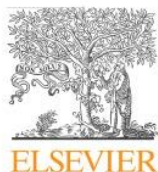
<sup>2</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>3</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

#### Résumé :

Les premières mousses rigides organiques très poreuses à base de tanins condensés extraits de bois de quebracho (*Schinopsis sp.*) sont rapportées. Des échantillons de différentes densités ont été préparés et caractérisés. Leur structure poreuse et leurs propriétés physiques ont été comparées avec celles de mousses préparées dans des conditions similaires, mais avec des tanins de mimosa ou de pin. Nous montrons que les propriétés des mousses de quebracho sont comparables, et dans certains cas meilleures que celles fabriquées à partir d'autres tanins. Les tanins de quebracho et de mimosa présentent des comportements très similaires, ceci étant attribués au fait que les unités flavonoïdes correspondantes ont des noyaux A de réactivités identiques. En revanche, les mousses de pin se comportent différemment en raison de leur noyau A différent. Les résultats indiquent que les tanins de quebracho sont donc une excellente alternative aux tanins de mimosa pour produire des mousses isolantes thermiques présentant de bonnes performances mécaniques.

Mots-clés : Tanins de quebracho, Mousse organique, Caractérisation, Propriétés physiques, Conductivité thermique.



## Structure and properties of rigid foams derived from quebracho tannin



A. Martinez de Yuso<sup>a</sup>, M.C. Lagel<sup>a,b</sup>, A. Pizzi<sup>b,c</sup>, V. Fierro<sup>a</sup>, A. Celzard<sup>a,\*</sup>

<sup>a</sup> Institut Jean Lamour, UMR CNRS – Université de Lorraine n°7198. ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex, France

<sup>b</sup> LERMAB, EA – Université de Lorraine n°4370. ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex, France

<sup>c</sup> King Abdulaziz University, Department of Physics, Jeddah, Saudi Arabia

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### ABSTRACT

The first highly porous organic rigid foams based on condensed tannin extracted from quebracho tree (*Schinopsis* sp.) are reported. Samples having different densities have been prepared and characterised. Their porous structure and physical properties have been compared with those of foams prepared in similar conditions but based on mimosa or pine tannins. We show that the properties of quebracho foams are comparable, and in some cases better, than those made from other tannins. Quebracho and mimosa present very similar behaviours, attributed to the fact that the corresponding flavonoid units have identical reactive A-rings. In contrast, pine foams behave differently, due to their different A-ring. The results indicate that quebracho is thus an excellent alternative to mimosa for producing thermally insulating tannin foams presenting good mechanical performances.

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### 1. Introduction

New materials are demanded nowadays due to the changing requirements of our society. The necessity of materials with specific properties and usefulness leads the development of new products to meet these requirements. One of the most important demands is the search of natural and sustainable materials. Phenolic foams are highly used as thermal insulators [1], but biosourced and cheap resins would be a great advantage for producing the same.

Tannin-based foams have been extensively described and shown to present excellent properties, making them able to compete with industrial phenol–formaldehyde foams, such as good insulating performances, low density, high resistance to chemicals and fire, and low cost [2]. Tannin foams have also been found to be suitable for other applications such as waste water treatment [3] or metal ion adsorption [4].

In order to get the best of these materials, not only their properties must be optimised but the tannin from which they are made should be available and cheap. Different kinds of condensed tannins can be used for the preparation of rigid foams, such as mimosa (*Acacia mearnsii*) [3,5], pine (*Pinus radiata* and *Pinus pinaster*) [6,7] or quebracho (*Schinopsis balansae* and *Schinopsis lorentzii*) [8]. The production of pine tannin is not developed yet, whereas that of mimosa is limited and the market is tight now. In contrast, the

annual production of quebracho tannin, although slightly lower than that of mimosa, benefits from a considerable growth potential.

Condensed tannins (or proanthocyanidins) are polymers of flavanol units that comprise a group of polyhydroxy-flavan-3-ol oligomers and polymers linked by carbon–carbon bonds between flavanol subunits [9]. Formaldehyde reacts with tannins to produce crosslinking, due to the phenolic nature of the flavonoid units. The main flavonoid species are different in the three aforementioned tannins as can be observed in Fig. 1.

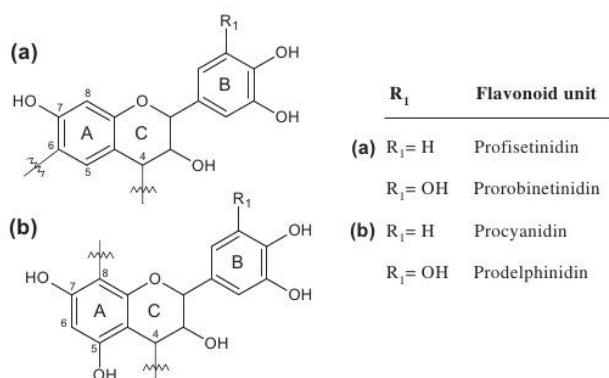
For mimosa tannin, the main polyphenolic unit is based on resorcinol A-rings and pyrogallol B-rings (i.e. prorobinetinidin flavonoid units). These constitute about 70% of the raw tannin extract. The secondary unit is based on resorcinol A-rings and catechol B-rings and represent about 25% of the total of the tannin fraction. The remaining part of the extract is the “non-tannins” [10].

For quebracho tannin, resorcinol A-ring and catechol B-ring (i.e. profisetinidin flavonoid units) are the main patterns constituting more than 80% of the phenolic content of the tannin itself [10]. In pine tannin, the main flavonoid units are based on phloroglucinol A-rings and catechol B-rings (i.e. procyanidin units). In much lower proportion, units based on phloroglucinol A-rings and phenol B-rings (i.e. prodelfinidin units) are present [6]. The A-rings of pine tannins then possess only the phloroglucinol-type structure, much more reactive towards formaldehyde than a resorcinol-type structure [10]. The differences in the flavonoid units, specifically at positions of R and C<sub>5</sub>, thus have a significant effect on tannin reactivity.

\* Corresponding author. Tel.: +33 329 29 61 14; fax: +33 329 29 61 38.

E-mail address: [alain.celzard@univ-lorraine.fr](mailto:alain.celzard@univ-lorraine.fr) (A. Celzard).





**Fig. 1.** Model structure for quebracho (proflisetinidin), mimosa (prorobinetinidin), and pine (procyanidin and prodelphinidin) condensed tannins.

In the present work, tannin-based rigid foams have been prepared from quebracho tree extract. The properties of quebracho foams have been studied and compared with the properties of foams prepared from mimosa and pine tannins in very similar – if not identical – conditions. The influence of the nature of the tannin on the final properties of the organic foams was discussed. A special attention was paid to thermal and mechanical properties, in order to see whether these new materials could be interesting thermal insulators for buildings.

## 2. Materials and methods

### 2.1. Materials

Quebracho tannin powder sulphited at 0.6%, known on the market under the name Fintan T and kindly supplied by the company SilvaChimica (St Miche Mondovi, Italy), was used for the preparation of the foams. Quebracho tannin was extracted industrially from 80 years old quebracho colorado trunks (*S. balansae* and *S. lorentzii*), an evergreen tree that grows wild in South America.

The chemicals used to prepare the foams were: furfuryl alcohol used as heat generator and strengthener, formaldehyde (37 wt.% aqueous solution) used as crosslinker, water used as solvent, diethyl ether used as blowing agent, and para-toluene-4-sulphonic acid (pTSA, 65 wt.% aqueous solution) used as catalyst. Changing the amount of blowing agent produced changes of foams' apparent density, and hence of porosity.

### 2.2. Foams preparation

Formaldehyde solution, furfuryl alcohol, water, and diethyl-ether were first intimately mixed together under stirring in a 250 mL polypropylene beaker at room temperature. Quebracho tannin powder was then added to the liquid mixture and the whole was again vigorously stirred. After complete homogenization, pTSA was added, the mixture was stirred for 20 s and subsequently put in a ventilated oven preheated at 35 °C. After an induction time of around 30 s, foaming occurred spontaneously in the oven.

Once fully hardened, i.e. within one minute only, the foams were dried at room temperature during 24 h and extracted from their moulds. The materials were put again in the oven at 35 °C during 4 additional hours, in order to remove the remaining vapours of blowing agent. For characterisation purposes, samples of typical size 3 × 3 × 1.5 cm were cut off the foam blocks. Given the vertical rising of the foams, the latter were slightly anisotropic and therefore all the subsequent measurements of physical properties were carried out along the vertical (foaming) direction.

Seven different quebracho foams were prepared, using one single formulation in which only the amount of blowing agent was changed. The formulations of all the materials discussed in this work are given in Table 1. It is important to note that formulations based on quebracho and mimosa are strictly identical (except for the amount of blowing agent), whereas those based on pine tannin are slightly different due to the much higher reactivity of the latter.

### 2.3. Foams characterisation

The apparent density, or bulk density  $\rho_b$ , of the samples was calculated as the weight/volume ratio of parallelepiped samples of known dimensions. The true density, or skeletal density  $\rho_s$ , is the density of the solid from which the considered material is made of, and was estimated by helium pycnometry using an Accupyc II 1340 (Micromeritics, USA) apparatus. From bulk and skeletal densities, the overall porosity,  $\Phi$  (dimensionless) of the materials was calculated as:

$$\Phi = 1 - \frac{\rho_b}{\rho_s} \quad (1)$$

The average cell diameter of the foams was obtained by counting the number of cells,  $N_c$ , per unit length of straight line drawn parallel to the principal directions of a number of scanning electron microscopy (SEM) images, obtained with an Hitachi S 4800 electron microscope [11]. If the measurements are made in a plane section, then the average cell diameter  $\bar{D}$  is given by [12]:

$$\bar{D} = \frac{1.5}{N_c} \quad (2)$$

The thermal conductivity was measured by the transient plane source method with a thermal conductivity analyzer Hot Disk TPS 2500 at room temperature. The method is based on a transiently heated plane sensor used as heat source and dynamic temperature sensor. This sensor consists of an electrically conducting pattern in the shape of a double spiral, which has been etched out of a thin nickel foil and sandwiched between two thin sheets of Kapton®. For the measurement of thermal conductivity, the plane sensor was fitted between two identical pieces of sample of dimensions 3 cm × 3 cm × 1.5 cm. The thermal conductivity was calculated with the Hot Disk 6.1 software.

Mechanical tests were carried out in compression using an Instron 5944 universal testing machine equipped with a 2 kN head, with which the full strain–stress data were recorded. The compression was carried out using a constant load rate of 2.0 mm min<sup>-1</sup>. Samples of cross-section 3 cm × 3 cm and height 1.5 cm were tested along the growing direction of the foam.

Young's modulus,  $E$ , was defined as the slope of the linear elastic phase in the initial part of the curve that presents the steepest slope [13]. After the elastic deformation, a strain maximum was sometimes followed by a decrease before reaching the long

**Table 1**  
Formulation of tannin-based foams.

Ingredients	Amounts (g)		
	Quebracho	Mimosa <sup>a</sup>	Pine <sup>b</sup>
Tannin	30	30	30
Furfuryl alcohol	10.5	10.5	19
Formaldehyde	7.4	7.4	7.4
Water	6	6	–
PEG 400	–	–	4.5
Diethyl ether	2.1–3.9	4–6	2–6
pTSA	11	11	11

<sup>a</sup> From [13].

<sup>b</sup> From [6].



serrated plateau, typical of elastic-brittle foams [11]. The compressive strength,  $\sigma_{pl}$ , has thus been taken as the highest height of the long serrated plateau (hence the subscript “pl”) for all the samples. Densification strain was defined as the strain at the intersection between the horizontal axis of the plot and the backward extended densification line [13].

### 3. Results and discussion

#### 3.1. Porous structure of quebracho foams

The apparent density of the foams is plotted in Fig. 2(a) as a function of the amount of blowing agent. The former work of Zhao [14], based on mimosa tannin, demonstrated both theoretically and experimentally that the bulk density of foams is inversely proportional to the amount,  $m$ , of blowing agent, i.e.  $\rho_b \propto m^{-1}$ . The same result was recovered here, as an excellent agreement was found when fitting a power law to the experimental data. The exponent of this power law was  $-1.04$ , very close indeed to the expected value. Plotting the inverse of the density as a function of the mass of blowing agent leads to a straight line with a correlation coefficient higher than 0.99 (not shown).

The same kind of law was found for the changes of average cell diameter as a function of bulk density, i.e.  $\bar{D} \propto \rho_b^{-1}$ , in agreement with what has been experimentally found and demonstrated elsewhere [14]. Since  $\rho_b \propto m^{-1}$  and  $\bar{D} \propto \rho_b^{-1}$ , then obviously the cell size is strictly proportional to the amount of blowing agent, as verified by Fig. 2(b). The linear fit to the experimental data indeed gave a correlation coefficient higher than 0.99.

The skeletal density was measured for each formulation of quebracho foam, and found to be  $1.46 \pm 0.01 \text{ g cm}^{-3}$ . This value is in

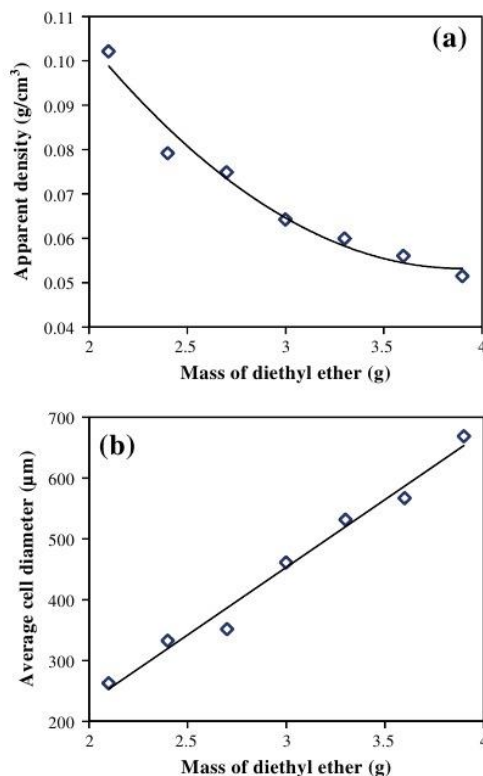


Fig. 2. (a) Apparent density, and (b) average cell size of quebracho foams as a function of the amount of blowing agent. The lines are power law and linear fits, respectively (see text).

good agreement, though a little lower, than the one obtained for the same formulation based on mimosa tannin [13]:  $1.59 \text{ g cm}^{-3}$ . From Eq. (1), the calculated overall porosity was found to be within the range 93–96.5%.

#### 3.2. Physical properties of quebracho foams

The thermal conductivity is shown in Fig. 3 as a function of bulk density. The conductivity of the foams was found to range from 0.047 to  $0.05 \text{ W m}^{-1} \text{ K}^{-1}$  and, as expected in this rather narrow range of porosity, it increased linearly with density. Such values are comparable with those of other phenolic foams, e.g.  $0.057 \text{ W m}^{-1} \text{ K}^{-1}$  at a density of  $0.12 \text{ g cm}^{-3}$  [15], among others [16]. These values were somewhat higher than those of similar foams made from other sources of tannin: mimosa and pine [6], and to those of expanded polystyrene foams for example [17].

This finding is explained by the values of cell size at fixed bulk density, which are the highest and the lowest in quebracho and pine foams, respectively, whereas mimosa foams present intermediate values. Fig. 2(b) indeed shows that the average cell size roughly ranges from  $650 \mu\text{m}$  to  $350 \mu\text{m}$  for densities of  $0.052 \text{ g cm}^{-3}$  and  $0.079 \text{ g cm}^{-3}$ , respectively. In the same range of density, mimosa and pine foams present cell sizes ranging from  $500 \mu\text{m}$  to  $300 \mu\text{m}$ , and from  $200 \mu\text{m}$  to  $170 \mu\text{m}$ , respectively [14]. However, the slope corresponding to quebracho foams was also lower than those of other tannin-based foams, making these materials better thermal insulators than mimosa- and pine-derived materials at densities higher than 0.1 and  $0.2 \text{ g cm}^{-3}$ , respectively.

Although a little less effective for thermal insulation, high-density foams are interesting as their mechanical properties significantly increase with density, as shown in Fig. 4. The shape of the obtained stress–strain curves is typical of other phenol–formaldehyde foams [18,19] and of other structural foams in general [20], with a long serrated plateau originating from the coexistence of collapsed and uncollapsed zones, representative of brittle foams undergoing successive cell wall fractures [16].

In the explored range of densities, quebracho foams presented higher values of both elastic modulus and compressive strength than those of mimosa [13] and pine [6] foams, as seen in Fig. 5(a and b). Extrapolation of the lines in these figures shows that pine foams present higher modulus and strength only at densities higher than 0.23 and  $0.13 \text{ g cm}^{-3}$ , respectively.

About the way the mechanical properties change with density, several micromechanical and phenomenological models have suggested the following power laws:

$$E = E_0 \rho_b^n \quad (3)$$

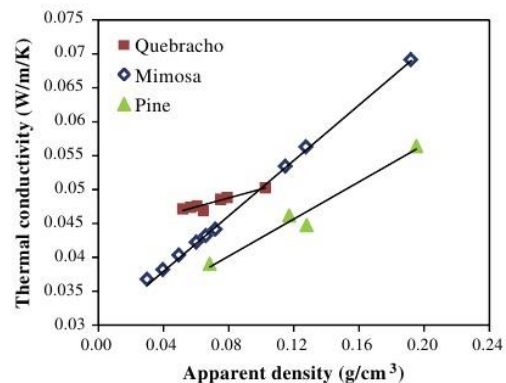
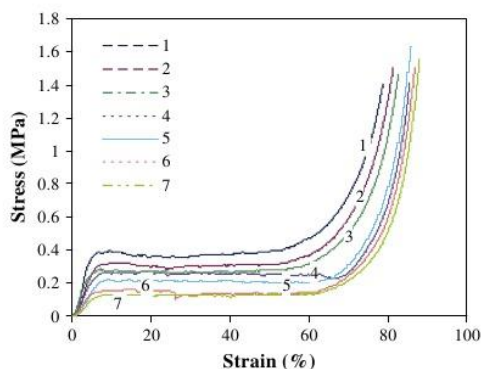


Fig. 3. Comparison of thermal conductivity of quebracho, pine and mimosa foams, as a function of bulk density.





**Fig. 4.** Stress–strain curves of quebracho foams having different bulk densities, according to: (1) 0.1021 g cm<sup>-3</sup>; (2) 0.0791 g cm<sup>-3</sup>; (3) 0.0748 g cm<sup>-3</sup>; (4) 0.0642 g cm<sup>-3</sup>; (5) 0.0599 g cm<sup>-3</sup>; (6) 0.056 g cm<sup>-3</sup> and (7) 0.0515 g cm<sup>-3</sup>.

$$\sigma_{pl} = \sigma_{pl,0} \rho_b^a \tag{4}$$

where  $E_0$  and  $\sigma_{pl,0}$  are the elastic modulus and the yield strength of the solid from which the cellular material is made of,  $n$  is an exponent which depends on the failure model, whereas the exponent  $a$  is associated to the structure and its deformation mechanics. The theoretical value of the exponent  $n$  is 2 [21], and that of  $a$  is 1.5 for open-cells foams [22].

Plotting the log of  $E$  and  $\sigma$  as a function of  $\log(\rho_b)$  confirms the validity of Eq. (3), (4). The same behaviour was observed for all other tannin-based foams [6,13,23]. The values of the corresponding exponents  $n$  and  $a$  have been reported in Table 2. Concerning the exponent of the elastic modulus, quebracho (2.12) and mimosa (1.92) presented similar values, and it is not clear yet why pine led to a value (3.31) higher than the theoretical one. The same applies to the exponent of compressive strength, the one for pine (2.79)

**Table 2**  
Exponents of power laws (Eqs. (3)–(5) and (7)) for the mechanical properties of tannin-based foams.

Exponents	Quebracho	Mimosa <sup>a</sup>	Pine <sup>b</sup>
$n$ (Elastic modulus)	2.12	1.92	3.31
$a$ (Compressive strength)	1.52	1.65	2.79
$x$ (Densification strain)	-0.30	-0.42	-0.09
$y$ (Absorbed energy)	1.23	1.13	2.70

<sup>a</sup> From [13].

<sup>b</sup> From [6].

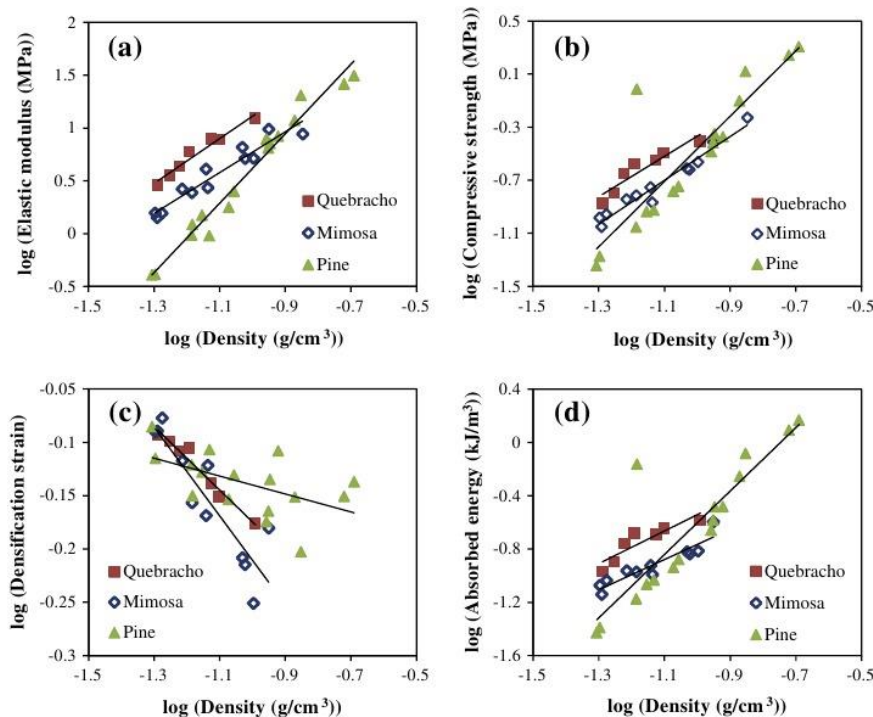
being hardly explained and significantly higher than those of quebracho and mimosa, 1.52 and 1.65, respectively. We believe that the high reactivity of pine tannin, more or less compensated by adjustments in the corresponding formulations (see again Table 1), might lead to foams whose solid backbone presents different mechanical properties than those of the other tannin-based materials, since no significant differences of porous structure could be observed.

A power law was again suggested here for correlating densification strain,  $\varepsilon_d$ , and bulk density:

$$\varepsilon_d \propto \rho_b^x \tag{5}$$

as the relationship of Gibson and Ashby [11] never applied to tannin-based foams. Fig. 5(c) shows that Eq. (5) works quite well for quebracho foams, whereas a high scattering of the data was found for other foams. The values of the new exponent  $x$  are listed in Table 2. Again, quebracho and mimosa foams presented similar behaviours,  $x = -0.30$  and  $-0.42$ , respectively, unlike pine foams,  $x = -0.09$ .

The energy absorbed by the foam during compression is defined as the area under the stress–strain curve prior to the onset of densification, and can be expressed as follows:



**Fig. 5.** Mechanical properties of tannin foams plotted as a function of bulk density in a double logarithmic scale: (a) elastic modulus; (b) compressive strength; (c) densification strain; and (d) absorbed energy.



$$U = \int_0^{\varepsilon} \sigma(\varepsilon) d\varepsilon \quad (6)$$

Given the shape of the curves presented in Fig. 4, Eq. (6) can be approximated by  $U \approx \sigma_{pl} \varepsilon_d$ . Considering Eqs. (4) and (5), the adsorbed energy should thus scale as:

$$U \propto d^y \quad (7)$$

where the new exponent  $y$  is such that  $y = a + x$ . Fig. 5(d) indeed shows a linear dependence when the absorbed energy is plotted as a function of the apparent density in a double logarithmic scale. Once again, the values of the exponent were similar for quebracho (1.23) and mimosa (1.13) foams, and were close to 1, suggesting that absorbed energy is roughly a linear function of the density. This behaviour has also been observed in other foams [24]. For pine foams, the very different value of the exponent, 2.70, indicates that the absorbed energy increases much faster with density.

The values reported in Table 2 confirm that the structures of the flavonoid units have a major influence on the properties of the resultant foams. The chemical reactivities are indeed very similar for quebracho and mimosa tannins, as most reactions occur on A-rings whereas B-rings are poorly reactive [25]. In contrast, the difference in the A-ring of pine tannin produces a very different, 6–7 times higher, reactivity [10], and therefore foams behaving differently.

#### 4. Conclusions

The influence of the flavonoid nature in the preparation of tannin-based foams has been analyzed. Rigid foams at different densities have been prepared from quebracho tannin for the first time, and their properties were compared with those of mimosa and pine foams. We have shown that, due to the identical A-ring of the flavonoid unit, which is the most reactive one and therefore mainly accounts for the observed reactions, quebracho foams can be prepared using the same formulation as for mimosa foams. This is a very important result *per se*, as the market of mimosa tannin is extremely tight, whereas that of quebracho tannin benefits from a huge development potential.

Not only the formulations are very similar when mimosa and quebracho tannin as precursors are compared. The porous structures of the foams themselves, as well as the thermal conductivity and the mechanical properties also present similar trends. Thus, the average cell size was found to be strictly proportional to the amount of blowing agent, a result already observed in the case of mimosa foams but not in the case of pine foams. The thermal conductivity was close to that of mimosa foams, although a little higher at low density. Relationships between absolute conductivity and average cell size were observed, the foams having the largest cells at a given density being those presenting the highest conductivity. From this point of view, pine foams were better thermal insulators, as they presented the smallest cells.

However, quebracho foams were those for which the thermal conductivity increased the least with density, suggesting that high-density foams are better insulators than mimosa foams. High density foams are also those presenting the highest mechanical properties, which may be an advantage for insulation of floors for example. Whatever the property: modulus, strength, densification strain or absorbed energy, quebracho and mimosa foams presented very similar trends, clearly different from those of pine foams. Quebracho foams were also those having the highest mechanical properties.

As a conclusion, the similar reactivity of quebracho and mimosa tannins produced foams having similar properties, slightly higher for quebracho foams, but totally different than those of pine due to its different nature.

#### Acknowledgements

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#### *4.4.4. Premiers outils pour la conception de mousses tanins-furaniques*

### **« *First tools for tannin-furanic foams design* »**

Auteurs : M.C. Basso<sup>1</sup>, M.C. Lagel<sup>1</sup>, A. Pizzi<sup>1,2</sup>, A. Celzard<sup>3</sup>, S. Abdalla<sup>2</sup>.

<sup>1</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>2</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

<sup>3</sup>IJL, Université de Lorraine, Epinal, France

#### Résumé :

Pour la première fois ont été préparées des mousses de tanins de quebracho exemptes de formaldéhyde. Plusieurs formulations simples ont été présentées dans le but d'étudier l'influence capitale que possède chaque composant sur la formation de mousse et donc sur les caractéristiques des mousses obtenues. L'utilisation d'un tensioactif non-ionique induit des cellules plus petites et une répartition plus homogène de la taille de celles-ci. De plus, les agents de réticulation améliorent les propriétés mécaniques des mousses. Une combinaison de différents catalyseurs permet de contrôler le rapport entre le processus d'expansion et celui de durcissement. La compréhension des rôles et des interactions des différents composants de la formulation rend possible la conception de mousses de tanins ayant des propriétés spécifiques souhaitées.

Mots-clés : Mousses de tanins de quebracho, Sans formaldéhyde, Effets réactifs, Propriétés spécifiques, Processus d'expansion et de durcissement, Conception de formulation.

## First Tools for Tannin-Furanic Foams Design

Mariá Cecilia Basso,<sup>a</sup> Marie-Christine Lagel,<sup>a,b</sup> Antonio Pizzi,<sup>a,c</sup> Alain Celzard,<sup>d</sup> and Soliman Abdalla<sup>c</sup>

Formaldehyde-free quebracho tannin foams were prepared for the first time. Several simple formulations have been presented in order to study the capital influence of each component on foaming and therefore on the characteristics of the obtained foams. Incorporation of a non-ionic surfactant leads to smaller cells and a more homogeneous cell size distribution. Cross-linking agents improve the mechanical properties of foams. A combination of different catalysts allows control of the ratio between the expansion/hardening processes. The understanding of the roles and interactions of the different components of formulation make possible the design of tannin foams having specific properties.

*Keywords:* Quebracho tannin foams; Without formaldehyde; Reactive effects; Specific properties; Expansion-hardening processes; Formulation design

*Contact information:* a: LERMAB, Université de Lorraine, 27 Rue Philippe Seguin, 88000 Epinal, France; b: SILVA-INDUNOR, Cerrito 1136 (C 1010AAX), Buenos Aires, Argentina; c: Dept. of Physics, King Abdulaziz University, Jeddah, Saudi Arabia; d: IJL, Université de Lorraine, 27 Rue Philippe Seguin, 88000 Epinal, France; \*Corresponding author: antonio.pizzi@univ-lorraine.fr

### INTRODUCTION

In the framework of sustainable development, biosourced materials represent an attractive alternative to products derived from petrochemical resources (Kaplan 1998; Gardziella *et al.* 2000; Raqueza *et al.* 2010). Tannin/furanic foams are approximately 95% composed of natural raw materials. Condensed polyflavonoid tannins are vegetal products obtained by water extraction from the wood and bark of trees, and furfuryl alcohol is obtained from agricultural waste after hydrolysis and catalytic reduction (Aguilar *et al.* 2002). These green, cheap, lightweight, cellular materials are prepared from a liquid resin mainly based on tannin and furfuryl alcohol dissolved in water, with a cross-linking agent and 4-paratoluene sulfonic acid as catalyst. A low boiling point solvent is used as the blowing agent (physical foaming) (Meikleham and Pizzi 1994; Tondi and Pizzi 2009; Basso *et al.* 2013a,b).

Polyflavonoid tannin-furanic foams have been extensively described and tested for a number of different applications showing great potential for replacing commercial, synthetic phenolic foams in most applications (Meiklenham and Pizzi 1994; Pizzi *et al.* 2008; Tondi *et al.* 2008a,b, 2009; Tondi and Pizzi 2009; Lacoste *et al.* 2013a,b).

Foam design, and thus the formulation of appropriate combinations of materials to achieve the properties wanted for particular applications, requires the understanding of (i) the influence of the different process variables, (ii) the role of each reactant during foaming, and (iii) the knowledge of the interactions of the different components involved. Recently, in this context, some research works have presented dynamic and kinetic studies of foaming for different formulations, describing in detail the foaming process



itself while correlating its parameters with the characteristic properties of mimosa and pine bark tannins (Basso *et al.* 2013a,b,c; Lacoste *et al.* 2013c).

In the present work, a formaldehyde-free quebracho tannin foam was prepared according to a base formulation. Several simple modifications were introduced to this starting formulation to show their influence on foaming, and consequently on the characteristics of the foams obtained, while discussing in detail the role played by each reactant. The aim of this work was to give some basic first principles for the appropriate formulation and design of tannin-furanic foams with desirable characteristics. This approach is not only descriptive of the foam but also predictive of the characteristics of the foams obtained, allowing foam design on demand.

## EXPERIMENTAL

### Materials

Quebracho (*Schinopsis lorentzii* and *balansae*) wood extracts were provided by Silva Chimica (S. Michele Mondovi', Italy). Furfuryl alcohol, glyoxal, and pentane were purchased at Acros Organics (Geel, Belgium), phenol sulfonic acid 65% water solution at Capital Resin Corporation (CRC 605, Columbus, OH, USA), silicone surfactant at Dow Corning (Xiameter OFX193, Paris, France), and para-toluene sulfonic acid at Sigma Aldrich (Saint-Louis, Missouri).

### Foams Preparation

The formaldehyde-free quebracho foams were prepared according to the mixture of components shown in Table 1 at  $32 \pm 2$  °C in an open plastic mould.

**Table 1.** Composition of Free-Formaldehyde Quebracho Tannin Foams

Sample name	TA	TB	TC	TD	TE
Tannin (g)	30	30	30	30	30
Furfuryl alcohol (g)	14	14	14	14	14
Water (g)	9	9	9	9	9
Pentane (g)	4.5	4.5	4.5	4,5	4.5
Phenol sulfonic acid (65%) (g)	8	8	8	8	-
Para-toluene sulfonic acid (65%) (g)	-	-	-	-	8
Silicone surfactant (g)	-	1	9	1	1
Glyoxal (g)	-	-	-	4,5	-
Apparent density (g/cm <sup>3</sup> )	0.042	0.031	0.041	0.037	0.041
Thermal conductivity (W/mK)	0.047	0.035	0.042	0.036	0.041
Average cell size (µm)	>500	-100	-100	-100	-500
Compression strength at 20% strain (MPa)	0.11	0.05	0.07	0.09	0.08

First, a liquid mixture was prepared and mechanically stirred for 20 s at room temperature. The liquid mixture was composed of furfuryl alcohol, silicone surfactant (except for the TA foam), and water. The tannins in powder form were then added to the mixture and strongly stirred for 90 s. Afterward, the glyoxal (TD foam) and subsequently the blowing agent, namely the pentane, and the acid catalyst were added by stirring for 15 s after the addition of each reagent to ensure homogenization. Finally, the mixtures were put in a ventilated oven preheated at  $32 \pm 2$  °C where foaming and hardening were carried out. After 30 min, the tannin-furanic foams obtained were dried at room



temperature. Before analysis, the samples were put in a climate chamber at 20 °C with a relative humidity of 65% for one week.

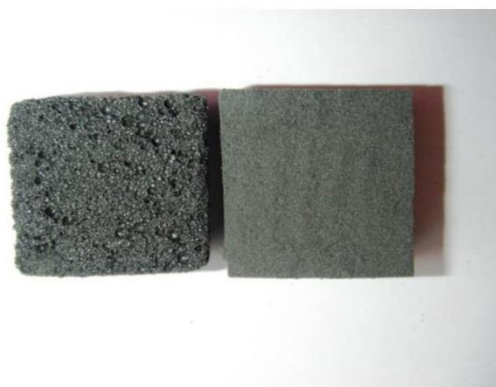
### Foams Characterization

Blocks of foam with dimensions of 3×3×1.5 cm were weighed to obtain the bulk density. The cellular morphologies of the foams were obtained by Hitachi S 520 Scanning Electron Microscope (SEM, Tokyo, Japan) at 30x magnification (TA and TE foam) and 200x magnification (TB, TC, and TD foam). Different magnifications were applied due to great differences in cell sizes of the evaluated samples. The thermal conductivity of the foam samples with dimensions of 3×3×1.5 cm was measured by the transient plane source method (Hot Disk TPS 2500, Piscataway, USA) at room temperature. The mechanical resistance to compression was investigated with an Instron 4467 universal testing machine (Norwood, MA, USA) at a load rate of 2.0 mm min<sup>-1</sup>. No significant differences in results were noticed within the specimens coming from the four repetition foams prepared for each case.

## RESULTS AND DISCUSSION

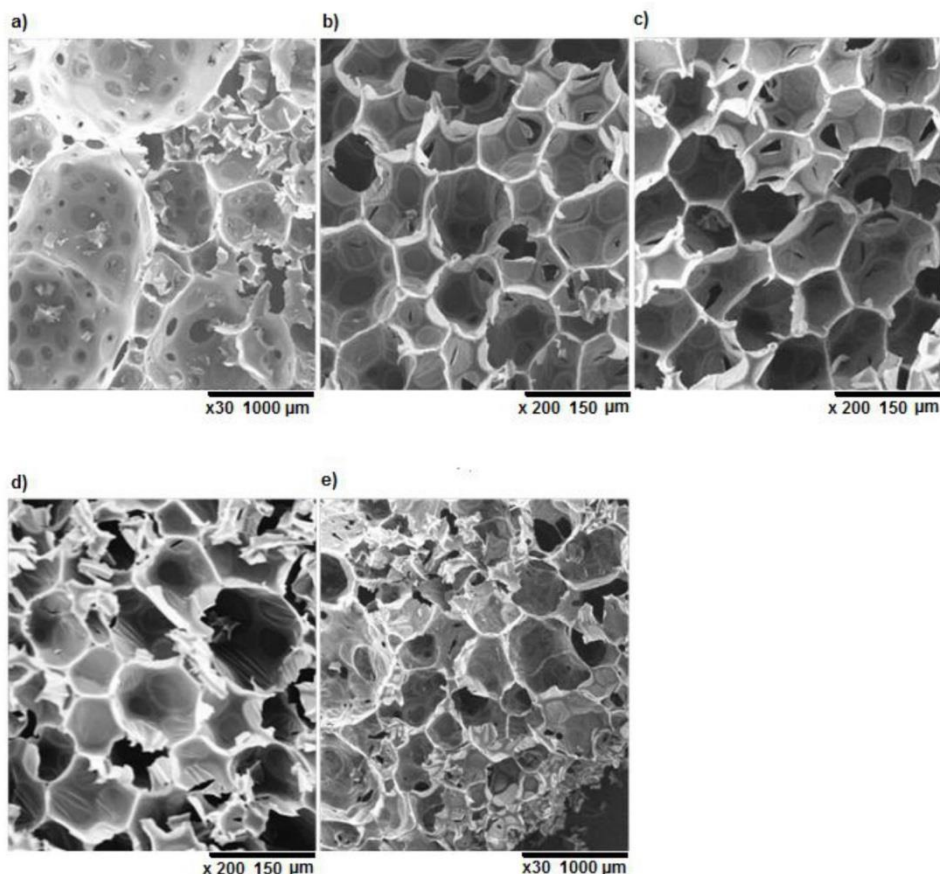
All of the mixtures presented in Table 1 yielded foams based on quebracho tannin and were completely formaldehyde-free. Thus, they are much more environmentally acceptable than the first quebracho tannin foams previously presented (Martinez de Yuso *et al.* 2014). These new tannin-furanic foams are rather lightweight (density lower than 0.1 g/cm<sup>3</sup>) and grey-coloured. Their measured thermal conductivities indicate good insulation properties, and they are comparable or better than those reported for other foams based on mimosa or pine tannins (Tondi *et al.* 2008b; Lacoste *et al.* 2013a) and other phenolic or lignophenolic foams (Shutov 1984, De Carvalho *et al.* 2003).

In particular, the TA foam is rigid, brittle, and has a cell distribution that is uneven and irregular. The TB foam, containing a small amount of a non-ionic surfactant, presents a density (0.031 g/cm<sup>3</sup>) lower than that of the TA foam (0.042 g/cm<sup>3</sup>), hence also presents a lower thermal conductivity (Table 1). Furthermore, at the macroscopic level, the aspect of these foams is very different (Fig. 1); namely the TB foam is more homogeneous, with finer and smaller cells than the TA foam which does not contain any surfactant.



**Fig. 1.** Free-formaldehyde Quebracho tannin based-foam samples. From left to right: without surfactant; with surfactant.

Scanning electron microscopy (SEM) also shows this same trend (Fig. 2a and b, Table 1). Such differences can be explained by the triple function of the surfactant: (i) to improve the compatibility of the reactants, mainly of the non-polar hydrophobic blowing agent with the resin and catalyst; (ii) to lower the surface tension of the system, thereby forming finer bubbles, and (iii) to prevent the cell wall from becoming thin and unstable during foaming, *i.e.* to prevent the developing foam from collapsing or rupturing (Iwasaki 1995; Zhang *et al.* 1999; Gardziella *et al.* 2000).



**Fig. 2.** SEM pictures of free-formaldehyde quebracho based-foam samples (a) TA foam; (b) TB foam; (c) TC foam; (d) TD foam; (e) TE foam

It is thus interesting that although it has a lower density, the cell size of the TB foam is lower than for the TA foam. This can be explained because the rise temperature is lower and later when a surfactant is used; curing process shows the same trend (Basso *et al.* 2013b). In this way, TB foam (with surfactant) becomes rigid more slowly than TA foam; then TB is more expanded, and so it is lighter than TA. Thus, the inclusion of a surfactant in the foam composition allows for the modification of the cell size independently of the density of the material, contrary to what was found by Zhao *et al.* (2010), Lacoste *et al.* (2013a), and Martinez de Yuso *et al.* (2014) for mimosa, pine, and quebracho tannin foams, respectively, who were limited to the variation of the blowing agent proportion. As a consequence, the capacity of achieving independence from the



other foaming parameters greatly increases formulation possibilities and the range of materials that can be developed, hence their greater diversity of properties and applications.

Figure 3 shows the compression resistance curves for the TA and TB foams. The former presents a higher mechanical resistance (Table 1) which is consistent with its greater density. The TB foam is instead more elastic as shown by the shape of its compression curve. This behaviour could depend on the temperature, hence the internal pressure generated during foaming, decreasing when a surfactant is included in the formulation (Basso *et al.* 2013). Thus, the foam with the surfactant is more elastic and less brittle.

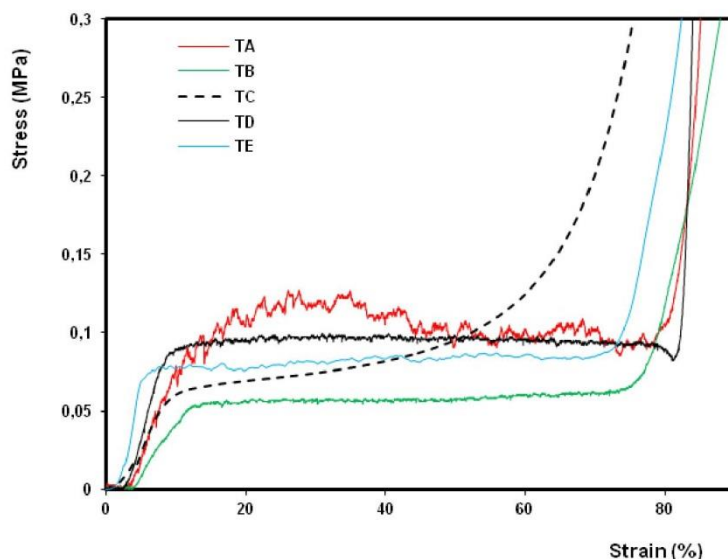


Fig. 3. Stress-strain curves of free-formaldehyde quebracho based-foams

This same trend has been observed (examples not shown in Table 1) when used in the foam composition small proportions (0.2 to 2 g) of either castor oil 35OE and 40OE, Pluronic PE6800 (blocks copolymers of polypropylene glycol-polyethylene glycol), or Tegostab B8406 and Tegostab B8244, two silicone surfactants currently used for the manufacture of polyurethane foams. All of these products are non-ionic surfactants.

Conversely, inclusion of other types of surfactants must be evaluated for each specific case. Adding anionic surfactants that are strongly hydrophilic, particularly sodium dodecylbenzenesulphonate or laureth sulphate (not reported in Table 1), provides a lack of compatibility with the pentane blowing agent and leads to collapse and destruction of the cellular structure. Such types of additives, often used in floral foams (dry flowers conservation, hydroponic cultures), must be combined with non-ionic surfactants which ease the emulsion formation for all the components of the formulation.

The TC foam (Table 1) containing a much higher proportion of non-ionic surfactant presents a structure as homogeneous as the TB foam due to the emulsion effect of the surfactant allowing for better mixing of the system components. Its cellular structure (Fig. 2c, Table 1) is similar to that of the TB foam. Nonetheless, its density is greater as well as its mechanical resistance and thermal conductivity. When a high proportion of surfactant is used, this compound acts as a plasticizer (Gardziella *et al.*

2000). Using plasticizers decreases the internal temperature of the foams, which decreases their internal foaming pressure and their rate of expansion (Basso *et al.* 2013a; Lacoste *et al.* 2013c). Such an effect would explain why the TC foam has a higher density than the TB foam as well as a certain degree of elasticity (Fig. 3). The foam density and its mechanical properties are then controlled by the proportions of surfactant used. In this way, the TC foam hardening is slower than for the TA and TB foams. For formulations TA and TB, the foams are sufficiently hardened 15 min after the catalyst addition and can be cut neatly with a knife. However, the TC foam remains semi-liquid and needs at least 20 to 25 min to solidify. This longer hardening time is due to a certain degree of elasticity (Fig. 3).

It has been shown that adding surfactant in proportions higher than those in Table 1 causes foam shrinking. This can be explained by the greater out of phase difference between foaming and hardening (Basso *et al.* 2013a), for which the structure of the foam while foaming is not sufficiently solid to support its cooling. This occurrence can be avoided by using moulds made with insulating materials, possibly closed or by increasing the outer temperature or by incorporating additives favouring polymerization.

Increasing the proportion of furfuryl alcohol in the formulation in order to limit foam shrinkage is not a valid approach, as it contributes even more to such an undesirable effect. An increase in the proportion of furfuryl alcohol, the heat generated by self-polymerisation of the foam system, would further exacerbate the time difference between foaming and hardening (Basso *et al.* 2013a,c). Thus, after a rather sharp temperature peak leading to an abrupt foam expansion, the system undergoes rapid cooling before the material can present a sufficiently solid structure in absence of either a cross-linker such as formaldehyde or a sufficiently high curing temperature. Furthermore, in addition to the shrinking problem, too quick an expansion is harmful to the integrity of the foam and hence to the mechanical properties of the final foam. In principle, it is preferable to control the kinetics of foam expansion by the external temperature used.

To improve the mechanical performance of the TB foam, a cross-linker other than the environmentally unacceptable formaldehyde has been added to the formulation obtaining the foam TD (Table 1). In particular, the addition of the non toxic and non-volatile glyoxal (Ballerini *et al.* 2005; El-Mansouri *et al.* 2007a,b), improves the foam's mechanical resistance and renders it more rigid (Table 1 and Fig. 3). This is because it favours polymerisation and cross-linking by forming new tannin-aldehyde and furan-aldehyde bonds (Lacoste *et al.* 2013b). The same effect is obtained by adding glutaraldehyde (Li *et al.* 2013 & 2014) and 1,6 diamino-hexane to the TB formulation. All of these additives favour cross-linking and polymerisation.

By the use of different additives it is possible to give the foam its desired characteristics. For example, a foam of improved mechanical resistance can be obtained by including a cross-linker in the formulation and the increased rigidity induced by this can be counterbalanced by the addition of an appropriate amount of a non-ionic surfactant. Finally, replacing the phenol sulfonic acid used as a catalyst in the TB foam with p-toluen sulfonic acid (pTSA) leads to obtaining the TE foam (Table 1). These two acid catalysts, which are currently used for the preparation of synthetic phenol-formaldehyde foams, both react and are included in the final foam structure (Gardziella *et al.* 2000; Tondi *et al.* 2008a; Basso *et al.* 2014). However, the composition and the characteristics of the catalyst as well as the curing/foaming relationship appear to determine the characteristics of the final foam.

The TE foam is denser and consequently presents both a higher mechanical resistance and a higher thermal conductivity than the TB foam (Table 1 and Fig. 3). TE foam hardening is slow (contrary to the TB foam); thus it cannot be cut with a knife after 15 minutes as in the case of foam TC. Moreover, it has larger cells than the TB foam (Fig. 2e, Table 1) and it shrinks because the pTSA used as catalyst favours more rapid foam expansion rather than polymerisation and cross-linking. Conversely, phenol sulfonic acid favours these last processes, *i.e.*, the curing foam. The molar weights of pTSA and phenol sulfonic acid are similar (172 and 174 g/mol, respectively), but the first is used as powder monohydrate (molecular weight 190 g/mol, 99% extra pure), while the phenol sulfonic acid is purchased as a 65% water solution including 2% sulphuric acid.

While the TC and TE foams suffer from some shrinkage due to their slower hardening, the cell size of the TC foam is not greater than for the TB foam because the excess surfactant decreases the foaming temperature of the system and thus slows down its expansion. For the TE foam, the lack of a plasticizer/surfactant leads to enlarged cells.

An interesting possibility is to combine the two acid catalysts in different proportions to obtain foams presenting specific characteristics by the precise control of the degrees of polymerisation/cross-linking and the equilibrium between the rate of foam expansion and hardening. For example, the pTSA acid could be combined with either the phenol sulfonic acid, another stronger organic acid, or even a very moderate proportion of sulphuric acid. In the case that alkaline catalysis is desired instead, the formulation needs to be changed by substituting the furfuryl alcohol with another hardener/cross-linker (Basso *et al.* 2014). In order to allow such foam expansion and hardening, the external temperature of the operation will need to be higher, due to the lack of the heat generated by the acid self-polymerisation of furfuryl alcohol.

## CONCLUSIONS

1. Incorporation of a small proportion of non-ionic surfactant leads to a more homogeneous cell size distribution and smaller cells in tannin/furanic foams.
2. Tannin foams having a high proportion of non-ionic surfactant present a certain degree of elasticity.
3. The mechanical performance of foams can be improved by using a cross-linking agent, such as an aldehyde.
4. The combination of different catalysts allows for controlling the ratio between the expansion/hardening processes.
5. The appropriate combination of different components and additives in the formulations leads to achieve specific properties for the obtained tannin foams.

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## 4.5. Matériaux abrasifs et de friction biosourcés

### *4.5.1. Développement et caractérisation de roues abrasives ayant comme matrices des résines tanins-furaniques*

## **« *Development and characterization of abrasive grinding wheels with a tannin-furanic resins matrix* »**

Auteurs : M.C. Lagel<sup>1</sup>, A. Pizzi<sup>1,2</sup>, M.C. Basso<sup>3</sup> et S. Abdalla<sup>2</sup>.

<sup>1</sup>LERMAB, Université de Lorraine, Epinal, France

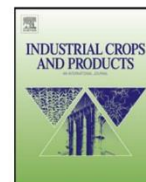
<sup>2</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

<sup>3</sup>Silva Chimica, San Michele Mondovi', Italie

### Résumé :

Un matériau thermodurcissable biosourcé à 100 % à base de résines thermodurcissables furaniques-tanins condensés a été utilisé comme matrice de roues abrasives solides. Ceci en utilisant des matières premières biosourcées. En outre, ce nouveau matériau thermodurci est produit par un procédé simple, qui peut être aisément industrialisé. Les meules réalisées avec cette résine qui lie différentes poudres abrasives organiques et minérales ont été élaborées et caractérisées. Ces meules présentent d'excellentes propriétés d'abrasivité par rapport à une meule commerciale.

Mots-clés : Biopolymères, Abrasifs biosourcés, Résines tanniques, Roues « vertes » abrasives.



## Development and characterization of abrasive grinding wheels with a tannin-furanic resins matrix



M.C. Lagel<sup>a,\*</sup>, A. Pizzi<sup>a,b</sup>, M.C. Basso<sup>c</sup>, S. Abdalla<sup>b</sup>

<sup>a</sup> LERMAB, University of Lorraine, 27 rue Philippe Seguin, 88051 Epinal, France

<sup>b</sup> Department of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

<sup>c</sup> Silva Chimica, via Torre 7, 12080 San Michele Mondovì, Italy

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### ABSTRACT

A 100% biosourced thermoset material based on condensed tannin-furanic thermoset resins, thus using biosourced raw materials, has been used as the resin matrix of solid grinding wheels. Moreover, this new thermoset material is produced by a simple process, which can be easily industrialized. Grinding wheels based on this resin bonding different mineral and organic abrasive powders were developed and characterized. These grinding wheels show excellent abrasiveness properties when compared to a commercial grinding wheel.

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### 1. Introduction

As a consequence of the continuous increase in oil prices biobased and biosourced materials are becoming more appealing. Many investigations have been done and are on course to replace oil-based materials with natural renewable materials. Among the biomass being explored for a variety of applications, furfuryl alcohol and condensed polyflavonoid tannins, one issued from agriculture and the other from forestry, have been investigated and used in last decades for wood adhesives (Pizzi, 1983, 1989, 1994) and more recently to develop new green materials such as fire-resistant foams (Tondi et al., 2008, 2009a, 2009b; Basso et al., 2014; Lagel et al., 2014; Martinez de Yuso et al., 2014), composites (Zhou et al., 2013; Sauguet et al., 2014) and high tech paper laminates (Abdullah et al., 2013). Recently a new thermoset plastic based on a natural tannin-furanic thermoset resin was developed (Li et al., 2013). This resin, based on the coreaction of mimosa tannins and furfuryl alcohol was developed to replace industrial oil-derived resins like phenolic resin for casting and moulding applications. In this article, firstly the possibility of preparing grinding wheels made with biobased resin as a bonding system was studied. The biobased resin used is a tannins/furfuryl alcohol condensation product. Moreover, the majority of vitreous-bonded grinding wheels in commercial use is composed of either fused aluminium oxide or silicon

carbide depending from the applications (Rue, 1985; Narayanan et al., 1988; Hay et al., 1990; Lee and Rue, 1992; Jackson et al., 2001). Secondly, a new type of resin based rather on quebracho tannins was developed. Thirdly, the formulation of the resin was extensively modified to cure in a few minutes at ambient temperature rather than the hours or days needed to cure without faults such as the original resin of Li et al. (2013). This is a crucial point in order to be used industrially. Abrasiveness characterization tests were done using a Taber Abraser.

### 2. Materials and methods

#### 2.1. Materials

Mimosa (*Acacia mearnsii* formerly *mollissima*, De Wildt) bark tannin extract (Mimosa OP) and quebracho (*Schinopsis lorentzii* and *balansae*) wood tannin extract (Fintan QSTW) powders were supplied by SilvaTeam (San Michele Mondovì, Italy).

Furfuryl alcohol (98%), ethylene glycol, glyoxal (40% in water) and para-toluene-4-sulphonic acid (pTSA, with a purity of 97.5%) were purchased from Acros Organics (Geel, Belgium).

Tung oil was purchased from Oleobois (Vendargues, France).

For this work, four different abrasives particles were used.

Three types of abrasive particles were supplied by Dup (Saint-Souplet, France):

- Two of aluminium oxide (Al<sub>2</sub>O<sub>3</sub>): Alu 24 (grain size of 0.71 mm) and Alu 16 (grain size of 1.19 mm).

\* Corresponding author. Tel.: +33 3 29 29 63 18; fax: +33 3 29 29 61 38.

E-mail address: [lagel.mc@gmail.com](mailto:lagel.mc@gmail.com) (M.C. Lagel).



- One of vegetal shot (grain size between 0.45 and 0.80 mm) made with coarsely ground walnut shells.

And one finer aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) was provided by Prake (Saint Pierre du Perray, France):

- PSG 100 (grain size of 0.63 μm).

## 2.2. Resins synthesis

### 2.2.1. Mimosa tannin resin

Firstly, 15 g of furfuryl alcohol and 5 g of mimosa tannins at 7.9% of relative humidity were mixed together with a mechanical stirrer during 15 s. Secondly 0.38 mL of a 65% water solution of *para*-toluene sulfonic acid (pTSA) was added as a catalyst under mechanical stirring for 2 min. Then the mixture was pre-polymerized at 60 °C using a vacuum rotary evaporator during 1.5 h. At this point the resin is ready to use. The viscosity is about 2600 mPa s at 25 °C.

### 2.2.2. Quebracho tannin resins

Firstly, furfuryl alcohol and quebracho tannins at 5.7% of relative humidity were mixed together with a mechanical stirrer. Secondly ethylene glycol was added and then a 65% water solution of pTSA. Every time the mixing time is 15 s. This is the basic formulation of the quebracho tannins resin based. The viscosity is also about 2600 mPa s at 25 °C. Finally the abrasive particles were added in a silicone mould to form the grinding wheels. In some case it is necessary to use some additives for the resin in order to have better wheels, for example without cracks.

## 2.3. Grinding wheels development

The shelf lives of resins are about a few weeks for mimosa tannin resin and about a few hours for quebracho tannin resin.

### 2.3.1. Grinding wheels made with mimosa tannin resin

Abrasive particles were added to the resin and mixed with a spatula. The mixture is easy to be performed. It was placed in an oven at 60 °C for 2 days for the curing and then at 100 °C for another 2 days, so the crosslinking reaction is completed. The samples were cooled and they were cut using a lathe in order to have the dimensions of a grinding wheel: thickness of 15 mm diameter of 50 mm and with a hole at the centre of 16 mm diameter. The proportions used are shown in Table 1.

### 2.3.2. Grinding wheels made with quebracho tannin resins

After having mixed all the component of the resin, the abrasive particles were added and incorporated with a spatula. The proportions used are shown in Table 2. Then the wheel matrix thermoset

**Table 1**  
Grinding wheels with mimosa tannin resins.

	Mass (g)			
	Alu 24		Nut shells	
Percentage of abrasive particles	150%	200%	75%	100%
Sample number	1	2	3	4
Resin	25	25	25	25
Abrasive particles	37.5	50	18.75	25

resin was cured at ambient temperature (25 °C) in a few hours, depending on formulations. The samples were cut using a lathe in order to have the dimensions of a grinding wheel: thickness of 15 mm, diameter of 50 mm and a hole at the centre of 16 mm diameter.

Initially, the matrix resins were composed of furfuryl alcohol, water, quebracho tannins and ethylene glycol (Table 2). However, with the ageing of the grinding wheel cracks appeared in the hardened resin matrix inducing fragility in the wheel. One sample was prepared without abrasive particles and the same cracks appeared indicating that the cause of this behaviour was not linked to the abrasive particles but just to the resin itself. Thus, to avoid cracks in the grinding wheels, at first the water in the formulation was replaced by furfuryl alcohol and afterwards a vegetable oil, such as tung oil and linseed oil, was added as a plasticizer. Glyoxal as an additional hardener was also added to some formulations (Table 2).

## 2.4. Grinding wheels characterization

### 2.4.1. Scanning electron microscopy (SEM)

SEM observations were done with a Hitachi TM-3000 scanning electron microscope.

Grinding wheels were observed at ×50 and ×100 magnifications, depending on the abrasive particles size.

### 2.4.2. Determination of the abrasiveness

The abrasiveness of the wheels was determined by the method described in the standard NF EN 13329+A1 by using an abrasimeter Taber Abraser 5130 (Taber Industries, USA). In this comparison work, the wheel was used with a 500 g weight load. Grinding wheels with tannins resins were compared with a Calibrade wheel H-18 from Taber Industries (North Tonawanda, USA). The abrasive tests were conducted on the surface of a sample of a 700 kg/m<sup>3</sup> commercial particle board. The size of the particle board sample was 1.9 cm × 10 cm × 10 cm. In order to set the sample on the machine, at the centre of particle board is drilled a 1.2 cm diameter hole.

According to the standard ATSM D4060-01 the wear index (*I*) of each sample was calculated as follows:

$$I = \frac{(A - B)1000}{C}$$

**Table 2**  
Grinding wheels with quebracho tannin resins and nut shells.

	Mass (g)															
	Nut shells		Alu 24				Alu 16				Alu PSG 100					
Percentage of abrasive particles	75%	100%	75%	100%	150%	200%	150%	200%	150%	200%	150%	200%	200%	25%	50%	
Sample number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	
Furfuryl alcohol	12	12	12	12	12	12	15	15	15	15	12	12	12	15	15	
Water	3.1	3.1	–	–	3.1	3.1	–	–	–	–	–	–	–	–	–	
Quebracho tannins	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	
Ethylene glycol	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	
Tung oil	–	–	2.15	2.15	–	–	–	–	–	–	–	2.15	2.15	–	–	
Glyoxal (at 40% in water)	–	–	0.86	0.86	–	–	–	–	–	–	0.86	0.86	–	–	–	
Linseed oil	–	–	–	–	–	–	–	–	–	–	–	–	3	–	–	
pTSA (at 65% in water)	–	–	0.5	0.5	–	–	0.07	0.25	0.3	1	1	1	1	0.02	0.02	
Abrasive particles	23.4	31.2	23.7	31.6	46.8	62.4	46.8	62.3	47.1	64.2	48.2	64.2	64.2	7.79	15.56	





Fig. 1. 150% Alu 24, quebracho resin (Sample 9).

where  $A$  is the weight (mg) of the sample before abrasion;  $B$  is the weight (mg) of the sample after abrasion and  $C$  is the number of cycles of abrasion recorded.

For each sample, the number of cycles was set at 500.

### 3. Results and discussion

#### 3.1. Macroscopic observations

Usually, the hardening of quebracho tannin resins took some hours, which is faster than the different type of resin originally used for mimosa tannin (Li et al., 2013). The chemistry used in this paper is not different than the one used by Li et al. (2013). It is still tannins reacted with furfuryl alcohol and acid. But it is the process which is now different. These thermosets present less cracks and harden faster than the one developed by Li et al. (2013). By using quebracho tannins (Fintan QSTW) instead of mimosa tannins (Mimosa OP), the reaction is faster. So this resin is easily and quickly prepared and the hardening is also faster. Although these two types of tannins are condensed tannins, their different types of extraction lead to different reactivity. Indeed, quebracho Fintan QSTW is extract by water and then with ethanol. Thus, there are no more carbohydrates which were present in tannins. So their reactivity is much higher. Indeed, carbohydrates are notorious for interfering in the curing of phenolic resins (Lacoste et al., 2014). This point allows production of grinding wheels in a few hours. The project started with mimosa tannin resin but a faster process was crucial in order to be used industrially. So with this new process, vacuum rotary evaporation of the resin is not necessary and the polymerization of the resin in an oven during four days neither.

In order to have a hardening in few minutes a small proportion of a 65% water solution of pTSA was added (Table 2).

Concerning abrasive particles, whatever aluminium oxide or nut shell particles are used: these are well coated by the mimosa and quebracho resins.

However, there some cracks were observed in the resin of Sample 4 (100% nut shells, mimosa resin); Sample 5 (75% nut shells, quebracho resin) (Fig. 1); Sample 9 (150% Alu 24, quebracho resin) and Sample 10 (200% Alu 24, quebracho resin). All these samples were made with resins in which water had been added. These cracks are the consequence of the evaporation of the water present in the resin. The reaction between tannins and furfuryl alcohol is an exothermic reaction. However, after curing some of the water remains included in the network. It is the evaporation of this water that leads to contraction of the material and so to cracks appearing.

Thus, the elimination of water was shown to be beneficial because no more cracks were detected in samples where the water had been replaced by furfuryl alcohol with a concomitant addition of pTSA (Fig. 2). Moreover, there were no more cracks in samples



Fig. 2. 150% Alu 16, quebracho resin without water addition and with pTSA (Sample 13).



Fig. 3. 150% Alu 16, quebracho resin without water addition, with tung oil and glyoxal and with pTSA (Sample 15).

where there was an addition of tung oil and glyoxal (Fig. 3) or even linseed oil (Fig. 4).

One further advantage was that samples made with aluminium oxide and quebracho resin without water addition and with pTSA were not friable. This aspect is of primary interest for the lifespan of the grinding wheel.

#### 3.2. Scanning electron microscopy (SEM)

Scanning electron microscopy was used to check the difference between the composition of the resins leading to cracks appearing in the grinding wheels made with quebracho tannin resins.



Fig. 4. 200% Alu 16, quebracho resin without water addition, with linseed oil and with pTSA (Sample 17).

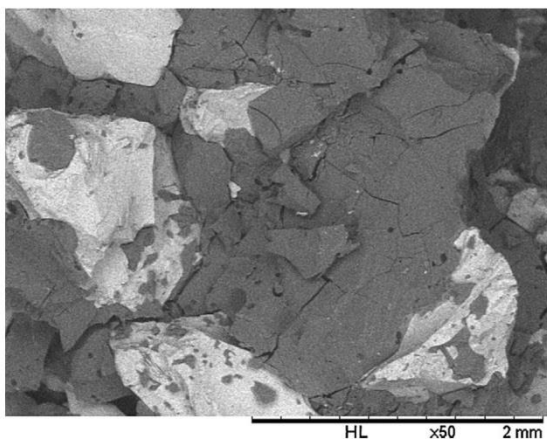


Fig. 5. 150% Alu 16 (1.19 mm) (Sample 13).

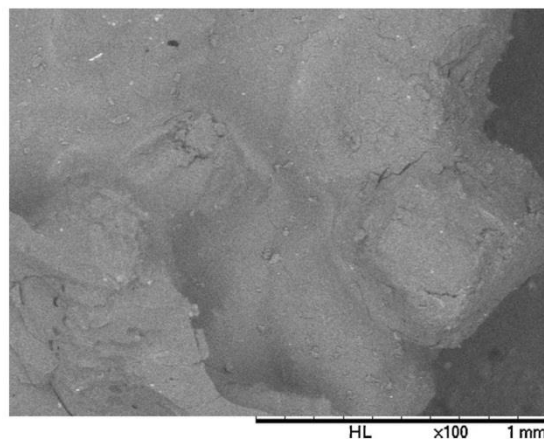


Fig. 7. 100% nut shells (0.45–0.80 mm) (Sample 6).

No cracks were visually observed in the sample made with 150% Alu 16 and the quebracho matrix resin where the water was replaced by furfuryl alcohol. Nevertheless, under microscope observation, some cracks in the resin were also observed (Fig. 5).

With the use of tung oil and glyoxal there are less cracks in the matrix resin and the abrasive particles are much better coated by the resin (Fig. 6).

In the sample with 100% on matrix resin of coarsely ground nut shells, there are some microcracks in the resin (Fig. 7). This was predictable because of the water evaporation in the resin. However, the compatibility between nut shell abrasive particles and tannin matrix resins is better than the one between aluminium oxide particles and tannin matrix resins. Furthermore, by replacing water by furfuryl alcohol and by using tung oil in the resin, there are much less cracks in the resin (Fig. 8). Abrasive particles are well coated by the resin, whatever be it with or without tung oil.

3.3. Abrasiveness of samples

Grinding wheels with tannins resins which were developed in this study are really competitive with the commercial Taber Calibrade wheel H-18 (Table 3) which was used as a control. Indeed, only four samples out of nineteen tested are not satisfying the requirements of the relevant ATSM D4060-01 standard. These were: 75% of nut shells with mimosa resin (Sample 3); 150% of Alu 24 particles with quebracho resin (Sample 9) and both made with PSG 100 particles with quebracho resin (Samples 18 and 19).

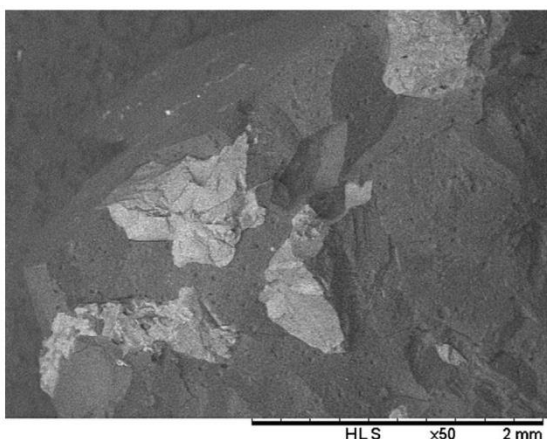


Fig. 6. 150% Alu 16 (1.19 mm) and tung oil (Sample 15).

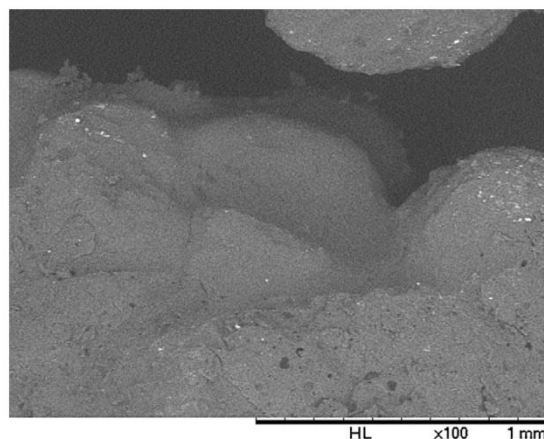


Fig. 8. 100% nut shells (0.45–0.80 mm) and tung oil (Sample 8).

As regards the sample with 75% of nut shells with mimosa tannin resin (Sample 3): we can assume that the mimosa tannins resin tends to coat better the lignocellulosic abrasives particles than the quebracho tannins resin. Indeed, mimosa tannins are composed mainly of robinetinidin flavonoid units and quebracho tannins are

Table 3  
Wear index of all grinding wheels tested.

Resin type	Abrasive particles type	Sample	Wear index	
Reference: Taber Calibrade wheel H-18			0	2.74E-05
Mimosa resin	Alu 24	1	9.79E-05	
		2	1.26E-04	
	Nut shells	3	6.12E-07	
		4	4.28E-05	
		5	4.40E-05	
		6	4.27E-05	
		7	9.43E-05	
Quebracho resin	Nut shells	8	1.63E-04	
		9	1.30E-05	
		10	1.83E-04	
	Alu 24	11	2.04E-04	
		12	2.31E-04	
	Alu 16	13	1.54E-04	
		14	1.19E-04	
		15	5.29E-05	
		16	1.52E-04	
		17	1.29E-04	
		PSG 100	18	5.06E-06
19			8.98E-06	



mainly composed of fisetinidin flavonoid units. Robinetinidin has one more hydroxyl group on the 5' position of B ring of the flavonoid unit than fisetinidin (Pasch et al., 2001; Pizzi, 1983, 1989, 1994). Moreover, samples made with nutshells and mimosa resins appear to be more mechanically resistant than those made with quebracho resins.

For samples with 150% of Alu 24 abrasive particles with quebracho resins (Sample 9), the sample is friable and presents cracks that cause its abrasiveness to be not so good. Thus, replacing water and adding pTSA are really an effective mean to improve the abrasiveness of the wheels.

Finally, for Samples 18 and 19, as the PSG 100 particles being very fine, the tannin resin coats too well and enrobes the particles to such an extent that wheel abrasiveness is poorer.

It is noteworthy that three wheels were broken when they were removed from the measuring instrument. These three wheels used natural abrasive: Samples 5, 6 and 7. Concerning the other wheels, they were perfectly usable again for new abrasion tests. Some dust was emitted during the test, but the wheels were still in good condition.

By comparing samples made with Alu 24 abrasive particles, the best grinding wheels were those made with quebracho resin and more precisely by replacing water with furfuryl alcohol and adding pTSA. These samples presented no cracks at all and were more abrasive to the touch than those made with mimosa resin. This can also be explained by the fact that the mimosa tannin resin appears to coat better the abrasive particles than the quebracho tannin resin.

For samples made with quebracho tannin resins by replacing water with furfuryl alcohol and adding pTSA the best wheels were those made with Alu 24 particles and not with Alu 16 particles. Moreover, grinding wheels made with Alu 24 particles were about eight times more abrasive than the Taber Calibrade control wheel H-18. Thus, wheels made with smaller abrasive particles were better. Indeed, it is more difficult to coat bigger particles than smaller particles with the resins, thus samples with bigger particles were slightly more friable.

Concerning the impact of the addition of tung oil and linseed oil to the matrix resin (by comparing Samples 14, 16 and 17), even if relatively comparable, the wheel which was a little more abrasive than the others was the one made with tung oil as an additive; the second best was the one with linseed oil as an additive and finally the last was the one without any oil additive. All these wheels were about five times more abrasive than the commercial control wheel. Visually, the wheels with oils as additives have quite the same appearance: the matrix resin coats very well the particles and the wheels are not at all friable. Thus, addition of a small proportion of oil improves both the abrasiveness and the lifespan of the wheel. As these wheels are not friable, the particles stay well attached to the wheel and so the wheel is more abrasive. This has to be optimized for a possible future industrial production. Indeed, the best wheel containing oil is the one where there is the smallest amount of added oil. It corresponds to the one with tung oil (addition of just 2.15 g of tung oil, comparing to 3 g of linseed oil).

#### 4. Conclusions

The preparation of grinding wheels with tannins/furfuryl alcohol resins has been shown to be possible.

Thus, in grinding wheels, the substitution of petrol-derived resins by a green resin is also possible. Moreover, the resin developed does not require a high temperature of curing contrary to commercial grinding wheels which require temperatures over 1000 °C for curing (Rue, 1985; Hay et al., 1990; Lee and Rue, 1992).

This approach is an alternative route to make green materials different from the condensed tannin/furanic foams or biocomposites already presented.

The use of quebracho resin (by replacing water with furfuryl alcohol and adding pTSA) gives better grinding wheels: no cracks are observed and the wheels are more abrasive to the touch than those made with mimosa resin. Furthermore, the novel quebracho resin developed for the purpose are also much faster curing than the older types such as those used in this paper for mimosa tannin resins.

Indeed, grinding wheels made with the mimosa tannin resin and Alu 24 particles (Samples 1 and 2) are four times more abrasive than the commercial control wheel used. Whereas grinding wheels made with quebracho resin and Alu 24 particles (Samples 11 and 12) are eight times more abrasive than the commercial control wheel.

Grinding wheels made with quebracho tannin resins and Alu 16 particles are about four to six times more abrasive than the commercial control wheel. Thus, the use of a vegetable oil in the preparation of the matrix resin is important to have good wheels. Moreover, the size of the particles is also important: bigger particles are not necessarily the most abrasive, while finer particles seem to have little or no interest when using the resin types presently developed.

As regards natural abrasives, grinding wheels made with quebracho resins containing tung oil and ground nut shells (Samples 7 and 8) are about 5 times more abrasive than the commercial control wheel. For grinding wheels of this type with natural tannin/furanic matrices it is better to use tung oil in the resin.

Finally, a new sort of green abrasives was developed in this work. Once more, oil-derived resins can be replaced by biosourced materials even for grinding wheels application.

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*4.5.2. Disques à tronçonner et à meuler pour meuleuse d'angle ayant comme matrice une biorésine*

**« Cutting and grinding wheels for angle grinders with a bioresin matrix »**

Auteurs : M.C. Lagel<sup>1</sup>, J. Zhang<sup>2</sup> et A. Pizzi<sup>1,3</sup>.

<sup>1</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>2</sup>Collège des Sciences et Technologies des Matériaux, Université forestière de Pékin, Pékin, Chine

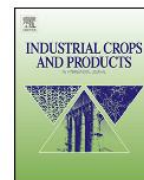
<sup>3</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

Résumé :

Une résine thermodurcissable biosourcée a été développée en utilisant des matières premières biosourcées comme les tanins condensés et l'alcool furfurylique. Celle-ci a été utilisée et testée pour une nouvelle application : en tant que matrice de disques abrasifs solides pour meuleuse d'angle. Le procédé de fabrication mis au point est particulièrement simple. Des disques à tronçonner et à meuler basés sur cette résine « verte » ont été développés en utilisant différentes tailles de particules abrasives de trioxyde d'aluminium. Ces disques ont été caractérisés et ont montré d'excellentes propriétés d'abrasivité et de découpe. Leurs résistances mécaniques se sont avérées être comparables à celles des disques commerciaux réalisés avec des résines phénoliques synthétiques. Ils tolèrent bien les contraintes sévères induites par leur utilisation avec une meuleuse d'angle fonctionnant à 11 000 tours par minute, en les utilisant en meulage ou en tronçonnage d'acier.

Mots-clés : Biopolymères, Abrasifs biosourcés, Résine tannique, Disques verts à meuler/tronçonner, Meuleuse d'angle.





## Cutting and grinding wheels for angle grinders with a bioresin matrix



M.C. Lagel<sup>a,\*</sup>, J. Zhang<sup>b</sup>, A. Pizzi<sup>a,c</sup>

<sup>a</sup> LERMAB, University of Lorraine, 27 rue Philippe Seguin, 88051 Epinal, France

<sup>b</sup> Beijing Forest University, College of Materials Science and Technology, 35 Tsinghua East Rd, Haidian District, Beijing, China

<sup>c</sup> Department of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

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### ABSTRACT

By using biosourced raw materials such as condensed tannins and furfuryl alcohol a biosourced thermoset resin was developed and used and tested for a new application: as a resin matrix of solid grinding wheels for angle grinders. The manufacturing procedure developed is particularly easy. Cutting and grinding discs based on this green resin were used for bonding different sizes of abrasive particles of aluminium trioxide. These discs were characterized and showed excellent abrasiveness and cutting properties. Their mechanical resistance was found to be comparable to that of commercial grinding discs bonded with synthetic phenolic resins. They tolerated well the severe stresses induced on them at 11,000 revolutions per minute (rpm) by operation in an angle grinder when grinding or cutting steel.

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### 1. Introduction

During the last decades there has been a continuous increase in oil prices. As a consequence of this, considerable research has been carried out in order to develop biobased and biosourced materials. Replacing petrochemicals is possible in many different industrial sectors. Natural and renewable materials coming from agriculture or forestry such as furfuryl alcohol and condensed polyflavonoid tannins have been used to develop new biobased materials: biobased adhesive resins (Pizzi, 1983, 1989, 1994; Zhou et al., 2013), insulation foams and floral foams (Tondi et al., 2008, 2009a,b; Basso et al., 2014a,b; Lacoste et al., 2013; Lagel et al., 2014a,b), fibre composites (Sauget et al., 2014), polyurethanes (Pizzi, 1979a,b; Basso et al., 2014a,b) even without isocyanates (Thebault et al., 2014a,b) and finally high tech paper laminates (Abdullah et al., 2013, 2014) and more recently new thermoset plastics based on a natural tannin-furanic thermoset resin (Li et al., 2013; Lagel et al., 2014a,b). These resins, based on the coreaction of tannins and furfuryl alcohol were developed to replace industrial oil-derived resins like phenolic resin in different applications, such as grinding wheels. In this article, firstly the possibility of preparing grinding discs made with biobased resin as a bonding system was studied. This is a difficult application as the stresses induced on a grinding wheel at 11,000 revolutions per minute (rpm) especially in contact with a hard material such as steel are rather

severe. Secondly, the formulation of the resin was further modified to cure quicker and with no faults than the original resin of Li et al. (2013). This is an important point in order to develop it for industrial production. Abrasiveness characterisation tests by grinding and cutting steel bars and tubes, and mechanical properties of the grinding discs were investigated.

### 2. Material and methods

#### 2.1. Materials

Quebracho (*Schinopsis lorentzii* and *balansae*) wood tannin extract (Fintan QSTW) powder was supplied by SilvaTeam (San Michele Mondovì, Italy). It must be pointed out that this tannin extract after water extraction from the wood, undertook a second extraction in ethanol to eliminate the majority of carbohydrates present. This type was used as while slightly more expensive it gives resins of much better performance.

Furfuryl alcohol (98%), polyethylene glycol 400 (PEG), ethylene glycol and *para*-toluene sulfonic acid (pTSA, with a purity of 97.5%) were purchased from Acros Organics, (Geel, Belgium).

Tung oil was purchased from Oleobois, (Vendargues, France).

Xiameter OFX-0193 Fluid (DC193) was purchased from Dow Corning, (Midland, United States).

Phenol liquified 80% w/w in water, pure was purchased from Fisher Scientific, (Loughborough, United Kingdom).

Formaldehyde solution 37% was purchased from Roth, (Karlsruhe, Germany).

\* Corresponding author. Tel.: +33 329296318; fax: +33 329296138.

E-mail address: [lagel.mc@gmail.com](mailto:lagel.mc@gmail.com) (M.C. Lagel).

**Table 1**  
Grinding discs with quebracho tannin resin.

	Mass (g)											
	150% Alu 24	200% Alu 24	150% Alu 36	175% Alu 36	200% Alu 36	150% Alu 60	175% Alu 60	200% Alu 60	150% Alu 36-60	150% Alu 24-60	150% Alu 60	150% Alu 60
Furfuryl alcohol	21.44	21.44	21.44	21.44	21.44	21.44	21.44	21.44	21.44	21.44	21.44	21.44
Tannins QSTW	25	25	25	25	25	25	25	25	25	25	25	25
PEG 400	8.76	8.76	8.76	8.76	8.76	8.76	8.76	8.76	8.76	8.76	8.76	8.76
Tung oil	3.59	3.59	3.59	3.59	3.59	3.59	3.59	3.59	3.59	3.59	3.59	3.59
DC 193	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
PF resin, F/P of 2.2	/	/	/	/	/	/	/	/	/	/	/	/
pTSA (65% in ethylene glycol)	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Abrasive particles	89.43	119.24	89.43	104.34	119.24	89.43	104.34	119.24	44.715+44.715	44.715+44.715	44.715+44.715	66.00

For this work, three different sizes of abrasive particles were used. There were purchased from Centre des Abrasifs, (Valenciennes, France). Abrasive particles are aluminium trioxide ( $Al_2O_3$ ): Alu 24 (grain size of 0.7 mm); Alu 36 (grain size of 0.4 mm) and Alu 60 (grain size of 0.25 mm).

Roving of fibreglass of 270 g/m<sup>2</sup> used came from Sinto (Aubagne, France).

An angle grinder Bosch GWS 1400 with a rotation of 11,000 rpm was used to test samples (Stuttgart, Germany).

A steel tube was used to test samples: round tube 6 mm × 1 mm and 1 m length, cold rolled steel from Alfer, (Wutöschingen-Horheim, Germany).

A commercial grinding disc of Opsial: A24R-BF27; thickness of 6.4 mm; diameter of 100 mm and a centre hole of 22.2 mm was used as a control.

## 2.2. Resins synthesis

### 2.2.1. Quebracho tannin resin

Firstly, furfuryl alcohol (21.44 g) and quebracho tannins (25 g) were mixed together with a mechanical stirrer during 15 s. Secondly, PEG (8.76 g), tung oil (3.59 g) and DC193 (0.13 g) were added. After each addition the mixing time is 15 s.

Finally, a 65% ethylene glycol solution of pTSA (0.7 g) was added as a catalyst under mechanical stirring for 15 s. The proportions were inspired by a previous work (Lagel et al., 2014a,b) and they are shown in Table 1. The viscosity of this tannin resin is about 3700 mPa s at 25 °C. This value was given by the use of a Brookfield DV-II + Viscometer, with S6 spindle and 60 RPM.

### 2.2.2. Acid catalysed phenol-formaldehyde (PF) resin

The PF control resin (molar ratio F/P=2.2) was synthesized as following reagents: 1 mole of phenol as 80% phenol mixed with 2.2 mole of formaldehyde as a 37% aqueous solution. Formaldehyde was added in 4 equal parts. The time between the additions of parts is 15 min.

Firstly, phenol and the first part of formaldehyde were heated at 94 °C under reflux and continuous stirring. The reaction mixture was slowly brought in about 45 min to reflux at 94 °C under continuous stirring. This time corresponds to the time necessary to the complete addition of formaldehyde.

Once 94 °C is achieved, the mixture is left to react until a viscosity about 57,000 mPa s at 25 °C (Brookfield DV-II + Viscometer, S6 spindle and 10 RPM). In this case it was 2 h and 15 min.

During all the process, the pH was controlled at 2 by adding some drops of pTSA at 65% in water.

## 2.3. Grinding discs development

By observing commercial abrasive discs and their product specification sheets, it was found that they were composed of a bonding resin which was a phenolic resin. Aluminium oxide particles were the abrasive particles. And the reinforcement of the disc was composed of three layers of roving of fibreglass (Fig. 1).

### 2.3.1. Grinding discs made with quebracho tannin resin

The amount of abrasive particles was added to the resin and it was well mixing. Samples were done in a silicone mold. Firstly, one layer of fibreglass was put in the bottom of the mold, after the half of the abrasive resin was placed. Then, a second layer of fibreglass was placed and above this the second part of abrasive resin. Eventually, a third layer of fibreglass was put on the top of that. A silicone sheet was placed in order to close the mold. This system was put in a press during 1 h at 150 °C and with a pressure of 80 kg/cm<sup>2</sup> on the disc of 100 mm of diameter. Then, samples were cooled and were drilled in their centres at 22 mm. So samples can be used



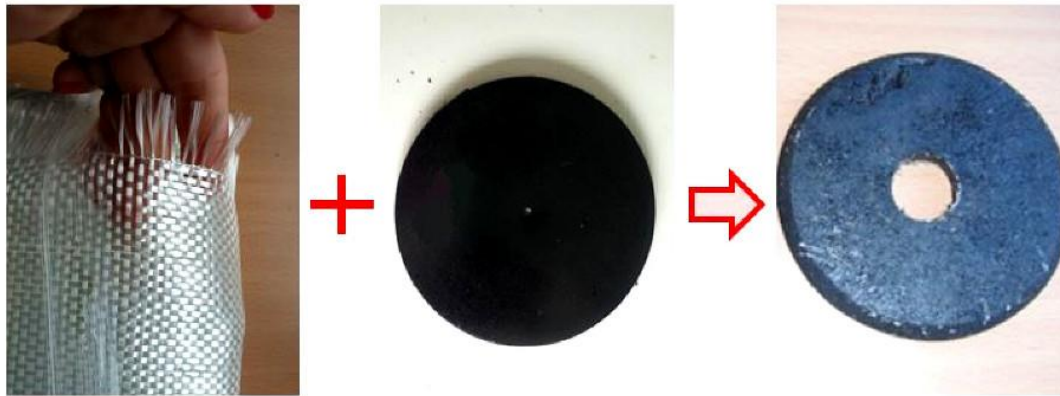


Fig. 1. Tannins resin bonded grinding disc development.

with an angle grinder. Concerning the quantity of abrasive particles, three amounts were tested: 150%, 175% and 200% (Table 1). These percentages are linked to the mass of the resin. For example, for a percentage of 150%: if there are 100 g of resin there will be 150 g of particles. These percentages above 150% were determined by macroscopic observation of the commercial disc. Abrasive particles used are aluminium trioxide ( $\text{Al}_2\text{O}_3$ ): Alu 24 (grain size of 0.7 mm); Alu 36 (grain size of 0.4 mm) and Alu 60 (grain size of 0.25 mm).

#### 2.3.2. Grinding discs made with a laboratory phenolic resin

The amount of abrasive particles was added to the resin and it was well mixing. Then a pTSA amount of 10% by mass relative to the resin was added, in order to decrease the pH and so to accelerate the hardening of the resin under heating.

After having mixed all the component of the resin, the method is the same than describe for abrasive discs with quebracho tannin resin. The proportions used are shown in Table 1.

### 2.4. Grinding discs characterization

#### 2.4.1. Determination of the abrasiveness

The abrasiveness of the grinding disc was determined by using an angle grinder Bosch GWS 1400 with a rotation of 11,000 rpm. A first test was done on steel bars. The visual comparison of the grinding depth was done between commercial grinding discs (The one bought and the one made in the laboratory) and tannin resin bonded discs. And a second test was done on a cold rolled steel tube was used to test samples (diameter of 6 mm and thickness of 1 mm). The test time was 10 s or less if the disc grinded/cut all the thickness of the tube. The comparison with a commercial disc was done.

The percentage of mass loss was calculated by weighting the disc before and after the abrasiveness test.

#### 2.4.2. Three points bending test

The tests were done on the basis of NF EN 301. The tests were done with an Instron 4467 machine. The dimensions of samples were: 8.5 mm × 20 mm × 100 mm. The distance between two supports was 80 mm. The loading rate was 1 mm/min. The flexural strength ( $f_m$  in N/mm<sup>2</sup>) was given by the formula (1).

$$f_m = \frac{3F_{\max}l_s}{2bt^2} \quad (1)$$

where  $F_{\max}$  is the breaking load (N),  $l_s$  is the distance between two supports (mm),  $b$  is the width of the sample (mm),  $t$  is the thickness of the sample (mm).

#### 2.4.3. Brinell hardness test

The tests were done on the basis of NF B 51–126. The tests were done with an Instron 4467 machine. The ball used for the tests had a diameter of 10 mm. The Brinell hardness (daN/mm<sup>2</sup>) was given by the formula (2).

$$HB = \frac{3.18}{1000} \times \frac{F}{P} \quad (2)$$

where  $F$  is the force that determined the retained depression (N),  $P$  is the depth of depression of the ball (mm).

## 3. Results and discussion

### 3.1. Macroscopic observations

For the first tests, the matrix resin was composed of furfuryl alcohol, water, quebracho tannins and PEG400 and pTSA in water. This quebracho tannin resin followed the one developed few months ago (Lagel et al., 2014a,b). However, with the ageing of the grinding wheels cracks appeared and induced fragility of the disc. These cracks are the consequence of the evaporation of the water

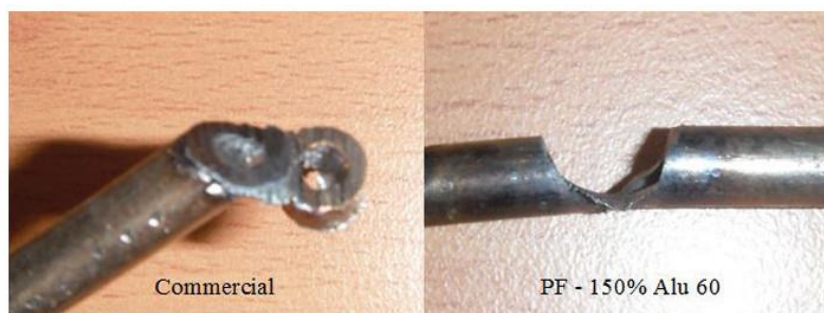


Fig. 2. Grinding tests on a steel bar.

**Table 2**

Time and mass loss of grinding discs after testing.

	Resin type	Mass loss (%)	Testing: steel tube cutting time (s)
Commercial Opsial	PF	0.1 ± 0.05	3
150% Alu 60	PF	3.3 ± 0.7	6
150% Alu 60	Quebracho tannin	18.7 ± 2.3	8
175% Alu 60	Quebracho tannin	47.0 ± 6.1	7
200% Alu 60	Quebracho tannin	44.1 ± 5.9	10
150% Alu 36	Quebracho tannin	34.6 ± 3.2	6
175% Alu 36	Quebracho tannin	47.0 ± 4.5	7
200% Alu 36	Quebracho tannin	48.8 ± 5.3	10
150% Alu 36–60	Quebracho tannin	43.5 ± 4.7	7
150% Alu 24–60	Quebracho tannin	58.9 ± 6.6	10

**Fig. 3.** Results of the tests of control discs: commercial disc and PF resin bonded disc with 150% Alu 60.

present in the resin which induces its contraction on drying. Thus, to avoid cracks in the grinding discs, firstly the water in the formulation was replaced by furfuryl alcohol and moreover a vegetable oil, tung oil, and also silicone oil (DC193), were added as plasticizers. Eventually, pTSA at 65% in water was replaced by pTSA at 65% in ethylene.

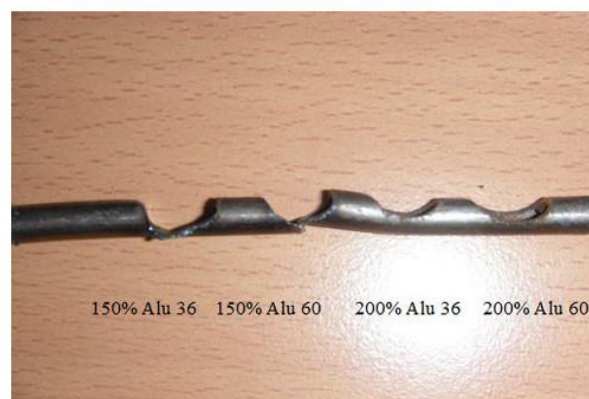
### 3.2. Abrasiveness of samples

The experimental grinding discs bonded with the tannin resins were compared with a commercial grinding disc (Opsial A24R-BF27) and a laboratory made abrasive grinding wheel bonded with a PF resin with 150% Alu 60 abrasive. Both of these latter were used as controls (Table 2). The first test was to visually compare the effect of tannins resin bonded grinding discs developed here with a commercial grinding disc to grind a steel bar (Fig. 2). For this test big abrasive particles (Alu 24) were used (Table 1). It was found that discs wear out quickly so it was decided to use finer particles in order to increase the abrasive properties of the tannins resin bonded grinding discs (Fig. 2).

Then second tests consisted in cutting a stainless steel tube with the different grinding discs prepared and measuring the extent of cutting/grinding and the time taken to cut the tube.

As regards the proportion of abrasive particles, discs with 200% of abrasive particles should have been more abrasive, but this was not the case as they did wear out quickly. They presented high mass loss percentages (Table 2). Moreover the testing times were 10 s because within 10 s they had not cut the steel tube contrary to the controls PF resin bonded grinding discs (Figs. 3 and 4). Thus, it was found that discs with 150% of abrasive particles were better. An intermediate amount of abrasive particles was tested: 175% (Fig. 5). But discs with 150% of abrasive particles were still more abrasive, faster cutting and presented less wear, and lower mass loss percentages (Table 2 and Fig. 4).

Regarding the abrasive particles size, the bigger particles were not those which gave the best discs. The bigger the particles were, the more they were easily removed from the disc because of the

**Fig. 4.** Results of the tests of the tannins resin bonded grinding discs: 150 and 200% of Alu 36 and 60.**Fig. 5.** Results of the tests of the tannins resin bonded grinding discs: 175% of Alu 36 and 60.



**Table 3**  
Three points bending tests.

	Commercial Opsial	PF – 150% Alu 60	T – 150% Alu 60	T – 150% Alu 36
$f(N/mm^2)$	25.83 ± 0.25	17.22 ± 0.12	22.92 ± 0.08	15.85 ± 0.14

**Table 4**  
Brinell hardness tests.

	Commercial Opsial	PF – 150% Alu 60	T – 150% Alu 60	T – 150% Alu 36
HB (daN/mm <sup>2</sup> )	9.79 ± 0.73	6.53 ± 0.81	5.82 ± 0.67	8.03 ± 0.76

matrix friability. Thus, wheels prepared with Alu 36 particles had high mass loss percentages (Table 2).

To try to further improve abrasiveness, mixing particles sizes was tried for discs with 150% of abrasive particles (Fig. 6). Thus, two intermediate discs were prepared:

- One with half proportion of particles of Alu 24 and half of Alu 60.
- One with half proportion of particles of Alu 36 and half of Alu 60.

However, the percentages of mass loss of both discs were very high. Thus, the best wheel was the one with 150% of Alu 60 (Fig. 4). It seems thus, that discs made with smaller abrasive particles are better.

Moreover, the mass loss of PF resin bonded disc is 33 times more than the one of Opsial commercial disc. So it can be presumed that in industrial conditions tannin resin bonded disc will have a very low mass loss.

As regards the testing time, the commercial disc Opsial took 3 s to cut the steel tube. For the two best quebracho tannins resin discs (150% Alu 60 and 150% Alu 36) this time was around 6–8 s (Fig. 4). However, to compare under equal conditions synthetic and bioresin discs a resin prepared in the laboratory according to a commercial PF formulation was used to prepare a control disc in the laboratory under the same conditions of the tannins resin discs. This disc, PF-150% Alu 60, took 6 s too as the bioresin one (Fig. 3).

After some research about the pressing conditions of the commercial grinding discs it was found that commercial discs were pressed at high temperature (200 °C) and with higher pressure: between 0.7 and 35 MPa. Whereas the quebracho tannins resin discs developed here were pressed at 150 °C and 8 MPa. The similarity of performance of the PF bonded control and of the bioresin discs indicates that future tannin resin grinding discs produced under



**Fig. 6.** Results of the tests of the tannins resin bonded grinding discs: 150% of mix of Alu 24, 36 and 60.

the same industrial conditions can be competitive with actual non-renewable resins bonded grinding discs.

### 3.3. Three points bending test

The results in Table 3 show that with the same abrasive particles size the discs made with the quebracho tannin resin is more resistant to bending (Table 3) than the disc made with the PF resin. By macroscopic observation it has been found that the laboratory PF resin discs present some bubbles which are not the case for the discs made with the quebracho tannin resin. The quebracho tannin resin appeared to coat better the aluminium trioxide particles, hence the composite was stronger.

By using the same resin, it has been shown that the discs made with bigger size aluminium particles (Alu 36) are less resistant to bending than the ones made with smaller size particles (Alu 60). This can be explained by the fact that bigger particles lead to greater resin friability.

Further industrial optimisation for a possible future industrial production is necessary but tannin-furanic based grinding discs appear really competitive with PF resin based grinding discs. Indeed, the value of flexural strength of commercial disc is about one and a half time higher than the one of PF resin bonded disc.

### 3.4. Brinell hardness test

In Table 4 are given the results of the Brinell hardness tests of the grinding discs composite material. It can be presumed that heat development leads to a quicker reaction and polymerization of the resin and leads to harder materials.

By using the same abrasive particles size (Alu 60) quebracho tannins resin was less hard than PF resin. But if bigger particles were used quebracho tannins resin was harder than PF resin.

This was consistent with the results of the bending test: with the same particles size quebracho resin yielded more flexible discs than PF resin. And with bigger particles, tannin-furanic bonded discs were less flexible than PF resin bonded ones. One could think that slightly greater flexibility or slightly greater rigidity could be possible be an advantage or disadvantage but the limited range of values within which this differences existed does not allow to say if greater flexibility or rigidity is the best choice for the experimental grinding discs.

However, all these results were within the same range of values so that tannin-furanic bonded grinding discs were at the same level than PF resin bonded ones. Even if the Brinell hardness of commercial Opsial disc is about one and a half time bigger than PF resin bonded disc, it can be presume that industrial tannins resin bonded disc will be competitive to synthetic resin bonded disc.

## 4. Conclusions

It is possible to prepare grinding discs with a tannins-furanic resin binder and inorganic abrasive particles embedded into it. Thus, the production of greener abrasive grinding discs is possible



and oil-derived resins can totally be replaced by a green resin. The condensed tannin-furanic resin without water yields discs which present no cracks and which age better than those previously developed by Li et al. (2013).

Furthermore, the quantity and the size of abrasive particles are also crucial: using bigger particles and a great quantity of abrasive particles does not necessarily lead to the most abrasive grinding disc.

Thus, these new green abrasive grinding discs are at their optimum with 150% of 0.25 mm (Alu 60) abrasive particles. But the optimum found in the laboratory may be not the same as in industrial conditions.

Moreover, concerning mechanical properties, these new green abrasive grinding discs (150% Alu 60) are more resistant to bending than PF resin control discs.

In addition to this, by producing and developing industrially these new green abrasive grinding discs under the same industrial conditions which are used for actual commercial discs (at a temperature of 200 °C and a pressure up to 35 MPa), they can be really competitive with oil-derived materials for the same application.

This shows once again that petrochemicals can be replaced by biosourced materials even for abrasive grinding discs which are quite a severe application.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.indcrop.2015.01.046>.

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#### *4.5.3. Plaquettes de frein automobile ayant comme matrice une biorésine*

### **« Automotive brake pads made with a bioresin matrix »**

Auteurs : M.C. Lagel<sup>1</sup>, L. Hai<sup>2</sup> et A. Pizzi<sup>1,3</sup>, M.C. Basso<sup>1</sup>, L. Delmotte<sup>4</sup>, S. Abdalla<sup>3</sup>, F. Bahabri<sup>3</sup> and H. S. M. Al-Zahrani<sup>3</sup>

<sup>1</sup>LERMAB, Université de Lorraine, Epinal, France

<sup>2</sup>Université forestière de Nanjing, Collège des Sciences et Ingénieries des Matériaux, Nanjing, Chine

<sup>3</sup>Département de Physique, Université du Roi Abdulaziz, Jeddah, Arabie Saoudite

<sup>4</sup>Institut de Science des Matériaux de Mulhouse, Université de Haute-Alsace, Mulhouse, France

#### Résumé :

En utilisant des matières premières biosourcées telles que les tanins condensés et l'alcool furfurylique, une résine thermodurcissable biosourcée a été élaborée, utilisée et testée pour une nouvelle application : comme matrice de plaquettes de frein automobile. Le procédé de fabrication mis au point est particulièrement simple. Les plaquettes de frein automobile basées sur cette résine « verte » ont été caractérisées et ont montré d'excellentes propriétés de freinage et de résistance à l'usure lors de leur test dans les conditions réelles : sur une voiture de série. Leur résistance mécanique a été jugée comparable à celle des plaquettes de frein automobile commerciales liées avec des résines phénoliques synthétiques. Ces nouvelles plaquettes « vertes » tolèrent bien les contraintes sévères induites par un puissant freinage comme un freinage d'urgence : 50 km/h jusqu'à l'arrêt complet du véhicule et elles ont montré des distances de freinage comparables ou plus courtes que les plaquettes de frein commerciales.

Mots-clés : Biopolymères, Plaquettes de frein biosourcées, Résine à base de tanins, Plaquettes de frein automobile « vertes ».

# AUTOMOTIVE BRAKE PADS MADE WITH A BIORESIN MATRIX

M.C. Lagel<sup>1</sup>, L. Hai<sup>2</sup>, A. Pizzi<sup>1,3\*</sup>, M.C. Basso<sup>1</sup>, L.Delmotte<sup>4</sup>, S.Abdalla<sup>3</sup>, F.Bahabri<sup>3</sup>, F.M.Al-Marzouki<sup>3</sup>

<sup>1</sup> LERMAB, University of Lorraine, 27 rue Philippe Seguin, CS60036, 88026 Epinal, France

<sup>2</sup> Nanjing Forestry University, College of Materials Science and Engineering, 159 Longpan Rd, Nanjing, China

<sup>3</sup> Dept. of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

<sup>4</sup>Material Science Institute of Mulhouse, CNRS UMR 7361, University of Haute Alsace, 15 rue Jean Starcky,  
BP 2488, 68057 Mulhouse Cedex, France

\*Corresponding authors. E-mail address: antonio.pizzi@univ-lorraine.fr

Phone number: +33 3 29 29 63 17/18, Fax: +33 3 29 29 61 38

## **Abstract**

By using biosourced raw materials such as condensed tannins and furfuryl alcohol a biosourced thermoset resin was developed and used and tested for a new application: as a resin matrix of automotive brake pads. The manufacturing procedure developed is particularly easy. Automotive brake pads based on this green resin were characterized and showed excellent braking properties and wear resistance when used under real car, full scale test conditions. Their mechanical resistance was found to be comparable to that of commercial automotive brake pads bonded with synthetic phenolic resins. They tolerated well the severe stresses induced by a strong braking like an emergency braking: 50 km/h (31 mph) until complete standstill and showed braking distances comparable or shorter than commercial brake pads.

**Keywords:** Biopolymers; Biosourced brake pads; Tannins resin; Green automotive brakes.

## **1. Introduction**

During the last decades a continuous increase of oil prices has occurred. As a result, considerable research has been done to develop new biobased materials. Replacing petrochemicals by biosourced chemicals is possible in many different industrial sectors. Natural and renewable materials coming from agriculture or forestry such as furfuryl alcohol and condensed polyflavonoid tannins have been used to develop new biobased materials: biobased adhesive resins (Pizzi, 1983, 1989 & 1994, Zhou et al., 2013), insulation foams and floral foams (Tondi et al., 2008, 2009a, 2009b; Basso et al., 2014; Lacoste et al., 2013; Lagel et al., 2014), high tech paper laminates (Abdullah et al., 2013, 2014), biobased composites (Sauget et al., 2014), and finally polyurethanes (Pizzi 1979a, 1979b; Basso et al., 2014) even without using isocyanates (Thebault et al., 2014, 2015). More recently new thermoset plastics based on a natural tannin-furanic thermoset resin were developed (Li et al., 2013; Lagel et al., 2014, 2015). These resins are based on the coreaction of furfuryl alcohol and tannins. They were developed to replace industrial oil-derived resins, like synthetic phenolic resins, which are used in different applications, like, for instance, in brake pads manufacture.

This work is a part of an approach of reduction and elimination of hazardous components for humans and the environment. Indeed after the ban of asbestos (since the 1st of January 1997 in France), which was used in brake pads preparation, the aim in few year is to replace formaldehyde by other component and also to use more and more biosourced chemicals and materials.

Development of biobased resins for brake pads has been thought before, and this based on a number of different materials. The use of biobased resins such as castor oil was already envisaged for brake lining in a USA patent in 1932 (Rosner 1932). Lignin based polymers were also proposed for this application (Lora and Glasser, 2002). The most actively researched materials, at present, for biobased brake pad matrices are cardanol (Voirin et al 2014), and biobased polyamides (Feldmann and Bledzki 2014), towards both of which it appears that considerable industrial research has been oriented.



In this article, firstly the possibility of preparing brake pads made with biobased resin based on tannins was studied for the first time. This application is rather demanding due to the stresses induced on the pad by the car braking system (Antanaitis 2016). Secondly, the formulation of the tannin resin was further modified from the ones developed earlier by Li et al. (2013) and Lagel et al. (2014, 2015) to obtain with ease a good performance and while improving greatly its ease of application. Both these improvements are essential and determining to be able to implement the new material in industrial production. Wear resistance (thickness and weight losses), emergency braking efficiency and Brinell hardness tests were investigated.

## **2. Material and methods**

### **2.1. Materials**

Quebracho (*Schinopsis lorentzii* and *balansae*) wood tannin extract (Fintan QSTW) powder was supplied by SilvaTeam (San Michele Mondovi', Italy). It must be pointed out that this tannin extract after water extraction from the wood, undertook a second extraction in ethanol to eliminate the majority of carbohydrates present. This type was used as while slightly more expensive it gives resins of much better performance.

Furfuryl alcohol (98%), polyethylene glycol 400 (PEG 400), ethylene glycol, *para*-toluene sulfonic acid (pTSA, with a purity of 97.5%) were purchased from Acros Organics, (Geel, Belgium).

Glycerol phosphate acidic ester was synthesized following Hoxie's example 1 (Hoxie 1968).

Tung oil was purchased from Oleobois, (Vendargues, France).

Xiameter OFX-0193 Fluid (DC 193), a silicone polyeter copolymer, was purchased from Dow Corning, (Midland, United States).

Graphite was provided by Condat, (Chasse-sur-Rhône, France).

Liquid neoprene glue was purchased from Würth, (Künzelsau, Germany).

For this work, two different sizes of abrasive particles were used. There were purchased from Centre des Abrasifs, (Valenciennes, France). Abrasive particles are aluminium trioxide ( $Al_2O_3$ ): Alu 36 (grain size of 0.4 mm) and Alu 60 (grain size of 0.25 mm).

Roving of fiberglass of 270g/m<sup>2</sup> used came from Sinto, (Aubagne, France). Roving of fiberglass are woven fiberglass.

Mineral wool (N°3 very thin) was purchased from Würth, (Künzelsau, Germany).

Commercial automotive brake pads from Brembo, (Curno, Italy) were used as a control.

## 2.2. Resin synthesis

The amounts are given for a pair of brake pads.

Firstly, furfuryl alcohol and quebracho tannins were mixed together during 15 sec. Secondly PEG 400, tung oil, DC 193 and neoprene were added. Thus graphite and glycerol phosphate acid were added for the relevant formulations. After each addition the mixing time is 15 sec.

Finally a 65% ethylene glycol solution of pTSA was added as a catalyst. The proportions were inspired by previous works (Lagel et al., 2014 & Lagel et al., 2015) and they are shown in Table 1.

## 2.3. Automotive brake pads development

By observing commercial automotive brake pads and after some research about this subject, it was found that in the 1960's, automotive and trucks brake pads were composed of fiberglass, mineral fibers, metal fibers, carbon and synthetic fibers to provide semi-metallic with higher performance than asbestos (which is now forbidden) (Blau 2001). Indeed, brake pads are most of the time composed by:

- Abrasives such as **aluminium oxide**, iron oxides, quartz, silica etc...
- Friction modifiers, such as antimony trisulfide, carbon (**graphite**), ceramic microspheres etc...
- Fillers, such as anti-oxidants, asbestos, barium sulfate, **rubber** etc...
- Reinforcements, such as fibers: **mineral wool, fiberglass** etc...
- Binder Materials, such as **phenolic resin** which is the most common binder.

After mixing all the components, the dough which will become the friction lining is compacted in mold and cooked at high temperatures (160 and 200°C). During this phase, the rubber binders are cured. Thus the material is definitively stabilized (Felten 2013).

In this work some additives, like glycerol phosphate acidic ester which is known to be a flame retardant, were added to the resin.

The amount of abrasive particles was added to the resin and it was well mixing. Samples were done in an aluminium mold whose walls were coated with silicone sheet. Firstly one layer of fiberglass was put in the bottom of the mold, after the half of the abrasive resin was placed. Then, a second layer of fibreglass was placed and above this the second part of abrasive resin. Eventually a third layer of fiberglass was put on the top of that.

This system was put in a hot press during 1 hour at 200°C (150°C was also used in order to decrease energy consumption) and with a pressure of 80 kg/cm<sup>2</sup>. Then, samples were cooled and were stuck on metallic plates in order to be identical to the commercial brake pads. These being also composed of a pad bonded onto a metallic plate (Figure 1). So samples can be used like automotive brake pads. Concerning the quantity of abrasive particles, three amounts were tested: 150%, 75% and 50% (Table 1). These percentages are linked to the mass of the resin. For example, for a percentage of 150%: if there are 100g of resin there will be 150g of particles. Abrasive particles used are aluminium trioxide (Al<sub>2</sub>O<sub>3</sub>): Alu 36 (grain size of 0.4 mm) and Alu 60 (grain size of 0.25 mm).

The fibers were incorporated in two different ways. Indeed, for fiberglass they can be placed on each side of the brake pad, or they can be cut in little (no more than 5 mm length) and mixed with the resin. For mineral wool, it can be placed in the middle of the brake pad or they can be cut in little (no more than 5 mm length) and mixed with the resin.

## **2.4. Automotive brake pads and resin characterization**

### ***2.4.1. Determination of the emergency braking efficiency and wear resistance***

The emergency braking efficiency of the automotive brake pads developed in this work was determined by testing them with a cycle of ten emergency braking (50 km/h counter until complete standstill of the car). The car was a Renault Scenic I (about 1300 kg).

The braking distance was reported and an average was done. Tests were all done by the same operator. The car was launched to 50 km/h and when the front wheels were at one precise place the operator

braked. The braking distance is between this precise place and the location of front wheels when the car is stopped. The comparison with commercial brake pads was done.

In order to characterize wear resistance, the percentages of mass loss and thickness loss were calculated by weighting and measuring the brake pads before and after the emergency braking tests.

#### **2.4.2. Brinell hardness test**

The tests were done on the basis of NF B 51-126. The tests were done with an Instron 4467 machine. The ball used for the tests had a diameter of 10 mm. The Brinell hardness (daN/mm<sup>2</sup>) was given by the formula (1).

$$HB = \frac{3.18}{1000} \times \frac{F}{P} \quad (1)$$

where:

F is the force that determined the retained depression (N),

P is the depth of depression of the ball (mm).

For each formulation one repetition was done

#### **2.4.3. MALDI-ToF analysis**

**MALDI-ToF-MS:** The spectra were recorded on a SHIMADZU AXIMA Performance MALDI instrument (Manchester, UK). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), 1000 pulses per spectrum. The delayed extraction technique was used applying delay times of 200-800 ns.

**MALDI-ToF Sample Preparation:** The samples were dissolved in acetone:water of 2:1 (5 mg/mL). The sample solutions were mixed with an acetone solution (10 mg/mL acetone) of the matrix. As the matrix 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation NaCl was added to the matrix (2 µL of NaCl at 0,1M in a mix of methanol:water of 1:1). The solutions of the sample



and the matrix were mixed in equal amounts and 1.5  $\mu\text{L}$  of the resulting solution were placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer.

#### ***2.4.4. NMR $^{13}\text{C}$ analysis in solid state***

Quebracho tannin and the tannin resin were analysed by solid state CP-MAS  $^{13}\text{C}$  NMR.

The solid-state  $^{13}\text{C}$  cross-polarization magic angle spinning NMR (CP-MAS  $^{13}\text{C}$  NMR) spectra were obtained on a Brüker Avance 400 MHz spectrometer at a carbon resonance frequency of 100.58 MHz, using a Brüker 4 mm CP-MAS probe.

The MAS spinning rate was 12000 Hz, sufficient for total suppression of side bands. The cross polarization contact time was 1ms with a recycle delay of 5 s; The  $^1\text{H}$   $90^\circ$  pulse length was 4.1 ns; the spin-lock field was 61 kHz. Spectral manipulation was performed in Topspin (version 3.0). Chemical shifts are referenced to tetramethylsilane (TMS) using adamantane as an external reference.

### **3. Results and discussion**

Considerable analytical results on the chemical reactions involved, products and chemical species obtained as well as their characterisation, both analytical and physical have already been abundantly reported (Li et al 2013; Nicollin et al 2013; Abdullah and Pizzi 2013; Basso et al. 2013; Lagel et al 2014, 2015). The formulation of tannins resin was further modified from the ones developed earlier by Li et al. (2013) and Lagel et al. (2014, 2015). Indeed in the past the following ameliorations were first done: the use of quebracho tannin instead of mimosa tannin; the addition of plasticizers: a vegetable oil (tung oil) and also silicone oil (DC 193). This was added to avoid cracks and fragility of the resin and also to have a quicker curing of the resin. This work was continued by adding neoprene (and others additives like graphite and glycerol phosphate acidic ester) which give to the tannin resin a better resistance and improve its Brinell hardness (for cutting and grinding discs developed by Lagel et

al. (2015). The neoprene gave faster adherence of the matrix on the abrasive particles, the graphite gave higher thermal resistance, and both contributed to a greater hardness of the system when the resin was cured: the Brinell hardness values obtained were between 6 and 8 daN/mm<sup>2</sup> for samples made with tannins resin and 150% of abrasive particles).

### **3.1. Emergency braking efficiency**

The experimental automotive brake pads bonded with the biobased resin were compared with commercial brake pads. These latter were used as control (Table 2). All biobased formulations developed in this work lead to better braking distances than commercial brake pads. Concerning formulation with 150% of abrasive particles, the one that has smaller thickness and weight loss is formulation 1 (Alu 36). Formulation 4 (Alu 60, with 2 layers of mineral wool) has also a good wear resistance. Its negative weight loss could be explained by the fact that some brake pad dust was on the brake disk and thus during testing of these brake pads the dust was stuck on their surface. Formulation 3 (Figure 2) is less wear resistant but has a good braking efficiency. Thus, the fact to add 2 layers of mineral wool in the middle of the brake pad leads to a better bonding pad when Alu 60 is used. This was necessary as the other samples made with 150% Alu 60 but with only one layer of mineral wool break after preparation when they were removed from the mold. When 150% of abrasive particles with fibers from woven fiberglass cut in small pieces (below 5 mm length) are mixed with the resin (Formulation 5), the brake pads are less wear resistant (Figure 3). Woven fiberglass placed on each side of the sample made with 150% of abrasive particles provided better cohesion of the pad. Brake pads made with 100% of abrasive particles (Formulation 7) have also a good wear resistance (Figure 4). Thus, by adding to the matrix resin more graphite and choosing an in-between proportion of abrasive, wearing is less but the braking distance is longer.

With an amount of 75% of abrasive particles it is not possible to obtain correct samples with only one layer of mineral wool in the middle because, after preparation, samples were broken in the middle along the layer of mineral wool. Mineral wool has to be cut in small pieces and mixed with the resin in order to have good brake pads (Formulations 10 & 11, Figure 5). By decreasing the amount of

abrasive and by adding cut mineral wool the brake pads are better. The best brake pads are those where Alu 60 was used. The Alu 60 abrasive particles appear to be more difficult to implement (because with 75% of abrasive particles: mineral wool needs to be cut but with a bigger or even a smaller amount of abrasive, mineral wool can be apply in layer) but have good performance. Moreover, a lower temperature of pressing is still suitable for the pad preparation.

With a smaller amount of abrasive particles (50%) it is possible to obtain correct samples with only one layer of mineral wool in the middle. As there are less particles the resin is less viscous and can better pass between the fibers of mineral wool. Thus, with Alu 36 (Formulation 12) these have good wear resistance (Figure 6). But with Alu 60 (Formulation 13) they were broken after testing (Figure 7). By decreasing the amount of abrasive particles from 75% to 50%, the braking distance is slightly shorter than with higher proportions of the Alu 36 abrasive, but the wear resistance is almost the same. However, with Alu 60 the behaviour is the opposite: less abrasive leads to more wear and a longer braking distance. The resin to which particles of a smaller size (Alu 60) were added is slightly more liquid than the one with bigger particles size (Alu 36). Thus, this implies that there is more resin without abrasive particles present in the middle of the pad. This leads to a slight heterogeneity of the pad and leads to a longer braking distance and finally to its rupture after removal from the braking rig. Furthermore, regarding the same formulation with 50% of abrasive particles when cut mineral wool is added to the resin, its braking efficiency is better but the samples are slightly less wear resistant (Formulation 16). It could be assumed that this is caused by the better homogeneity of the pad which is obtained in this manner.

Yet when glycerol phosphate acidic ester is added (Formulations 14 & 15), the samples broke after preparation. However, when cut mineral wool is added while also adding glycerol phosphate acidic ester (Formulations 18 & 19) the pad samples are good and have a good braking efficiency. As glycerol phosphate acidic ester is a flame retardant, while radical mechanisms are involved, it is well known as also having the effect of blocking or retarding the increase in temperature. (Schartel 2010). This indicates that its addition may be able to retard the brake pad temperature increase during braking thus improving their performance. With glycerol phosphate acidic ester alone the sample was too

brittle without the support of the mineral steel wool. The combination of the two instead, gave the wanted balance of properties.

### **3.2. Brinell hardness test**

In Table 3 are given the results of the Brinell hardness tests for the biobased automotive brake pads. Of all the biobased automotive brake pads only 3 samples completed the Brinell hardness test without too much cracks or even breaking (Figure 8). In all these others cases, the maximum force (N) was reported and an approximate Brinell hardness was calculated. The standard NF B 51-126 recommends applying an increasing force at a rate such that the depth P of  $2.5 \pm 0.5$  mm is reached in  $15 \pm 5$  s and then, maintaining the force corresponding to that depth during  $25 \pm 5$  s.

With the results found in this work it can be say that more abrasive particles do not lead necessarily to a higher Brinell hardness. Thus, it is the relative proportions of the different additives and of their combination that leads to the wanted effect. Thus, the Brinell hardness average for brake pads made with 150%; 100%; 75% and 50% abrasive particles is respectively 3.0; 4.7; 6.2; 2.8 times smaller than that of commercial brake pads. Four out of the six samples prepared with only 50% of abrasive particles have a Brinell hardness only 2 times smaller than commercial brake pad. As a consequence, an optimum level for the proportion of abrasive particles added should be determined for a possible future industrial application.

As an example, one of the best formulations (formulation 11) has a very low Brinell hardness value but also very low weight and thickness losses. Thus, a good wear resistance doesn't necessary lead to a high value of Brinell hardness. The most important factor correlating wear resistance and Brinell hardness could then be the lack of torsion stresses, bending stresses or impact stresses on all the surfaces of the brake pad.



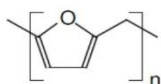
Concerning, the fibers used: mineral wool and fiberglass, it can only be assumed that if mineral wool is not cut into small pieces it leads to a better Brinell hardness (3 times smaller than commercial brake pads, but when it is cut it is 4 times smaller).

However, the higher values of Brinell hardness obtained for commercial brake pads could also indicate a greater brittleness of these, a possibly unfavourable characteristics in hard breaking situations due to higher surface smoothness, lower grip and partial slipping of the pad on the brake disc. Thus, even if the Brinell hardness of commercial brake pads is about 3 times bigger than that of biobased resin bonded brake pads, industrial tannins resin bonded automotive brake pad show real promise to become competitive with synthetic resin bonded brake pad.

### 3.3. MALDI-ToF analysis

The tannin resin was analysis by MALDI-ToF, this basic resin being composed of: Furfuryl alcohol, quebracho tannins QSTW, PEG 400, tung oil, DC 193 and neoprene.

By observing the spectrum of the resin obtained by a linear ionisation mode analysis, with the ion gate off (Figure 9), a repeating period of 80 Da is evident. In reality it is a repeating period of 82-83 Da (in theory 80 Da), alternating. It is a furfuryl alcohol chain of the repeating unit: -furan-CH<sub>2</sub>- (Formula 1).



*Formula 1*

In Table 4 and Figure 9 are given the furanic reaction products obtained.

As regard the tannin reaction products, quebracho tannins monomers (Figure 10) often appear in MALDI in their deprotonated form (Pasch et al 2001). Fisetinidin deprotonated which is the predominant unit of quebracho tannins is observed here at 270.25 Da. Protonated robinetinidin and catechin are also present at 292.24 Da. Deprotonated gallocatechin is also present at 303.02 Da and at

330.21 Da and at 334.92 Da but under its highly protonated form but linked also to to the Na<sup>+</sup> matrix aid.

There is also a major peak at 360.24 Da which is related to gallocatechin-CH<sub>2</sub>OH, this hydroxymethyl group being derived from the formaldehyde split off by rearrangement of the furane-CH<sub>2</sub>-O-CH<sub>2</sub>-furane methylene ether bridges formed by a side reaction of the furfuryl alcohol.

From 381 Da, there are a series of peaks which are related to reaction between gallocatechin and furfuryl alcohol. They are explained in Table 5.

Galocatechin is the monomer which is then appearing to predominantly react, as it is the more reactive one. Other monomers can only react afterwards in the formation of the resin. This is the reason why in the MALDI-ToF spectrum reported for the resin only the reaction with furfuryl alcohol of galocatechin and some catechin appears. Reaction products between furfuryl alcohol and other monomers which are less reactive either appear later in the reaction or indeed do not occur at the stage of the reaction which was used for MALDI-ToF analysis.

#### **3.4. NMR 13C analysis**

In the solid state resin spectrum of the resin three peaks that are either smaller or not present in the tannin alone spectrum take particular importance (Figs 11 and 12) (Wehrli and Wirtlin 1878 ; Pizzi 1994). These are the peaks at 152.5 ppm, 107 ppm and the 70-71 ppm. These peaks exist but are considerably smaller in the spectrum of the tannin. The 152.5 ppm and 107ppm peaks correspond to the signals of the two carbons of the furanic ring coreacted in the resin. They are superimposed to the smaller peaks from the C7 and C9 of the tannin and one of the types of interflavonoid linkage of the tannin alone. The much more pronounced 70-71 ppm signal is characteristic of unreacted hydroxymethyl groups (-CH<sub>2</sub>OH) belonging to furfuryl alcohol and to furfuryl alcohol chains linked or not to the flavonoids, while the clear peak at 61 ppm belongs to the -CH<sub>2</sub>-O- carbons of methylene ether (-CH<sub>2</sub>-O-CH<sub>2</sub>-) bridges between furanic rings, confirming the MALDI ToF results.

The three clear shifts at 38 ppm, 28 ppm and 13 ppm in the resin in relation to the 34 ppm and 22 ppm of the unreacted tannin, indicate that different -CH<sub>2</sub>- bridges exist in the resin, different from what

present in the unreacted tannin. A part the shifted C4 of the flavonoid, the peaks at 28 ppm and 13 ppm are particularly indicative, representing the  $-\text{CH}_2-$  bridges between two furanic rings and equally between one furanic ring and the C6 of a flavonoid A-ring. The 13 ppm does particularly indicate a minor number of strongly sterically hindered  $-\text{CH}_2-$  bridges do also occur.

#### **4. Conclusions**

It is possible to prepare automotive brake pads with a tannins-furanic resin binder and inorganic abrasive particles embedded into it. Thus, the production of greener automotive brake pads is totally possible and oil-derived resins can be replaced by a biobased resin. MALDI-ToF and NMR analysis show that tannins react closely with furfuryl alcohol in order to form a resistant thermoset matrix.

Furthermore, the quantity and the size of abrasive particles are also crucial for the performances of the brake pads. At the same time, fibers (mineral wool & fiberglass) which serve as reinforcements are also crucial by the way they are integrated in the brake pads.

Regarding the averages of thickness and weight loss and the average of braking distance, the three best formulations are:

- Formulation 1: 150% Alu 36; one layer of mineral wool in the middle; one layer of fibreglass on each side of each pad.
- Formulation 11: 75% Alu 60; mineral wool and fiberglass cut and mixed with the resin; with graphite.
- Formulation 18: 50% Alu 36; mineral wool and fiberglass cut and mixed with the resin; with graphite and glycerol phosphate acidic ester.

However, the optimum found in the laboratory may be not the same as under industrial conditions.

Moreover, concerning braking performances, these new green brake pads are more efficient during an emergency braking than commercial brake pads. However the Brinell hardness results of these new biobased brake pads are lower than the one of commercial brake pad, this however not being necessarily a negative characteristics, indicating their lower brittleness.

But in addition to this, by producing and industrially developing these new green brake pads under the same industrial conditions which are used for actual brake pads (at a temperature of 200°C and higher pressure), they can be really competitive with oil-derived materials for the same application.

This study demonstrates once again that petrochemicals can be replaced by biosourced materials even for applications under severe conditions such as automotive brake pads.

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## TABLES

**Table 1: Automotive brake pads with quebracho tannins resin**

Sample	Mass (g)								
	1	2	3	4	5	6	7	8	9
Percentage	150% Alu 36	150% Alu 60	150% Alu 36	150% Alu 60	150% Alu 36	150% Alu 60	100% Alu 36	75% Alu 36	75% Alu 60
Furfuryl alcohol	36.37	36.37	36.37	36.37	36.11	36.11	44.81	51.59	51.59
Tannins QSTW	42.41	42.41	42.41	42.41	42.10	42.10	52.24	60.15	60.15
PEG 400	14.86	14.86	14.86	14.86	14.75	14.75	18.31	21.08	21.08
Tung oil	6.09	6.09	6.09	6.09	6.05	6.05	7.50	8.64	8.64
DC 193	0.22	0.22	0.22	0.22	0.22	0.22	0.28	0.31	0.31
Al <sub>2</sub> O <sub>3</sub>	156	156	156	156	156	156	130	111.43	111.43
Graphite	/	/	/	/	0.76	0.76	1.88	1.08	1.08
Neoprene	2.85	2.85	2.85	2.85	2.83	2.83	3.51	4.05	4.05
Glycerol phosphate acidic ester	/	/	/	/	/	/	/	/	/
pTSA (65% in ethylene glycol)	1.19	1.19	1.19	1.19	1.18	1.18	1.47	1.68	1.68
Temperature (°C)	200	200	200	200	200	200	150	150	150
Mineral wool (for each pad)	1 layer in the middle	1 layer in the middle	2 layers in the middle	2 layers in the middle	1 layer in the middle	1 layer in the middle	5 grams cut	1 layer in the middle	1 layer in the middle
Fiberglass (for each pad)	1 layer on each side	1 layer on each side	1 layer on each side	1 layer on each side	2 grams cut	2 grams cut	1 layer on each side	2 grams cut	2 grams cut
Observations	/	Broken after preparation	/	/	/	Broken after preparation	/	Broken after preparation	Broken after preparation



Mass (g)

Sample	10	11	12	13	14	15	16	17	18	19
Percentage	75% Alu 36	75% Alu 60	50% Alu 36	50% Alu 60	50 % Alu 36	50% Alu 60	50% Alu 36	50% Alu 60	50% Alu 36	50 % Alu 60
Furfuryl alcohol	51.59	51.59	60.18	60.18	59.50	59.50	60.18	60.18	59.50	59.50
Tannins QSTW	60.15	60.15	70.17	70.17	69.37	69.37	70.17	70.17	69.37	69.37
PEG 400	21.08	21.08	24.59	24.59	24.31	24.31	24.59	24.59	24.31	24.31
Tung oil	8.64	8.64	10.08	10.08	9.96	9.96	10.08	10.08	9.97	9.97
DC 193	0.31	0.31	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36
Al <sub>2</sub> O <sub>3</sub>	111.43	111.43	86.67	86.67	85.68	85.68	86.67	86.67	85.68	85.68
Graphite	1.08	1.08	1.26	1.26	1.25	1.25	1.26	1.26	1.25	1.25
Neoprene	4.05	4.05	4.72	4.72	4.66	4.66	4.72	4.72	4.66	4.66
Glycerol phosphate acidic ester	/	/	/	/	2.97	2.97	/	/	2.97	2.97
pTSA (65% in ethylene glycol)	1.68	1.68	1.96	1.96	1.94	1.94	1.96	1.96	1.94	1.94
Temperature (°C)	150	150	150	150	150	150	150	150	150	150
Mineral wool (for each pad)	5 grams cut	5 grams cut	1 layer in the middle	1 layer in the middle	1 layer in the middle	1 layer in the middle	5 grams cut	5 grams cut	5 grams cut	5 grams cut
Fiberglass (for each pad)	2 grams cut	2 grams cut	2 grams cut	2 grams cut	2 grams cut	2 grams cut	2 grams cut	2 grams cut	2 grams cut	2 grams cut
Observations	/	/	/	/	Broken after preparation	Broken after preparation	/	/	/	/

**Table 2: Thickness & mass losses and braking distance of biobased automotive brake pads**

<i>Formulation</i>	<i>Thickness loss average (%)</i>	<i>Weight loss average (%)</i>	<i>Braking distance average 50 km/h to stop (m)</i>	<i>Observations</i>
<i>Commercial</i>	1.51	0.27	8.85	/
<i>1</i>	0.24	0.71	6.86	/
<i>3</i>	1.40	2.67	4.92	/
<i>4</i>	-0.17	1.31	6.48	/
<i>5</i>	4.28	6.35	7.26	/
<i>7</i>	0.49	1.03	6.92	/
<i>10</i>	1.72	1.59	6.63	/
<i>11</i>	0.57	0.48	6.40	/
<i>12</i>	1.41	0.86	7.21	/
<i>13</i>	4.71	3.51	6.79	Broken after test
<i>16</i>	2.14	1.44	5.48	/
<i>17</i>	4.39	3.43	7.22	/
<i>18</i>	1.11	0.67	6.36	/
<i>19</i>	1.59	1.32	6.40	/

**Table 3: Brinell hardness tests of biobased automotive brake pads**

<i>Formulation</i>	<i>Formulation</i>	<i>Brinell hardness (daN/mm<sup>2</sup>)</i>	<i>Observations</i>
<i>Commercial</i>	<i>Commercial</i>	70.41	/
<i>1</i>	<i>A</i>	26.55	Break
<i>3</i>	<i>B</i>	24.73	Break
<i>4</i>	<i>D</i>	18.10	/
<i>5</i>	<i>E</i>	26.08	Break
<i>7</i>	<i>T</i>	14.86	/
<i>10</i>	<i>P</i>	15.42	Break
<i>11</i>	<i>Q</i>	9.00	Break
<i>12</i>	<i>G</i>	29.77	/
<i>13</i>	<i>H</i>	19.61	Break
<i>16</i>	<i>K</i>	13.84	Break
<i>17</i>	<i>L</i>	45.12	Break
<i>18</i>	<i>R</i>	29.39	Break
<i>19</i>	<i>S</i>	39.37	Break

**Table 4: Furanic reactions in MALDI-ToF spectrum of tannins resin analysis**

$M + Na^+$ ( <i>exp.</i> )	$M + Na^+$ ( <i>calc.</i> )	<i>Molecules</i> (where FA is furanic nuclei)
231.00	230	FA-CH <sub>2</sub> -O-CH <sub>2</sub> -FA-CH <sub>2</sub> OH
334.92	338	FA-CH <sub>2</sub> -O-CH <sub>2</sub> -FA-O-CH <sub>2</sub> -FA
491.03	492	(FA-CH <sub>2</sub> ) <sub>5</sub> -FA
641.11	643	(FA-CH <sub>2</sub> -O-CH <sub>2</sub> ) <sub>5</sub> -CH <sub>2</sub> O-CH <sub>2</sub> OH <sup>*</sup> and/or (FA-CH <sub>2</sub> -O-CH <sub>2</sub> ) <sub>5</sub> -FA <sup>**</sup>
797.00	797	HOCH <sub>2</sub> -(FACH <sub>2</sub> OCH <sub>2</sub> FA) <sub>4</sub> -CH <sub>2</sub> OH or HOCH <sub>2</sub> -(FA-CH <sub>2</sub> ) <sub>8</sub> -FA-CH <sub>2</sub> OH

<sup>\*</sup> Due to condensation between formaldehyde that has split off from FA-CH<sub>2</sub>-O-CH<sub>2</sub>-FA bond to give FA-CH<sub>2</sub>-FA + HCHO that has reacted again with the hydroxymethyl group of the furfuryl alcohol.

<sup>\*\*</sup> Due to the same, the HCHO split off but has reacted with the furanic nuclei rather than with the hydroxymethyl group.

**Table 5: Gallicocatechin and furan nuclei reactions in MALDI-ToF spectrum of tannins resin analysis**

$M + Na^+$ ( <i>exp.</i> , Da)	$M + Na^+$ ( <i>calc.</i> , Da)	<i>Molecules</i> (where FA is furanic nuclei)	<i>Observations</i>
381.86	386	Gallicocatechin-CH <sub>2</sub> -FA	Without Na <sup>+</sup>
421.01	421	Gallicocatechin-CH <sub>2</sub> -FA	Gallicocatechin highly protonated, with Na <sup>+</sup>
464.36 or 465.36	466 or 469	Gallicocatechin-CH <sub>2</sub> -FA-CH <sub>2</sub> -FA or (Gallicocatechin-CH <sub>2</sub> -FA)-(CH <sub>2</sub> OH) <sub>2</sub>	Without Na <sup>+</sup> or with Na <sup>+</sup>
551.47	549	(Gallicocatechin-CH <sub>2</sub> -FA-CH <sub>2</sub> -FA)-(CH <sub>2</sub> OH) <sub>2</sub>	With Na <sup>+</sup>

## FIGURES LIST

**Figure 1: Commercial brake pad after braking test**

**Figure 2: Formulation 3 after braking test**

**Figure 3: Formulation 5 after braking test**

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**Figure 5: Formulation 11 after braking test**

**Figure 6: Formulation 12 after braking test**

**Figure 7: Formulation 13 after braking test**

**Figure 8: Formulation 13 after Brinell hardness test**

**Figure 9: MALDI-ToF analysis of tannins resin**

**Figure 10: Main quebracho tannins monomers**

**Figure 11: CP MAS  $^{13}\text{C}$  NMR analysis of resin**

**Figure 12: CP MAS  $^{13}\text{C}$  NMR analysis of tannin**

## FIGURES

**Figure 1: Commercial brake pad after braking test**



**Figure 2: Formulation 3 after braking test**



**Figure 3: Formulation 5 after braking test**





**Figure 4: Formulation 7 after braking test**



**Figure 5: Formulation 11 after braking test**



**Figure 6: Formulation 12 after braking test**



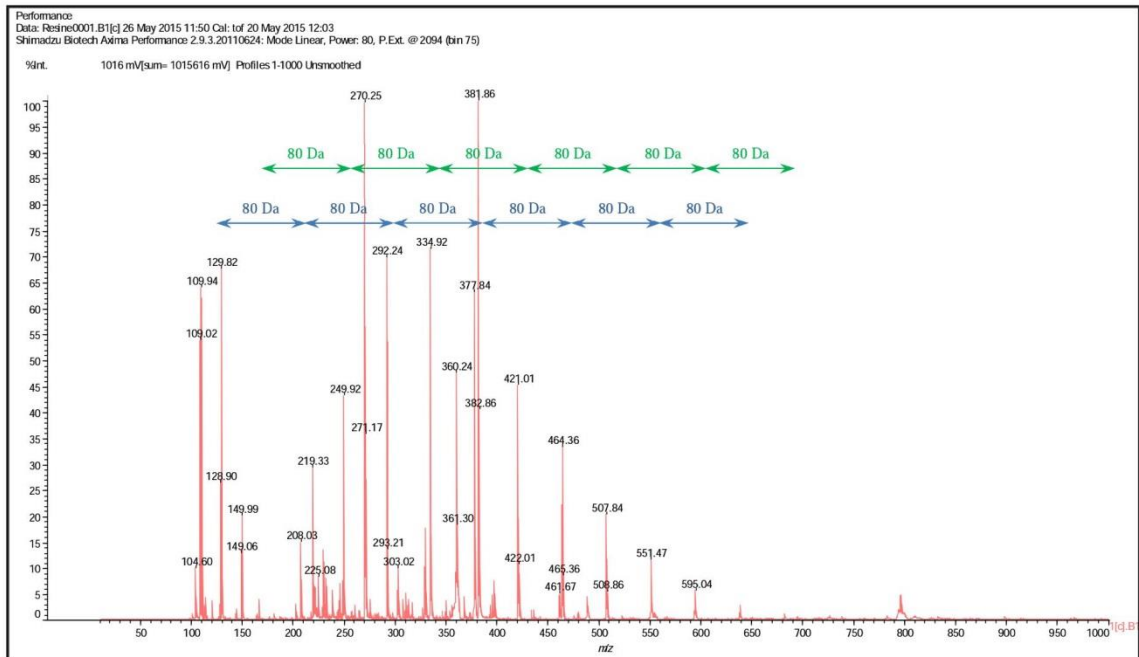
**Figure 7: Formulation 13 after braking test**



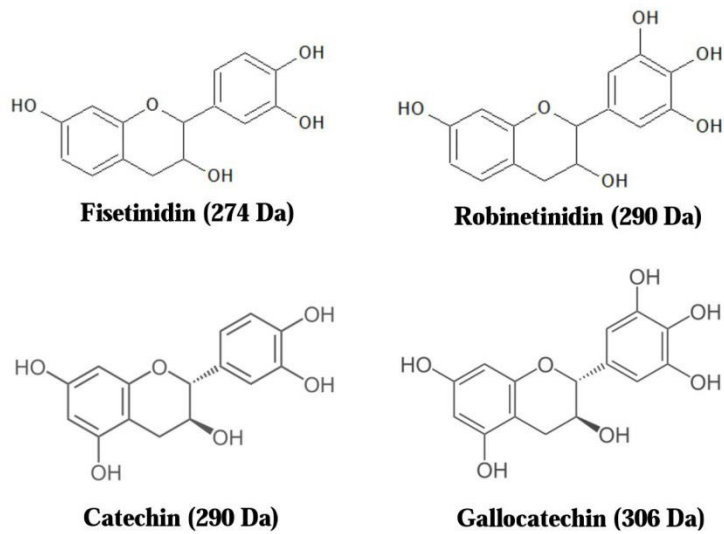
**Figure 8: Formulation 13 after Brinell hardness test**



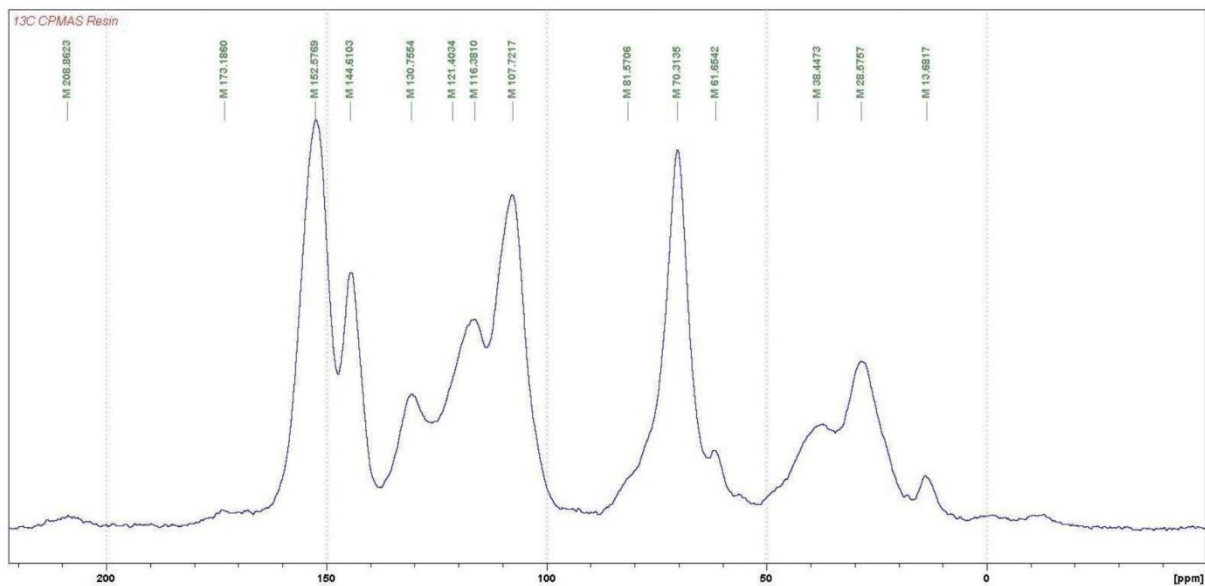
**Figure 9: MALDI-ToF analysis of tannins resin**



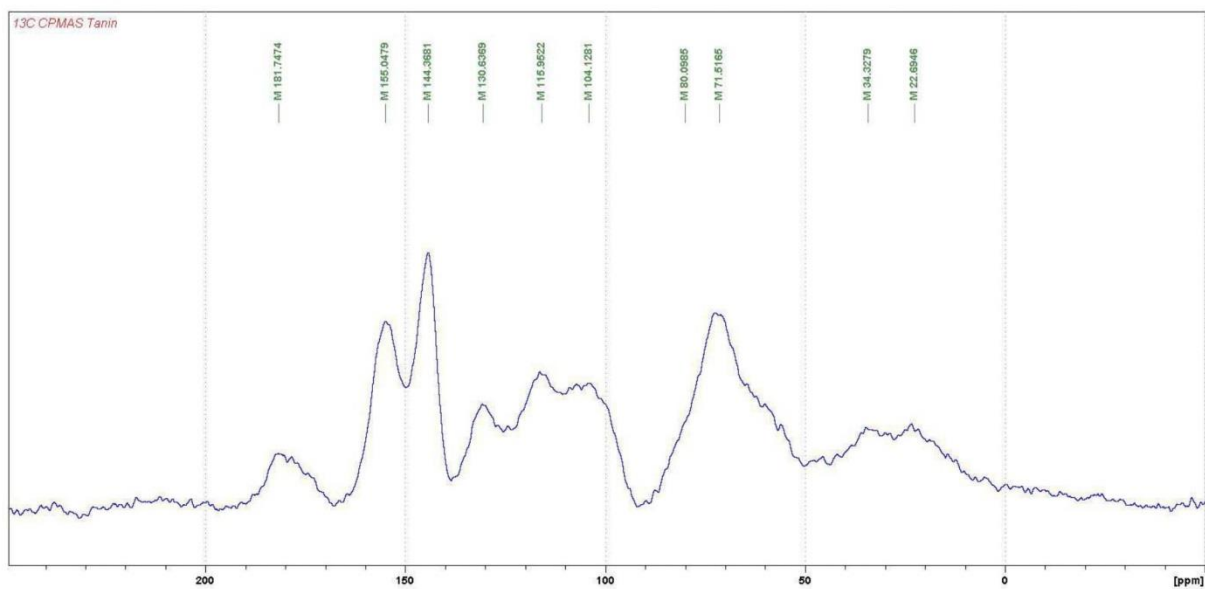
**Figure 10: Main quebracho tannins monomers**



**Figure 11: CP MAS  $^{13}\text{C}$  NMR analysis of resin**



**Figure 12: CP MAS  $^{13}\text{C}$  NMR analysis of tannin**





## **5. CONCLUSIONS GENERALES ET PERSPECTIVES**

### **5.1. Les adhésifs pour matériaux lignocellulosiques**

Lors de cette thèse une première approche de développement de colles pour matériaux lignocellulosiques a été explorée en utilisant des hydrolysats de protéines de blé. En effet, les panneaux de particules utilisés en milieu extérieur sont le plus souvent fabriqués avec des colles phénoliques (phénol-formaldéhyde). Bien que les taux d'émissions de formaldéhyde des panneaux soient faibles et afin que ces colles soient plus respectueuses de l'environnement et de la santé humaine, deux solutions sont le plus souvent essayées : la diminution du formaldéhyde et la substitution partielle du phénol par des composés naturels.

Les panneaux développés lors de ce travail ont des taux de substitution du phénol par les protéines de 10 à 30 %. Pour les meilleurs panneaux (masse volumique cible de 700 kg/m<sup>3</sup>) les cohésions internes sont de 0,94 N/mm<sup>2</sup> avec un taux de substitution de 10 % (LMW Protein) et 0,86 N/mm<sup>2</sup> avec un taux de substitution de 20 % (Solpro 050). Des taux de substitution plus importants pourraient être explorés afin de déterminer un optimum et également de déterminer les meilleurs hydrolysats de protéines de blé pour cette application précise.

Une étude resterait néanmoins à caractériser et à réaliser, ce serait celle de la résistance de ces panneaux contenant de grandes proportions de gluten par rapport aux insectes et aux champignons.

Enfin, les panneaux développés dans cette étude avec une substitution partielle du phénol par des hydrolysats de protéines de blé sont une étape de plus vers le développement et la commercialisation de colles partiellement ou totalement biosourcées.

Ce même but a amené le développement de résine phénolique où une partie du phénol a été substituée par des tanins de châtaignier afin de produire non pas des panneaux de particules mais des mousses solides.

### **5.2. Les mousses phénoliques avec substitution partielle du phénol par des tanins**

Le travail suivant est toujours en relation avec la substitution d'une partie du phénol par des ressources naturelles : les tanins de châtaignier. Il a été possible de synthétiser une résine phénol-

formaldéhyde-tanins (PFT) avec un ratio molaire P/F de 1/1,7 et en remplaçant 30 % en masse du phénol par les tanins de châtaignier.

De manière générale lors de la réalisation de mousses de tanins, le catalyseur de réaction utilisé est une solution aqueuse d'acide para-toluène sulfonique à 65 %. Mais lors de cette étude il a été remarqué que ce n'est pas le plus approprié pour la fabrication de mousses phénoliques où le phénol est partiellement substitué par des tanins. En effet, les mousses sont assez friables. D'autres catalyseurs ont été testés et il s'est avéré que l'acide sulfurique et l'acide phénol sulfonique donnent des mousses beaucoup plus homogènes et moins friables. Ces mousses sont d'ailleurs plus résistantes mécaniquement et elles sont également plus résistantes à l'eau que les mousses phénoliques classiques. Enfin, la conductivité thermique à masse volumique égale est équivalente à celle des mousses phénoliques classiques.

De plus, un moussage chimique est également possible avec l'utilisation de pMDI, les mousses obtenues sont beaucoup plus denses et donc plus rigides et résistantes mécaniquement.

En outre, l'utilisation de tanins dans les résines PFT les rendraient plus stables dans le temps et donc utilisables plus longtemps afin de fabriquer des mousses. Des tests complémentaires seraient utiles afin de caractériser cette observation. Un travail complémentaire pourrait être d'optimiser la quantité de tanins utilisés en substitution du phénol, afin d'avoir des mousses les plus « vertes » possibles mais possédant les caractéristiques comparables aux mousses commerciales.

L'analyse MALDI-ToF des résines PFT montre bien que les tanins ont réagi avec le phénol et le formaldéhyde et qu'ils ne sont pas de simples charges dans la résine. En effet, même si les anneaux aromatiques des tanins de châtaignier sont moins réactifs que les sites réactifs du phénol ; les tanins de châtaignier ont réagi avec le formaldéhyde en formant des ponts méthylène reliant le phénol (sites ortho et para) et les anneaux phénoliques des tanins (sites méta de l'acide gallique). Mais comme ces sites méta sont encombrés stériquement, la réaction la plus importante est celle entre les groupes méthylol formés dans les oligomères phénol-formaldéhyde et les anneaux aromatiques des tanins de châtaignier.

Ce travail constitue une étape importante entre les mousses issues totalement de la pétrochimie et les mousses biosourcées.

### 5.3. Les mousses solides biosourcées à base de tanins

Les tanins sont présents dans une multitude de plantes, ainsi il y a une multitude de variation de composition, et donc une multitude de mousses rigides possibles.

En premier lieu, afin d'obtenir des mousses rigides à base de tanins il faut trouver un optimum entre la vitesse de polymérisation, d'expansion et de durcissement de la résine.

Les mousses de tanins ont été initialement développées en utilisant des tanins de mimosa, mais de plus en plus sont également utilisés les tanins de quebracho. En effet, ils sont composés de molécules de type robetinidine/fisetinidine en différentes proportions, mais ils possèdent une réactivité chimique similaire. Les mousses de tanins sont d'excellents isolants thermiques au même titre que le liège ou la laine de verre, et elles possèdent des résistances mécaniques intéressantes. Les mousses à base de tanins sont caractérisées par le nombre très important de combinaisons possibles des différents composants et additifs présents dans leurs formulations. Ceci induit la possibilité d'obtenir des propriétés spécifiques (densité apparente, conductivité thermique, résistance mécanique...) pour chaque mousse de tanins réalisée. Ces mousses naturelles possèdent d'ailleurs de très bonnes caractéristiques mécaniques, caractéristiques thermiques, résistances au feu et bien-sûr sont respectueuses de l'environnement. Il a été révélé que la taille des cellules est proportionnelle à la quantité d'agent moussant. De plus, à une certaine densité : plus les tailles de cellules sont grandes, plus la conductivité thermique des mousses est importante.

Lors des dernières recherches sur le sujet des mousses de tanins, l'utilisation de tensioactifs s'est développée car ceux-ci permettent de modifier la microstructure de la mousse. Ainsi, par exemple, les tensioactifs non-ioniques impliquent des tailles de cellules plus petites et une plus grande homogénéité de la distribution de celles-ci. Une quantité plus importante de tensioactif non-ionique implique une mousse de tanins relativement élastique.

En outre, une autre approche a été d'étudier une alternative aux mousses tanins-furaniques qui sont catalysées en milieu acide. Car en effet, leur caractère acide pourrait être un frein à leur mise en œuvre dans les matériaux d'isolation : la compatibilité entre les mousses de tanins et les panneaux de bois semble délicate. En effet, lorsque les mousses acides sont en contact avec des matériaux lignocellulosiques l'hydrolyse de la cellulose et des hémicelluloses peuvent être observées. Ainsi, des mousses de tanins catalysées en milieu basique ont été développées et ceci en utilisant le glutaraldéhyde qui est un durcisseur intéressant lorsqu'il n'y a pas d'alcool furfurylique. Leurs caractéristiques thermiques et mécaniques sont de l'ordre de celles observées pour les mousses tanins-furaniques.

De manière générale, les mousses de tanins sont assez faciles à mettre en œuvre, ce qui est un point positif pour un éventuel développement industriel. Néanmoins, il reste quelques études à mener afin de déterminer les optimums des différents paramètres afin de pouvoir être parfaitement compétitifs vis-à-vis de mousses commerciales issues de l'industrie pétrochimie. Ainsi, il serait utile d'étudier les résines (pré-mélange sans l'agent moussant et sans le catalyseur) afin de pouvoir passer de l'environnement du laboratoire à une échelle industrielle. De plus, leur comportement dans le temps est un point crucial : l'évolution de leur viscosité, leur durée de conservation...

Enfin, il serait intéressant de mener une étude poussée sur les possibles attaques d'insectes et de champignons sur les mousses à base de tanins. En effet, les tanins jouent un rôle d'arme chimique défensive pour les arbres car ils sont difficilement assimilables par les insectes et les champignons. De plus, les agents pathogènes (champignons, bactéries) qui attaquent le bois en sécrétant des enzymes extracellulaires sont neutralisés car les tanins inhibent ces enzymes en complexant avec celles-ci. Il serait donc intéressant de voir s'il en va de même dans le cas des mousses à base de tanins.

#### **5.4. Les matériaux abrasifs et de friction biosourcés**

Ces recherches ont pour la première fois permis de mettre au point une matrice « verte » à base de tanins condensés suffisamment résistante mécaniquement afin d'être utilisée dans la préparation de roues abrasives, de disques abrasifs pour meuleuse d'angle ou encore de plaquettes de frein automobile. Ceci étant possible grâce à la réaction des tanins avec l'alcool furfurylique en présence d'huiles naturelles et/ou de plastifiants. Cette nouveauté vise de nouveaux domaines d'application industrielle où les oligomères naturels, issus des cultures agricoles ou de déchets forestiers, peuvent être utilisés en tant que matières premières.

Un premier travail a été de mettre au point des petites roues abrasives réalisées à température ambiante et non à très hautes températures (plus de 1000°C) comme les roues abrasives commerciales. Ceci étant un point important dans la réduction des consommations d'énergie.

De plus, en utilisant les tanins de quebracho, il a été possible de réaliser des plastiques thermodurcissables en quelques minutes au lieu de plusieurs jours comme c'était le cas dans les travaux précédents. Quelques ajustements de la formulation ont permis de diminuer grandement

les fissures présentes sur les échantillons après leur séchage, comme par exemple la suppression de l'eau ou encore l'addition d'huiles (huile de bois de Chine, de lin). Le choix de la quantité et de la taille des particules abrasives (trioxyde d'aluminium) est également important vis-à-vis des performances des roues obtenues.

Les tests d'abrasion des roues sont très positifs, ce qui permet d'imaginer un probable développement industriel de ces roues abrasives « vertes ».

Un second travail a été mené avec succès et est innovant dans la mesure où c'est la première fois qu'un plastique dur thermodurcissable copolymérisé à base de tanins et d'alcool furfurylique a été utilisé dans la fabrication de disques abrasifs (à tronçonner ou à meuler). C'est donc la première fois qu'un plastique totalement « vert » est utilisé dans un domaine où la résistance mécanique doit être importante afin de supporter des forces de rotation très hautes (11 000 tours/min) et bien-sûr que l'abrasivité du produit soit optimum et efficace. C'est une avancée majeure que ce type de produit « vert » puisse rivaliser avec des résines synthétiques dérivées du pétrole. En caractérisant et en comparant les disques « verts » avec des disques liés avec une résine phénolique préparée en laboratoire et aussi avec des disques abrasifs commerciaux.

De même dans ce travail, la quantité et la taille des particules abrasives sont très importantes. En effet, une plus grande quantité de particules abrasives ne mène pas forcément à un disque plus abrasif.

Les formulations ont encore été améliorées. Les tanins étant assez réactifs, l'utilisation de plastifiants (comme le polyéthylène glycol 400, l'huile de bois de Chine, etc...) est intéressante car ils permettent de mettre de la distance entre les sites réactifs, ainsi le durcissement du polymère est mieux maîtrisé et mène donc à des plastiques thermodurcissables plus homogènes. De plus, le catalyseur (pTSA) qui était en solution aqueuse est maintenant utilisé en solution dans l'éthylène glycol afin de limiter au maximum l'eau dans la formulation et donc de la même manière l'apparition de fissures lors du séchage du disque. Et le mode de fabrication essaie de se rapprocher de celui utilisé dans l'industrie mais ce travail reste toute de même à l'échelle du laboratoire (température de 200°C et pression de 35 MPa). Notre optimum trouvé au laboratoire ne correspond pas forcément à celui de l'industrie. Des travaux de faisabilité en chaîne de production et l'optimisation des formulations semblent donc être les prochaines étapes à ce travail de recherche.

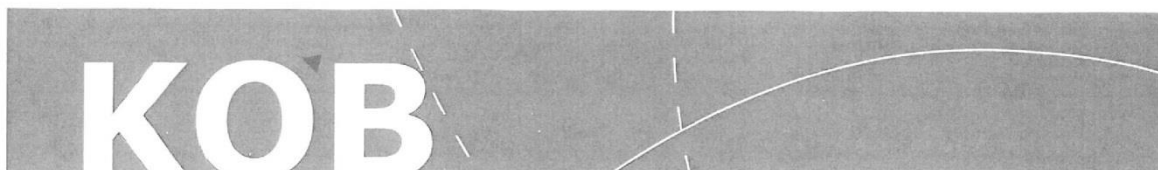


Un dernier travail utilisant ce type de plastique thermodurcissable a été le développement de plaquettes de frein automobile biosourcées. Ceci constitue encore une nouveauté dans ce secteur : les plaquettes de frein sont toujours exclusivement réalisées avec des matrices issues de la pétrochimie. Les formulations ont été adaptées à cette application : du graphite (agent de frottements), du néoprène (charge), de l'ester acide de glycérol phosphate (ignifugeant) et des fibres de verre & laine d'acier (renforts) ont été utilisés. Encore une fois, le choix de la quantité et de la taille des particules abrasives est important par rapport aux caractéristiques finales des plaquettes de frein : les pertes de masse et d'épaisseur après test ; l'efficacité de freinage en freinage d'urgence (50 km/h jusqu'à l'arrêt total du véhicule) et la dureté Brinell. Les plaquettes de freins « vertes » développées ici semblent réellement être compétitives par rapport à celles que l'on trouve dans le commerce. Ceci même si les optimums trouvés lors de ce travail sont des optimums de laboratoire et ne seront sûrement pas les mêmes en conditions industrielles. Les formulations sont plus complexes et donc il faut mener des études complémentaires afin de pouvoir trouver l'optimum à appliquer dans l'industrie. Il serait intéressant de réaliser d'autres tests de freinage à plus hautes vitesses, sans pour autant qu'il s'agisse de freinage d'urgence. Ou encore réaliser différents cycles de freinage afin d'évaluer les performances des plaquettes dans le temps. De même, des tests en situation sèche et humide pourraient être intéressants afin d'observer le comportement de ces plaquettes de frein biosourcées lors de différentes situations que tout automobiliste est amené à rencontrer.

Cette étude démontre une nouvelle fois que les produits pétrochimiques de synthèse peuvent être remplacés par des matériaux naturels biosourcés et ceci même dans le cas d'une application très sévère comme les plaquettes de frein automobile.

## 6. ANNEXES

### Brevet PCT/IB2014/065129, 7 Octobre 2013



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I.N.P.I  
15 rue des Minimes – CS 50001  
92677 Courbevoie Cedex  
FRANCE

Fax: +33 (0)1 56 65 86 00

#### RECOMMANDÉE

V. Réf. :  
N. Réf. : 1949-50 FR KCH/CHS

Kortrijk, le 7 octobre 2013

Messieurs,

**Concerne :** dépôt d'une demande de brevet  
**Au nom de Syral Belgium nv et Université de Lorraine**  
**Titre :** "Colles à bois pour la préparation de panneaux de particules"

Veillez trouver ci-joint les documents nécessaires au dépôt de la demande de brevet mentionnée ci-dessus. Nous vous demandons de bien vouloir procéder au dépôt de la demande de brevet.

Les originaux ainsi que le texte vous seront envoyés par la poste.

Vous remerciant d'avance, nous vous prions d'agréer, Messieurs, nos salutations les meilleures.

Ing. F. OSTYN

KOB nv  
Pres. Kennedypark 31c, B-8500 Kortrijk  
Tel. +32 56 21 35 38  
Fax +32 56 21 60 14 (octr.)  
Fax +32 56 21 04 63 (merk./mod.)  
info@kob.be, www.kob.be

bankrekeningen | comptes bancaires | bank accounts  
KBC-Kortrijk no. 460-0471121-32 IBAN BE 90 4600 4711 2132 SWIFT : KREDBEBB  
DEXIA-Kortrijk no. 068-2157844-09 IBAN BE 52 0682 1578 4409 SWIFT : GKCCBEBB

BTW/TVA/VAT BE 0450.490.071, RPR Kortrijk

Veillez remplir cette requête à l'encre noire

DB 540 - 10 - 12

<p style="text-align: center;">Réservé à l'INPI</p>		<p><b>1 NOM ET ADRESSE DU DEMANDEUR OU DU MANDATAIRE À QUI LA CORRESPONDANCE DOIT ÊTRE ADRESSÉE</b></p> <p>▪ KOB nv - Frans OSTYN, Ing. President Kennedypark 31c B-8500 KORTRIJK BELGIQUE</p> <p>▪</p>	
<p>REMISE DES PIÈCES DATE LIEU N° D'ENREGISTREMENT NATIONAL ATTRIBUÉ PAR L'INPI DATE DE DÉPÔT ATTRIBUÉE PAR L'INPI</p>			
<p><b>Vos références pour ce dossier</b> <i>(facultatif)</i> 1949-50 FR KCH/CHS</p>			
<p><b>Confirmation d'un dépôt par télécopie</b></p>		<p><input type="checkbox"/> N° attribué par l'INPI à la télécopie</p>	
<p><b>2 NATURE DE LA DEMANDE</b></p>		<p><b>Cochez l'une des 4 cases suivantes</b></p>	
<p>Demande de brevet <input checked="" type="checkbox"/></p>			
<p>Demande de certificat d'utilité <input type="checkbox"/></p>			
<p>Demande divisionnaire <input type="checkbox"/></p>			
<p style="text-align: center;"><i>Demande de brevet initiale</i></p>		N°	Date
<p style="text-align: center;"><i>ou demande de certificat d'utilité initiale</i></p>		N°	Date
<p>Transformation d'une demande de brevet européen <i>Demande de brevet initiale</i></p>		<input type="checkbox"/>	Date
<p>N°</p>			Date
<p><b>3 TITRE DE L'INVENTION (200 caractères ou espaces maximum)</b></p> <p>"Colles à bois pour la préparation de panneaux de particules"</p>			
<p><b>4 DÉCLARATION DE PRIORITÉ OU REQUÊTE DU BÉNÉFICE DE LA DATE DE DÉPÔT D'UNE DEMANDE ANTÉRIEURE FRANÇAISE</b></p>		<p>Pays ou organisation Date</p>	
			N°
		Pays ou organisation Date	N°
		Pays ou organisation Date	N°
<p><input type="checkbox"/> <b>S'il y a d'autres priorités, cochez la case et utilisez l'imprimé «Suite»</b></p>			
<p><b>5 DEMANDEUR (Cochez l'une des 3 cases)</b></p>		<p><input type="checkbox"/> Personne morale à compter de 1000 salariés</p>	
		<p><input type="checkbox"/> Personne morale de moins de 1000 salariés</p>	
		<p><input type="checkbox"/> Personne physique</p>	
<p>Nom ou dénomination sociale</p>		<p>Syral Belgium nv</p>	
<p>Prénoms</p>			
<p>Forme juridique</p>		<p>société anonyme</p>	
<p>N° SIREN</p>			
<p>Code APE</p>			
<p>Domicile ou siège</p>	<p>Rue</p>	<p>Burchtstraat 10</p>	
	<p>Code postal et ville</p>	<p>9 3 0 0 AALST</p>	
	<p>Pays</p>	<p>BELGIQUE</p>	
<p>Nationalité</p>			
<p>N° de téléphone <i>(facultatif)</i></p>		<p>N° de télécopie <i>(facultatif)</i></p>	
<p>Adresse électronique <i>(facultatif)</i></p>			
<p><input checked="" type="checkbox"/> <b>S'il y a plus d'un demandeur, cochez la case et utilisez l'imprimé «Suite»</b></p>			

Remplir impérativement la 2<sup>ème</sup> page

REMISE DES PIÈCES DATE LIEU N° D'ENREGISTREMENT NATIONAL ATTRIBUÉ PAR L'INPI		Réservé à l'INPI	DB 540 - 10-12
<b>6 MANDATAIRE (s'il y a lieu)</b>			
Nom		OSTYN	
Prénom		Frans	
Cabinet ou Société		KOB nv	
Nationalité		Belge	
N° de pouvoir permanent et/ou de lien contractuel			
Adresse	Rue	President Kennedypark 31c	
	Code postal et ville	L 8 5 0 0   KORTRIJK	
	Pays	BELGIQUE	
N° de téléphone (facultatif)		+32 56 21 35 38	
N° de télécopie (facultatif)		+32 56 21 60 14	
Adresse électronique (facultatif)		info@kob.be	
<b>7 INVENTEUR (S)</b>		<b>Les inventeurs sont nécessairement des personnes physiques</b>	
Les demandeurs et les inventeurs sont les mêmes personnes		<input type="checkbox"/> Oui <input checked="" type="checkbox"/> Non : <b>Dans ce cas remplir le formulaire de Désignation d'inventeur(s)</b>	
<b>8 BÉNÉFICIAIRE DE LA RÉDUCTION DU TAUX DES REDEVANCES</b>		<input type="checkbox"/> Personne(s) physique(s) <input type="checkbox"/> Entreprise de moins de 1000 salariés ( <b>attestation à fournir dans le mois du dépôt</b> ) <input type="checkbox"/> Organisme à but non lucratif dans le domaine de l'enseignement ou de la recherche ( <b>attestation à fournir dans le mois du dépôt</b> )	
<b>9 SÉQUENCES DE NUCLEOTIDES ET/OU D'ACIDES AMINÉS</b>		<input type="checkbox"/> Cochez la case si la description contient une liste de séquences	
Le support électronique de données est joint		<input type="checkbox"/>	
La déclaration de conformité de la liste de séquences sur support papier avec le support électronique de données est jointe		<input type="checkbox"/>	
<b>Si vous avez utilisé l'imprimé «Suite», indiquez le nombre de pages jointes</b>			
<b>10 SIGNATURE DU DEMANDEUR OU DU MANDATAIRE (Nom et qualité du signataire)</b>		<b>VISA DE L'INPI</b>	
		OSTYN Frans - Mandataire	

Conformément aux dispositions de la loi n° 78-17 du 6.01.1978 modifiée relative à l'informatique, aux fichiers et aux libertés, vous bénéficiez d'un droit d'accès et de rectification pour les données vous concernant auprès de l'INPI. Les données à caractère personnel que vous êtes tenu(e) de nous fournir dans ce formulaire sont exclusivement utilisées pour identifier le titulaire de la demande et son éventuel mandataire.





**REQUÊTE EN DÉLIVRANCE DE BREVET  
ANNEXE**

**Détail des redevances versées**

A remplir par le demandeur

	Redevances	Tarif	Quantité	Montant
062	Dépôt		1	36,-
062	Dépôt à taux réduit			
063	Rapport de recherche		1	500,-
063	Rapport de recherche à taux réduit			
068	Revendication, à partir de la onzième			
068	Revendication, à partir de la onzième à taux réduit			
077	Rapport de recherche sous priorité étrangère reconnu équivalent			
			<b>TOTAL À PAYER</b>	<b>536,- Euros</b>

**Mode de règlement**

Mandat       Chèque       Virement       Autres :

Autorisation de prélèvement sur le compte client ouvert à l'INPI

Signature du représentant autorisant le prélèvement sur compte client

N° du compte :

Nom Prénom du signataire

**Vos références pour ce dossier**

*(facultatif)* 1949-50 FR KCH/CHS

<p><b>1</b> NOM ET ADRESSE DU DEMANDEUR OU DU MANDATAIRE</p> <p>▪ KOB nv - Frans OSTYN, Ing. President Kennedypark 31c B-8500 KORTRIJK BELGIQUE</p> <p>▪</p>	<p>NOM ET ADRESSE DE LA PERSONNE À QUI DOIT ÊTRE ADRESSÉ LE REÇU DE PAIEMENT (si différent du cadre 1)</p> <p>▪</p> <p>▪</p>
<p>Nom ou dénomination sociale du demandeur</p>	<p>Syral Belgium nv</p>



## RESUME

Avec la constante augmentation des prix du pétrole et la diminution des ressources fossiles, des alternatives « vertes » doivent être trouvées. Ainsi, des premières recherches ont été menées sur la possibilité de mettre au point des colles pour panneaux à base de bois dans lesquelles une partie du phénol a été substituée par des protéines de blé.

De même, les tanins sont des molécules polyphénoliques naturelles et peuvent être une alternative aux produits chimiques de synthèse issus du pétrole. Les tanins de châtaignier, tanins hydrolysables, ont été utilisés afin de substituer une partie du phénol lors de la synthèse de résines phénoliques. Ces résines ont été étudiées et utilisées pour la fabrication de mousses phénoliques rigides. Cette démarche constitue un pas de plus vers la mise au point et la future commercialisation de matériaux plus respectueux de l'environnement.

En outre, les tanins ont également été utilisés lors du développement de mousses rigides biosourcées tanins-furaniques, cette fois-ci il s'agit de tanins condensés : tanins de quebracho, couplés à de l'alcool furfurylique (d'origine agricole). Ces mousses « vertes » présentent une bonne résistance mécanique, de bonnes performances thermiques et elles ne brûlent pas, ainsi, elles sont totalement adaptées à une utilisation pour l'isolation des bâtiments.

Enfin, de nouveaux types de matériaux issus de produits naturels (tanins et alcool furfurylique) ont été mis au point lors de cette thèse : des matériaux abrasifs et de friction biosourcés. Des roues abrasives et des disques abrasifs ont été développés et testés. Et des plaquettes de frein automobile ont été fabriquées et testées en conditions réelles. Tous ces nouveaux matériaux présentent d'excellentes propriétés par rapport aux matériaux commerciaux.

## ABSTRACT

With the constant increase of oil prices and with the dwindling of fossil resources, "green" alternatives must be found. Thus, first research was conducted on the possibility to develop synthetic phenolic adhesives for wood-based panels where a part of phenol was substituted by wheat proteins.

Similarly, tannins which are natural polyphenolic molecules can be used as an alternative to synthetic chemical products. Chestnut tannin, a hydrolysable tannin was used to substitute part of phenol during the synthesis of phenolic resins. The characteristics of these resins were studied and the resins used for the manufacture of rigid phenolic foams. This is a new step towards the development and future commercialization of more environmentally friendly materials.

Furthermore, condensed flavonoid tannins were also used in the development of tannins-furanic biobased rigid foams. Quebracho wood tannin extract was coupled with furfuryl alcohol another material of natural, agricultural origin. These "green" foams show good mechanical strength, good thermal performance and do not burn, thus they are entirely suitable for use in building insulation.

Finally, new types of materials made from the same natural products (tannins and furfuryl alcohol) were developed during the research described in this thesis: biobased abrasive and friction materials. Abrasive wheels and abrasive discs for steel molding and steel cutting using a biobased matrix were thus developed and tested. Moreover, automotive brake pads were prepared and were tested under real vehicle application conditions. All these new materials showed excellent properties compared to commercial materials and yielded excellent results comparable and sometime superior to their synthetic commercial equivalents.