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## Matériaux biosourcés originaux dérivés de tanins

Elham Azadeh

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UNIVERSITÉ  
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SIMPPÉ



# THÈSE

Pour l'obtention du grade de

**Docteur de l'Université de Lorraine**

*Spécialité : Sciences du bois et des fibres*

Par **Elham AZADEH**

Sous la direction

du **Professeur Christine Gérardin** et du **Professeur Philippe Gérardin**

Soutenance publique prévue le 20/10/2023

## **Matériaux Biosourcés originaux dérivés de Tanins**

### **Membres du jury**

<b>Rapporteur</b>	<b>Mme. Fatima Charrier</b>	<b>MCF HDR</b> Université de Pau et des Pays de l'Adour
<b>Rapporteur</b>	<b>M. Mark Irlé</b>	<b>Directeur de Recherches</b> Ecole Supérieure du Bois, Nantes
<b>Présidente du jury</b>	<b>Mme. Rachida Zerrouki</b>	<b>Professeur</b> Université de Limoges
<b>Examineur</b>	<b>M. Guo-Hua HU</b>	<b>Professeur</b> Université de Lorraine
<b>Directrice de thèse</b>	<b>Mme. Christine Gérardin Charbonnier</b>	<b>Professeur</b> Université de Lorraine
<b>Co-directeur de thèse</b>	<b>M. Philippe Gérardin</b>	<b>Professeur</b> Université de Lorraine
<b>Membre invité</b>	<b>M. Antonio Pizzi</b>	<b>Professeur émérite</b> Université de Lorraine
<b>Membre invité</b>	<b>Mme. Umami Han Abdullah</b>	<b>Senior lecturer</b> Putra Malaysia University



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**تقدیم به روح پدرم که همیشه حاضر بود بی آنکه باشد**

**تقدیم به لبخند تو مادرم که هر چه دارم از توست**

**تقدیم به تو ایمان عزیزم که نه برادر که عزیزترین دوست منی**

## Tables des Matières

Remerciements .....	1
Avant-Propos .....	1
Liste des abréviations .....	2
Liste des Figures .....	3
Liste des Tableaux .....	5
Liste des Annexes.....	6
Introduction .....	8
<b>Chapitre I- Etat de l'art .....</b>	<b>10</b>
1.Présentation générale des Tanins .....	13
1.1. Historique .....	13
1.2. Description et propriétés .....	13
1.3. Classification et structure chimique .....	15
1.3.1-Tanins hydrolysables :.....	15
Gallotanins .....	15
Ellagitanins .....	16
1.3.2. Tanins condensés .....	17
2. Matières tanantes végétales utilisées dans cette étude.....	21
2.1. Extraction de tanins .....	21
2.2. Tanins extraits du bois .....	22
2.3. Tanins issus des écorces : .....	23
3.Réactivité des tanins condensés .....	24
3.2- Réactivité des sites nucléophiles .....	25
3.2.1. Réaction avec l'alcool furfurylique .....	26
3.2.1.1. Caractéristiques physico-chimiques de l'alcool furfurylique .....	26
3.2.1.2-Production de l'alcool furfurylique .....	26
3.2.1.3-Réactivité de l'alcool furfurylique .....	27
3.2.1.4- Réaction des tanins avec l'alcool furfurylique .....	28



3.2.2-Réaction des tanins avec des aldéhydes .....	29
3.3- Fonctionnalisation des groupes hydroxyles .....	30
3.3.1. Acylation .....	30
3.3.2. Estérification des polyphénols par un chlorure acide .....	31
4. Matériaux biosourcés dérivés des tanins .....	32
4.1- Les mousses : description et classification .....	32
4.2. Les mousses d'isolation naturelles dérivées des tanins.....	34
4.3-Conception de mousses polyuréthanes non isocyanates (NIPU).....	37
4.4-Conception de composites bois / tanin / alcool furfurylique .....	40
<b>Chapitre II-Conception de mousses naturelles dérivées de tanins condensés.....</b>	<b>44</b>
1. Introduction générale .....	47
2. Development of Water Repellent, Non-Friable Tanin-Furanic-Fatty Acids Bio foams (Publication. I) .....	51
Introduction .....	51
Materials and Methods .....	53
Results and Discussion .....	57
Conclusions.....	74
3.Flexible, Water Repellent Tannin-Furanic-Fatty Acids Biofoams (Publicaion.II) .....	75
Introduction .....	76
Materials and Methods .....	78
Results and Discussion .....	81
Conclusions.....	102
4.Discussion et conclusion.....	103
<b>Chapitre III- Synthèse et caractérisation de mousses d'isolation thermique bio-polyuréthane sans isocyanate à base de tanins hydrolysable .....</b>	<b>108</b>
1.Introduction générale.....	111
2.Self-Blowing Non-Isocyanate Polyurethane Foams Based on Hydrolysable Tanins (Publication. III) .....	113
Introduction .....	114
Materials and Methods .....	116
Results and Discussion .....	118

<b>Conclusions.....</b>	<b>125</b>
<b>3.Hydrolysable Chestnut Tannin Extract Chemical Complexity in Its Reactions for Non-Isocyanate Polyurethanes (NIPU) Foams (Publication.IV) .....</b>	<b>128</b>
<b>Introduction .....</b>	<b>129</b>
<b>Materials and Methods .....</b>	<b>131</b>
<b>Results and Discussion .....</b>	<b>133</b>
<b>Conclusion.....</b>	<b>145</b>
<b>4.Discussion et conclusion.....</b>	<b>147</b>
<b>Chapitre IV : Conception de composites bois/tanin/alcool furfurylique .....</b>	<b>150</b>
<b>1.Introduction générale.....</b>	<b>153</b>
<b>2.Optimizing Furfuryl Alcohol/Tanin Concentration and Ratio for Enhanced Biosourced Thermoset Resins in Wood Protection.....</b>	<b>158</b>
<b>Introduction .....</b>	<b>159</b>
<b>Materials and Methods .....</b>	<b>160</b>
<b>Results and Discussion .....</b>	<b>165</b>
<b>Conclusion.....</b>	<b>181</b>
<b>3.Optimizing Esterified Tannins and Fatty Acids to Enhance European Beech Properties .....</b>	<b>183</b>
<b>Introduction .....</b>	<b>184</b>
<b>Materials and Methods .....</b>	<b>160</b>
<b>Results and Discussion .....</b>	<b>165</b>
<b>Conclusion.....</b>	<b>197</b>
<b>4.Discussion et conclusion.....</b>	<b>199</b>
<b>Conclusion Générale .....</b>	<b>201</b>
<b>Annexes .....</b>	<b>211</b>
<b>Références.....</b>	<b>231</b>
<b>Résumé .....</b>	<b>245</b>
<b>Abstract.....</b>	<b>246</b>

## **Avant-Propos**

La présente thèse est composée d'un recueil de publications scientifiques soumises à des revues internationales à comité de lecture, ainsi que d'un chapitre rédigé selon le format standard et présenté dans des conférences. Les introductions de chaque chapitre ainsi que les conclusions ont été rédigées en français.

Cette approche de rédaction s'inscrit dans le cadre d'une démarche scientifique visant à diffuser les résultats de mes recherches de manière complète et conforme aux exigences de publication des revues scientifiques internationales. En rassemblant ces publications dans le cadre d'une thèse, je souhaite offrir une synthèse cohérente de mes travaux de recherche et les mettre à la disposition de la communauté scientifique.

Je tiens à souligner que le choix de cette structure a entraîné certaines redondances, inhérentes à la compilation de publications indépendantes, qui peuvent être rencontrées lors de la lecture de cette thèse. Je vous prie de faire preuve d'indulgence à cet égard.

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Enfin, j'espère que cette thèse sera un apport significatif à la compréhension et au développement de mon domaine de recherche, et qu'elle suscitera de nouvelles perspectives et opportunités pour des travaux futurs.

Merci de consacrer du temps à la lecture de cette thèse et j'espère qu'elle sera enrichissante et stimulante pour vous.

## Liste des abréviations

- AF : Alcool furfurylique
- ASE : Percentage of anti-swelling efficiency
- B : Bulking value
- C13 RMN : Résonance Magnétique Nucléaire du Carbone-13
- CP : Coniophora puteana
- DMAP : 4-diméthylaminopyridine
- DM : Densité de masse
- DTG : Derivative Thermogravimetry
- Et3N : triméthylamine
- FTIR : spectroscopie infrarouge à transformée de Fourier
- HDI : Hexaméthylène diisocyanate
- IPDI : Isophorone diisocyanate
- L : is Leaching Value
- MEB : microscope électronique à balayage
- MC : Percentage of moisture content of wood sample
- MOE : Module Young
- MOLDI-TOF : Matrix-Assisted Laser Desorption/Ionization Time-of-Flight
- NIPU : mousses polyuréthanes sans isocyanate
- NU : Resine NIPU
- pTSA : para-toluene-sulfonic acid
- RPE : Résonance Paramagnétique Électronique
- S : Swelling at saturation state
- STD : Standard
- SU : Solution uptake
- SFE : Surface free energy
- TDI : 2,4-tolylène diisocyanate
- TGA : Thermogravimetric Analysis
- TV : Trametes versicolor
- $WL_D$  : weight loss percentage of the wood sample due to decay
- WL : Weight Loss after Leaching
- $WPG_1$  : weight percentage gain before leaching process
- $WPG_2$  : weight percentage gain after leaching process
- WU : Water uptake

## Liste des Figures

Figure.1. 1-Constituants principaux des tanins hydrolysables .....	15
Figure.1. 2-la structure de gallotannins .....	16
Figure.1. 3-la structure des acides ellagiques .....	16
Figure.1. 4- Schéma d'un flavonoïde et sa numérotation[1], [2], [4] .....	17
Figure.1. 5-les quatre type de poly flavonoïde à partir de deux anneaux [19] .....	18
Figure.1. 6-Structure d'un tanin condensé (proanthocyanidine).....	19
Figure.1. 7- Structure de la castaline/vescaline et de la castalagine/vescalagine .....	23
Figure.1. 8-Les réactions variées des tanins condensés.....	24
Figure.1. 9- Dégradation des tanins en catéchines et anthocyanidines en conditions acides [19].....	25
Figure.1. 10-Auto-condensation acide par hydrolyse de l'hétérocycle. ....	25
Figure.1. 11-la procédure de fabrication l'alcool furfurylique .....	26
Figure.1. 12-la réaction avec le formaldéhyde .....	27
Figure.1. 13- la réaction autocondensation de l'alcool furfurylique.....	27
Figure.1. 14- Produits de réaction de l'alcool furfurylique sur la catéchine .....	28
Figure.1. 15- Sites d'attaque du formaldéhyde sur des flavonoïdes.....	29
Figure.1. 16-Réaction entre le tanin et le formaldéhyde .....	29
Figure.1. 17- Acylation de la quercétine par le chlorure d'acétyle .....	30
Figure.1. 18-Schéma de l'estérification de la quercétine en 7-oléylquercétine.....	31
Figure.1. 19-Schéma de Gréffage d'une chaîne grasse sur des flavonoïdes utilisés .....	32
Figure.1. 20-Disposition schématique pour une mousse [4] .....	33
Figure.1. 21 Applications commerciales des mousses élastiques [53].....	34
Figure.1. 22-Applications commerciales des mousses rigides .....	34
Figure.1. 23-Image de la structure d'une mousse tanin-furanique de première génération (à gauche) et macro-apparence de la même (à droite).....	36
Figure.1. 24- Schématique de la synthèse de polyuréthanes non isocyanates à base de tanin. ....	38
Figure.2. 2-Comparison of FTIR spectra of mimosa tannin, oleic acid, oil-grafted tannin using oleoyl chloride, and oleoyl chloride .....	58
Figure.2. 3-(c). Comparison of FTIR spectra of mimosa tannin, lauric acid, oil-grafted tannin using lauryl chloride, and lauryl chloride.....	59
Figure.2. 4-Comparison of different compositions to produce oil-grafted tannin using palmitoyl chloride.....	60
Figure.2. 5-The structure of the four flavonoid types constituting mimosa tannin is shown. A- and B-rings are indicated, and the site numbers have been indicated on the fisetinidin structure. ....	61
Figure.2. 6-Two of the possible isomer structures for the (fisetinidin)2-(palmitate)2 oligomer, showing that the palmitoyl residue can have reacted both on the C3 alcoholic -OH and on one of the phenolic -OHs. ....	62
Figure.2. 7-Two of the possible isomer structures for the (fisetinidin)2-(palmitate)2 oligomer.....	65
Figure.2. 8 -Example of the structures of two possible isomers of the identified species glucose(fisetinidin)2-(palmitate)3 at 1442 Da .....	65
Figure.2. 9-MALDI-TOF mass spectra of oil-grafted tannin with palmitoyl chloride (a) from 400 Da to 800 Da, (b) from 800 Da to 1200 Da, (c) from 1200 Da to 1600 Da.....	66
Figure.2. 10-Examples of the structure of a robinetinidin-(oleate) <sub>3</sub> , with Na+. ....	67
Figure.2. 11-MALDI-TOF mass spectrum of oil-grafted tannin with oleoyl chloride (a) from 400 Da to 800 Da, (b) from 800 Da to 1200Da, (c) from 1200 Da to 1600 Da, (d)from 1600 Da to 2400 Da .....	68
Figure.2. 12-From left to right: examples of cubes of standard foam, Foam A, Foam B, Foam C, and Foam D. ..	71
Figure.2. 13- Surface friability test of the standard foam and the four oil-grafted foams A, B, C.....	72
Figure.2. 14- Wetting angle and its variation as a function of time of the ( ) standard foam, ( ) foam A, ( ) foam B, ( ) foam C, and ( ) foam .....	73
Figure.2. 15-Chemical Structure of One Esterified Flavonoid.....	77
Figure.2. 16- Comparison of FTIR spectra of mimosa tannin, lauric acid, and fatty acid-grafted tannin using lauroyl chloride.....	81
Figure.2. 17- Schematic visualization of the esterification of a commercial condensed tannin extract.....	82

Figure.2. 18- Comparison between unmodified foams without (STSD.R) and with glycerol (STD.F).....	84
Figure.2. 19- Comparison between rigid (C12,16,18-R) and flexible (C12,16,18-F) fatty acid-grafted tannin foams .....	84
Figure.2. 20-The average compression strength of the rigid unmodified and oil-grafted foam with three chains of fatty acid.....	86
Figure.2. 21-The average compression strength of the modified and flexible oil-grafted foam with three chains of fatty acid.....	86
Figure.2. 22-schematic figure to explain the elasticity calculation. ....	88
Figure.2. 23-Ccomparison between load at the yield point and MOE for unmodified and rigid oil-grafted foams	89
Figure.2. 24-Comparison between load at the yield point and MOE for unmodified and flexible fatty acids grafted foams. ....	90
Figure.2. 25-Compression results of unmodified and rigid oil-grafted foams with three chains of fatty acid.....	91
Figure.2. 26-Comparison between flexible fatty acid-grafted foams with three different fatty acid chains .....	91
Figure.2. 27-Cyclic compression tests for the unmodified rigid foam (STD-R) without plasticizer and with glycerol plasticizer (STD-F).....	92
Figure.2. 28-Schematic differences at the level of the polymer network between rigid and flexible foams.....	93
Figure.2. 29-Ten cycles strain-stress curves of rigid foams added with lauric acid -grafted tannin at 10, 20 and 40% strain.....	94
Figure.2. 30- 10 Cycles strain-stress of flexible foams with added lauric acid-grafted tannin at strains of 10, 20 and 40% .....	95
Figure.2. 31- Ten cycles strain -stress of flexible foams with added oleic acid-grafted tannin at strains of 10, 20and 40% .....	96
Figure.2. 32- Comparison of rigid standard foam and rigid foams added of fatty acid-grafted tannin different chain length. ....	98
Figure.2. 33-Comparison between standard flexible foam and flexible foams added fatty acid-grafted tannin of different chain lengths. ....	98
Figure.2. 34-Comparison of TGA and DTG weight curves as a function of time, between an unmodified rigid foam (STD-R) and rigid foams added of fatty acids-grafted tannin with fatty acid chains of three different kinds. ....	99
Figure.2. 35- Comparison of TGA and DTG curves weight curves as a function of time, between an unmodified flexible foam (STD-F) and rigid foams added of fatty acids-grafted tannin with fatty acid chains of three different kinds .....	100
Figure.2. 36- Comparison of TGA and DTG between unmodified foams (STD-R, STD-F) and rigid (C12-R) and flexible(C12-F) lauric grafted-tannin foam .....	100
Figure.3. 1-Schematic structural formulas of oligomers of pentagalloyl glucose (I), and its rearrangements to castalagin (II), and vescalin (III). ....	114
Figure.3. 2-Example of a urethane species isolated by reaction of carbonated gallic acid with hexamethylene diamine in chestnut tannin [8] .....	115
Figure.3. 3-Example of a urethane species formed by glucose present in chestnut extract after carbonation with dimethyl carbonate with hexamethylene diamine .....	115
Figure.3. 4- FTIR spectrum of chestnut tannin extract.....	119
Figure.3. 5- FTIR spectrum of NIPU resin before foaming, Oil Bath reacted. ....	119
Figure.3. 6-FTIR spectrum of Hardened Foam after hardening it in the oven. ....	120
Figure.3. 7-Thermogravimetric Analysis (TGA) curves of the four chestnut tannin foams. To note that the curves are practically coincidental.....	121
Figure.3. 8- Superimposed DTG curves for the four-chestnut tannin NIPU experimental foams .....	121
Figure.3. 9- Ignition test images with time scale in seconds for (a) foams 1.2, (b) foam 1.3, (4) foam 1.4, (d) foam1.5. For foam1.3 the afterburning before self-extension is shown.....	125
Figure.3. 10-SEM images of chestnut tannin extract-based non-isocyanate polyurethane (NIPU) bio-foam.....	133
Figure.3. 11-SEM images of chestnut tannin extract-based non-isocyanate polyurethane (NIPU) bio-foams.....	134
Figure.3. 12-(MALDI ToF spectra of chestnut tannin extract non-isocyanate polyurethane (NIPU) bio-foam ...	136
Figure.3. 13- (MALDI ToF spectra of chestnut tannin extract non-isocyanate polyurethane (NIPU) bio-foam ..	137

Figure.3. 14-(MALDI ToF spectra of chestnut tannin extract non-isocyanate polyurethane (NIPU) bio-foam.(g) 1600–2000 Da range, (h) 2000–250,000 Da range .....	138
Figure.3. 15-Reaction scheme showing that all the free-OH groups in a glucose.....	142
Figure.3. 16-CP-MAS <sup>13</sup> C NMR of non-isocyanate polyurethane (NIPU) chestnut tannin extract bio-foam .....	143
Figure.4. 1- Results of the effect of different concentration of solution on the leaching Process (GroupF1).....	166
Figure.4. 2- Results of the effect of different ratio of TAN/FA Ratios on the leaching Process (GroupF2).....	166
Figure.4. 3-The reaction between the polyphenolic groups and furfuryl alcohol.....	168
Figure.4. 4-Mechanism of crosslinking in the polycondensation of furfuryl alcohol: a) Conjugation of structure and b) Diels-Alder cycloaddition of different chains [11].....	168
Figure.4. 5- Autocondensations of furfuryl alcohol under acid conditions [242]. .....	169
Figure.4. 6- Autocondensation of condensed tannin under acidic conditions through the hydrolysis of flavonoids heterocycles .....	169
Figure.4. 8-Infrared spectroscopy of untreated beech wood and mimosa tannin. ....	170
Figure.4. 9-Infrared spectroscopy of different polymerized solutions with varied ratios of Tan/FA.....	170
Figure.4. 10-Infrared spectroscopy of different polymerized solutions with varied ratios of Tan/FA.....	171
Figure.4. 11-FTIR spectra of untreated beech vs tannin-furanic polymer vs tannin-furanic-treated beech.....	172
Figure.4. 13-Effect of varied concentration on decay durability for the group(F1) against white-rot and Brown-rot .....	175
Figure.4. 14-Illustration of Decay Durability: Comparison of untreated and treated samples with varied ratios of Tan/FA against whiter rot and brown rot, including leaching rate.....	177
Figure.4. 15-Thermogravimetric Analysis (TGA) of Untreated and Treated Samples with Varied Solution (F2) .....	178
Figure.4. 16-Thermogravimetric Analysis (DTG) of Untreated and Treated Samples with Varied Solution (F2). .....	179
Figure.4. 17-Comparaision of Leaching Values and Mass Gain Results .....	189
Figure.4. 18-The Comparaision between Unmodified Tannin and Modified Tannin .....	190
Figure.4. 19-FTIR spectroscopy of the polymers for the polymers:STD, C18,I, and C18,II.....	191
Figure.4. 20-Comparison FTIR spectroscopy of impregnated samples (STD, C16.I, and C16.II) with Unmodified Beech Wood. ....	191
Figure.4. 21-Results of biological durability under the influence of white and brown rot.....	193
Figure.4. 22-Thermogravimetric Analysis (TGA) of treated and control samples. ....	194
Figure.4. 23-Thermogravimetric analysis (DTG) of treated and control samples.....	195
Figure.4. 24-Wettability results of untreated samples, treated Samples without modified Tannin (STD), and modified Tannin (Beech-C12, C16, C18) .....	196

## Liste des Tableaux

Tableau.2. 1-Composition of standard tannin-based foams and tannin-based foams formulated with oil-grafted tannins .....	55
Tableau.2. 2-Yield of oil-grafted tannins using different fatty acid chlorides. ....	59
Tableau.2. 3-Different compositions used to produce oil-grafted tannin using palmitoyl chloride .....	60
Tableau.2. 4-Characterization by MALDI-TOF of oil-grafted tannins using palmitoyl chloride .....	63
Tableau.2. 5-Density of tannin foams with oil-grafted tannin.....	71
Tableau.2. 6-Contact angle measurement and value of total surface free energy (SFE).....	73
Tableau.2. 7-Surface energy of liquids with polar and dispersion surface energy components.....	74
Tableau.2. 8-Formulations used to prepare the rigid and flexible foams .....	79
Tableau.2. 9-The initials observation for the modified rigid foams .....	82
Tableau.2. 10-The initials observation for the modified flexible foams .....	82
Tableau.2. 11-The results of the compression test at maximum and yield point for the rigid foams.....	88
Tableau.2. 12-Results of the compression test at maximum and yield point for the flexible foams.....	89

Tableau.3. 1-Relative proportion of the proportions of materials used to prepare the chestnut tannin NIPU resin.	116
Tableau.3. 2-Proportion of materials used to prepare the NIPU foams.	117
Tableau.3. 3-Compression tests compression.	123
Tableau.3. 4- Ignition test comparison	124
Tableau.3. 5-The relative proportion of materials used to prepare the chestnut tannin NIPU resin.	130
Tableau.3. 6-The proportion of materials used to prepare the NIPU foams.	132
Tableau.4. 1-Sample dimension and their corresponding characterization	161
Tableau.4. 2-Formulation of the applied impregnating solution (F1)	161
Tableau.4. 3-Formulation of the applied impregnating solution (F2)	162
Tableau.4. 4-The results of leaching process (F1)	165
Tableau.4. 5-The results of leaching process (F2)	166
Tableau.4. 7.The results of decay durability against brown-rot (CP)for the group(F1)	174
Tableau.4. 8.The results of decay durability against White-rot (CP) for the group (F1)	174
Tableau.4. 9- The decay durability of untreated and tannin-furanic treated samples with varied ratios of Tan / FA against white rot ( <i>Coriolus versicolor</i> ).	176
Tableau.4. 10- The decay durability of untreated and tannin-furanic treated samples with varied ratios of Tan / FA against brown rot ( <i>Coniophora puteana</i> ).	176
Tableau.4. 11-Sample dimensions and their corresponding characterization	186
Tableau.4. 12The formulations of the impregnation solutions with proportion equal (TAN: FA) (1:1)	187
Tableau.4. 13-Results of Leaching Test Following Modification Process	188
Tableau.4. 14-Biological durability of treated and untreated samples against brown and white rot.	192

## Liste des Annexes

Annex. 1-Characterization of oil-grafted tanin with oleoyl chloride by MALDI-TOF	211
Annex. 2. MALDI-TOF mass spectrum of oil-grafted tanin with oleoyl chloride (a) from 400 Da to 800 Da, (b) from 800 Da to 1200Da,(c) from 1200 Da to 1600 Da , (d)from 1600 Da to 2400 D.	213
Annex. 3-Characterization of oil-grafted tanin with lauryl chloride by MALDI-TOF	214
Annex. 4-MALDI-TOF mass spectrum of oil-grafted tanin with lauryl chloride (a) from 400 Da to 800 Da, (b) from 800 Da to 1200 Da, (c) from 1200 Da to 1600 Da, (d) from 1600 Da to 2000 Da.	219
Annex. 5-Species assignments of MALDI ToF analysis for a chestnut tanin extract non-isocyanate polyurethane (NIPU) foam.	220





## **Introduction**

Les matériaux issus des ressources fossiles, notamment le pétrole, font partie intégrante de notre vie quotidienne. Malgré les pollutions causées par ces ressources, la demande pour leur utilisation dans diverses applications augmente chaque année. Cependant, étant donné que les ressources fossiles s'épuisent progressivement, il est essentiel de trouver des alternatives issues de ressources renouvelables afin de réduire notre dépendance à ces ressources. Le monde scientifique s'investit massivement dans la recherche de nouvelles technologies visant à créer de nouveaux matériaux respectueux de l'environnement.

Ces dernières décennies, la préservation de l'environnement et le développement durable ont suscité un grand nombre de recherches scientifiques à l'échelle mondiale. La sensibilisation accrue aux enjeux environnementaux a conduit à des recherches scientifiques approfondies sur le développement de matériaux biosourcés, moins nocifs et renouvelables, en remplacement des matériaux synthétiques. De nombreuses études ont été réalisées afin de trouver les meilleurs matériaux naturels applicables dans le cadre de la chimie.

Les matériaux biosourcés offrent une alternative durable et respectueuse de l'environnement aux matériaux traditionnels dérivés des ressources fossiles. Parmi ces matériaux, le bois et ses dérivés, tels que la cellulose, la lignine et les tanins extractibles, présentent un potentiel prometteur pour la conception de matériaux innovants.

En effet, le bois représente une véritable source d'innovation offrant de nombreuses possibilités d'utilisation dans le contexte actuel du développement durable. Il contient des composés polymères tels que la cellulose, les hémicelluloses et les lignines, ainsi que des composants extractibles polymérisables comme les tanins [1]. Les propriétés du bois et des composés extractibles du bois offrent non seulement des opportunités d'amélioration des propriétés des matériaux, mais permettent également la production de matériaux respectueux de l'environnement tels que des colles, des isolants et des composites à base de bois.

Les tanins, en raison de leurs groupes phénoliques qui sont similaires à ceux issus des ressources fossiles, offrent un potentiel significatif pour les remplacer dans le développement de matériaux biosourcés et la synthèse de polymères respectueux de l'environnement. Cependant, en raison de l'abondance de groupes hydroxyles, ils sont très hydrophiles, ce qui entraîne certains problèmes lors de leur utilisation dans le domaine des matériaux, notamment dans la fabrication de mousses, tels qu'une faible hydrophobicité et une forte friabilité.

Cette thèse se concentre principalement sur la conception de matériaux biosourcés à base de tanins tels que les mousses et les composites du bois. Le premier objectif de cette thèse consiste à explorer le

potentiel des tanins condensés et hydrolysables dans la conception de mousses isolantes. Ces matériaux présentent un intérêt particulier dans la recherche de solutions plus durables pour l'isolation des bâtiments et des infrastructures. Pour ce faire, différentes approches ont été suivies, notamment le développement de mousses tanin-furaniques, de mousses de type NIPU (polyuréthanes sans isocyanate). Ces matériaux ont été soigneusement évalués en termes de propriétés d'isolation thermique et de résistance à l'absorption d'eau.

Le deuxième objectif de cette thèse est d'exploiter le potentiel des tanins pour permettre une modification chimique du bois. Le bois est en effet un matériau naturel de plus en plus utilisé mais qui nécessite des traitements de protection dans le cas des essences peu durables susceptibles d'être dégradées par différents facteurs biotiques ou abiotiques. Nous avons étudié la possibilité d'insérer des tannins en tant que comonomères lors de la furfurylation du bois par l'alcool furfurylique.

Après une revue de l'état de l'art tel que présenté dans le chapitre I, les résultats obtenus sont présentés dans trois chapitres distincts : le chapitre II présente la modification chimique des tanins condensés (Mimosa) en vue de diminuer leur caractère hydrophile et de les utiliser afin de concevoir des mousses tanins furaniques avec des propriétés améliorées. De plus, le chapitre III traite de la conception de mousses polyuréthanes sans isocyanate à partir de tanins hydrolysables (Châtaignier). Ces deux chapitres fournissent une analyse détaillée des performances et des caractéristiques de ces matériaux innovants, permettant ainsi d'évaluer leur pertinence dans le domaine de l'isolation. Dans le chapitre IV, nos recherches se sont concentrées sur la conception de composites à base de bois utilisant des tanins condensés. Différents paramètres ont été variés, notamment le rapport entre le tanin et l'alcool furfurylique, ainsi que la présence de tanin modifié, dans le but d'améliorer les propriétés du bois.

Ce manuscrit de thèse se termine par une conclusion générale qui résume de façon synthétique les principaux résultats obtenus et qui offre quelques perspectives à nos travaux.

D'une façon générale, la recherche et le développement de matériaux biosourcés dérivés des tanins ouvrent de nouvelles perspectives pour la conception de matériaux respectueux de l'environnement.

# **Chapitre I- Etat de l'art**



## **1.Présentation générale des Tanins**

### **1.1. Historique**

Le nom tanin a été officiellement attribué à la procédure de tannage dans la production du cuir. Pendant très longtemps, les matières tannantes naturelles ont été utilisées directement pour l'industrie de tannage. En principe, la peau était trempée dans une solution aqueuse de matière tannante broyée. Le tanin se dissolvait d'abord dans l'eau, puis était progressivement absorbé par la peau, ce qui la transformait peu à peu en cuir.

L'histoire de la chimie des tanins remonte au milieu du XVIIe siècle, lorsque le chimiste italien Giovannetti a étudié les interactions entre les solutions de fer et les substances appelées à l'époque des astringents. Au niveau universitaire, les chercheurs de l'Université de Dijon ont identifié la présence d'un acide dans ces composés et l'ont nommé acide gallique. Jusqu'au début du XIXe siècle, les tanins étaient reconnus comme un groupe discret de molécules qui ont des propriétés variées en fonction de leur teneur en acide gallique.

Au début du XXe siècle, la France était le premier pays producteur de tanins en Europe. Cette production était seulement pour l'industrie du cuir.

Après la deuxième guerre mondiale, le remplacement du cuir par des matériaux synthétiques a réduit la production commerciale de tanin. À partir des années 70, la troisième période d'utilisation industrielle commence grâce à l'apparition des enjeux environnementaux, notamment l'application de tanin dans le domaine des nouveaux matériaux biosourcés tels que les mousses, les adhésifs [1], [2].

### **1.2. Description et propriétés**

Les tanins sont des produits végétaux qui se trouvent dans presque toutes les parties des plantes supérieures comme les racines, l'écorce, le bois et les feuilles. Ils sont des métabolites secondaires, des composés polyphénoliques, et leur rôle principal est la défense contre des agents de biodégradation tels que les insectes, les infections alimentaires, les champignons ou les bactéries [3]. La structure des composés polyphénoliques dans les tanins ressemble aux composés phénoliques issus des ressources fossiles. Les tanins peuvent donc être utilisés dans la chimie verte et de la conception de matériaux renouvelables comme les adhésifs en particulier les adhésifs [2] pour le bois ou les mousses [4].

Les tanins ont des propriétés très variables et cette diversité est liée aux différents types d'arbres et à leur zone de stockage dans les plantes : le pin (*Pinus radiata*), le chêne (*Quercus robur*) et le mimosa (*Acacia mearnsii* ou *mollissima*) contiennent la majorité de leurs tanins dans l'écorce,

le gambier (*Uncaria Gambir*) dans les feuilles, le pecan (*Carya illinoensis*) dans les noix de moelle, tandis que le châtaignier (*Castanea sativa*) et le quebracho (*Schinopsis lorentzii* ou *balansae*) stockent leurs tanins dans toute leur structure [1], [4].

Ils peuvent exister dans diverses parties des plantes :

- Racines ou rhizomes (Ratanhia, Rhubarbe)
- Écorces (Chêne, Quinquina),
- Bois (Acacia à cachou)
- Feuilles (Hamamélis)
- Fleurs (Rose rouge)
- Graines (noix d'Arec, Kola).

Cependant, il y a une accumulation dans les écorces âgées et les tissus présentant des pathologies telles que les galles [4]–[6].

Les tanins sont des composés à faible masse moléculaire qui peuvent être extraits du bois et de l'écorce à l'aide de solvants polaires tels que l'eau, l'éthanol et l'acétone, ou de solvants apolaires tels que le toluène, le cyclohexane et le dichlorométhane.

Même s'ils ne sont présents qu'en faible quantité, les tanins ont une influence significative sur les caractéristiques des plantes telles que l'odeur, la couleur et la résistance aux agents de dégradation biologique de la substance à partir de laquelle ils sont extraits [7].

Ces composés phénoliques peuvent s'associer aux protéines pour former des complexes qui peuvent être solubles ou insolubles. Bien que leurs structures chimiques varient, ces composés ont des propriétés commune [1], [2], [4]–[6]:

- Ils précipitent les protéines de leur solution, en particulier la gélatine [1], [4].
- Ils donnent avec les sels et des métaux lourds des laques de couleurs variées ; en particulier avec les sels de fer [1], [4]
  - Bleu-noir avec les tanins hydrolysables
  - Brun-vert avec les tanins condensés
- Ils sont un corps généralement amorphe et sans point de fusion précis.
- Ils sont plus ou moins solubles dans l'eau, dans l'alcool et l'acétone, insolubles dans les solvants organiques apolaires. En raison de la grosseur de leurs molécules et de leur tendance à se polymériser par oxydation, les solutions aqueuses de tanin se comportent comme des dispersions colloïdales [1], [4].

- Ils sont capables de se fixer sur la substance dermique de la peau en tripe et de la transformer en cuir [1], [4].

### 1.3. Classification et structure chimique

Du point de vue composition ou structure chimique, il existe deux catégories de tanins : les tanins hydrolysables et les tanins condensés ou flavonoïdes. En général, les tanins hydrolysables comprennent les gallotanins et les ellagitanins, tandis que les tanins condensés, tels que les tanins poly flavonoïdes, sont stables et peu sujets à l'hydrolyse [2], [7], [8].

#### 1.3.1-Tanins hydrolysables :

Les tanins hydrolysables se présentent en faibles quantités dans les plantes, ils sont un mélange des groupes phénoliques comme l'acide gallique et l'acide ellagique. Ils sont classés selon les produits obtenus après hydrolyse, en gallotanins (composés d'acide gallique et de glucose) et en ellagitanins (composés de 106 motifs biaryliques et de glucose). Ils sont constitués de produits phénoliques simples : ce sont des esters d'acide gallique et de ses dimères (acide digallique, acide ellagique) et de monosaccharides (surtout le glucose) [4]. Ils libèrent une partie non phénolique et une partie phénolique constituée principalement d'acide gallique (cas des gallotanins) ou de l'acide ellagique qui est un dimère de l'acide gallique (cas des ellagitanins) après hydrolyse [8]–[10](Figure.1.1).

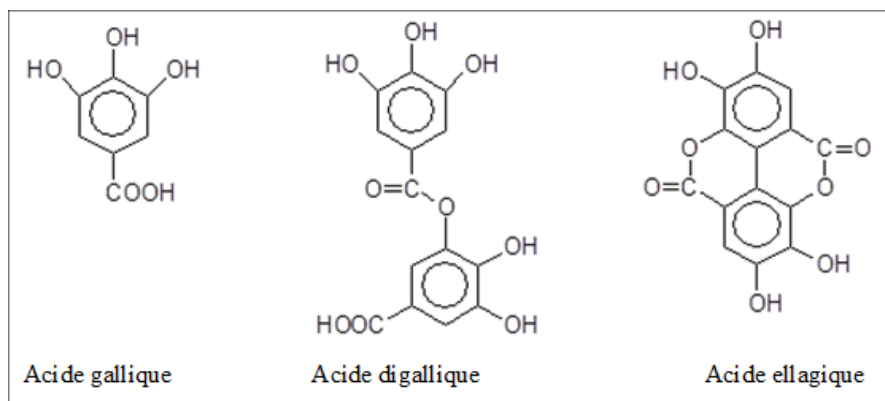


Figure.1. 1-Constituants principaux des tanins hydrolysables

#### Gallotanins

Les Gallotanins sont des tanins simples hydrolysables. Ils sont des polymères naturels formés par l'estérification des groupes hydroxyles des monomères D-glucose et gallique acide. Bien que les gallotanins soient formés par les groupes polyols, polyphénoliques, ils sont attachés à des sucres. Les groupes hydroxyles sont capables d'être substitués partiellement ou complètement par les unités de gallyol. Si cette substitution est partielle, les groupes hydroxyles



libres peuvent être substitués par d'autres résidus comme penta-(digalloyl)-glucose( $\beta$ -PGG) et des tétra-(digalloyl)-glucose(TGG) ou tri-(digalloyl)-di-(galloyl) glucose(Figure.1.2) [10], [11].

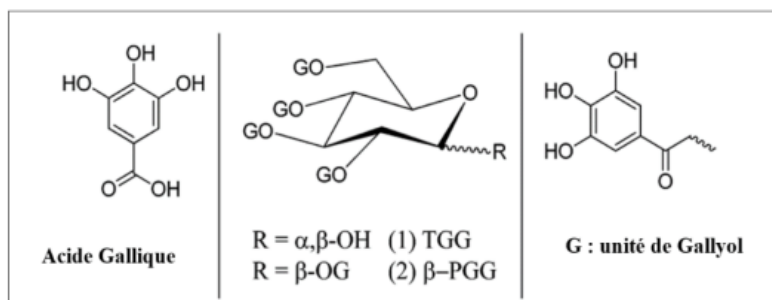


Figure.1. 2-la structure de gallotanins

### Ellagitanins

Contrairement aux gallotanins, les ellagitanin contiennent des motifs de liaison supplémentaires qui proviennent de réactions de couplage oxydatif entre les fragments galloyl. La biosynthèse des ellagitanin est donc une progression enzymatique oxydative des gallotanins. La première étape est une oxydation du 1,2,3,4,6-pentagalloylglucose dans l'ellagitanin monomère. La seconde étape consiste essentiellement en une dimérisation après une seconde oxydation spécifique à médiation par une enzyme pour former un hexahydroxydiphényle(Figure.1.3) [10]–[12].

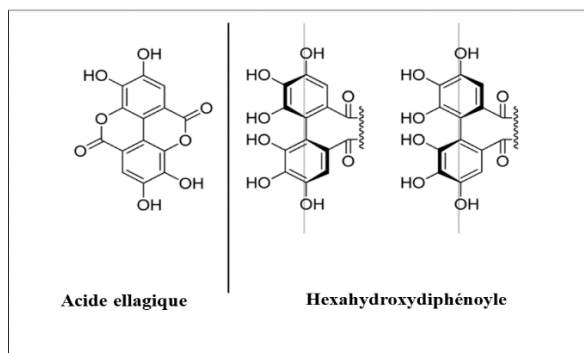


Figure.1. 3-la structure des acides ellagiques

Les tanins hydrolysables ont déjà été utilisés comme substituts partiels du phénol dans la fabrication de résines phénol formaldéhyde [4], [13], [14] , Leur utilisation reste très limitée dans le domaine des colles en raison de leur faible réactivité avec le formaldéhyde. Récemment, ce type de tanin a démontré sa capacité à participer aux réactions de création de liaisons polyuréthane en présence de diamines et sans isocyanate [15]. C'est pour cette raison que ce

type de tanin a fait l'objet de la conception d'une mousse isolante thermique avec la technique de bio polyuréthane non isocyanate.

### 1.3.2. Tanins condensés

Les tanins condensés représentent plus de 90% de la production mondiale de tanins commerciaux. Ils sont constitués d'unités flavonoïdes (Figure.1.4) présentant différents degrés de polymérisation, ils sont associés à leurs précurseurs : catéchines (c), leucoanthocyanes (flavanes-3,4-diols) [6], [16], [17] et à des carbohydrates dont la plus ou moins grande proportion influence la viscosité et la réactivité du tanin.

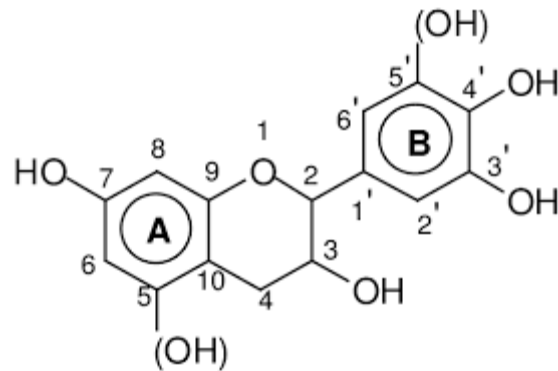


Figure.1. 4- Schéma d'un flavonoïde et sa numérotation[1], [2], [4]

Comme le montre le schéma précédent, il est possible d'obtenir deux types d'anneau A et deux types d'anneau B[1], [2], [4], [6] :

- Cycle A porte un seul groupe hydroxyle en C7 : cycle résorcinol.
- Cycle A porte deux groupes hydroxyles en C5 et C7 : cycle phloroglucinol.
- Cycle B porte deux groupes hydroxyles en C3' et C4' : cycle catéchol.
- Cycle B porte trois groupes hydroxyles en C3', C4' et C5' : cycle pyrogallol.

A partir de ces différents types de cycles, il a été défini une nomenclature des polyflavonoïdes [1], [2], [4], [16] – [18] (Figure.1.5).

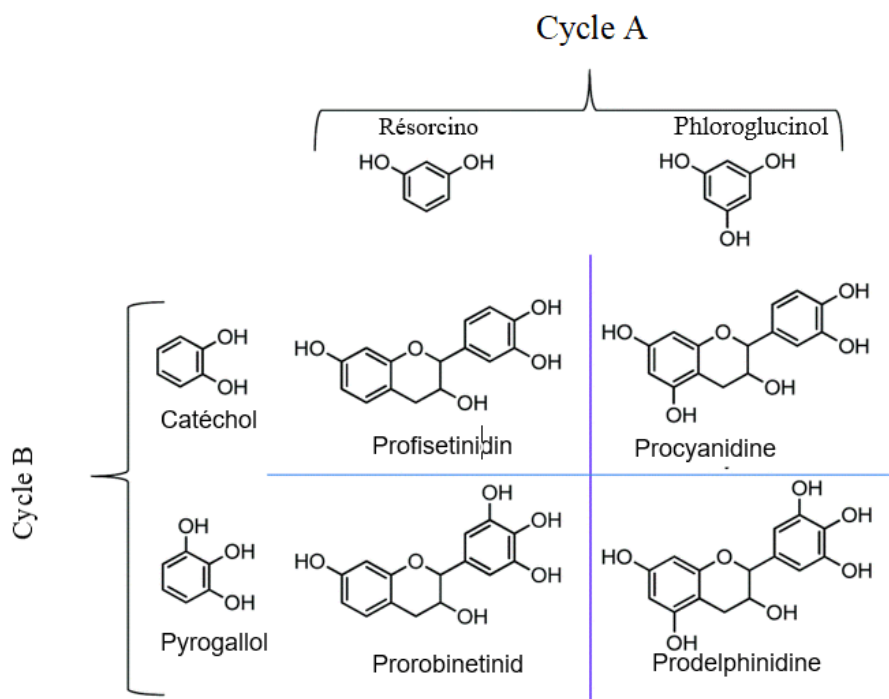


Figure.1. 5-les quatre type de poly flavonoïde à partir de deux anneaux [19]

- Cycle A type phloroglucinol et cycle B type pyrogallol : prodelphinidine (l'élément de base est la gallocatéchine).
- Cycle A type phloroglucinol et cycle B type catéchol : procyanidine (l'élément de base est la catéchine).
- Cycle A type réSORCINO et cycle B type pyrogallol : prorobinetinidine (l'élément de base est le robinetinidol).
- Cycle A type réSORCINO et cycle B type catéchol : profisetinidine (l'élément de base est le fisetinidol) [4], [5], [10], [19].

Les tanins condensés sont toujours constitués d'un mélange, présentant des proportions diverses des quatre types de polyflavonoïdes définis en Figure 1.5. Ainsi, pour le type de cycle A, la fréquence du cycle de type phloroglucinol par rapport au type réSORCINO permet de déterminer la réactivité du tanin vis-à-vis d'un aldéhyde et de prévoir la qualité du réseau d'enchevêtrement. Concernant le cycle B, la fréquence des cycles de type pyrogallol par rapport à ceux de type catéchol influence l'ouverture de l'hétérocycle pyranique et détermine le type de réarrangement à envisager pour la structure sous conditions alcalines ou basiques [20], [21].

L'utilisation de la technique d'analyse  $C^{13}$  RMN pour les tanins condensés a révélé les types de polyflavonoïdes présents dans un tanin spécifique. Cependant, cette méthode ne permet pas de distinguer entre les prodelphinidines et les procyanidines, ni entre les prorobinetinidines et les profisetinidines [20]–[22]. C'est la raison pour laquelle on compare (prodelphinidines + procyanidines) à (prorobinetinidines + profisetinidines).

Les tanins condensés sont formés par une répétition de 3 à 8 unités de flavonoïdes. Ces flavonoïdes sont principalement de deux types : les flavan-3-ols et les flavan-3,4-diols. La condensation des unités flavonoïdes repose sur des liaisons interflavonoïdes 4,6, résultant d'une formation initiale de liaisons interflavonoïdes 4,8 entre une unité de type A-phloroglucinol, comme la catéchine, et des unités de type réSORCINOL possédant le cycle A (Figure.1.6) [2],[18],[20].

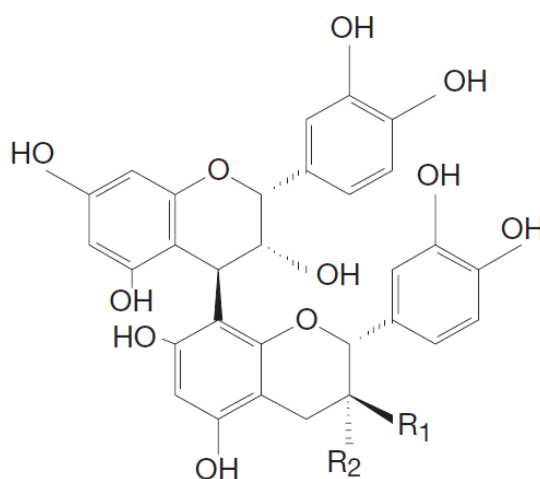


Figure.1. 6-Structure d'un tanin condensé (proanthocyanidine)

Il y a eu de nombreuses recherches sur l'utilisation de ces tanins condensés [23]–[26].

Les polyflavonoïdes sont capables d'assister dans des réactions radicalaires d'autocondensation en présence de bases ou d'acides faibles de Lewis [27]–[33].

Ainsi, une résine est produite sans dégagement de formaldéhyde libre mais elle peut être utilisée uniquement à l'intérieur [34]. L'analyse thermomécanique en flexion trois points a permis de quantifier l'enchevêtrement du réseau par détermination du nombre moyen de degré de liberté des segments de polymères au cours de l'autocondensation des tanins [4], [35].

Dans l'analyse des thermogrammes obtenus, l'augmentation du module d'Young est liée à deux phénomènes : la progression de la réaction d'autocondensation du tanin par paliers successifs correspondant aux différences de réactivités des sites disponibles sur le cycle A et le cycle B mais aussi l'autocondensation à basse température initiale qui conduit à la formation de polymères linéaires dont la longueur augmente jusqu'à une valeur limite qui dépend de la

température et de la concentration, longueur critique à partir de laquelle se forme un réseau d'enchevêtrement de ces polymères linéaires qui correspond à un autre palier sur la courbe du Module d'Young[35], [36].

L'analyse TMA a été utilisée pour étudier les résines de type phénol-formaldéhyde. Cette analyse a permis de déterminer deux points importants : le point de gel, qui correspond au début de l'augmentation du module d'Young, et le point de vitrification de la résine, qui correspond au point d'inflexion de la courbe du module [37]–[39].

Pour les tanins condensés, qui sont des composés phénoliques complexes, il n'est pas possible de définir clairement ces deux concepts car la courbe du module d'Young présente plusieurs pics et plusieurs paliers. Par conséquent, il est nécessaire d'identifier les différents points d'inflexion de la courbe en se basant sur les pics de la dérivée première du module, dans l'ordre où ils apparaissent : Le premier point d'inflexion correspond au début de l'enchevêtrement des polymères linéaires, une sorte de pseudo vitrification. Ensuite, on observe le vrai début de la vitrification, qui est dû à la formation du réseau d'enchevêtrement tridimensionnel résultant de la réactivité des sites du cycle A. Enfin, on observe le renforcement du réseau précédemment formé par des réactions sur les sites du cycle B[4], [35], [36].

L'analyse des mécanismes réactionnels radicalaires a permis de découvrir que les composés phénoliques sont capables de produire des radicaux phénoxyles (de type  $\Phi-O\bullet$ ) qui sont relativement stables. Ces radicaux ont la capacité de ralentir ou même d'empêcher la progression de la polymérisation radicalaire des tanins [39], [40].

En étudiant les finitions pour la protection du bois, il est intéressant de considérer les capacités antioxydantes des tanins. Cette propriété est évaluée par leur capacité à former rapidement des radicaux, soit par transfert de radicaux préexistants chez les tanins vers un radical phénoxy plus stable, soit par action de l'irradiation lumineuse sur le tanin. La vitesse de disparition des radicaux phénoxyles formés est également prise en compte. Cette étude a été menée à l'aide de la Spectroscopie de Résonance Paramagnétique Électronique (RPE). Elle a permis de déterminer que quatre paramètres, classés par ordre décroissant d'importance, influent sur les capacités antioxydantes des tanins. Ces paramètres sont [1], [4] :

- L'état colloïdal de la solution de tanin, lié à la présence de carbohydrates [31], [32], [41].
- La stéréochimie des tanins étudiés est liée à la facilité de formation des liaisons inter flavonoïdes [41], [42].
- Facilité d'ouverture de l'hétérocycle pyranique [2], [42].

- Nombre de groupes hydroxyles présents sur l'anneau A et l'anneau B du tanin.

En conséquence, il est possible de conclure que les tanins condensés présentent des propriétés antioxydantes nettement supérieures à celles des tanins hydrolysables. De plus, le tanin de quebracho est un antioxydant plus efficace que le tanin de mimosa [41], [42].

Différentes techniques d'analyse ont également permis d'isoler et d'identifier les molécules constituant les tanins, ainsi que leur degré de polymérisation, en utilisant notamment la chromatographie liquide haute performance [43], par chromatographie à perméation de gel [44]. La spectroscopie d'absorption de l'ultraviolet [45], [46] permet d'identifier globalement la famille d'un tanin alors que la spectroscopie infrarouge à transformée de Fourier permet de définir un tanin donné [47]. La spectroscopie de l'infrarouge a également permis de déterminer la proportion d'extractibles, de tanins et de non-tanins pour une espèce de tanin donnée [47], [48].

## **2. Matières tannantes végétales utilisées dans cette étude**

### **2.1. Extraction de tanins**

Les tanins sont des matériaux extractibles. L'extraction de tanin est une procédure de la circulation d'un solvant à travers des matières tannantes afin d'extraire des molécules solubles.

Un extrait tannant est le résultat de la concentration par évaporation de l'eau de la solution obtenue par lessivage méthodique de la matière tannante naturelle.

La préparation des matières tannantes et la procédure d'extraction exercent une sérieuse influence sur la composition finale de l'extrait de tanin.

Les composés phénoliques peuvent être extraits des plantes fraîches, congelées ou séchées. En général, après le séchage des matières tannantes, il faut les broyer et homogénéiser. La technique de séchage a également une influence sur la composition finale des extraits de tanin. Les méthodes d'extraction sont généralement basées sur des solvants [4], [5], [43]. La méthode traditionnelle utilisée en industries est basée sur l'eau bouillante. Les matières tannantes soit le bois (tanin châtaignier) soit l'écorce (tanin mimosa) sont découpées en taille maximum de 1,5-2 cm et l'épaisseur de 5-10mm.

Le processus d'extraction est mené méthodiquement en suivant le principe du contre-courant afin d'extraire le maximum de tanin et d'obtenir des solutions les plus concentrées possibles. Pour ce faire, les conditions d'extraction sont telles que le bois le plus épuisé est en contact avec la solution la moins concentrée, tandis que le bois le plus riche est en contact avec la solution la plus concentrée [4]. Cette procédure est effectuée avec la proportion égale de la matière

tannate et l'eau en température de 50-110 °C sous la pression 0,8 bar maximum dans plusieurs cycles de 6-10 h. La solution obtenue contient 4-5% de tanin en masse avec un rendement d'extraction de 60-65%. la concentration à l'aide de plusieurs cycles de l'évaporation sous vide conduit à une solution de 40- 50% en masse. Cette solution à l'aide d'un séchage par atomisation peut arriver à la concentration de 90-96% de la masse sèche. L'opération consiste à pulvériser l'extrait liquide sous forme de très fines gouttelettes (d'un brouillard) dans une enceinte traversée par un courant d'air chaud. L'eau s'évapore presque instantanément et les gouttelettes se transforment en poussière. Il suffit ensuite de séparer ces particules solides de l'air et de la vapeur d'eau [4], [43], [44]. L'extraction peut se faire seulement avec l'eau mais la plupart du temps, les solvants organiques comme l'éthanol [43] , le méthanol [45] ou un mélange [47] des solvants s'utilisent sans ou avec l'eau afin d'augmenter l'efficacité de l'extraction. Ces nouvelles méthodes apportent une forte amélioration dans l'extraction des tanins. Les méthodes d'extraction sont variées et chaque matière tannate demande un solvant et une procédure d'extraction spéciale. Le rendement et la composition des extraits dépendent totalement du type de solvant (polarités), du temps et de la température d'extraction et de proportion d'échantillon/solvant [47], [48].

## **2.2. Tanins extraits du bois**

### **Tanins de châtaignier (*Fagaceae, Castanea sativa*)**

Le tanin châtaignier est extrait d'un arbre qui pousse dans les régions tempérées du sud de l'Europe. Cependant, seul le tronc et les grosses branches de l'arbre sont utilisés pour obtenir le tanin. La quantité de tanin présent dans les arbres augmente avec l'âge. Ainsi, la teneur en tanin d'un arbre de 8 ans est d'environ 1,5%, tandis que pour un arbre de 70 ans, elle peut atteindre 10-13%. Les arbres entre 50 et 70 ans sont considérés comme étant les plus adaptés pour l'extraction de tanin.

Le tanin châtaignier est un ellagitannin et plus de 78% de sa composition sont constitués par la vescalagine et la castalagine [49]. Les tanins anomères correspondants sont appelés vescaline et castaline et sont les constituants principaux des extraits de tanin comme le montre la figure suivante (Figure.1.7).

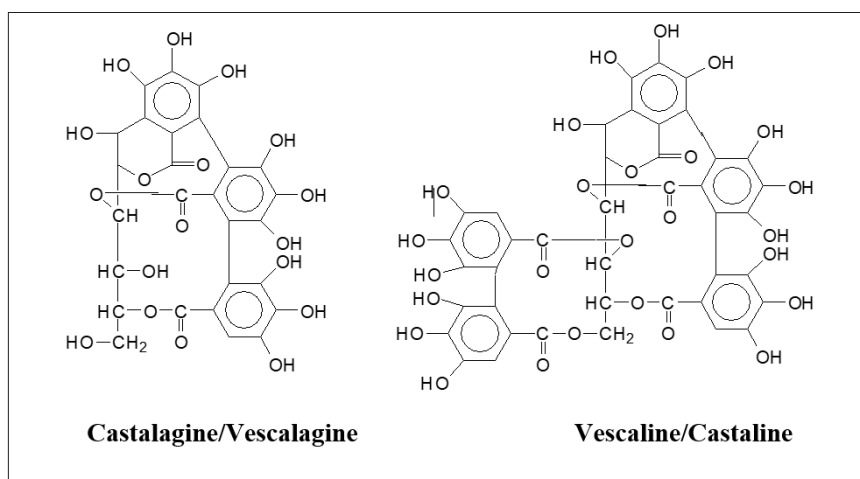


Figure.1. 7- Structure de la castaline/vescaline et de la castalagine/vescalagine

L'extrait commercial de tanin châtaignier est composé de castalagine, vescalagine, castaline et vescaline à 70% [50], [51] et 30% par des autres composés comme pentagalloyl glucose [50], [52]. En réalité, les principaux constituants sont des chaînes de glucose sur lesquelles plusieurs unités de glucose sont estérifiées par l'acide gallique ou l'acide digallique [50]–[52].

### 2.3. Tanins issus des écorces :

#### **Tanin de mimosa** (*Leguminosae, Acacia mearnsii*)

Ce type de tanin, à l'origine, est l'extrait de l'écorce d'un acacia en Australie. Il y a 350 espèces de cet arbre dans les régions boisées de ce continent. Aujourd'hui, cet extrait commercialisé provient par une large plantation surtout dans les régions de l'Afrique du Sud.

Normalement, les arbres ont 20 mètres de hauteur à l'âge de 15 en ayant 35% de teneur moyenne en tanin. Ce type de tanin condensé a été étudié en détail pour les applications variées surtout dans le domaine des colles et des mousses.

À partir de ces écorces on prépare l'extrait de tanin de mimosa très utilisé par les tanneurs du monde entier. C'est un tanin condensé qui a été étudié en détails [2], [23], [24]. Il est constitué de 87 % de polyflavonoïdes de type (prorobinetinidines + profisetinidines) et de 13 % de (prodelphinidines + procyanidines). La condensation des unités flavonoïdes se produit par le biais de liaisons interflavonoïdes entre les carbones C4 et C6.



### 3. Réactivité des tanins condensés

Les tanins ont la capacité de participer à diverses réactions chimiques, ce qui ouvre de nombreuses possibilités de modifications. Ces modifications peuvent améliorer les caractéristiques des tanins, les substituer par d'autres groupes et les utiliser dans des réactions de polymérisation pour la conception de nouveaux matériaux.

Les réactions principales de tanin, notamment des tanins condensés sont classées en trois grandes catégories (Figure 1.8) [19].

- Réactivité des sites hétérocycles
- Réactivité des sites nucléophiles
- Réactivité des sites hydroxyles

Ces réactions peuvent également être considérées comme des modifications chimiques. Elles jouent un rôle important dans la synthèse des polymères en permettant la création de nouveaux blocs.

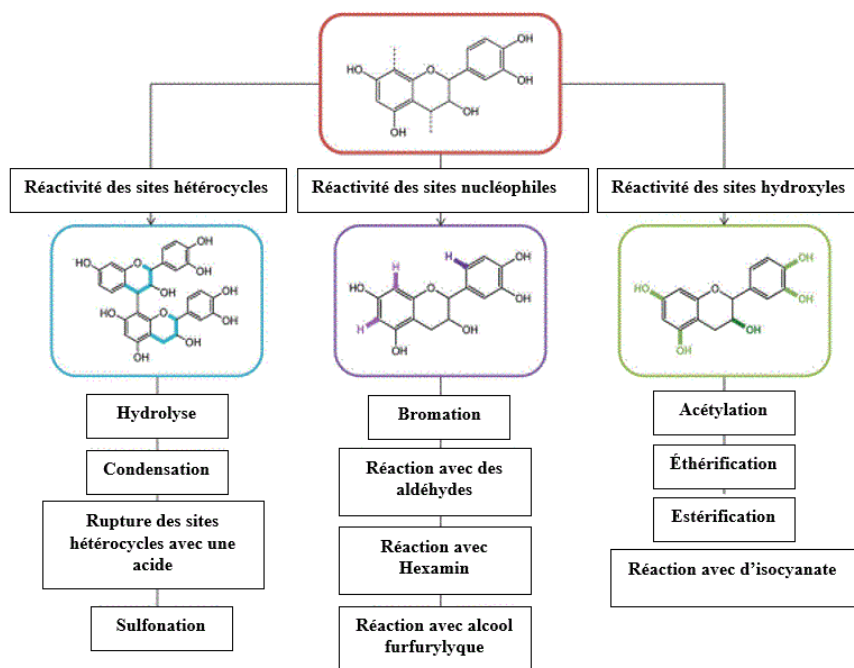


Figure.1. 8- Les réactions variées des tanins condensés.

#### 3.1. Réactivité des sites hétérocycles

Dans les deux conditions acide et basique, il est très possible d'observer des réarrangements comme l'hydrolyse [19] et l'autocondensation [2]. La rupture des liaisons interflavonoïdes peut également se réaliser en milieu acide, ce qui conduit à la formation de catéchines et d'anthocyanidines (Figure 1.9). La deuxième réaction est la condensation après hydrolyse de

l'hétérocycle. Les groupes formés à la suite à l'hydrolyse peuvent se condenser avec les sites nucléophiles d'une autre unité de tanin (Figure. 1.9).

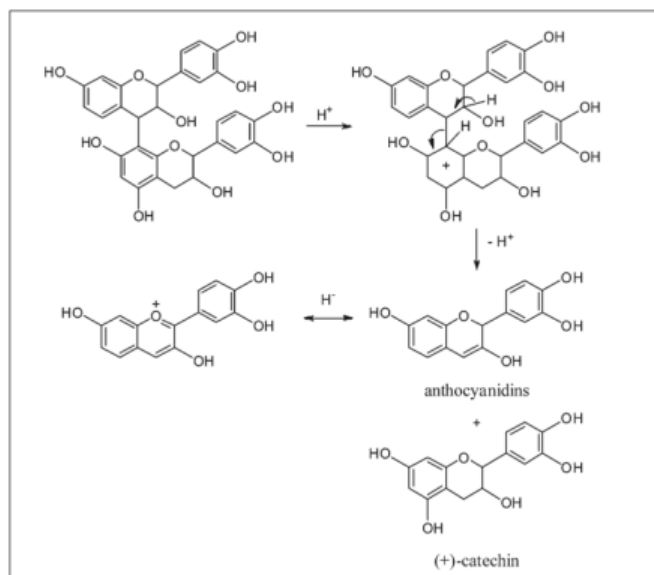


Figure.1. 9- Dégradation des tanins en catéchines et anthocyanidines en conditions acides [19]

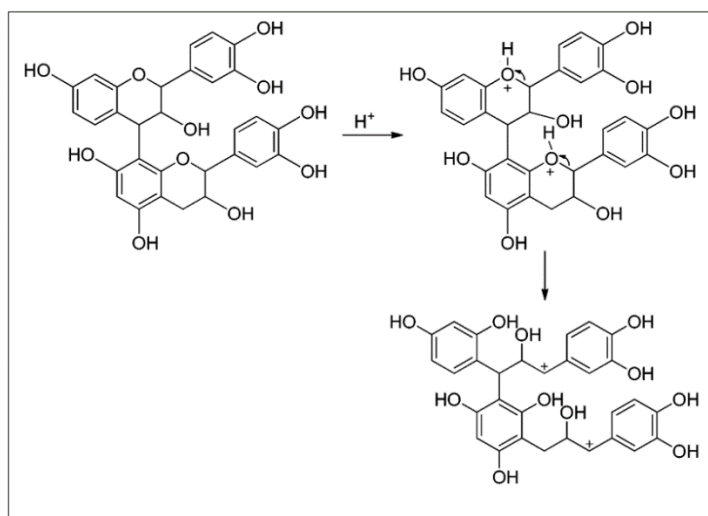


Figure.1. 10-Auto-condensation acide par hydrolyse de l'hétérocycle.

### 3.2- Réactivité des sites nucléophiles

En ayant des groupes phénoliques, les tanins ont la possibilité d'avoir des réactions sur les sites nucléophiles. Ces types de réactions, comme ceux avec des alcools et des aldéhydes, sont très importantes pour produire des matériaux dérivés du tanin. Les réactions principales des groupes phénoliques pour créer des chaînes de polymères, telles que la réaction avec l'alcool furfurylique ou les aldéhydes, se produisent sur ces sites.

En raison de la structure aromatique, la réaction de couplage peut également se produire avec un acide carboxylique et des aldéhydes.

### 3.2.1. Réaction avec l'alcool furfurylique

#### 3.2.1.1. Caractéristiques physico-chimiques de l'alcool furfurylique

Etant donné que l'alcool furfurylique est l'un des composés organiques importants dans cette étude, il est indispensable de le connaître en détail. L'alcool furfurylique est un liquide transparent et incolore à température ambiante, mais peut devenir jaune clair en fonction de son état de conservation. Ce produit est considéré comme nocif par inhalation [1], [4], [53], [54]. Ce composé organique présente des caractéristiques aromatiques et alcooliques.

L'alcool furfurylique est soluble dans l'eau et les alcools à faible poids moléculaire, et il présente une forte réactivité chimique dans le cadre des oxydations et des polymérisations. Ce produit est utilisé principalement dans la chimie des résines, des peintures, des matériaux synthétiques et surtout dans les fonderies.

#### 3.2.1.2-Production de l'alcool furfurylique

L'alcool furfurylique joue un rôle important dans la formation des mousses de tanin, car il représente environ 20% du poids des mousses une fois qu'elles sont produites. Ce produit chimique est généralement obtenu à partir des hémicelluloses de différents types de produits agricoles, principalement par des pentosanes des hémicelluloses (Figure.1.11).

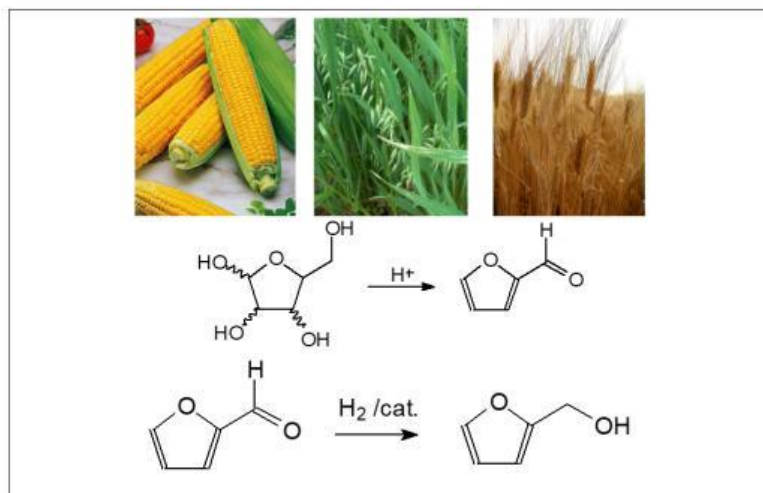


Figure.1. 11-la procédure de fabrication l'alcool furfurylique

Il existe de nombreux procédés et produits de départ documentés dans la littérature pour fabriquer du furfural [55], [56]. Les catalyseurs utilisés sont généralement constitués de métaux tels que le cobalt (Co) et le molybdène (Mo). Des études récentes ont montré l'efficacité des

mélanges de ces deux métaux (Co-Mo) ainsi que l'utilisation de bore (B) comme co-catalyseur [57] et Cu-MgO [58].

### 3.2.1.3-Réactivité de l'alcool furfurylique

L'alcool furfurylique peut être transformé en 2,5-bis(hydroxyméthyl)furan par réaction avec le formaldéhyde (Figure.1.12) [59]. La réaction avec le formaldéhyde permet de générer un composé qui peut servir d'intermédiaire très efficace dans la polymérisation mixte avec les tanins condensés [1], [5].

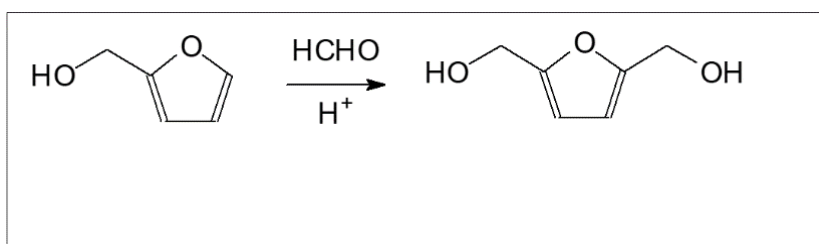


Figure.1. 12-la réaction avec le formaldéhyde

L'alcool furfurylique a la capacité d'assister une réaction d'autocondensation très exothermique dans un milieu acide, ce qui permet de renforcer les liaisons polymériques issues de ce composé organique (Figure.1.13).

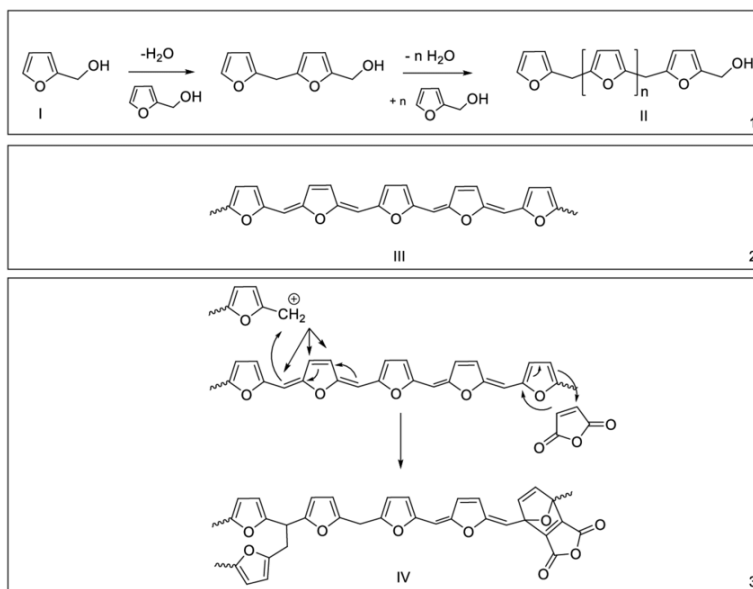


Figure.1. 13- la réaction autocondensation de l'alcool furfurylique

Une fois que l'énergie d'activation de cette réaction est atteinte, le processus devient auto-entretenu et tout l'alcool furfurylique est rapidement converti en polyalcool furfurylique. Afin de mieux comprendre le mécanisme de polymérisation de l'alcool furfurylique, des études ont été menées en utilisant des techniques telles que la spectrométrie UV, la spectroscopie infrarouge à transformée de Fourier (FTIR) et la résonance magnétique nucléaire (RMN) sur des polymères furaniques préparés en utilisant un solvant et sous une atmosphère d'azote [4], [60]. La réaction de polycondensation peut conduire à la formation de différents types de structures polymériques en fonction des conditions de catalyse appliquées. En effet, cette réaction peut conduire à la formation de polymères linéaires, ramifiés ou même à des structures tridimensionnelles.

De nombreuses recherches ont été effectuées pour évaluer la résistance thermique et à la corrosion de ces matériaux, ainsi que leur nature hautement ignifuge. Grâce à ces propriétés, ces produits sont fréquemment employés dans l'industrie de la fonderie et des revêtements anticorrosion [1], [4], [5].

### 3.2.1.4- Réaction des tanins avec l'alcool furfurylique

Des études initiales ont examiné la réactivité de l'alcool furfurylique, ainsi que celle de l'alcool furfurylique avec le tanin et la catéchine en milieu acide [61]–[63].

Les conditions mises en œuvre dans ce processus ont été choisies de manière à tenir compte de la réactivité très élevée de l'alcool furfurylique sur lui-même en milieu acide. Après séparation et purification via HPLC en phase inverse, deux flavonoïdes substitués en positions C8 et C6 par des groupements furanyles ont été obtenus avec des rendements respectifs de 4 % et 1,5 %. (Figure 1.14). Cependant, ces réactions ont montré un rendement très faible. Ceci peut être attribué à l'autocondensation de l'alcool furfurylique en milieu acide, ce qui entraîne la formation du poly(alcool furfurylique).[19].

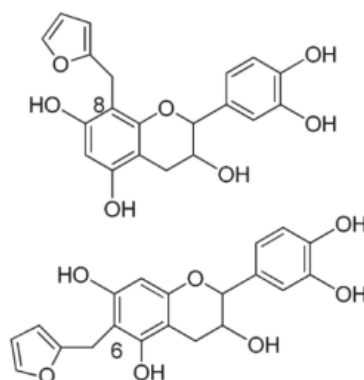


Figure.1. 14- Produits de réaction de l'alcool furfurylique sur la catéchine

### 3.2.2-Réaction des tanins avec des aldéhydes

La réaction avec des aldéhydes, notamment le formaldéhyde a un rôle très important lors de la préparation des matériaux dérivés de tanin tels que des colles et des mousses.

Le formaldéhyde est l'aldéhyde le plus utilisé lors de la préparation des matériaux dérivés de tanin comme un durcisseur. Le formaldéhyde réagit avec des tanins pour amorcer la polymérisation à travers des ponts méthylène dans les sites actifs des molécules de flavonoïdes, principalement les cycles A. Lorsque le noyau A est du type résorcinol, le site réactif se trouve en position C8 et lorsque le noyau A est de type phloroglucinol, ce site réactif se trouve en position C6 (Figure -1.15,1.16) [25].

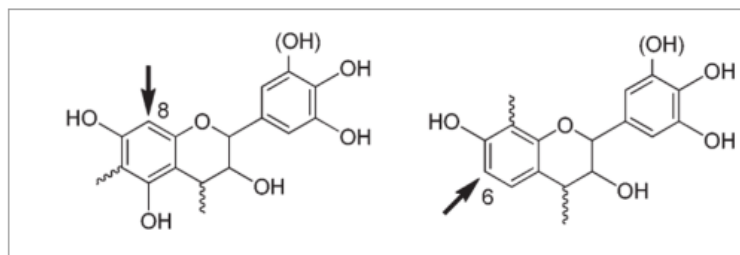


Figure.1. 15- Sites d'attaque du formaldéhyde sur des flavonoïdes

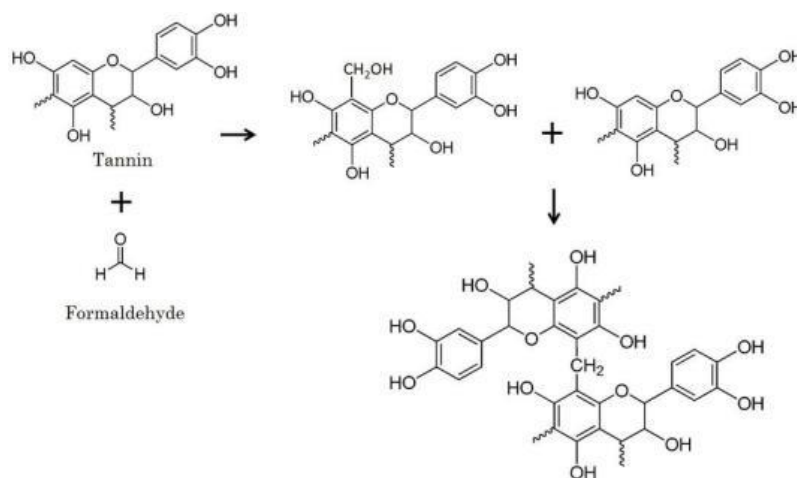


Figure.1. 16-Réaction entre le tanin et le formaldéhyde

Les sites nucléophiles présents sur le noyau A de n'importe quel flavonoïde sont plus réactifs que ceux du cycle B. Ceci est dû aux groupements hydroxyles qui provoquent une activation de la globalité du cycle B sans localisation de la réactivité comme cela se produit sur le noyau A. Les cycles B de type pyrogallol ou catéchol ne sont donc pas réactifs, sauf lorsqu'il y a formation d'anions à des pH relativement élevés ( $\approx 10$ ) et parfois, les noyaux B de type catéchol sont réactifs à température plus élevée [49], [64].

Les autres types d'aldéhydes sont moins réactifs que le formaldéhyde mais afin de diminuer l'utilisation de formaldéhyde, le glutaraldéhyde, acétaldéhyde ont été utilisés dans quelques recherches [65]. Le glutaraldéhyde réagit beaucoup plus lentement que le formaldéhyde, tandis que l'acétaldéhyde peut produire des résultats intéressants sous certaines conditions.

### 3.3- Fonctionnalisation des groupes hydroxyles

Les groupes hydroxyles phénoliques et aliphatiques présents dans les tanins sont des fonctionnalités réactives qui peuvent être modifiées pour obtenir différents dérivés. De plus, les tanins, également, peuvent être modifiés afin améliorer son efficacité.

Les hydroxyles phénoliques sont les groupes les plus réactifs. Différentes modifications, telles que l'acylation, l'éthérisation, la substitution par l'ammoniac, ainsi que les réactions avec des groupes époxy ou des isocyanates, ont été réalisées et étudiées par différentes recherches.

#### 3.3.1. Acylation

L'acylation de tanins est une méthode bien connue pour modifier certains caractères des tanins. Le tanin solubilisé dans l'anhydride acétique en présence de la pyridine a été caractérisé et peut être analysé par RMN. Tous les OH (phénoliques et aliphatiques) sont soumis à l'acylation. Quel que soit le niveau d'acylation, le dérivé du tanin perd sa solubilité dans l'eau [66]. Les agents d'acylation sont soit des acides carboxyliques, soit des dérivés plus réactifs tels que les chlorures d'acyle ou les anhydrides d'acide [67]. Il est également possible de synthétiser des groupes d'esters par plusieurs méthodes telles que l'estérification de Fischer.

L'acétylation des polyphénols donne la possibilité de dériver une partie ou la totalité des groupes hydroxyle. Les méthodes couramment employées utilisent le chlorure d'acétyle ou l'anhydride acétique dans la pyridine comme l'agent d'acétylations (Figure.1.17) [68].

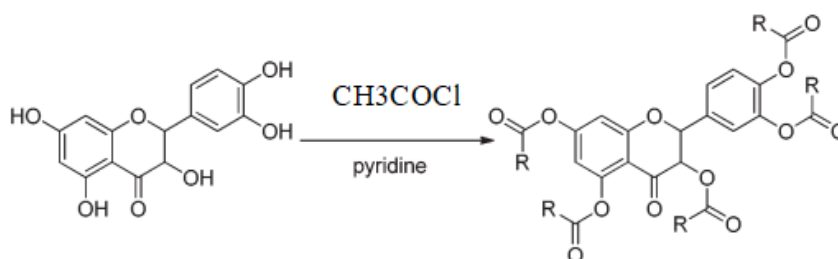


Figure.1. 17- Acylation de la quercétine par le chlorure d'acétyle

Les chaînes plus longues du propyle à l'octadodécyle peuvent être introduites par estérification dans ce cas, les chlorures ou anhydrides d'acide sont couramment utilisés. Par exemple, les

tanins de Nutgall ont été acylés par le chlorure de propanoyle, le chlorure d'hexanoyle et le chlorure de lauryle. La réaction a été conduite dans de l'acétone en présence de pyridine ou de triéthylamine à température ambiante pendant 2 heures. Aux alentours de 40% des hydroxyles ont été acylés lorsque le chlorure de lauryle était utilisé [68], [69].

### 3.3.2. Estérification des polyphénols par un chlorure acide

L'estérification d'un composé par un chlorure d'acide gras est une méthode pouvant impliquer la totalité ou une partie des groupements hydroxyle du composé. Elle a fait l'objet de nombreuses études dont quelques-unes sont rapportées ci-après.

Takizawa et coll. (1992) ont montré que la stabilité oxydative du saindoux peut être obtenue à l'aide de dérivés de la quercétine. Dans un premier temps, de la quercétine dissoute dans un mélange benzène - tétrahydrofurane a réagi avec du chlorure d'acide dodécanoïque en présence de triéthylamine commecatalyseur.

La 7-dodécanoylquercétine ainsi qu'une tridodécanoylquercétine ont été obtenues. Dans un second temps, comme précédemment, de la quercétine a été ajoutée à du chlorure d'acide oléique et il en a résulté de la 7-oléylquercétine (Figure.1.18) [68], [69].

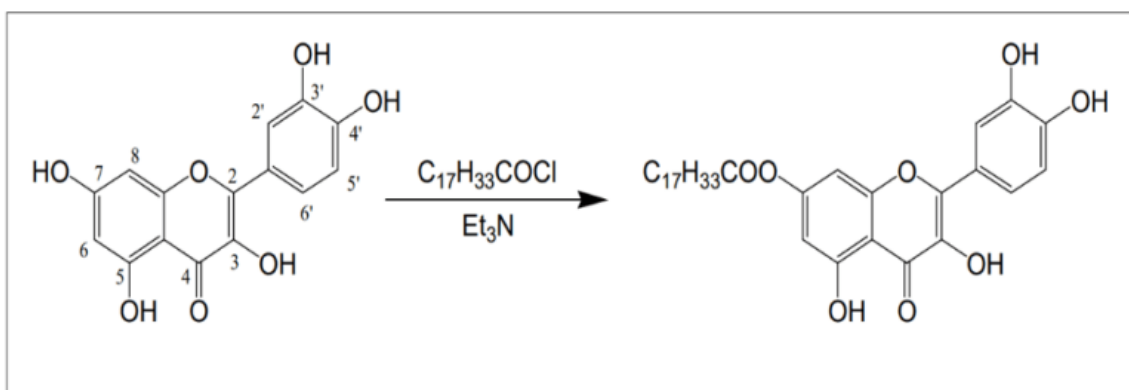


Figure.1. 18-Schéma de l'estérification de la quercétine en 7-oléylquercétine

L'un des moyens de modifier les propriétés chimiques des polyphénols, tels que les tanins, est l'estérification. Cette méthode consiste à créer des liaisons esters en combinant les polyphénols, comme les tanins, avec des acides gras. Cette formation d'esters peut modifier les propriétés chimiques et physiques des polyphénols.

L'estérification des polyphénols peut être réalisée par plusieurs méthodes différentes, mais l'utilisation de chlorures et d'anhydrides d'acides est bien connue comme méthode courante



Récemment, le greffage de tanins ou de flavonoïdes tels que la catéchine avec des acides gras a été étudié pour obtenir des produits plus hydrophobes ou amphiphiles. La même approche a été utilisée pour greffer des acides gras sur des flavonoïdes (Figure.1.19) [70], [71]. L'objectif principal de cette étude est de trouver une formulation de greffage qui permet de réduire les coûts de production des tanins modifiés et de moduler l'hydrophobie des mousses tanin-furanique afin de les rendre plus compétitives sur le marché.

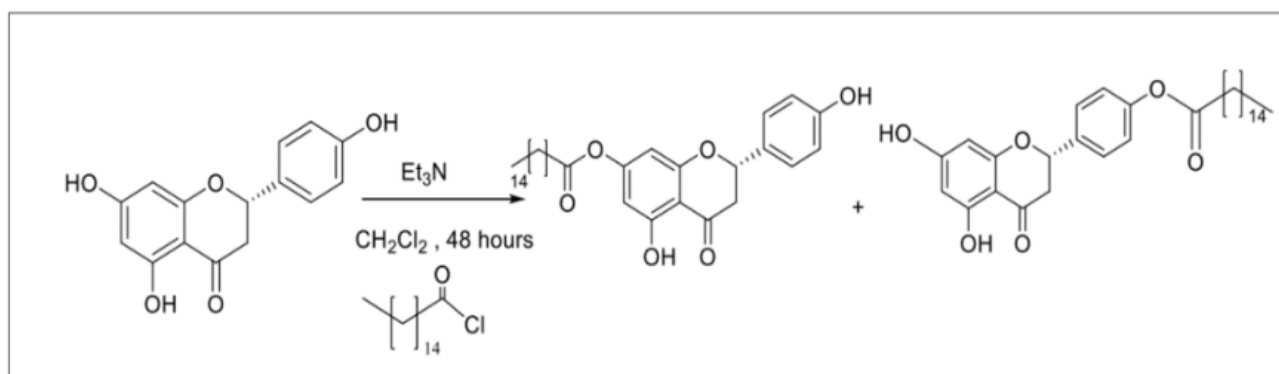


Figure.1. 19-Schéma de Greffage d'une chaîne grasse sur des flavonoïdes utilisés

#### 4. Matériaux biosourcés dérivés des tanins

##### 4.1- Les mousses : description et classification

Les mousses sont des matériaux poreux dotés d'une structure cellulaire complexe, composée de cellules vides contenant du gaz entouré d'une phase liquide ou solide condensée. La structure cellulaire des mousses peut influencer leurs propriétés et caractéristiques, qu'il s'agisse de cellules fermées ou ouvertes.

Par exemple, la structure cellulaire peut affecter la souplesse ou la rigidité. Les mousses ont des applications variées et peuvent être classées en deux catégories principales : mousses liquides et mousses solides. Les mousses liquides sont couramment utilisées dans notre quotidien, comme les mousses tensioactives, la mousse à raser ou la mousse de lait.

Les mousses solides sont synthétisées. En général, elles sont produites à partir de trois étapes principales :

- **Induction** : consiste à préparer une résine contenant la plupart ou tous les matériaux constitutifs des mousses, y compris l'ajout de catalyseur, d'agent d'expansion et de durcisseur. Les systèmes de production de mousses rigides les plus couramment utilisés reposent sur des formulations liquides relativement complexes. Pour obtenir une mousse de

qualité, il est nécessaire d'inclure certains composants tels qu'un solvant, un durcisseur, un catalyseur et un agent d'expansion.

- **Expansion / moussage** : cette étape implique le dégagement de gaz et la formation de bulles. En général, ce processus est exothermique. L'expansion peut être mécanique, chimique ou une combinaison des deux.
- **Polymérisation et stabilisation du polymère** : lors de cette étape, la structure globale de la mousse se forme et les chaînes macromoléculaires réagissent pour créer une structure tridimensionnelle autour des bulles. Cette étape est cruciale pour assurer la stabilité de la structure de la mousse. Si la polymérisation se produit trop rapidement, la microstructure cellulaire n'a pas suffisamment de temps pour former une mousse adéquate avec une bonne structure cellulaire. En revanche, si la polymérisation démarre trop tard, la structure peut s'effondrer en raison de l'écoulement et le rendement de la mousse peut diminuer.

Des études sur la distribution et la forme des différentes cellules dans une structure mousseuse statique ont été menées dans les années 90 [72], [73]( Figure.1.20).

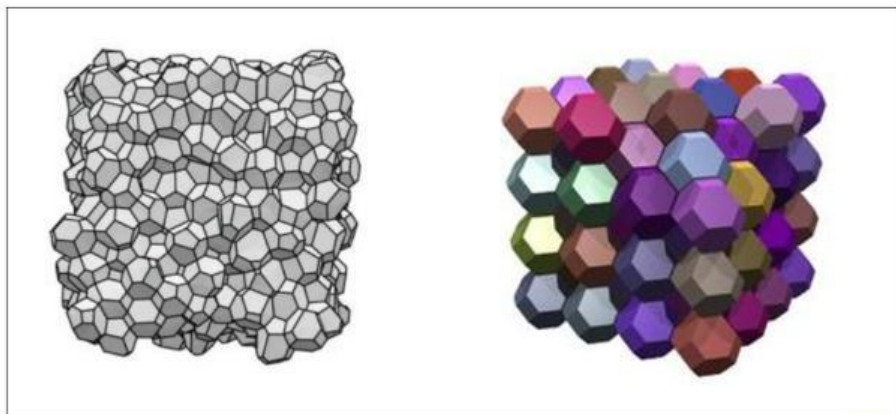


Figure.1. 20-Disposition schématique pour une mousse [4]

Les mousses solides sont des matériaux polymérisés et réticulés qui présentent une variété de caractéristiques et d'applications. Elles peuvent avoir des cellules ouvertes ou fermées. Les mousses avec des cellules ouvertes sont plus légèrement perméables. Egalement, elles peuvent être classifiées comme des mousses élastiques. Les mousses élastiques les plus connues sur le marché sont les mousses de polyuréthanes. Les mousses élastiques ou flexibles sont déformables tout en retrouvant leur forme initiale lorsque la contrainte appliquée est relâchée. Les mousses polyuréthane dominent actuellement le marché de ces mousses, mais les latex et les mousses EVA sont également largement utilisées dans des secteurs spécifiques tels que les matelas et les accessoires sportifs (Figure.1.21).



Figure.1. 21 Applications commerciales des mousses élastiques [53]

Les mousses rigides sont des matériaux qui ne se déforment pas et sont principalement utilisées pour l'isolation thermique et acoustique des bâtiments. Contrairement aux mousses flexibles, elles ne sont pas utilisées pour leur capacité à se conformer à des surfaces irrégulières. Les mousses rigides peuvent également être utilisées dans les automobiles comme matériaux antichoc en raison de leur capacité à absorber les contraintes et les énergies mécaniques, ainsi que par leur poids léger (Figure.1.22).



Figure.1. 22-Applications commerciales des mousses rigides

#### 4.2. Les mousses d'isolation naturelles dérivées des tanins

Il existe différents développements dans le domaine des mousses rigides isolantes. Tout d'abord, pour remplacer les polyuréthanes synthétiques qui impliquent l'utilisation d'isocyanates, deux approches ont été explorées. Premièrement, des mousses basées sur la réaction d'un tanin modifié par benzylation ont été développées pour le rendre plus réactif en tant que polyol lors de la réaction avec des isocyanates polymériques [74]–[78]. Cette première approche suit la même méthodologie qui a été utilisée pour étudier un autre polyphénol naturel, la lignine [78]. C'est une approche traditionnelle dans laquelle le tanin ne fonctionne que comme

polyol. La deuxième approche de ce type utilise une stratégie très différente, basée sur la réaction d'un tanin avec un aldéhyde et la réaction subséquente des groupes méthylols (-CH<sub>2</sub>OH) ainsi formés avec l'isocyanate. Cette approche est aujourd'hui utilisée pour la fabrication de colles à base de tanins [2], [79] soit pour d'autres colles à base de formaldéhyde comme UF, MUF et PF [80], [81].

À l'aide de cette deuxième approche, des mousses rigides de type phénolique-polyuréthane ont été développées en utilisant des matériaux naturels, tels que les tanins et l'alcool furfurylique, co-traités avec de l'isocyanate polymérique. Les proportions utilisées prennent en compte les contraintes liées aux installations industrielles pour la production continue de mousses de polyuréthane [82].

Une variété d'oligomères de copolymérisation différents a été détectée. Les polyuréthanes semblent avoir été formés à partir de deux sites de tanins flavonoïdes, principalement au niveau du groupe hydroxyle flavonoïde en C3, mais aussi, bien que moins fréquemment, sur les groupes hydroxyles phénoliques des oligomères flavonoïdes. Les polyuréthanes ont également été formés à partir de plusieurs types de diisocyanates, notamment l'hexaméthylène diisocyanate (HDI), l'isophorone diisocyanate (IPDI) et le 2,4-tolylène diisocyanate (TDI).

Les polyuréthanes sont également formés avec du glyoxal dans la formulation, qu'il soit pré-réagi ou non avec le tanin, avec le catalyseur, l'acide phénol sulfonique et avec le furfural. Cependant, ce dernier favorise grandement la réaction avec le cycle A des flavonoïdes par l'intermédiaire d'un pont méthylène plutôt que par la réaction avec les groupes isocyanates pour former des uréthanes. Tous les matériaux semblent avoir co-réagi pour former des ponts uréthanes et méthylènes entre tous les principaux composants utilisés. Ainsi, le tanin, l'alcool furfurylique, l'isocyanate, le glyoxal et même le durcisseur, l'acide phénol sulfonique, ont formé un certain nombre d'espèces mélangées liées par les deux types de liaison. Plusieurs espèces mixtes composées de 2, 3 et même 4 composants différents co-traités ont été observées.

Des formulations de mousses rigides autogonflantes chimiquement à base d'extrait de tanin ont été développées depuis 1994 [83]. Ces mousses, composées à 95% de matériaux d'origine naturelle, présentent des propriétés mécaniques et physiques comparables à celles des mousses PF synthétiques. À l'origine, la phase fluide avant moussage est composée d'un tanin et de formaldéhyde utilisé comme durcisseur. Ces deux éléments sont mélangés avec de l'alcool furfurylique, qui agit comme agent de production d'énergie ou de montée en température nécessaire pour la polymérisation par sa réaction d'auto-polymérisation et par sa réaction avec le tanin [83]. Sous des conditions acides, une expansion vers une phase mousse de la substance

fluide est déclenchée par un agent d'expansion physique à bas point d'ébullition, tout en permettant simultanément une réticulation du mélange résineux pour obtenir une stabilisation dimensionnelle à la faible densité souhaitée. [83]. Ces mousses ont été testées et sont totalement résistantes au feu, cela étant leur intérêt majeur.

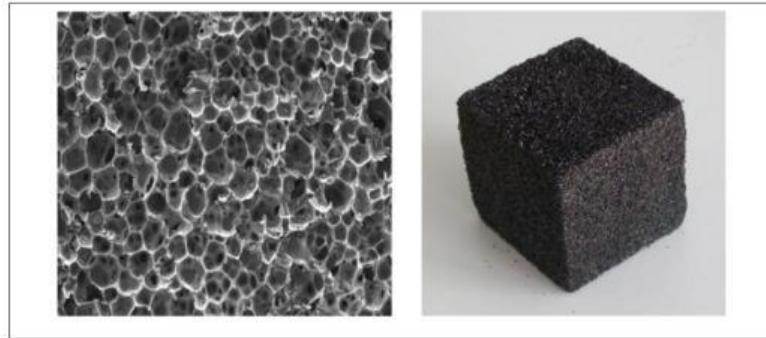


Figure.1. 23-Image de la structure d'une mousse tanin-furanique de première génération (à gauche) et macro-apparence de la même (à droite)

Pendant ces dix dernières années, la recherche a été conduite pour améliorer ces mousses, en les formulant sans formaldéhyde [84], [85], sans aldéhydes, sans un solvant organique comme agent gonflant [86], sans alcool furfurylique gonflant en milieu alcaline [87] et pas seulement acide, avec cellules ouvertes et cellules fermées, en les copolymérisant avec des résines synthétiques comme des résines phénolique [88] et isocyanates [89], en les copolymérisant avec des protéines [90], en introduisant des variations dans leurs systèmes de préparation [91], [92], en améliorant leur tenue à l'eau par greffage sur une petite proportion du tanin des longues chaînes hydrorepellantes [70], et aussi gonflant à la chaleur sans être autogonflants ou simplement gonflée par agitation mécanique pour l'utilisation comme mousses projetées [93], [94]. En plus des mousses rigides, des mousses flexibles ont été développées [95]–[97].

Les mousses avec les plus réactifs des tanins de type procyanidin, comme le tanin de pin, ont été aussi développées [98], [99] et la filière de carbonisation de ces mousses a été aussi poursuivie et améliorés [100]. Les variétés de ces mousses sont vraiment nombreuses [101], [102] et la littérature sur ce sujet est aujourd'hui assez vaste, trop vaste pour être résumée ici.

Un certain nombre d'applications ont été développées pour ces mousses, notamment les mousses à cellules ouvertes qui offrent une excellente isolation acoustique [103], ainsi que les mousses carbonisées qui peuvent être utilisées dans de nombreuses applications [102], [104], et aussi plus récemment pour la réparation osseuse par ostéogenèse avec des cellules souches [105]. Prenons l'exemple de cette dernière application : étant donné les options de traitement limitées, l'ingénierie des tissus osseux offre la possibilité de cultiver une quantité illimitée de

produits tissulaires ayant un potentiel thérapeutique accru pour la gestion des cas cliniques caractérisés par une perte osseuse sévère.

L'ingénierie osseuse repose sur l'utilisation d'échafaudages biomatériaux conformes, de cellules ostéocompétentes et d'agents biologiquement actifs. Entre autres, la poudre séchée par pulvérisation de tanin poreux (PTSDP) a été approuvée pour une utilisation humaine. Ainsi, la poudre dérivée par broyage des mousses tanin-furaniques a été utilisée comme matériau de reconstruction à faible coût, avec une biocompatibilité et une capacité potentielle à être remplacée par de l'os *in vivo*.

Dans cette étude, des échafaudages macro-PTSDP avec une géométrie, une porosité et des propriétés mécaniques définies ont été fabriqués en combinant la technologie de coulée et la lixiviation des porogènes en mélangeant PTSDP et hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  avec des macro-particules de polyéthylène glycol. Il a été démontré que les échafaudages développés dans ce travail soutiennent l'attachement, la viabilité à long terme et la différenciation ostéogénique des progéniteurs mésenchymateux dérivés de cellules souches pluripotentes induites humaines. La combinaison de certains échafaudages macroporeux PTSDP avec des cellules ostéocompétentes spécifiques au patient offre donc de nouvelles opportunités pour développer des greffes osseuses autologues avec un potentiel clinique accru pour des reconstructions squelettiques complexes.

La répulsion à l'eau et la friabilité superficielle de ces mousses ont été fortement améliorées par l'introduction de petites quantités de tanins estérifiés avec des acides gras [70], [71].

La variété d'utilisation de ces mousses est telle que de nombreuses autres applications peuvent être envisagées, voire non envisagées à l'heure actuelle, et seront développées à l'avenir.

#### **4.3-Conception de mousses polyuréthanes non isocyanates (NIPU)**

Les polyuréthanes non isocyanates (NIPU) ont été développés assez récemment afin d'éliminer les isocyanates toxiques de leur préparation. Cette méthode consiste à faire réagir des polyols synthétiques avec des carbonates cycliques ou bicycliques, suivis d'une réaction avec des diamines [106]–[118]. Certains travaux ont contribué de manière pionnière à cette technique, comme le montrent les références [106], [113], [116], [118]. Cette approche permet non seulement d'utiliser des matériaux synthétiques, mais également un certain nombre de matériaux biosourcés différents pour préparer des NIPU [119]–[125]. Cependant, peu d'entre elles ont été utilisées pour préparer des mousses NIPU, à quelques rares exceptions notables avec des matériaux synthétiques [122] ou naturels [123].

Récemment, les tanins ont été utilisés pour produire des polyuréthanes sans isocyanates (NIPU) pour un certain nombre d'applications, principalement pour les revêtements de surface [124]–[126]. La réaction des polyhydroxyuréthanes est basée sur la réaction d'un extrait de tanin avec du carbonate de diméthyle (ou avec des carbonates cycliques plus complexes) suivie d'une réaction du tanin carbonaté avec une diamine (Figure.1.24).

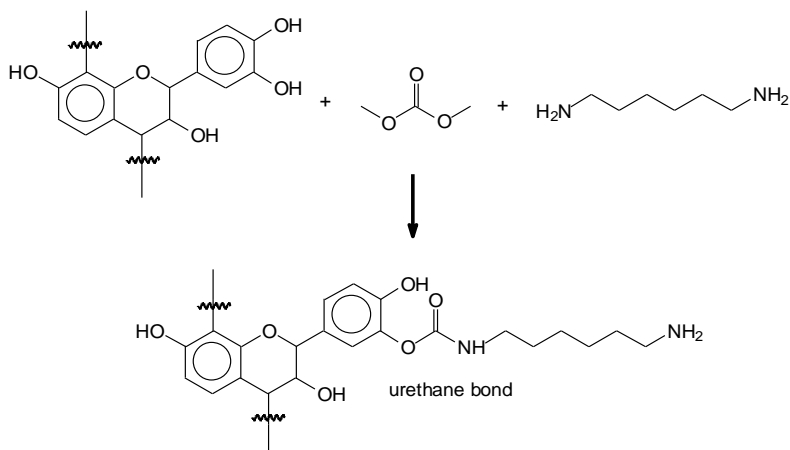


Figure.1. 24- Schématisation de la synthèse de polyuréthanes non isocyanates à base de tanin.

La synthèse de polyuréthane à partir de tanin est obtenue par la réaction des groupes hydroxyles des unités flavonoïdes tanniques avec du carbonate de diméthyle., suivi d'une réaction avec de l'hexaméthylène diamine.

Au cours de ces travaux, notamment dans le cas des tanins hydrolysables [126], dont le squelette est riche en glucides, il a été observé que non seulement les tanins mais aussi les glucides eux-mêmes dans les extraits de tanins réagissaient pour former des NIPU. Cette observation a conduit par la suite à essayer d'obtenir des NIPU à partir de glucose et de saccharose, et à les appliquer pour différentes applications [127]. Ainsi, la plupart des polyuréthanes biosourcés non isocyanates (NIPU) ont été préparés à partir de glucose et de saccharose, par réaction avec du diméthyl carbonate et de l'hexaméthylène diamine, et les oligomères NIPU obtenus ont été déterminés. Des NIPU linéaires et ramifiés ont été formés.

Les NIPU dérivés du glucose ont été appliqués comme revêtements de surface pour le bois et l'acier, avec des résultats très encourageants [127]. Les résines de glucose NIPU ont également été testées comme adhésifs thermodurcissables pour les joints de bois [127], et les NIPU de saccharose pour les adhésifs pour panneaux de particules de bois [128], avec également des résultats les plus encourageants.

Les polyuréthanes non isocyanates à base de glucose (NIPU) ont également été utilisés pour préparer des mousses de polyuréthane partiellement biosourcées par réaction avec du  $\text{NaHCO}_3$  comme agent gonflant, et par l'ajout d'un agent de couplage silane [123]. Les mousses ont été moussées et durcies par application de chaleur. À la différence des mousses tanin-furanique décrites précédemment, ces mousses présentaient une résistance au feu très limitée, indiquant que comme pour les mousses synthétiques de polyuréthane, l'utilisation éventuelle d'un ignifuge semble vraiment nécessaire. Plus caractéristique est leur comportement de contrainte-déformation. Alors que la compression aplatit effectivement les parois cellulaires, la structure cellulaire est néanmoins maintenue, et les parois cellulaires n'ont pas été détruites. Cela indique un certain niveau de mousses et confirme cette explication.

Ce développement des mousses NIPU décrit ci-dessus ouvre un certain nombre de nouvelles perspectives sur les bio mousses à base de tanins, d'hydrates de carbone et d'autres matériaux naturels tels que la lignine et autres. Encore plus intéressant, des variations de mousses peuvent être obtenues par le mélange de ces différents matériaux naturels.

En conclusion, les mousses rigides à base de tanin semblent adaptées à une large gamme d'applications. Outre l'isolation thermique et l'isolation acoustique, évidemment deux des domaines les plus intéressants, un troisième domaine est également d'une actualité particulière. L'un de ces développements est la carbonisation des mousses de tanin pour former des mousses de carbone utilisées dans diverses applications. Ce domaine a fait l'objet de nombreuses recherches au cours des trois dernières années, et une littérature considérable existe déjà à ce sujet [100], [104], [129]–[133].

Un autre domaine d'application d'intérêt pour les mousses tanin-furaniques naturelles est le domaine de la culture hydroponique [134]. Des mousses de tanin de quebracho sans formaldéhyde ont été développées pour les applications horticoles/hydroponiques et florales. Ces mousses incluaient dans leur composition un agent mouillant et au moins un composé capable de neutraliser l'acidité résiduelle issue du catalyseur acide. Cela était nécessaire pour aligner le pH sur ce dont les plantes ont besoin. Leurs densités étaient comprises entre 0,048 et 0,066  $\text{g/cm}^3$  et leur résistance à la compression entre 0,07 et 0,09 MPa. Les images de microscopie électronique à balayage (MEB) ont montré une porosité ouverte et une taille moyenne de cellule de 125 à 250  $\mu\text{m}$ . L'absorption d'eau a atteint 98 % (volume), tandis que le pH résiduel est de 5. Ces nouvelles mousses de tanin ne sont pas phytotoxiques et conviennent à la conservation des fleurs fraîches coupées et comme matrices de support pour l'horticulture et la culture hydroponique. Elles ont montré des performances comparables ou supérieures à la



mousse florale phénolique synthétique commerciale utilisée comme référence. Il est clair qu'un certain nombre d'autres applications peuvent être envisagées et sont susceptibles d'être développées à l'avenir, en particulier avec la nouvelle perspective des mousses NIPU tanin-carbohydate.

Aujourd'hui, une grande variété de mousses NIPU est disponible, comprenant des mélanges de tanins avec des hydrates de carbone et d'autres biomatériaux [135]–[140].

#### **4.4-Conception de composites bois / tanin / alcool furfurylique**

Le bois, en tant que matériau naturel, peut être confronté à une perte de propriété due au vieillissement et aux agents dégradatifs biologiques notamment dans le sens des matériaux durables. C'est pour résoudre ce problème que l'homme a toujours cherché des méthodes pour préserver le bois et améliorer sa durabilité.

Les premières techniques de préservation du bois dans l'histoire comprenaient l'utilisation d'huiles ou de goudron pour recouvrir les surfaces en bois. À partir de la révolution industrielle, des méthodes plus nocives et chimiques telles que le Créosote et l'arsenic ont fait leur apparition. Bien qu'efficaces pour empêcher la dégradation du bois, ces méthodes sont généralement basées sur l'utilisation de produits toxiques, comme les biocides, qui sont dangereux pour l'environnement et pour les êtres humains. Pour cette raison, de nouvelles techniques utilisant des produits non-biocides ont été approuvées et développées, notamment dans le domaine de la modification chimique du bois. L'apparition de composés organiques pour la préservation du bois a fait l'objet de nombreuses recherches[141]–[144].

Aujourd'hui, l'un des sujets importants dans le domaine du bois est de trouver des méthodes de préservation avec des matériaux naturels à faible impact environnemental et d'éviter l'utilisation de produits chimiques toxiques. Ces types de matériaux ont fait l'objet de nombreuses recherches ces dernières années. Globalement, il s'agit de traitements thermiques et de méthodes de modification du bois, comme l'acylation ou furfurylation. Les traitements thermiques sont appliqués sur le bois à une température moyenne de 180 à 230 C° et permettent d'éviter l'utilisation de produits biocides [142], [143], [145], [146].

La modification chimique du bois, comme l'acétylation, est basée sur la modification du bois au niveau moléculaire par de l'anhydride acétique. Grâce à cette méthode, les groupes hydroxyles libres du bois sont greffés par des groupes acétyles. L'acétylation permet d'obtenir un bois avec une très forte stabilité dimensionnelle et une augmentation considérable de sa durabilité biologique contre les champignons ainsi que les insectes[143], [144] .

Des méthodes basées sur l'utilisation de produits naturels ont été développées pour être appliquées sur le bois, tels que l'alcool furfurylique, les tanins et d'autres composés organiques. Une des méthodes de modification chimique du bois à partir des produits renouvelables est la furfurylation du bois. La furfurylation du bois est un processus de modification chimique qui consiste à introduire de la résine d'alcool furfurylique (FA) dans les parois cellulaires du bois. Ce processus augmente la durabilité et la stabilité dimensionnelle du bois, tout en conservant ses propriétés mécaniques et esthétiques. La furfurylation peut être effectuée sur différentes essences de bois, telles que le pin, le hêtre, ou toutes les essences imprégnables, et elle peut être utilisée pour diverses applications en extérieur.

La furfurylation est considérée comme une alternative écologique aux traitements chimiques conventionnels utilisant des produits toxiques. Elle vise à éviter l'utilisation de biocides tout en valorisant des matériaux d'origine renouvelable. Les produits employés dans le processus de furfurylation, dont l'alcool furfurylique est dérivé de l'hémicellulose présente dans les plantes, sont fabriqués à partir de matières premières renouvelables et présentent un faible impact environnemental. De plus, la furfurylation permet de réduire la consommation de bois de qualité supérieure en augmentant la durabilité des bois moins résistants.

Des recherches récentes portant sur l'utilisation de la furfurylation en combinaison avec d'autres composé naturelle, tels que les tanins en tant que copolymère avec l'alcool furfurylique, ou l'optimisation de la furfurylation à l'aide de différents acides en tant que catalyseur, ont été étudiées [142], [147], [148].

L'utilisation des tanins est une nouvelle approche dans le domaine de la préservation du bois[147]. Les tanins sont reconnus pour leurs propriétés antioxydantes, ce qui signifie qu'ils ont le pouvoir de neutraliser les radicaux libres. Ces radicaux libres endommagent les cellules et accélèrent leur vieillissement. De plus, les tanins précipitent les protéines présentes dans les champignons en perturbant leurs processus métaboliques, réduisant ainsi la dégradation biologique du bois. Les tanins se sont avérés être d'excellents partenaires de l'alcool furfurylique pour créer des polymères tanin-furaniques[147], [148]. C'est pourquoi ils ont été choisis pour la préservation du bois en tant que copolymères, renforçant ainsi le réseau polymérique lors du processus de furfurylation

Au sein du laboratoire LERMAB, l'utilisation du tanin pour optimiser la furfurylation a démontrée l'amélioration des propriétés du bois, notamment sa résistance aux champignons. Dans le cadre de cette thèse, la quantité de tanin a été considérablement augmentée dans le but

d'utiliser un matériau moins coûteux que l'alcool furfurylique. De plus, l'effet du tanin modifié sur l'amélioration des propriétés du bois a été observée.



# **Chapitre II-Conception de mousses naturelles dérivées de tanins condensés**



**Ce chapitre a fait l'objet de deux articles :**

**Article. I :** Azadeh, E., Abdullah, U. H., Ali, N. B. M., Pizzi, A., Gérardin-Charbonnier, C., Gérardin, P., ... & Ashari, S. E. (2022). Development of Water Repellent, Non-Friable Tannin-Furanic-Fatty Acids Biofoams. *Polymers*, 14(22), 5025.

**Article. II:** Azadeh, E., Abdullah, U. H., Gérardin, C., Pizzi, A., Gérardin, P., & Segovia, C. Flexible Biofoams Based on Furanics and Fatty Acids Esterified Tannin.

Ce chapitre est une étude sur les mousses naturelles dérivées de tanins condensés et de tanins hydrolysables. Il est possible de classer ce chapitre en deux parties :

1. Modification chimique des extraits phénoliques, notamment les tanins condensés, pour améliorer le caractère hydrophobe des mousses tanin-furaniques.

Dans la première section de cette étude, la modification chimique de tanins condensés, notamment du mimosa, a été réalisée pour améliorer les propriétés physico-chimiques des tanins afin d'étendre leur utilisation dans différentes applications telles que les mousses d'isolation.

2. Conception de mousses rigides et flexibles à base de tanins condensés et de tanin modifié en utilisant de l'acétaldéhyde (Publication -II).

Dans cette section les de tanins modifiés ont été utilisés pour concevoir des mousses tanin-furaniques hydrophobes. Cet extrait phénolique modifié a joué un rôle important dans cette étude.

## 1. Introduction générale

Ce chapitre se concentre sur la conception et l'optimisation des mousses tanin-furaniques à partir de tanin condensé, en particulier les extraits de mimosa, dans le but d'améliorer leur caractère hydrophobe et la friabilité. Pour atteindre cet objectif, deux étapes ont été réalisées : la modification chimique du tanin et la conception des mousses en utilisant le tanin modifié.

La première phase de cette étude visait à déterminer les conditions optimales et simples pour la réaction d'estérification. Cette section s'est concentrée sur la recherche de la méthode la plus simple et efficace pour la modification des tanins, tout en mettant l'accent sur leur caractérisation. Des techniques de caractérisation telles que la spectroscopie infrarouge et la spectrométrie de masse MALDI-TOF ont été utilisées pour confirmer le succès de cette méthode de modification.

Cette partie de la recherche met en évidence l'importance de trouver des méthodes optimales pour la modification du tanin dans le but d'obtenir des matériaux de haute qualité et de mieux comprendre les propriétés de ces mousses spécifiques. De plus, le tanin modifié obtenu au cours de cette étude a été utilisé pour améliorer les propriétés des mousses.

Dans la deuxième étape, les tanins modifiés ont été utilisés pour améliorer l'hydrophobicité des mousses. Différents types de mousses ont été conçus, et l'incorporation de tanin modifié par des chlorures d'acide gras a eu un impact non seulement sur les propriétés hydrophobes, mais aussi sur les caractéristiques physiques et mécaniques des mousses obtenues. Deux types de mousses ont été fabriqués et caractérisés : les mousses rigides et les mousses flexibles.

Les mousses à base de tanin-furanique sont généralement produites en réagissant les tanins avec de l'alcool furfurylique en présence d'aldéhydes et d'un agent d'expansion. Cette réaction forme un polymère réticulé qui confère à la mousse sa rigidité et sa résistance mécanique.

Cependant, les mousses de tanin naturelles présentent certaines limitations, notamment en termes de friabilité, de faible résistance à l'eau et de compatibilité limitée avec les composés hydrophobes. Pour surmonter ces limitations et améliorer les propriétés des bio-mousses de tanin, des chercheurs ont développé différentes méthodes de modification, notamment l'estérification avec des acides gras.

Plusieurs formulations ont été testées pour simplifier la procédure courante d'estérification du tanin. L'ajout de ce tanin modifié a eu un impact significatif sur l'amélioration des propriétés hydrophobes des mousses. L'hydrophobicité des mousses a été évaluée en mesurant l'angle de



contact. De plus, afin d'augmenter le rendement des mousses, différentes formulations ont été proposées et testées, telles que l'utilisation de glycérol comme agent de dispersion de la température ou l'utilisation d'autres aldéhydes que le formaldéhyde. L'ajout de tanin estérifié en présence de glycérol a permis de concevoir une mousse flexible.

Cette étude constitue la partie complémentaire de la recherche précédente, qui se concentrait sur la conception des deux types de mousses hydrophobes, à savoir rigides et flexibles, en utilisant du tanin modifié par des chlorures d'acide gras tels que le chlorure d'acide lauryl, le palmitoyle et l'oléyle.

Il convient de noter que l'acétaldéhyde a été utilisé comme agent de réticulation en remplacement définitif du formaldéhyde, ce qui a joué un rôle crucial dans l'amélioration et l'optimisation des résultats de cette étude. En effet, cet aldéhyde possède un point d'ébullition plus élevé que le formaldéhyde, ce qui a permis de mieux contrôler la température de réaction et de favoriser la formation de la structure des mousses. L'utilisation de glycérol a également permis d'ajuster la température de réaction et de produire un type de mousse flexible. Il est donc possible de dire que l'obtention de ce type de mousse constitue un aspect important de cette partie de la recherche, étant donné ses nombreuses applications dans les industries au quotidien.

Les caractéristiques visuelles, physiques et morphologiques des mousses conçues ont été étudiées et comparées. Des analyses approfondies ont été réalisées pour évaluer les propriétés telles que la densité, la résistance mécanique, la porosité, et la structure cellulaire des mousses. Des techniques d'imagerie ont été utilisées pour examiner la morphologie et la distribution des pores dans les échantillons de mousses. Les résultats obtenus ont démontré l'efficacité de la modification du tanin et de l'utilisation de l'acétaldéhyde dans la création de mousses hydrophobes présentant des caractéristiques prometteuses pour diverses applications industrielles.

Dans l'ensemble, ce chapitre contribue à l'avancement des connaissances sur la modification du tanin et l'utilisation de cet extrait modifié dans la conception de mousses hydrophobes. Les méthodes de caractérisation utilisées permettent de mieux comprendre les propriétés des mousses modifiées et ouvrent la voie à de nouvelles applications potentielles dans divers domaines industriels. Ces recherches offrent des perspectives prometteuses pour l'utilisation des tanins modifiés comme alternative durable aux matériaux synthétiques et soulignent l'importance de l'innovation dans le développement de matériaux respectueux de l'environnement. En outre, la recherche a permis de développer et de caractériser avec succès

des mousses rigides et flexibles hydrophobes à partir de tanin modifié par des chlorures d'acide gras. Les propriétés physiques et morphologiques des mousses ont été soigneusement évaluées, confirmant leur potentiel pour une large gamme d'applications industrielles. Les résultats obtenus ouvrent la voie à de futures recherches visant à optimiser davantage les propriétés des mousses et à explorer de nouvelles possibilités d'utilisation dans divers domaines industriels.



## **2. Development of Water Repellent, Non-Friable Tannin-Furanic-Fatty Acids Bio foams (Publication. I)**

### **Abstract:**

Tannin-furanic foams were prepared with a good yield using the addition of relatively small proportions of a polyflavonoid tannin extract esterified with either palmitic acid, oleic acid, or lauric acid by its reaction with palmitoyl chloride, oleyl chloride, or lauryl chloride. FTIR analysis allowed us to ascertain the esterification of the tannin, and MALDI-TOF analysis allowed us to identify several multi-esterified flavonoid oligomers as well as some linked to residual carbohydrates related to the equally esterified tannin. These foams presented a markedly decreased surface friability or no friability at all, and at densities lower than the standard foam they were compared to. Equally, these experimental foams presented a much-improved water repellence, as indicated by their initial wetting angle, its small variation over time, and its stabilization at a high wetting angle value, while the wetting angle of the standard foam control went to zero very rapidly. This conclusion was supported by the calculation of the total surface energy of their surfaces as well as of their dispersive and polar components.

**Keywords:** tannin-furanic foams; esterified tanins; friability; water repellence; surface free energy.

FTIR; MALDI-TOF

### **1.Introduction**

Tannins are renewable, natural materials that are readily available. They can be extracted from the bark and wood of certain trees and from agricultural waste. They have been traditionally extracted industrially for more than a century for use in the manufacture of heavy leathers. Their use has been extended in the last decades to several other industrial applications. They are widely used to manufacture wood adhesives [2], [148], [149], but extensive research on their utilization has led to a variety of other possible applications, such as metal primers, pharmaceuticals, and many other uses [150], [151]. Among these, one of the most interesting applications is for bio-based foams for thermal and acoustic insulation.

Tannin-based foams have been prepared from renewable, natural raw materials to substitute for petrochemical resources [83], [152]. Tannin-based foams are one example of biobased foams, composed of 95% relatively inexpensive natural raw materials that are considered less- or nontoxic. Condensed tannin and hydrolysable tanin are two different types of tannin possessing different structures. The structure of hydrolysable tannins is gallic and ellagic acid-based, taking

the form of chains of pentagalloyl glucose and of their degradation products, such as castalagin and castalin. Some authors have stated they are not recommended for producing foams due to their fragility and friability [153], [154]. However, recent work on hydrolysable tannin-based non-isocyanate polyhydroxy urethane foams has shown these conclusions to be incorrect [140], [155].

Polyflavonoid tannin extract from the bark of the black mimosa (*Acacia mearnsii*, formerly *mollissima*, de Wildt) is one of the two most common commercial condensed tannins [156]. Such condensed tannins consist of 2–10 flavonoid units, which are reactively responsive towards aldehydes [2], [157], [158]. Tannin-based foams, or more exactly tannin-furanic-based foams, are prepared by the reaction of tannin with furfuryl alcohol with or without aldehydes, mainly formaldehyde [153], although recent research has succeeded in preparing them using other aldehydes [123], [138], [159] or even with no aldehydes at all [86]. Formaldehyde reacts with both tannins' phenolic aromatic ring sites [2] as well as with the furanic ring of the furfuryl alcohol cross-linking them [160]. These foams can be produced at room temperature without any pre-polymerization. These materials can compete with synthetic, industrial phenol-formaldehyde foams [63], [134], [157], [161].

Notwithstanding their excellent fire resistance imparted by both the tannin and the furanic moieties, some drawbacks still do persist for these foams. One of the most annoying observed and reported drawbacks is their surface friability and their over-absorption of water when used as thermal insulating material. An initial indication that both such drawbacks could possibly be solved was the coupling of small amounts of fatty acid esterified tannins to the tannin constituting the majority of the foam [70]. Esterification of several different flavonoids and of flavonoid tannins is known in the literature in a variety of application fields and using several different approaches. Thus, in the medical pharmaceutical field enzymatic esterification of model flavonoid compounds with unsaturated fatty acids has been reported [162], [163], where enzymatic conversion showed a better percentage at between 70% and 85% yield with different flavonoids with oleic acid and linoleic acid than transesterification for linoleic acid [162]. Conversely, esterification of glycosylated model flavonoid compounds was showed by NMR to occur mainly on the glucosides linked to the flavonoids [164]. More recently, a study on tannin esterification for use in materials using anhydrides was investigated as a route to synthesize tannin esters possessing varying ester chain length and degree of substitution (DS) to study the impact on polylactic acid comparing it with other systems of flavonoid esterification [165]. These various routes to tannin ester formation included (i) with acetic

anhydride [166]; (ii) with acyl chloride with stearyl chloride [167]; and (iii) transesterification with vinyl laurate [168]. These routes indicated the favoured flavonoid sites where esterification occurred, namely on all the phenolic and C3 alcoholic sites by anhydride, on the flavonoid B-ring phenolic-OHs by a transesterification approach, and mainly on the phenolic -OH groups of both the B- and A-rings by reaction with an acyl chloride. This latter is also confirmed by two other studies on model compounds such as catechin, naringenin, and mesquitol, where the phenolic hydroxyls were esterified with ease [169], [170] It is however strange that an alcoholic -OH such as the one on the flavonoid C3 is esterified with an anhydride and not found with an acyl chloride, as it does not really make sense.

With these premises, the work presented here is a more in-depth investigation of how to solve such drawbacks in the best and most effective way, to determine the control parameters to achieve this, and finally to eliminate such drawbacks.

## **2. Materials and Methods**

### **2.1. Materials**

Spray-dried mimosa tannin (*Acacia mearnsii* formerly *mollissima*, de Wildt) extract powder was supplied by Silva Chimica (St. Michele Mondovi', Italy). Furfuryl alcohol and lauroyl chloride were purchased from Acros Organics (Geel, Belgium). Para-toluene-sulphonic acid (pTSA), diethyl ether, acetaldehyde, and glutaraldehyde were purchased from SigmaAldrich (St. Louis, MO, USA). Formaldehyde was provided by Merck-Schuchardt OHG

(Hohenbrunn, Germany). Oleoyl chloride and palmitoyl chloride were acquired from Alfa Aesar (Kandal, Germany). Chloroform was obtained from Merck (Darmstadt, Germany).

### **2.2. Synthesis of Oil-Grafted Tannin**

The method to synthesize the oil-grafted tannin was modified from that reported by Rangel et al. [70] to improve the preparation of the oil-grafted tannin. To begin, 5 g of commercial mimosa tannin extract was weighed and transferred into a 250 mL round bottom flask. Then, 5 g of palmitoyl chloride was added, followed by 80 mL of chloroform. At room temperature, the reaction mixture was magnetically agitated for at least 12 h and then evaporated until dry under reduced pressure, while maintaining the temperature below 40 °C. Finally, a dark brown solid of oil-grafted tannin was obtained. The same procedure outlined above for palmitoyl chloride was used for both oleyl chloride and lauroyl chloride (maintaining the same molar ratio addition of fatty acid) to examine the effect of different fatty acid chains on synthesis percentage yield.

## **2.3. Testing and Characterization of Oil-Grafted Tannin Extract**

### **2.3.1. Fourier Transform Infrared (FTIR) Spectroscopy Analysis**

The FTIR spectra were collected on a Perkin Elmer Spectrum One (Villebon-sur-Yvette, France) supplied with an ATR-FTIR unit. A few milligrams of each oil-grafted tannin sample were placed on a diamond/ZnSe crystal sample holder. The spectra were acquired by accumulation of 10 scans at a resolution of 4 cm<sup>-1</sup> and in the 650–4000 cm<sup>-1</sup> wavelength range. The results obtained were recorded and examined using Spectrum software (Perkin Elmer, Waltham, MA, USA). A natural tannin extract spectrum was used as control.

### **2.3.2. Matrix-Assisted Laser Desorption Ionization–Time-of-Flight (MALDI-TOF) Analysis**

Water/acetone (50/50 volume) was used to dissolve the oil-grafted tannin (4 mg/mL), and the solutions were added to the matrix solution of 10 mg/mL in acetone. 2,5-dihydroxy benzoic acid was used as the matrix to ease placing the sample on the sample-holder plate. Red phosphorus was used for instrument calibration (LaserBio Labs, Valbonne, France). A concentrated solution of 10 mg/mL of sodium chloride (NaCl) in distilled water was mixed into the matrix to enhance ion formation. The sample was added to the matrix solution and was divided into three parts. From 0.5 to 1 µL of three parts of the sample solution and one part of the NaCl solution was put on the MALDI target. The MALDI target was placed into the spectrometer after solvent evaporation. The peaks in the spectrum can present themselves at the actual molecular weight of the chemical species or increased by 23 Da, this being the molecular weight of the Na<sup>+</sup> linked to the molecule from the NaCl added to the matrix to facilitate the flight of heavier oligomers. Sometimes both forms of the same species, with and without Na<sup>+</sup>, can be present in the same spectrum.

The MALDI-TOF spectra were recorded on an AXIMA Performance instrument (Shimadzu Scientific Instruments, Manchester, UK). The irradiation source was a pulsed nitrogen laser with 3 ns intervals at a wavelength of 337 nm. The measurements were carried out using the following conditions: polarity, positive; flight path, linear; mass, high (20-kV accelerating voltage); and 100 to 150 pulses per spectrum. The delayed extraction technique was used to apply delay times of 200 to 800 ns, and the ion gate was set at 400 Da. The spectra are exact at ±1 Da.

## 2.4. Foam Preparation

Mimosa tannin extract was thoroughly mixed by hand in a beaker with water, furfuryl alcohol, and formaldehyde (37% solution). Oil-grafted mimosa tannin was added into the mixture according to the formulations in Table 2.1. Then, para-toluene-sulfonic acid (pTSA) catalyst as a 65% solution in water and diethyl ether (blowing agent) were added to the mixture, followed by 20 s of vigorous stirring. Within 2–3 min of the addition of the catalyst and blowing agent, a black foam was obtained. The foam was left for at least 24 h to allow evaporation and eliminate the residual blowing agent trapped in it. An equivalent tannin foam without the addition of oil-grafted mimosa tannin was also prepared as a control.

Table 2.1. Composition of standard tannin-based foams and tannin-based foams formulated with oil-grafted tannins

Formulation	STD	A	B	C	D
Mimosa tannin extract (g)	15	13.75	13.75	13.75	13.75
Oil-grafted mimosa tannin (g)	-	1.25	1.25	1.25	1.25
Formaldehyde (g)	3.7	3.7	0	0	0
Furfuryl alcohol (g)	6	5.5	5.5	5.5	6
Water (g)	2	0	0	0	2
Glycerol (g)	0	3	2.5	2.5	0
pTSA (g)	5.5	5.5	6	6	5.5
Diethyl ether (g)	1.7	1.7	1.7	1.7	1.7
Glutaraldehyde (g)	0	0	3.7	0	0
Acetaldehyde (g)	0	0	0	3.7	3.7

## 2.5. Characterization of Tannin-Based Foam

### 2.5.1. Density

After fully drying the samples, the bulk density,  $\rho$ , was calculated as the weight/volume ratio of each sample of a standard dimension of 30 mm  $\times$  30 mm  $\times$  30 mm. The density of each sample was recorded.

### 2.5.2. Friability

Evaluation of friability was conducted manually according to Rangel et al. [70]. The samples were rubbed without stress or adding pressure 5 times against the wipe tissue paper surface along a 3.5 cm distance. The foam with the added oil-grafted tannin was rubbed at the same time as the standard foam against the wipe tissue paper to provide comparison. The comparison was based on visual evaluation of the amount of foam residue that was left on the paper after rubbing. The friability was assessed manually [70], [171] in accordance with the following protocol: Each sample was rubbed five times, without additional pressure or stress, against the



paper surface along a 3.5 cm distance. Kimtech Science paper was used (Precision Wipes Tissue Wipers, Kimberly-Clark Professional, Nanterre, France). For each formulation, the hydrophobized foam and the standard one was rubbed simultaneously on the paper to afford comparison to the control experiment.

### 2.5.3. Contact Angle Measurement

The contact angle measurements were determined according to Martha et al.[172]. The determination of the contact angle of water to measure the wettability of the tannin foam was performed with a video measuring system from Krüss Gmb (Villebon-sur-Yvettes, France), equipped with a high-resolution CCD camera. The tannin foams were placed on the top of a table in front of the CCD camera. A water droplet of 20 microlitre was placed onto the foam surface using a micropipette to always obtain the same size droplet. The drop shapes on the surface of the tannin foam were captured by the CCD camera and measured for a period of 180 s. Image J 1.46 software with DropSnake plugin analysis was used to measure the contact angle for both the left and the right side of the individual image of the droplet. The values obtained were then averaged. In total, 19 images were taken for each recorded drop to obtain a curve of contact angle versus wetting time.

Surface free energy (SFE) calculations were determined using Young's equation[173]. Young's equation states that:

$$\text{Equation (1)}-\gamma_s = \gamma_{sl} + \gamma_l \cos \theta$$

where  $\gamma_s$ ,  $\gamma_{sl}$ , and  $\gamma_l$  are regarded as the SFE of a solid, the SFE of the solid–liquid interface, and the SFE of the liquid, respectively, and  $\theta$  is the value of the contact angle between the solid and the measuring liquid. However, the value of  $\gamma_s$  and  $\gamma_{sl}$  cannot be obtained directly from Young's equation and using another equation by Dupré is needed[174]. Dupré introduced the concept of work adhesion between phase a and phase b by the following equation:

$$\text{Equation (2)}-W_{ab} = \gamma_a + \gamma_b - \gamma_{ab}$$

By assuming “a” is a solid and “b” is a liquid, Equation (3), the Young–Dupré[174]equation, will be obtained by exchanging Equation (1) to Equation (2):

$$\text{Equation (3)}-W_{sl} = \gamma_l(1 + \cos \theta)$$

The work of cohesion of a solid and liquid can be defined as

$$\text{Equation (4)}-W_{ss} = \gamma_s + \gamma_s - 0 = 2\gamma_s$$

$$\text{Equation (5)}-W_{ll} = \gamma_l + \gamma_l - 0 = 2\gamma_l$$

According to Berthelot's assumption, the adhesion work between the solid and liquid

$W_{sl}$  is equal to the geometric mean of the cohesion work of a solid and liquid individually:

$$\text{Equation (6)-} W_{sl} = (W_{ss}W_{ll})$$

The basis for the surface energy calculation, Equation (7), was obtained by combining all the equations from Equations (3)– (6):

$$\text{Equation (7)-} W_{sl} = 2(\gamma_s\gamma_l)^{\frac{1}{2}} = \gamma_l(1 + \cos \theta)$$

Many other methods have been introduced to identify the amount of SFE of a sample. One of the approaches that can be used was by Owens–Wendt–Rabel–Kaelble [175]–[177], where total surface free energy is the combination of polar and dispersive parts:

$$\text{Equation (8)-} \gamma_l = \gamma_{ld} + \gamma_{lp}$$

$$\text{Equation (9)-} \gamma_s = \gamma_{sd} + \gamma_{sp}$$

where  $\gamma_{ld}$  and  $\gamma_{sd}$  are represented as the dispersive surface energy for liquid and solid,

$\gamma_{lp}$  respectively. Meanwhile,  $\gamma_l$  and  $\gamma_s$  are the polar surface energy components of the liquid and solid, respectively.

### 3. Results and Discussion

#### 3.1. FTIR Results of Oil-Grafted Tannin

Figure 2.1 shows the FTIR spectra of mimosa tannin, palmitic acid, palmitoyl chloride, and oil-grafted tannin using palmitoyl chloride. In the FTIR spectra of the oil-grafted tannin, a sharp peak appeared at  $1742\text{ cm}^{-1}$ , proving the presence of ester groups in the oil grafted tannin. The spectrum for palmitoyl chloride shows that a sharp peak at  $1804\text{ cm}^{-1}$  is due to the presence of the C=O stretch band for acid chlorides [178]. This sharp peak disappears when using palmitoyl chloride to synthesize oil-grafted mimosa tannin. The absorption band at  $1616.12\text{ cm}^{-1}$  in the tannin spectrum is attributed to the C–H vibration in the aromatic ring of the mimosa tannin [179], [180]. A sharp peak appearing at  $1706\text{ cm}^{-1}$  in the palmitic acid spectrum is assigned to the C=O stretch band for the carboxylic acid group [178]. Figure 2.2 shows the FTIR spectra of mimosa tannin, palmitic acid, palmitoyl chloride, and oil-grafted tannin using palmitoyl chloride [178]–[182]. Figure 2.3 shows the FTIR spectra of mimosa tannin, lauric acid, lauroyl chloride, and oil-grafted tannin using lauroyl chloride [178]–[182]. It can be concluded that different fatty acid chloride chains did not influence the FTIR result but that they affected the yield of oil-grafted tannin, as shown in (Table 2.2).

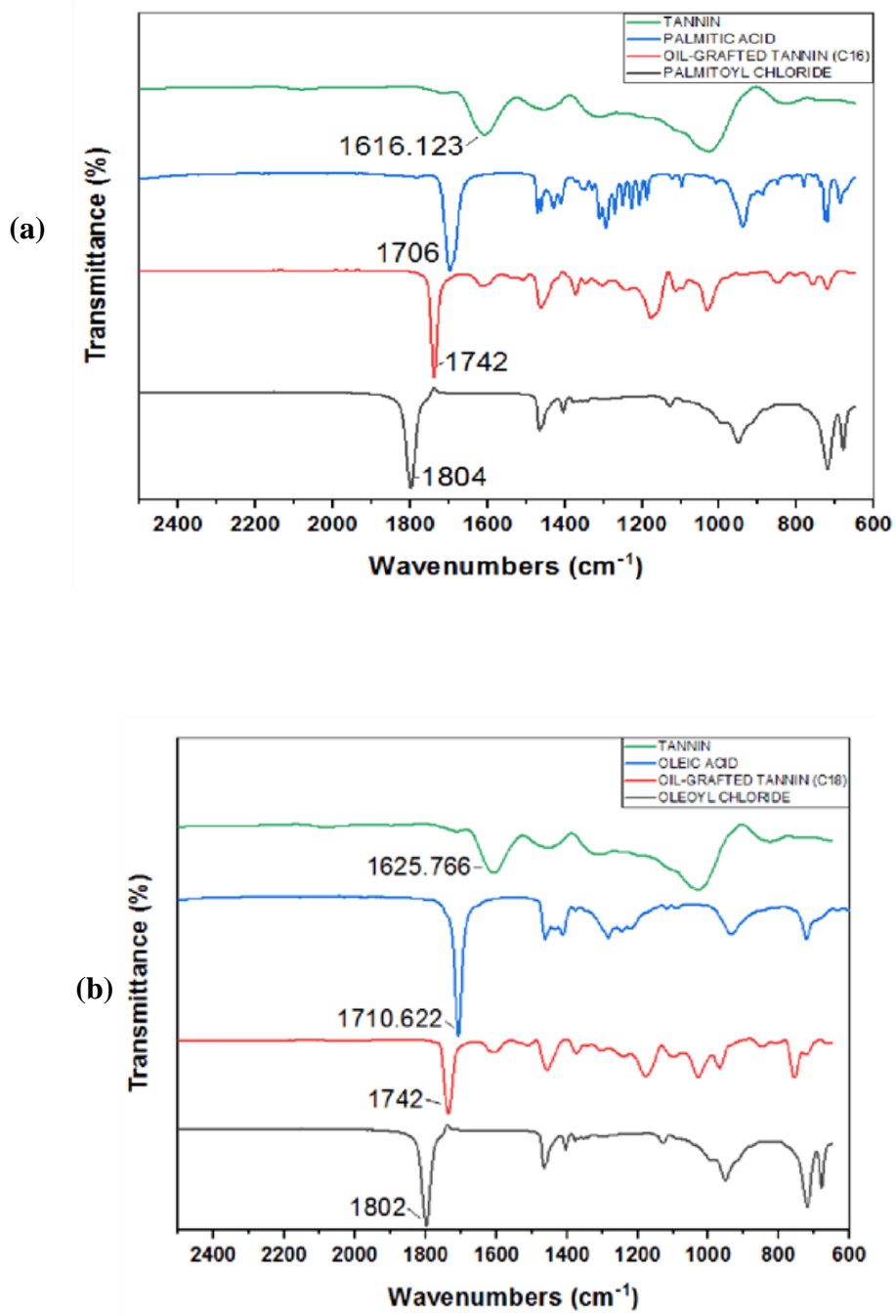


Figure.2. 1-Comparison of FTIR spectra of mimosa tannin, oleic acid, oil-grafted tannin using oleoyl chloride, and oleoyl chloride

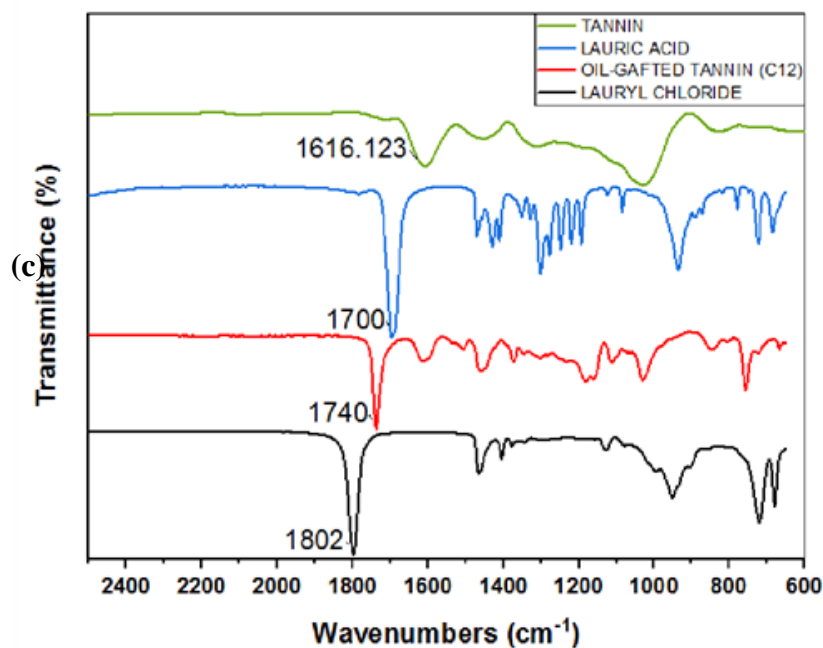


Figure.2. 2-(c). Comparison of FTIR spectra of mimosa tannin, lauric acid, oil-grafted tannin using lauryl chloride, and lauryl chloride

Tableau.2. 2-Yield of oil-grafted tannins using different fatty acid chlorides.

Fatty Acid Chloride	Weight percent gain of Oil-Grafted Tannin after Drying (g)
Lauryl	7.60
Palmitoyl	7.85
Oleyl	8.36

Oil-grafted tannins using different mass ratios of fatty acid chlorides and tannin were also prepared. As different fatty acid chloride chains did not influence the FTIR result, only palmitoyl chloride was consequently maintained for further investigation. Table 2.3 shows different compositions used to synthesize the oil-grafted tannin by using palmitoyl chloride [178]–[182]. Based on Figure 2.4, an absorption band appears at 1804 cm<sup>-1</sup> and 1808 cm<sup>-1</sup> in the spectra of the oil-grafted tannins using palmitoyl chloride with mass ratios of 1:8 and 1:4, respectively. This peak is due to the presence of an excess of the acid chloride group of palmitoyl chloride in the oil-grafted tannin [178]. Contradictorily, the spectra for mass ratios of 1:1 and 2:1 show that there was no presence of peaks from the acid chloride group but only an ester group existed. Therefore, the 1:1 mass ratio was used to prepare the oil-grafted tannin.

Tableau.2. 3-Different compositions used to produce oil-grafted tannin using palmitoyl chloride

Mass Ratio T:P	Palmitoyl Chloride (g)	Chloroform (g)	Tannin (g)
2 :1	0.25	30	0.5
1 :1	0.5	30	0.5
1 :4	2	30	0.5
1 :8	4	30	0.5

(T = Tannin, P = Palmitoyl chloride).

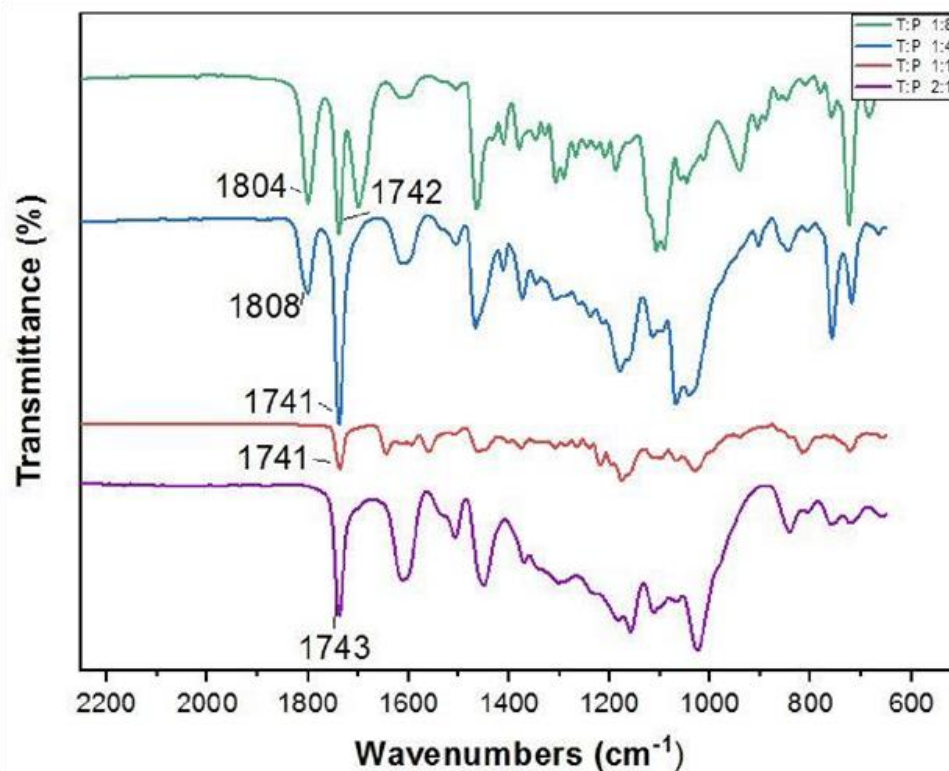


Figure.2. 3-Comparison of different compositions to produce oil-grafted tannin using palmitoyl chloride.

### 3.2. Analyse MALDI-TOF

#### 3.2.1. MALDI-TOF Analysis of Oil-Grafted Tannins from Palmitoyl Chloride

Mimosa tannin is a natural polymer that consists of various types of polyphenolic oligomers. As the commercial tannin extract was used, there were also some residual carbohydrates present, generally fragments of hemicelluloses [2]. Basically, the formation of the oligomers in the condensed tannin consists of four types of flavonoid units, which are fisetinidin (A), robinetinidin and catechin (B), and galocatechin (C), with respective masses of 274.3 Da, 290.3 Da, and 306.3 Da [2]. They are linked to each other mainly at C4-C6 but also C4-C8 (Figure 2.5). It must be pointed out that robinetinidin and catechin have the same molecular mass, but

in mimosa tannin robinetinidin constitutes 70% of the flavonoids present while catechin constitutes only approximately 5% [2] (Figure 2.5). It must be kept in mind however that whenever robinetinidin is mentioned in an oligomer it could also be catechin. These four flavonoid units are shown in Figure 2.5.

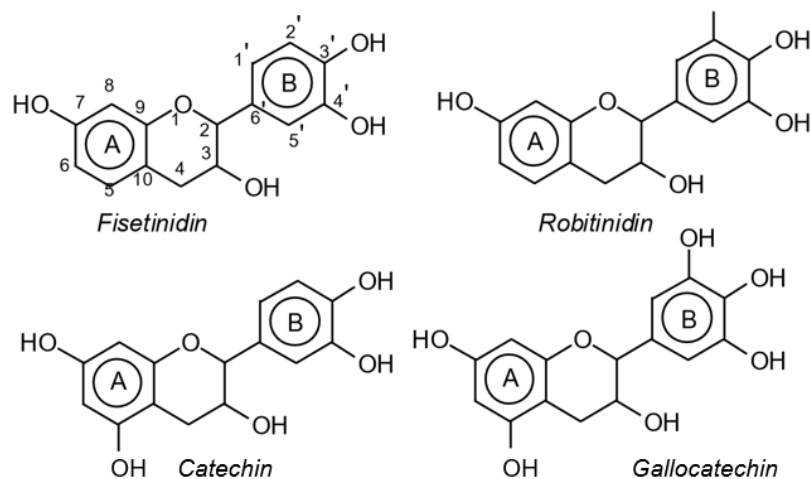


Figure.2. 4-The structure of the four flavonoid types constituting mimosa tannin is shown. A- and B-rings are indicated, and the site numbers have been indicated on the fisetinidin structure.

MALDI-TOF analysis of condensed flavonoid tannins is a proven and established technique [183]–[187]. Table 2.4 shows the characterization of oil-grafted tannin with palmitoyl chloride by MALDI-TOF. Fisetinidin-palmitate (calculated at 515 Da) is protonated and without Na<sup>+</sup>, indicating that the palmitate residues can be on any of the tannin –OHs. Nonetheless, it is most likely to be on the C3, the OH of which has a more alcoholic character. However, it is at least likely that many isomers of each flavonoid-monopalmitate do occur, with the C3-substituted one possibly predominating, as shown by the structures proposed for the species at 515 Da, 529 Da, 747 Da, 782 Da, and 807 Da (Table S1). This is also valid for all the higher oligomers identified and shown in Table S1, except for diesterified flavonoid monomers, triesterified flavonoid monomers, and dimers such as the species at 747 Da, 1027 Da, 1281 Da, 1297 Da, 1315 Da, and 1331 Da (Table S1). In these, at least one of the palmitate residues has reacted on one of the phenolic –OHs of the flavonoids and is thus linked to a phenolic aromatic ring. Robinetinidin-palmitate is protonated without a Na<sup>+</sup> (calculated 529 Da). The same site of reaction is valid for the diprotonated gallocatechin-palmitate, which appears at 545 Da without Na<sup>+</sup>. The species fisetinidin-

(palmitate)<sub>2</sub> without Na<sup>+</sup> (calculated 747 Da) is the first showing that both the alcoholic –OH on the flavonoid C3 and one of the phenolic’s –OHs are also esterified without being able to define if the site esterified on the aromatic ring is on the flavonoid B-ring –OHs or A-ring OHs. The compound (fisetinidin)<sub>2</sub>-(palmitate)<sub>2</sub>, without and with Na<sup>+</sup> at 782 Da and 807 Da, indicates that the second palmitate residue on this flavonoid dimer is more probably or more abundantly on the C3 of the second flavonoid unit, but reaction with one of the phenolic groups (although in a minority) cannot be excluded (Table.2. 6).

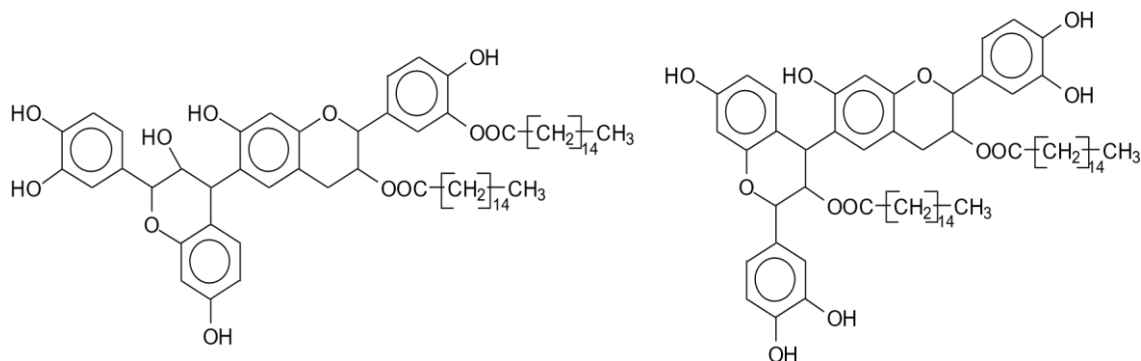
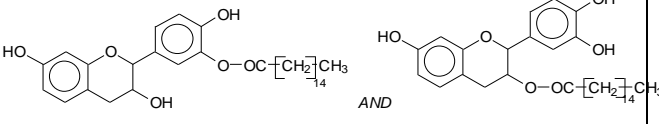
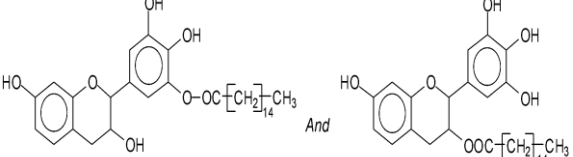
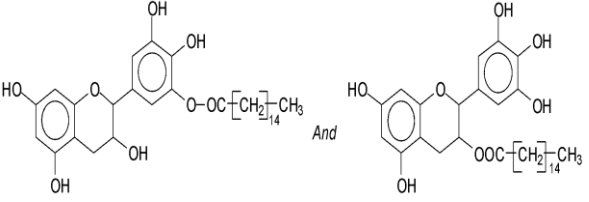
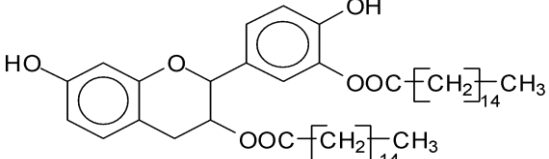
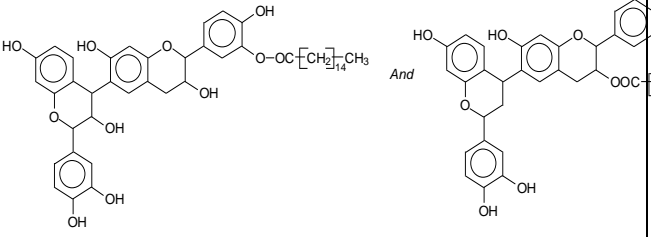
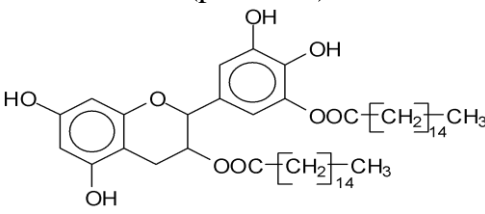
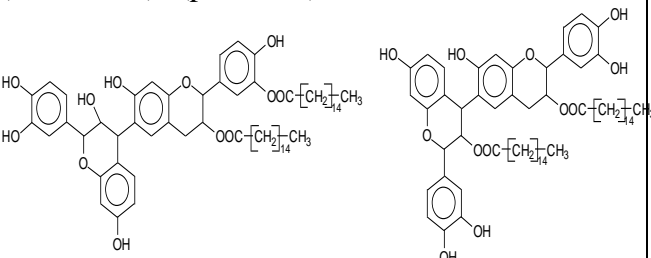


Figure.2. 5-Two of the possible isomer structures for the (fisetinidin)<sub>2</sub>-(palmitate)<sub>2</sub> oligomer, showing that the palmitoyl residue can have reacted both on the C3 alcoholic –OH and on one of the phenolic –OHs.

Tableau.2. 4-Characterization by MALDI-TOF of oil-grafted tannins using palmitoyl chloride

Molecular Species	Experimental (Da)	Calculated (Da)	Remarks
<p>Fisetinidin-palmitate, protonated</p> 	515 Da	513 Da	Free flavonoid monoester
<p>Robinetinidin-palmitate, protonated, no Na<sup>+</sup></p> 	529 Da	528 Da	Free flavonoid monoester, protonated
<p>Gallocatechin-palmitate</p> 	545 Da No Na <sup>+</sup>	544 Da No Na <sup>+</sup>	Free flavonoid monoester, protonated
<p>Fisetinidin-(palmitate)<sub>2</sub>, no Na<sup>+</sup></p> 	747 Da	750 Da	Free flavonoid diester, deprotonated
<p>(Fisetinidin)<sub>2</sub>-palmitate</p> 	784 Da No Na <sup>+</sup> 807 Da with Na <sup>+</sup>	784 Da No Na <sup>+</sup> 807 Da with Na <sup>+</sup>	Flavonoid dimer monoester
<p>(Robinetinidin)<sub>2</sub>-palmitate</p>	801 Da	800 Da	Flavonoid dimer monoester, protonated



Gallo catechin-(palmitate) <sub>2</sub> + Na <sup>+</sup> 	782 Da No Na <sup>+</sup> 805 Da with Na <sup>+</sup>	782Da No Na <sup>+</sup> 805 Da with Na <sup>+</sup>	Free flavonoid diester
(Fisetinidin) <sub>2</sub> -(palmitate) <sub>2</sub> 	1021Da No Na <sup>+</sup> 1046 Da with Na <sup>+</sup>	1021Da No Na <sup>+</sup> 1046 Da with Na <sup>+</sup>	Flavonoid Dimer diester
Robinetinidin-(palmitate) <sub>3</sub>	1027 Da with Na <sup>+</sup>	1027 Da with Na <sup>+</sup>	Flavonoid monomer triester
(Fisetinidin) <sub>2</sub> -(palmitate) <sub>3</sub>	1281 Da with Na <sup>+</sup>	1282 Da with Na <sup>+</sup>	Flavonoid Dimer triester
Robinetinidin-fisetinidin-(palmitate) <sub>3</sub>	1297 Da with Na <sup>+</sup>	1298 Da with Na <sup>+</sup>	Dimer triester
(Robinetinidin) <sub>2</sub> -(palmitate) <sub>3</sub> , protonated	1315 Da with Na <sup>+</sup>	1314 Da with Na <sup>+</sup>	Dimer triester
Robinetinidin-Gallo catechin-(palmitate) <sub>3</sub> , protonated	1331 Da with Na <sup>+</sup>	1329 Da with Na <sup>+</sup>	Dimer triester,
Glucose-(fisetinidin) <sub>2</sub> -(palmitate) <sub>3</sub>	1442 Da with Na <sup>+</sup>	1443 Da with Na <sup>+</sup>	Glucoside dimer triester
Robinetinidin-(fisetinidin) <sub>2</sub> -(palmitate) <sub>3</sub>	1571 Da with Na <sup>+</sup>	1571 Da with Na <sup>+</sup>	Trimer triester
(gallo catechin) <sub>2</sub> -(palmitate) <sub>4</sub>	1580 Da no Na <sup>+</sup>	1580Da no Na <sup>+</sup>	Dimer tetraester
(Robinetinidin) <sub>2</sub> -fisetinidin-(palmitate) <sub>3</sub>	1587 Da with Na <sup>+</sup>	1587 Da with Na <sup>+</sup>	Trimer triester

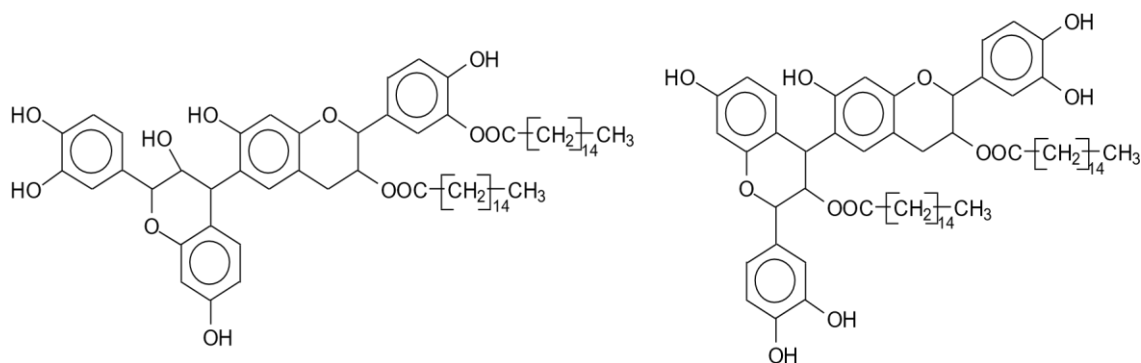


Figure.2. 6-Two of the possible isomer structures for the (fisetinidin)2-(palmitate)2 oligomer

This schema is showing that the palmitoyl residue can have reacted both on the C3 alcoholic –OH and on one of the phenolic –OHs.

This demonstrates that flavonoid oligomers are also esterified. The compound (galocatechin)2-(palmitate)4- without Na<sup>+</sup> indicates that at least two of the phenolic –OHs do esterify, not just the two alcoholic –OHs in C3s. Figure 6a–c shows a MALDI-TOF analysis of modified oil-grafted mimosa tannin extract using palmitoyl chloride with the molecular weight ranging from 400 to 1600 Da. One unusual but indicative species formed that is worth noting is the one at 1442 Da, where a triesterified flavonoid dimer is linked to a glucose residue. It is well-known that in flavonoid tannin extracts there are residual carbohydrates and fragments of hemicelluloses, some of which even link to flavonoid moieties [184], [185].

This is the case of the species at 1442 Da but considering the high proportion of –OH groups on glucose, one cannot say if the palmitoyl residues are linked just to the flavonoids or if some are linked onto the carbohydrate (Figure 2.7). Two of the possible isomer structures are shown in Figure 5, but other isomers where the distribution of the palmitoyl residues can be different could equally be present (Figure 2.8). The results of MALDI-TOF between 400 and 1600 Da are shown in (Figure 2.9)

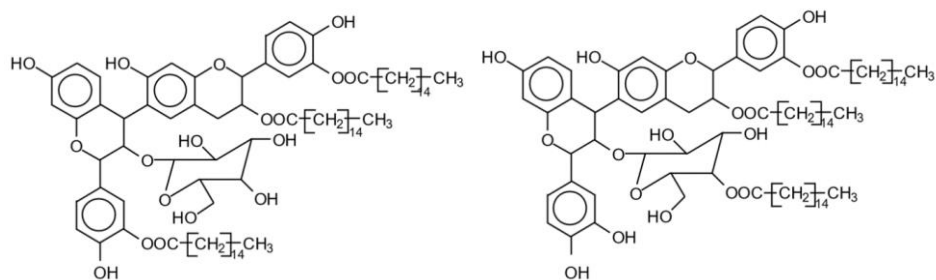
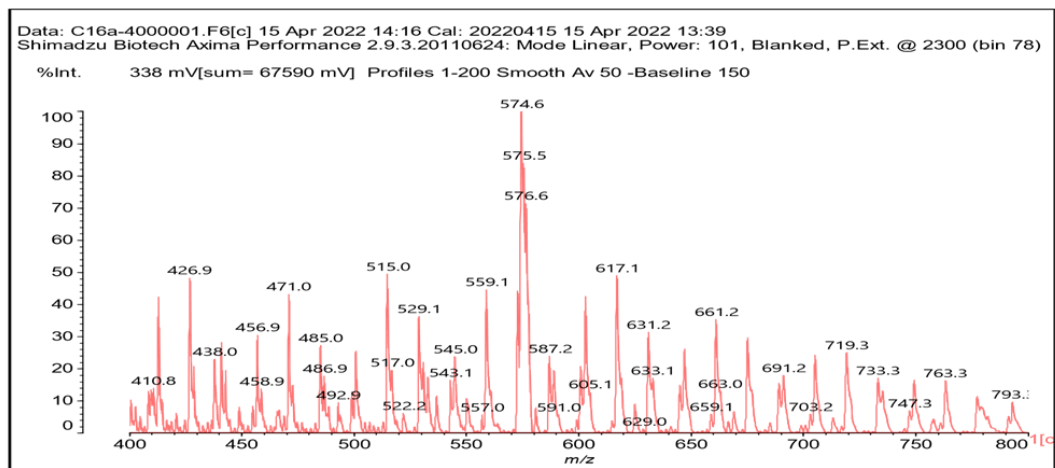
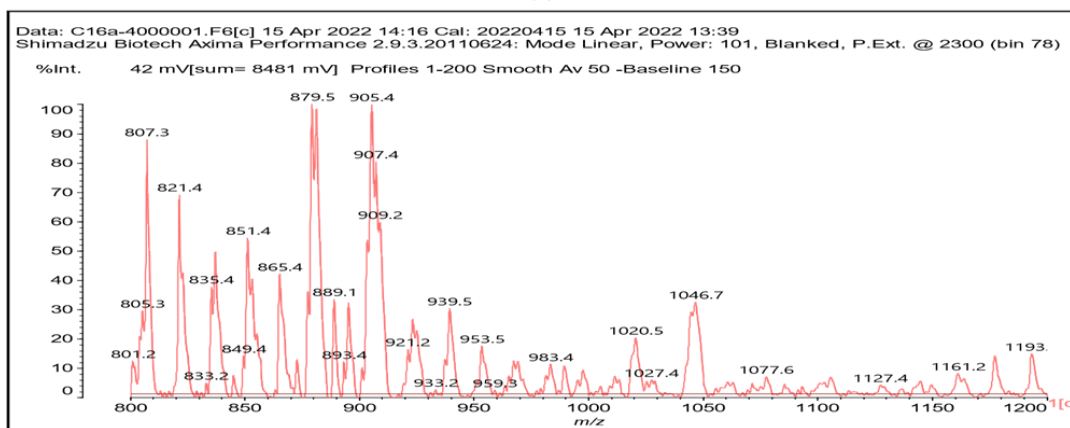


Figure.2. 7 -Example of the structures of two possible isomers of the identified species glucose(fisetinidin)2-(palmitate)3 at 1442 Da



(a)



(b)

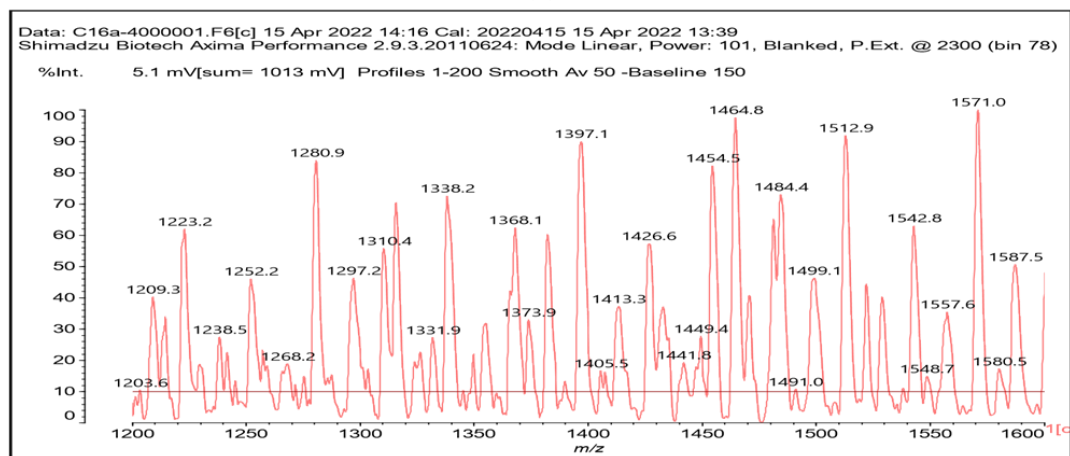


Figure.2. 8-MALDI-TOF mass spectra of oil-grafted tannin with palmitoyl chloride (a) from 400 Da to 800 Da, (b) from 800 Da to 1200 Da, (c) from 1200 Da to 1600 Da

### 3.2.2. MALDI-TOF Analysis of Oil-Grafted Tannins from Oleoyl Chloride

Figure 2.11 shows the results of MALDI-TOF for oil-grafted tannin with oleoyl chloride with the molecular weight ranging from 400 to 1600 Da and the Table S1 (Annex.1) and Figure S1a–d (Annex) (Supplementary Material) shows the characterization of oil-grafted tannin with oleoyl chloride using MALDI-TOF with the details. The compound fisetinidin-oleate monoester is protonated with Na<sup>+</sup> (calculated 561 Da), indicating that the oleate residues can be on any of the –OHs, but they are most likely to have reacted with the –OH on the C3 that has a more alcoholic character. The same is true for the robinetinidin-oleate monoester, normal and deprotonated with Na<sup>+</sup> (calculated 575–577 Da). The fisetinidin-(oleate)<sub>2</sub> diester at 801 Da is the first compound that demonstrates that both the alcoholic –OH on C3 and one of the phenolic –OHs are also esterified, without being able to define if it is with the B-ring or A-ring –OHs. The same can be said for the series of compounds in Table S2 at 841 Da, 1105 Da, 1331 Da, 1355 Da, 1609 Da, and 1630 Da. Of these the species at 1105 Da, a robinetinidin trioleate, must be particularly noted (Figure 2.10), indicating that a flavonoid can be extensively esterified on the majority of its –OH groups.

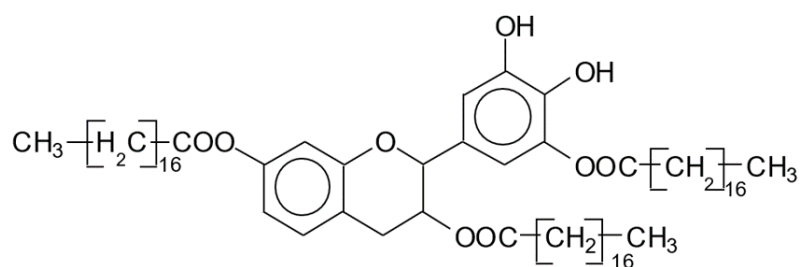


Figure.2. 9-Examples of the structure of a robinetinidin-(oleate)<sub>3</sub>, with Na<sup>+</sup>.

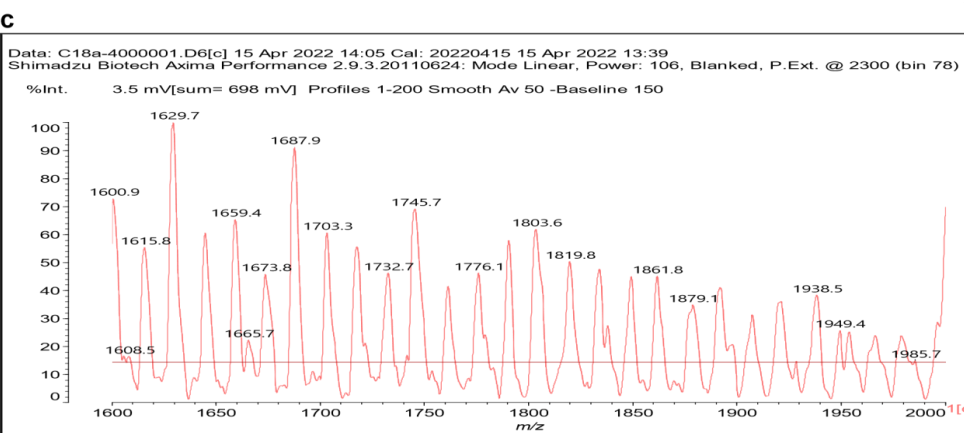
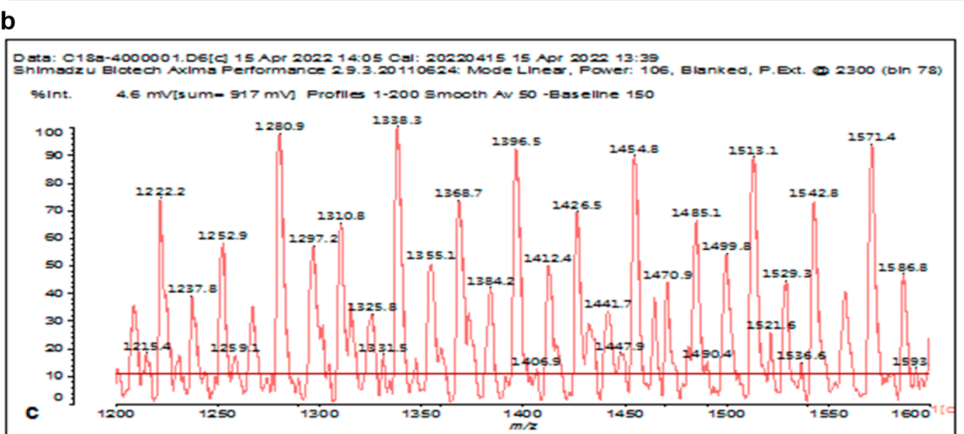
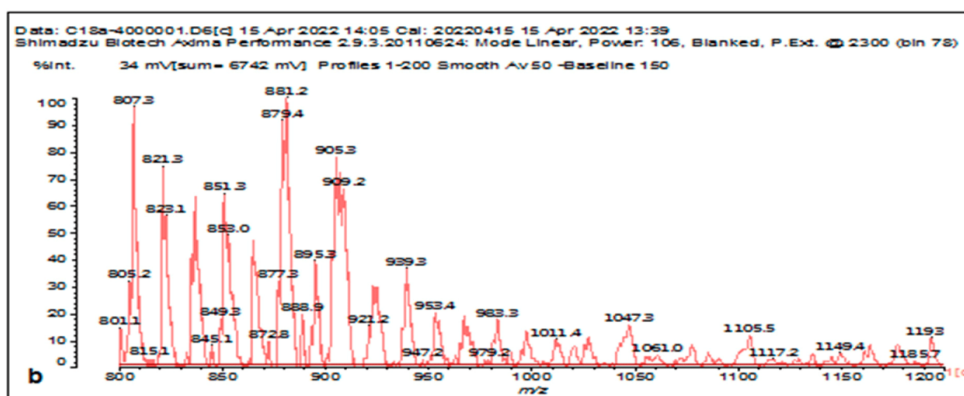
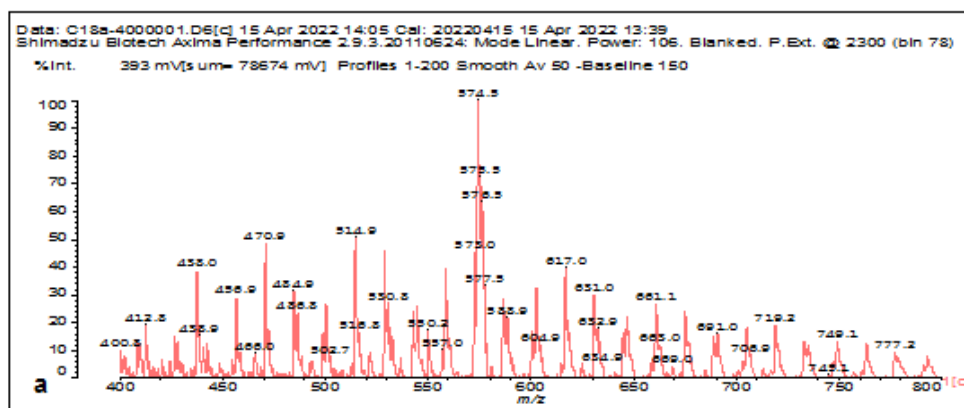


Figure.2. 10-MALDI-TOF mass spectrum of oil-grafted tannin with oleoyl chloride (a) from 400 Da to 800 Da, (b) from 800 Da to 1200Da, (c) from 1200 Da to 1600 Da, (d)from 1600 Da to 2400 Da

At 1609 and 1630 Da is a robinetinidin pentaoleate ester that has all the –OHs of the flavonoid esterified, indicating that phenolic –OHs do react with the fatty acid with ease, notwithstanding their slightly acid behaviour (Annex.2). Their several flavonoid dimers esterified, such as the ones at 1149 Da, 1331 Da, 1355 Da, 1338 Da, 1500 Da, 1601 Da, 1609 Da, 1630 Da, and 1688 Da, which shows that higher flavonoid oligomers are also esterified with ease. As for the flavonoid palmitates, a species at 1500 Da is an oleate triester linked to a flavonoid dimer to which, as in the palmitate esters' case, is also linked a glucose residue of the hemicelluloses present in a small amount in the extract.

In principle, the pattern of compounds formed is very similar to what was observed for the flavonoid palmitate esters. Figure S2a–d show the MALDI-TOF spectra of modified oil-grafted tannins using oleoyl chloride with the molecular weight ranging from 400 to 2000 Da.

### **3.2.3. MALDI-TOF Analysis of Oil-Grafted Tannins from Lauryl Chloride**

Table S2(Annex.3) and Figure S2 (Annex.4) show the characterization of oilgrafted tannins with lauryl chloride using MALDI-TOF mass spectrometry. The chemical species found for the esterification of tannin with lauryl chloride are rather like what was already observed in Tables 4 and 5 for tannin esterified with palmitoyl chloride and oleyl chloride, but series of oligomers are more and more clearly visible in the spectrum, probably due to the lower molecular weight of the laurate residue and its possibly higher mobility. Thus, there are four clear peak series, each separated by a repeating motive of 182 Da, that are clearly identifiable in this particular case. The first of these is formed by the peaks at 1011 Da, 1193 Da, 1375 Da, 1557 Da, 1740 Da, 1922 Da, 2104 Da, 2286 Da, and 2468 Da. These are formed by the progressive addition of one lauryl residue at a time on a glucose-(robinetinidin)<sub>2</sub>-fisetinidin oligomer at 1011 Da, starting with the glucose(robinetinidin)<sub>2</sub>-fisetinidin-laurate (no Na<sup>+</sup>) oligomer at 1193 Da and ending with the glucose-(robinetinidin)<sub>2</sub>-fisetinidin-(laurate)<sub>8</sub> (no Na<sup>+</sup>) oligomer at 2468 Da. As inferred, the esterification of a carbohydrate side chain linked to the flavonoid also occurs extensively with the tannin laurate (Table S2) (Supplementary material).

The second clearly identifiable series of peaks, also separated by a repeating mass of 182 Da, is the one formed by the peaks at 633 Da, 815 Da, 997 Da, 1179(s) Da, 1361(s) Da, 1543 Da, 1724 Da, 1906 Da, 2089 Da, and 2271 Da. These are formed by the progressive addition of one lauryl residue at a time on a (galocatechin)<sub>2</sub> oligomer at 633 Da (with Na<sup>+</sup>), starting with the (galocatechin)<sub>2</sub>-laurate (with Na<sup>+</sup>) oligomer at 815 Da and ending with the (galocatechin)<sub>2</sub>-(laurate)<sub>9</sub> (with Na<sup>+</sup>) at 2271 Da.

The third series is composed of the peaks at 617 Da, 981 Da, 1163 Da, 1344 Da, 1526 Da (shoulder), 1708 Da, 1890 Da, 2072 Da, and 2254 Da. These are formed by the progressive addition of one lauryl residue at a time on a gallo catechin-robinetinidin oligomer at 617 Da (with Na<sup>+</sup>). However, an expected peak at 798 Da that should represent a gallo catechinrobinetinidin-laurate oligomer does not appear in the spectrum. Thus, the series of laurate peaks starts with the 981 Da gallo catechin-robinetinidin-(laurate)<sub>2</sub> and ends with the 2254 Da gallo catechin-robinetinidin-(laurate)<sub>9</sub>, all with Na<sup>+</sup>. The peak at 1526 Da is really a barely visible shoulder. There then exists a fourth series of rather small peaks, namely 587–589 Da, 953 Da, 1317 Da, 1499 Da, 1681 Da (shoulder), 1863 Da, and 2045 Da. These are formed by the progressive addition of one lauryl residue at a time on a fisetinidin-robinetinidin oligomer represented by 585–589 Da peaks (with Na<sup>+</sup>). The oligomer sequence here starts with the peak at 953 Da, being a fisetinidin-robinetinidin-(laurate)<sub>2</sub>, and ends with the peak at 2045 Da, being fisetinidin-robinetinidin-(laurate)<sub>8</sub>, all with Na<sup>+</sup>. Two peaks that should be in the series are not present, namely one that should be at 771 Da and the other at 1135 Da. These represent the absent oligomers fisetinidin-robinetinidin-laurate and fisetinidin-robinetinidin- (laurate)<sub>3</sub>, respectively, both absent from the spectra. One can only speculate why this occurs, but it could be that these two species might be particularly reactive, and they are not replenished once a further lauryl chloride reacts with them, hence not surviving to the conditions of esterification of the tannin that have been used.

### **3.3. Density and Friability**

In Table 2.1 are shown the formulations used to prepare the oil-grafted tannin foams. A small amount of oil-grafted tannin prepared with palmitoyl chloride was added into the formulation to increase the wettability of the foam. Figure 2.12 shows examples of foam cubes of each formulation listed in Table 1, while the respective densities of the five different formulations in which the additive was palmitoyl-grafted tannin are shown in Table 2.5. Table 5 shows that the density of the standard foam was higher than the densities of the foams in which a palmitoyl-grafted tannin additive had been included. This is worth keeping in mind when measuring the respective friability of these foams, as in general, for the standard formulation the lower the density the more friable the foam.

Tableau.2. 5-Density of tannin foams with oil-grafted tannin.

Foam Sample	Density (g/ cm <sup>3</sup> )
Standard foam	0.12
Formulation A	0.0815
Formulation B	0.0853
Formulation C	0.0849
Formulation D	0.1061

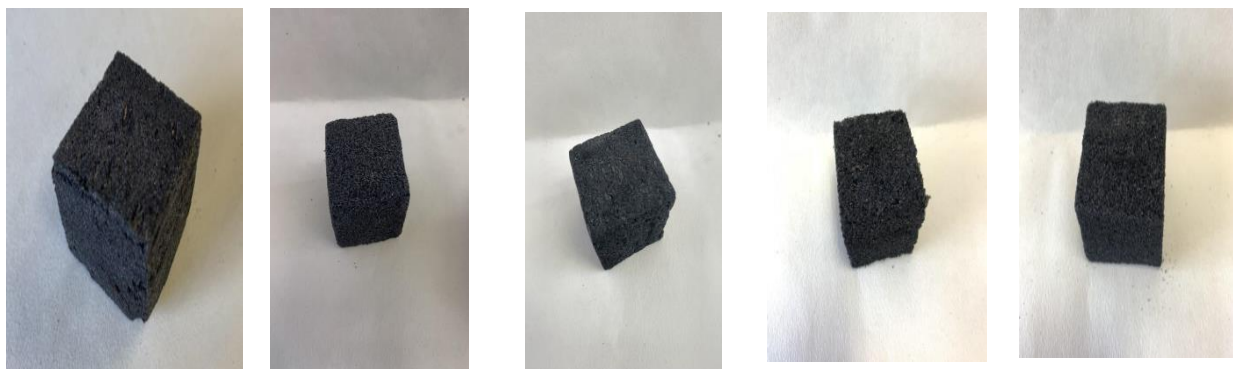


Figure.2. 11-From left to right: examples of cubes of standard foam, Foam A, Foam B, Foam C, and Foam D.

Figure 2.12 shows the improvement in friability that occurred with the different foams to which the palmitic oil residues grafted to the tannin had been used as an additive in a relatively small amount [70], [171]. The figures show, from the black trace of foam material produced by friction on the white paper, that the four experimental formulations are in general markedly less friable than the standard foam, and this at a lower density of the standard foam (Table 2. 5). From more friable to less friable, their order is Standard>D>A>C>>B (Figure 2.13). Thus, Formulation B is clearly the best of the four experimental foams, with a non-friable surface, a considerable advantage for its application in several uses. The main difference from the other foams is the presence of glutaraldehyde as a cross-linker, while the use of acetaldehyde is not as performant in terms of eliminating friability, as can be seen from the friability of foam C that is worse than for foam D.



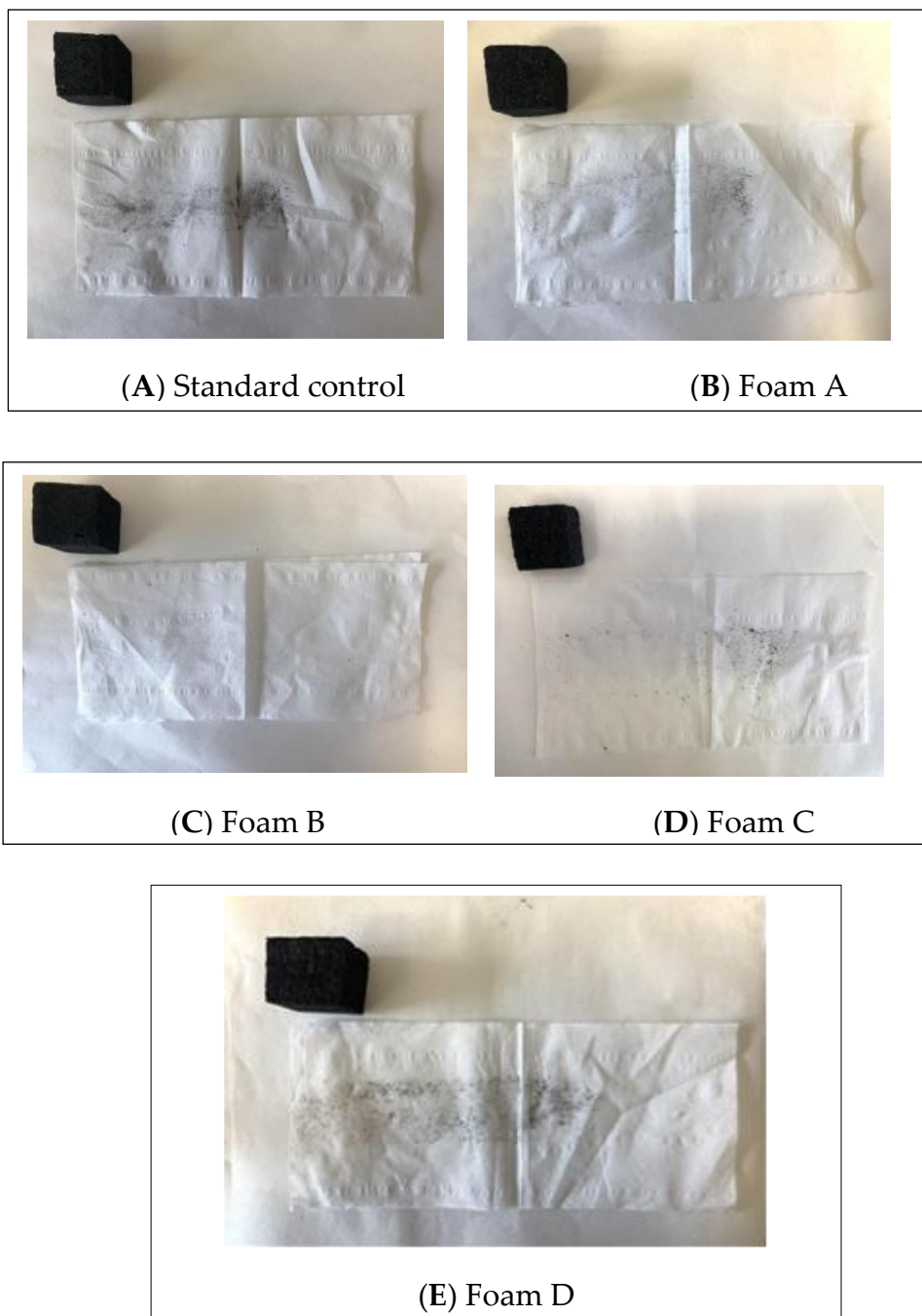


Figure.2. 12- Surface friability test of the standard foam and the four oil-grafted foams A, B, C.

### 3.4. Wettability

Figure 2.14 shows the results of the initial contact angle of a sessile water drop on the surface of the five foams, and the variation of the contact angle as a function of time in the first 180 s. The contact angle of the standard foam is high, around  $90^\circ$  at the first second of measure, but it decreases abruptly after 10 s and after 50 s the water droplet has completely penetrated the foam. This is not the case, however, for the foams with an oil-grafted tannin additive. After 150 s the contact angle reading became static and remained the same for samples A, B, and C. For sample D it became static after just 20 s. This means that adding the oil-grafted tannin additive increases the water-repellent property of the four experimental foams. Thus, the water drop

contact angle becomes stable in the order from the best to the worst of D>B=C>A>Standard. The respective surface energies were also calculated (Table 2.6).

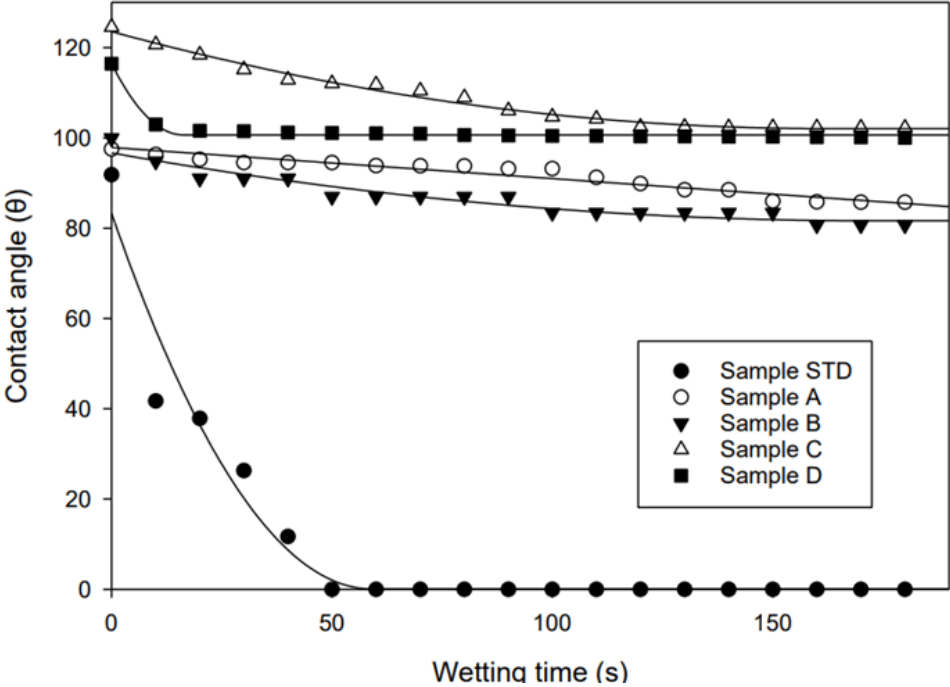


Figure.2. 13- Wetting angle and its variation as a function of time of the (●) standard foam, (○) foam A, (▼) foam B, (△) foam C, and (■) foam

Tableau.2. 6-Contact angle measurement and value of total surface free energy (SFE).

Sample	Contact Angle (°)	Surface Energies (mN m <sup>-1</sup> )		
	Water	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$
STD	91.83 (19.81)	17.06	8.26	8.8
A	97.51 (3.89)	13.76	7.91	5.85
B	99.93 (5.21)	12.47	6.66	5.81
C	124.54 (7.07)	3.41	3.94	-0.53
D	116.44 (3.66)	5.60	5.05	0.55

where  $\gamma_s$  = total surface free energy of foam's solid,  $\gamma_s^d$  = dispersive surface energy of foam's solid, and  $\gamma_s^p$  = polar surface energy component of foam's solid.

Table 2.6 shows the total surface free energy (SFE) for all the foams, both the standard one and the four with a palmoyl-grafted tannin additive. The total  $\gamma_s$  value decreases as the contact angle of the surface increases. It can be shown that samples A, B, C, and D are hydrophobic, since the value of the polar SFE component  $\gamma_s^p$  is smaller than that of the value of the dispersive SFE  $\gamma_s^d$ , thus proving that the addition of palmitic oil-grafted mimosa tannin to a tannin foam increases its water repellence. This confirms that Foams D and C are the most water-repellent, while A and B are less water-repellent, and the standard foam is not water-repellent, thus confirming the results of the contact angle test.

Table.2.7 reports the values of  $\gamma_l$  = total surface free energy of liquid;  $\gamma_l^p$  = polar surface energy component of liquid;  $\gamma_l^d$  = dispersive energy component of liquid. This shows that water is a very polar liquid and supports the water repellence of the foams as discussed above from the results in Table2.7.

Tableau.2. 7-Surface energy of liquids with polar and dispersion surface energy components.

Liquid	$\gamma_l$ (mN m <sup>-1</sup> )	$\gamma_l^p$ (mN m <sup>-1</sup> )	$\gamma_l^d$ (mN m <sup>-1</sup> )
Water	72.8	51	21.8

#### 4. Conclusions

Commercial mimosa tannin extract was esterified with palmitic, oleic, or lauric acid by reaction with their respective chlorides, with good yields. When used as a small proportion additive in tannin-furanic foams, the esterified tannins rendered the surface of these foams much less or even not at all friable, and very markedly improves both their water repellence and its maintenance over time in relation to a tannin-furanic foam control without this additive. Chemical analysis indicated that esterification of the tannin occurred and indicated a range of esterified tannin oligomers which were formed. These results indicate that this route is viable for eliminating the two problems of friability and wettability of these bio foams.

### **3.Flexible, Water Repellent Tannin-Furanic-Fatty Acids Biofoams (Publicaion.II)**

#### **Abstract**

Water repellent, flexible biofoams using tannin esterified with various fatty acid chains, namely lauric, palmitic and oleic acids, by reaction with lauryl chloride, palmitoyl chloride, and oleyl chloride were developed and their characteristics compared with the equivalently esterified rigid biofoams. Glycerol, while initially added to control the reaction temperature, was used as a plasticizer yielding flexible biofoams presenting the same water repellent character that the equivalent rigid foams. Acetaldehyde was used as the cross-linking agent instead of formaldehyde, as it showed a better performance with the esterified tannin. The compression results showed a significant decrease of the Modulus of Elasticity (MOE) of the flexible foams in relation to that of the rigid foams, confirming their flexible character. The lauryl- and palmitoyl-esterified biofoams presented similar mechanical properties, while the oleyl-esterified biofoam presented different mechanical and morphological result not really showing the expected flexibility. Both the esterified rigid and flexible tannin-based biofoams showed good water resistance and their sessile drop contact angle analysis as a function of time confirmed this characteristic. Scanning electron microscope (SEM) analysis showed the flexible foams to present a higher proportion of closed cells than the rigid foams. Conversely, the cells depth of the flexible foams was lower than that of the rigid foam. As regards their thermal resistance, the flexible foams showed a slight loss of mass compared to the rigid ones without glycerol. Both types of foams presented much lower surface friability of non-esterified rigid foams.

#### **KEYWORDS**

Flexible tannin-furanic foams; esterified tannins; water repellence; TGA; SEM; compression

## 1-Introduction

Tannins are a complex class of natural polyphenols that are widely distributed in plant species, including fruits, vegetables, and trees. Due to their unique chemical structure [188], tannins, especially commercial condensed flavonoid tannin extracts have been used for a number of different applications in biomaterials science [102], [150]. Tannins have been used as binders to create composites either alone [189] with other renewable materials, such as lignin [190] and proteins such as soy [191]–[193]. They have unique properties, including high mechanical strength and low flammability, making them suitable for use in the production of insulation materials. Their addition to composites can enhance their thermal stability and flame resistance, further increasing their potential as insulation materials [145]. Moreover, tannin-based composites could be biodegradable, making them a more sustainable alternative to traditional insulation materials.

Tannins have been shown to possess excellent thermal stability and can be easily modified to enhance their performance as insulation materials. In addition, tannins are abundantly available in nature and can be extracted using sustainable methods, making them a promising candidate for the development of eco-friendly insulation materials [102], [150], [63], [194]. One promising application is in the development of insulation foams [83], [103], [139].

Rigid tannin foams are typically produced through reacting furfuryl alcohol, another biosourced material [195] with tannins in the presence or absence of aldehydes and with or without a blowing agent [83], [86] or by the formation of non-isocyanate polyurethanes foams for both condensed flavonoid tannins [123], [136], [137], [139] and hydrolysable tannins [140], [188].

The reaction leads to the formation of a crosslinked polymer network, which imparts rigidity and mechanical strength to the foam. These foams are typically used in applications such as fire and acoustic insulation [98], [103], [150], with also applications in hydroponics [134].

Conversely, flexible tannin foams have been reported by incorporating plasticizers or other additives into the tannin reaction mix. The plasticizers reduce the crosslinking density of the foam and increase its flexibility, making it suitable for use in other applications [95], [196].

Tannin-based bio foams, however, also exhibit some limitations, such as, friability, low water repellency and their somewhat inadequate compatibility with hydrophobic compounds. Therefore, to overcome these limitations and improve the properties of tannin bio foams, researchers have developed various methods to modify them, including their esterification with

a fatty acid [70]. Recently rigid foams presenting lower friability and increased water repellence have been obtained by adding to tannin-furanic foams a relatively small proportion of tannin the flavonoid units of which were esterified by lauroyl, palmitoyl and oleyl chlorides [71] to obtain structures of the type:

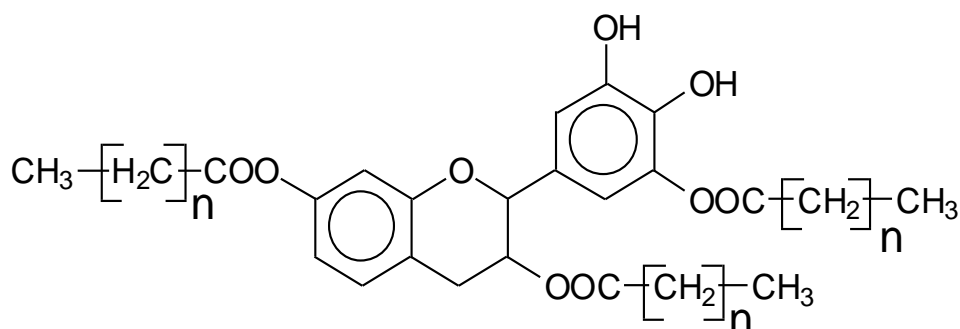


Figure.2. 14-Chemical Structure of One Esterified Flavonoid.

with  $n=12$  (lauroyl), 16 (palmitoyl) and 18 (oleyl). The esterification with fatty acids of condensed tannins can be achieved through various methods, such as esterification [68], [70], [71], [165], amidation, or transesterification, which results in the formation of amphiphilic molecules with both hydrophilic and hydrophobic properties. This modification enhances the emulsifying and dispersing properties of tannins, as well as their solubility and compatibility with hydrophobic compounds, making them suitable for use in various applications, such as coatings, adhesives, and bio- forms.

There are works reporting successful modification of tannins using fatty acids grafting such as oleic acid [68], [70], stearic acid [68], and lauric acid [71] and palmitic acid [70], [71], which have resulted in improved hydrophobicity and dispersing properties, enhanced thermal stability, and better compatibility with hydrophobic compounds. Furthermore, the degree of modification and the type of fatty acid used can be tailored to suit specific applications, making fatty acid-grafted tannins a promising avenue for developing new materials with improved properties.

The main unresolved problem to extend the applicability of these foams is the lack of the coupling of the fatty acid esterification technology with the flexibility technology due to the addition of plasticizers. The coupling of these two technologies would allow easier fitting foams for applications such as thermal insulation to steam or water pipes, as well as more adaptable acoustic insulation fitting to several different surface geometry. The work presented here does then aim to combine fatty-acid esterification of a commercial condensed flavonoid tannin extract with the addition of glycerol to obtain flexible, water-repellant, non-friable, fire-resistant

flexible bio foams and to compare their characteristics with those of rigid tannin-based foams both with and without fatty acids esterification.

## **2. Materials and Methods**

This research is divided into two parts:

- 1) Preparation of esterified tannin that is involved in the reaction between the flavonoid's groups and a fatty acid compound such as oleoyl chloride and palmitoyl chloride in a solvent. The method applied to synthesize the fatty acid-grafted tannin was obtained from previous work [71].
- 2) The conception of water repellent tannin-based biofoams. Their formulations are indicated in Table 2.8

### **2.1. Materials**

Mimosa (*Acacia mearnsii* formerly *mollissima*, de Wildt) tannin extract as the main structural compound of this work was supplied by Silva Chimica (St. Michele Mondovi', Italy). Furfuryl alcohol were purchased from Acros Organics (Geel, Belgium). Para-toluene-sulphonic acid (pTSA), diethyl ether, acetaldehyde, and glutaraldehyde were purchased from Sigma-Aldrich (St. Louis, MO, USA). Lauroyl chloride, oleoyl chloride and palmitoyl chloride were acquired from Alfa Aesar (Kandal, Germany). Chloroform was obtained from Merck (Darmstadt, Germany).

### **2.2. Synthesis of Oil-Grafted Tannin**

The method to synthesize the oil-grafted tannin was modified from that reported from previous work [71]; 5 g of commercial mimosa tannin extract was weighed and transferred into a 250 mL round bottom flask and then 80 g of chloroform was added, followed by 3.75 g of fatty acid chloride acid.

The reaction was left for at least 16 hours while maintaining the temperature below 40 °C and then evaporated. This procedure gives an esterified tannin that doesn't have to be washed by a solvent and it can be used directly afterwards.

### **2.3. Foam Preparation**

Each esterified mimosa tannin extract was mixed with furfuryl alcohol. Then, the non-esterified mimosa tannin extract was added and mixed with acetaldehyde (99% solution) and water. For the flexible foams glycerol was added at this stage and mixed rapidly. Last, para-toluene-

sulfonic acid (pTSA) 65% solution in water as catalyst, and diethyl ether (blowing agent) were added to the mixture, followed by 40 s of vigorous stirring. The rigid foam was obtained rapidly and the flexible foam acquired its final structure within 2-3 minutes. The foam was then left for at least 24 h to allow evaporation and elimination of the residual blowing agent trapped in it. The formulations used are shown in Table.2.8.

Tableau.2. 8-Formulations used to prepare the rigid and flexible foams

Formulation	STD rigid foam	Esterified rigid foams(R)	Esterified flexible foams(F)
Category of foam	STD	(C12, C16, C18)	(C12, C16, C18)
Mimosa tannin extract (g)	15	13.75	13.75
Fatty acid-grafted mimosa tannin (g)	0	1.25	1.25
Furfuryl alcohol (g)	5.5	5.5	5.5
Acetaldehyde	3	3	3
Water (g)	3	3	2
Glycerol (g)	1.5	0	5
Diethyl ether (g)	1.7	1.7	1.7
pTSA (g)	5.5	5.5	5.5

**R** (C12, C16, C18) are the rigid water repellent tannin foams with added tannin esterified with three types of fatty acids

**F** (C12, C16, C18) are the flexible water repellent tannin foams with added tannin esterified with three types of fatty acids

**STD:** Unmodified foam

## 2.4. Characterization of Tannin-Based Foam

### 2.4.1. Initial Observations

First, some properties such as apparent density, induction time (min), and the absorption resistance time of a drop of water on the surface of a foam have been registered. The bulk density was calculated as each sample's weight/volume ratio of a sample of dimension of 30 mm × 30 mm × 30 mm.

The induction time is the time necessary to complete the foaming procedure.

### 2.4.2. Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM, Hitachi TM-3000) (Milexia, Paris, France) was used to analyze the microstructure and morphology of the foams obtained. All samples were made into 0.5 cm<sup>2</sup> cross-sections. Then, a thin layer of gold-palladium was sputtered on the surface of the foams to obtain a better definition of the image.



This analysis was carried out to compare the effect of different types of esterified tannin on the foams cell structure, and additionally to observe the differences between the rigid and flexible foams.

### **2.4.3-Compression Resistance**

The samples were cut into a uniform size of 30 mm × 30 mm × 20 mm. A universal testing machine (Instron 4301, Elancourt, France) was used to test the compression strength of the foams. The direction of the load was parallel to that of the foam rise under ambient conditions. The crosshead rate was fixed at 2.0 mm·min<sup>-1</sup>. At least three sample were tested for each foam.

Three samples of 30x30x20 mm were placed under 10 cycles of compression at a strain of 10%, 20% and 40%. The Modulus of Elasticity (MOE), strain, and stress values were calculated and compared to observe the different behavior of rigid and flexible foams.

### **2.4.4-Contact Angle Measurement**

The determination of the water contact angle to measure the wettability of the tannin foam, and its maintenance as a function of time, was carried out using a video measuring system from Krüss Gmb (Villebon-sur-Yvettes, France), equipped with a high-resolution CCD camera. The tannin foams were placed on the top of a table in front of the CCD camera. A water droplet of 20 microliter was placed onto the foam surface using a micropipette to always obtain the same size droplet. The drop shapes on the surface of the tannin foam were captured by the CCD camera and measured during a period of 180 s. In total, 60 images were taken for each recorded drop to obtain a curve of contact angle versus wetting time.

### **2.4.5-Thermogravimetric Analysis (TGA)**

A thermogravimetric (TGA) analysis was performed by TGA/DSC1-TMA/SDTA 84Xe instrument from Mettler Toledo (Viroflay, France) equipped with a STARE v.11 fr System program. This analysis was realized to measure the foam's thermal stability. Ten milligrams (±1.00 mg) of each sample powder were placed in an alumina crucible (the exact mass was automatically weighed by the instrument) followed by heating the sample at a temperature rate of 25 °C up to 600 °C.

### 3. Results and Discussion

#### 3.1-FTIR result of oil-grafted tannin.

The FTIR characterization of oil-grafted tannin has been reported in recent research [71] as the three oil-grafted tannins showed almost the same results, the FTIR of the tannin grafted with acid lauroyl chloride has been studied in this research work (Fig. 2.16). In the FTIR spectra of the oil-grafted tannin, a sharp peak appeared at  $1740\text{ cm}^{-1}$ , is a C=O stretch band indicating the presence of ester groups in the fatty acid grafted tannin, while for unreacted lauroyl chloride and lauric acid this peak appears in  $1802$  and  $1700\text{ cm}^{-1}$ , respectively this being the stretch bands for the carboxylic acid C=O. The absorption band at  $1616.12\text{ cm}^{-1}$  in the tannin spectrum is attributed to the C–H vibration in the aromatic ring of the mimosa tannin [179], [180].

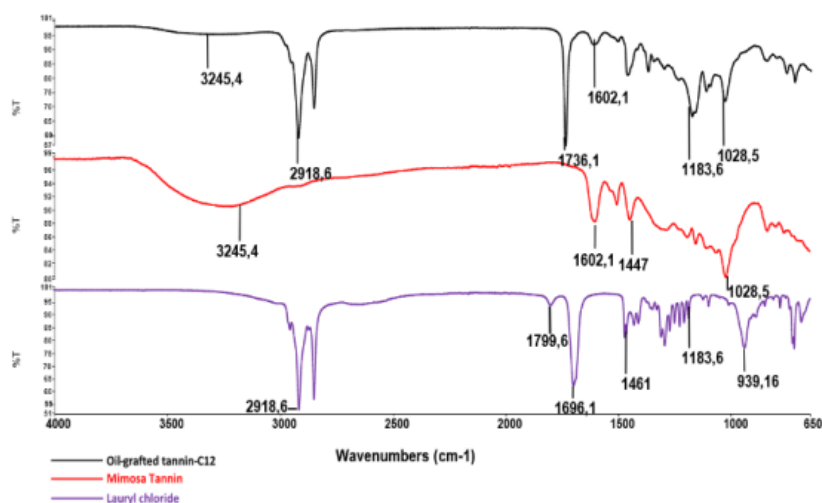


Figure.2. 15- Comparison of FTIR spectra of mimosa tannin, lauric acid, and fatty acid-grafted tannin using lauroyl chloride.

The mechanism of formation of the grafted tannins is shown in Fig.2.16 The tannin used was a commercial tannin extract, thus it contained a minor percentage of carbohydrates oligomers either linked to the phenolic part of the tannin [184] or free [197], derived from the fragmentation of hemicelluloses in the extraction process. As a consequence, the esterification with fatty acid chlorides occurred both on the hydroxyl groups of the tannin as well as on some hydroxyl groups of the carbohydrates fraction. The species illustrated in Scheme 2.17 were identified doing the esterification of tannins for rigid foams [71].

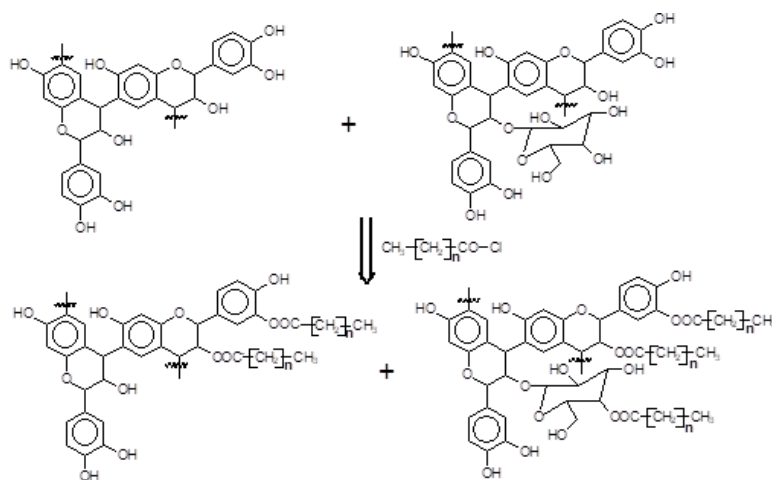


Figure.2. 16- Schematic visualization of the esterification of a commercial condensed tannin extract

### 3.2- Initials Observations

The initials observation for the two series of foams are shown in Tables 2.9 and 2.10.

In all the modified foams, flexible and rigid ones, the lengths of time taken for water absorption and wettability have increased, indicating that water repellency is much improved when a percentage of the tannin is esterified with a fatty acid. The density increases slightly with the addition of glycerol. The induction time increases with the addition of glycerol because as the addition of the glycerol has reduced the temperature, the induction time for completing the foaming has increased and the flexible foams are smaller than the rigid foams. This could be attributed to the diminution of temperature and energy of foaming.

Tableau.2. 9-The initials observation for the modified rigid foams

Formulation	STD.R	C12-R	C16-R	C18-R
Induction time (s)	10	24	21	28
Density (g/cm <sup>3</sup> )	0.09	0.093	0.11	0.13
Water absorption (min)	1	120	120–180	110

Tableau.2. 10-The initials observation for the modified flexible foams

Formulation	STD.F	C12-F	C16-F	C18-F
Induction time (s)	48	50	56	52
Density (g/cm <sup>3</sup> )	0.10	0.11	0.12	0.14
Water absorption (min)	5	180	150–180	150

In the two series of foam, the modified foam with oleyl-grafted tannin shows a cell structure slightly different from the other modified foams but the glycerol addition has markedly increased this difference and the water repellency of the flexible foam. The foam modified with an oleyl-grafted tannin showed a smaller size cell than the rigid modified foam grafted with the same fatty acid. Elastic foams are appeared visually less brittle than rigid foams.

The unmodified foam STD without glycerol is very brittle and the temperature of the reaction didn't allow it to complete the procedure of foaming correctly, but the addition of glycerol made it less fragile. Another point important in this work is the quantity of acetaldehyde as a cross-linker agent. The classic formulation to prepare tannin furanic foams with formaldehyde indicated 3.7 g of acetaldehyde for 15 g of tannin but this proportion crushed the structure of the cell, and a part of the foam was useless and destroyed. For this reason, the quantity of acetaldehyde was decreed to 2.5-3 g for 15g of tannin.

### **3.3. Scanning Electron Microscopy (SEM) Analysis**

Scanning electron microscopy (SEM) was used to investigate the morphology and microscopic structure of the different foam formulations. The SEM images of foam samplers include unmodified foams (STD.R and STD.F, Figure 2.18), modified rigid foams with fatty acid-grafted tannin (C12-R, C 16-R, C 18-R), and flexible modified foam (C12-F, C16-F, C18-F). All these were compared.

The comparison between the unmodified foams (STD.R and STD.F) shows the change in the size and form of the structure of the cell in the foam with glycerol. The cells of foams with a high proportion of glycerol are stronger than the foam without or with a small proportion of glycerol. In the foam STD-R which contains 1.5 g of glycerol, the holes are bigger, and the wall structure of the cells seems weaker than the cells in the STD-F which contains more quantity of glycerol. The cells in the unmodified foam with the glycerol are the same or slightly bigger than the foam STD.R but the cells are closer. Both foams were fragile and brittle, but they have shown a result different in reaction with oil-grafted tannins.

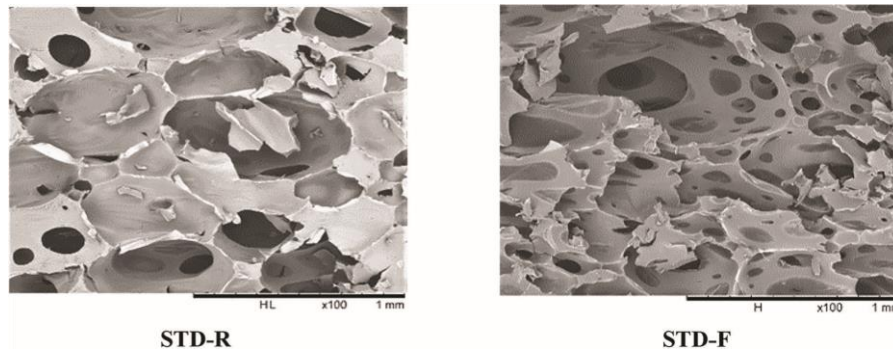


Figure.2. 17- Comparison between unmodified foams without (STD.R) and with glycerol (STD.F)

In the second step, the water repellent foams including rigid and semi-flexible ones were compared and the results are presented in Figure 2.18. The foams containing the glycerol appear to have cells slightly bigger than the rigid foams. but the cells have a somewhat closer structure (Fig.2.19).

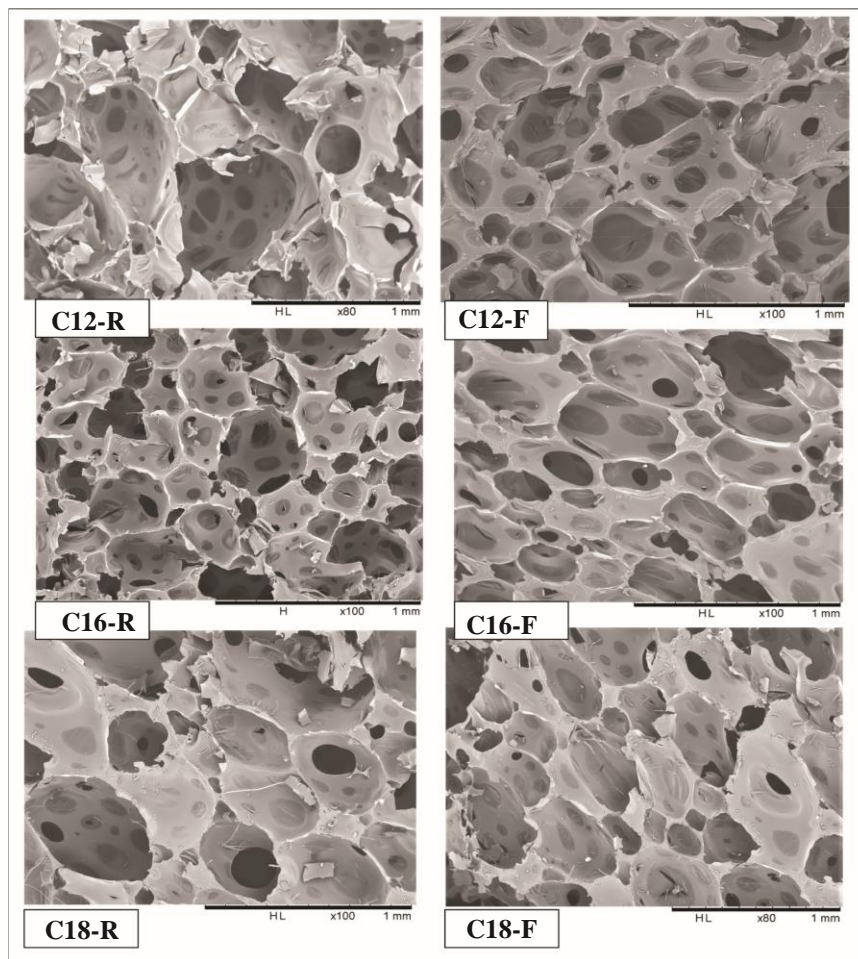


Figure.2. 18- Comparison between rigid (C12,16,18-R) and flexible (C12,16,18-F) fatty acid-grafted tannin foams

(C12-R) : Rigid lauric acid-grafted foam ; (C12-F) : flexible lauric acid-grafted foam.

(C12-R) : Rigid palmitic acid-grafted foam ; (C12F) : flexible palmitic acid-grafted foam.

(C12-R) : Rigid oleic acid-grafted foam ; (C12-F) : flexible oleic acid-grafted foam.

### 3.3. Compression Resistance and module elasticity

The test of compression has been investigated to observe the flexibility comportment of semi-flexible foam and to have a comparison between the rigid and semi-flexible foams some rigid foams have also been studied.

Two methods have been effectuated that include the rupture and plural cycle in certain strains. All the foam is cut into 30\*30 mm with a height of 20mm.to observe the resistance against rupture force, the foams were placed under 2KN force with a displacement rate of 2mm/min.

The elastic behavior of the foams was evaluated in the direction perpendicular using an instrument universal(cetelore) and 1 KN for each foam. 3 samples of 30\*30\*20 mm were placed under 10 of compression cycle to a strain of 10,20,40%.

The modulus of elasticity was calculated based on the relation between stress and strain value in the yield point.

The modulus of elasticity (also known as Young's modulus) can be calculated using the following formula:  $E = \sigma / \varepsilon$

where:(E) = modulus of elasticity (Pa or MPa) and ( $\sigma$ ) = stress (force per unit area, typically in N/m<sup>2</sup> or MPa)

( $\varepsilon$ ) = strain (change in length per unit length, typically expressed as a decimal or a percentage).

In the first step, the average strength of the rigid and semi-flexible foams has been calculated (Figueur.2.18) (Figueur.2.19).

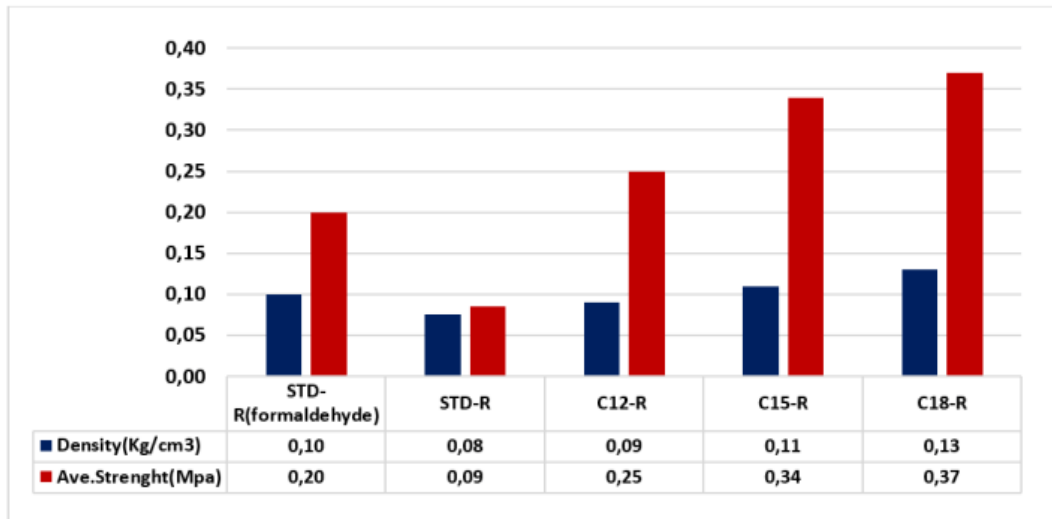


Figure.2. 19-The average compression strength of the rigid unmodified and oil-grafted foam with three chains of fatty acid

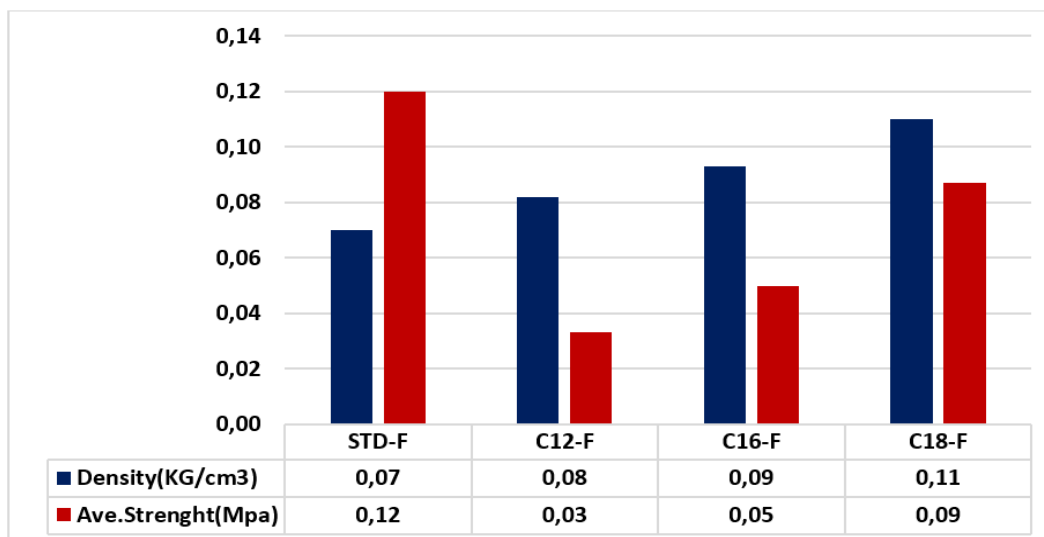


Figure.2. 20-The average compression strength of the modified and flexible oil-grafted foam with three chains of fatty acid.

The comparison between the two classes of foams that include rigid and semi-flexible showed: As the unmodified rigid foam using acetaldehyde has a nature more flexible than a rigid foam using formaldehyde, to have a standard value to compare the rigidity, an unmodified foam using formaldehyde has been prepared (STD-R-formaldehyde).

It must be noted that for both the rigid and the flexible foams there is some correlation between foam density and the foam resistance to compression. This correlation is not linear as the number of carbon atoms of the grafted ester increases, the density increases almost linearly

while the resistance to compression increases much more sharply. This is evident from both Figs. 2.18 and 2.19. While the differences in density for the rigid foams grafted with the three fatty acids in Fig. 2.18 possibly contribute to somewhat partially justify the resistance to compression, this is not the case in Fig. 2.19 for the case of the flexible foam. Such an effect is particularly evident in Fig. 2.19 for the flexible foams where the differences in density of the three fatty acids grafted foams are really non-significant. It indicates that for both rigid and flexible foams, but particularly for the flexible foams, the length of the fatty acid chain contributes to the compression strength imparted to a tannin-furanic foam. The question is then, why the longer the fatty acid chain esterifying the tannin, the higher is the contribution of its length to the foam compression resistance. Firstly, what can possibly be advanced is that over the tannin-furanic covalent network formed in the foam is superposed also a strength contribution by a physical entanglement network due to the long chains of the fatty acid esters present. Second, the carbohydrate oligomer chains, linked or not to the tannin, that in general do not contribute to the strength of a tannin-furanic foam, being now partly esterified also contribute to the physical entanglement network formed and thus to the increase in strength.

The compression curve always shows an elastic failure with three regions: elastic deformation or linear elasticity, plateau, and densification (Fig.2.22). However, the tensile stress-strain curve showed a fragile break[63] (Tondi et al. 2009). Crack formation is always the result of an effect of the concentration of stress. This damages the material in either tension or compression. Tension, nonetheless, causes a far more rapid crack propagation causing tannin-furanic foams to be brittle in tension and elastic while being compressed. The first step can give information like stress, strain, and MOE at the yield point or the elastic region. The calculation and compression of the MOE and at the yield point make a difference between the rigidity of the foams. The foam with a smaller MOE is more elastic or flexible. The results of compression analysis for the rigid and flexible sample's weight/volume ratios are shown in Tables 2.11, Fig.2.23.



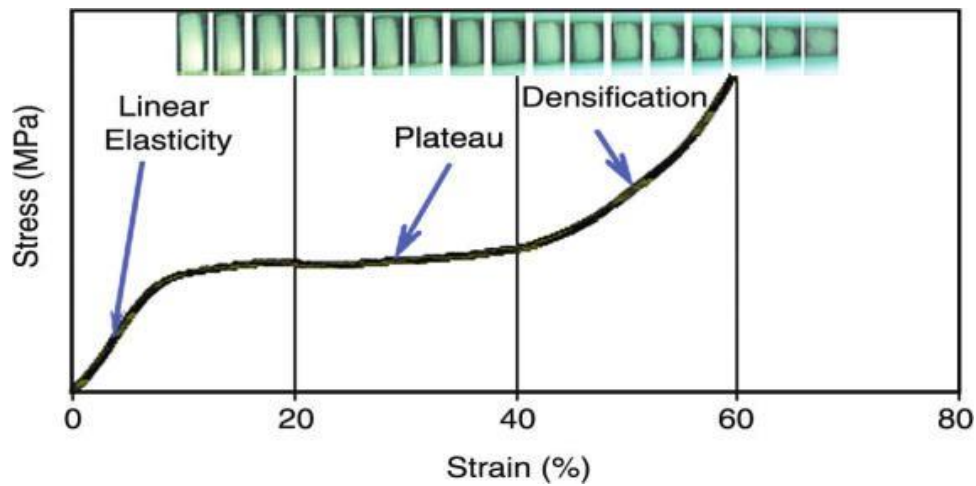


Figure.2. 21-schematic figure to explain the elasticity calculation.

Tableau.2. 11-The results of the compression test at maximum and yield point for the rigid foams.

Sample	Load Maximum (KN)	Displacement Maximum (mm)	Stress Maximum (MPa)	Strain at Maximum (%)	Load at Yield (KN)	Displacement at Yield (mm)	Stress Yield (MPa)	Strain Yield	Module elasticity at Yield (MPa)
STD-R-formaldehyde	0.45	14	0.38	55	0.19	1.63	0.21	8.28	0.026
STD-R-acetaldehyde	0.38	17	0.15	85	0.09	3.51	0.17	15.8	0.010
C12-R	0.51	16.7	0.56	66	0.18	2.48	0.21	13.25	0.015
C16-R	0.74	16.6	0.83	83	0.32	2.58	0.36	14.35	0.024
C18-R	0.815	15.5	0.905	77	0.40	1.97	0.44	13.26	0.033

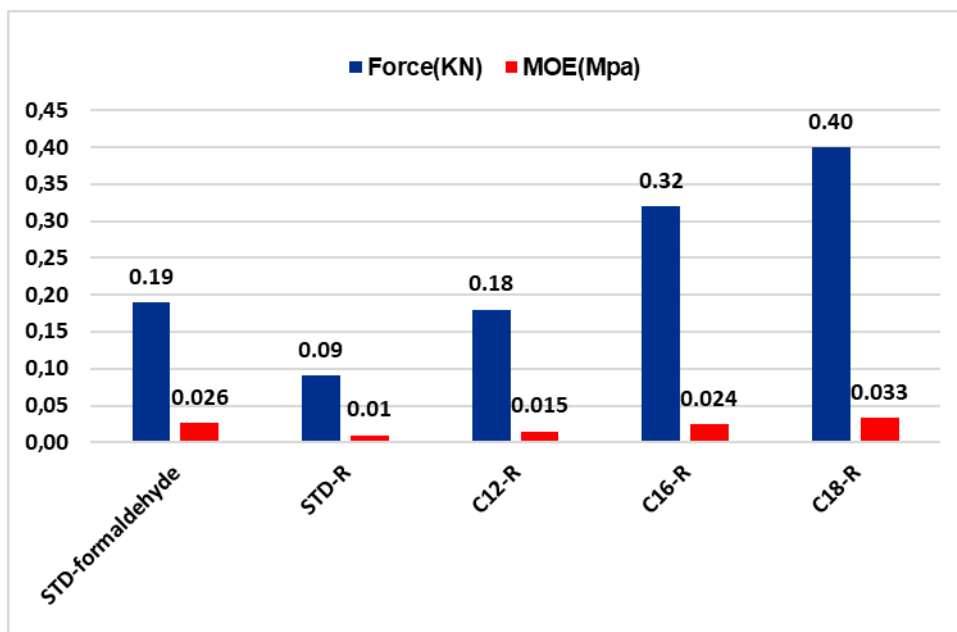


Figure.2. 22-Comparison between load at the yield point and MOE for unmodified and rigid oil-grafted foams

In the second part of the project with the substitution of tannin with 8.3% fatty acid-grafted tannin and the addition of glycerol, a grafted foam with high water repellency and less rigidity has been obtained. This foam is indeed flexible and can stand up the pressure more than a rigid foam. This foam is flexible and did not crush as rigid foam under the pressure of compression, recovering its shape during the cyclic test (Table 2.12). Its elasticity is thus proven by the calculation the of MOE yield. As is shown in Table 2.12 and Fig. 2.24, the MOE of the tannin foams to which fatty acids-grafted tannin, especially with lauric and palmitic acids is very low, in line with their increase in elasticity

Tableau.2. 12-Results of the compression test at maximum and yield point for the flexible foams

Sample	Load Maximum (KN)	Displacement Maximum (mm)	Stress Maximum (MPa)	Strain at Maximum (%)	Load at Yield (KN)	Displacement at Yield (mm)	Stress Yield MPa	Strain yield	Module elasticity at Yield (MPa)
STD-F	0.16	15	0.18	77	0.096	2.73	0.11	18.20	0.0060
C12-F	0.049	15.83	0.054	79	0.021	2.12	0.024	8.11	0.0029
C16-F	0.080	15.1	0.089	84	0.036	2.024	0.040	6.86	0.0058
C18-F	0.12	12.52	0.318	62	0.058	1.67	0.064	5.39	0.011

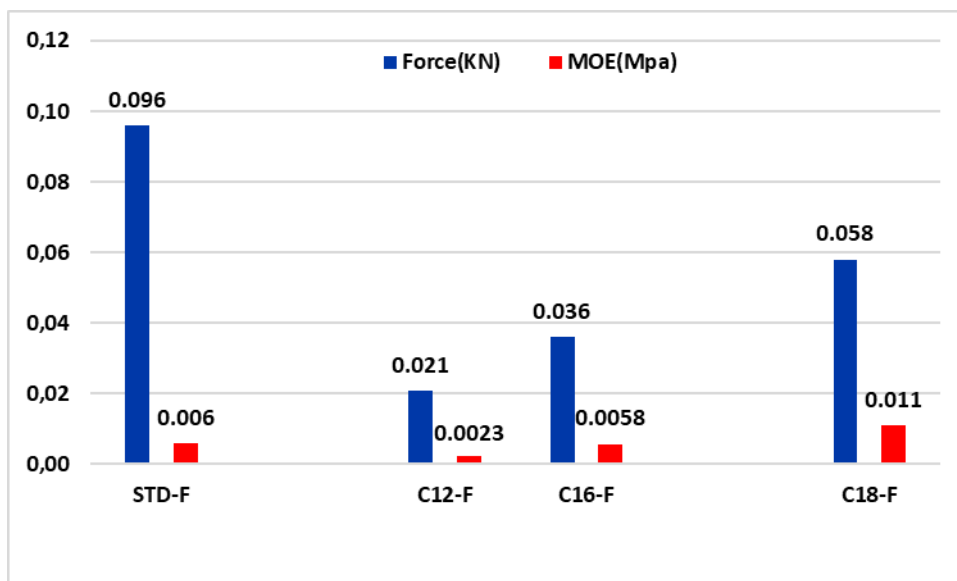


Figure.2. 23-Comparison between load at the yield point and MOE for unmodified and flexible fatty acids grafted foams.

As is shown in Table 2.12 and Fig. 2.24, the MOE of the tannin foams to which fatty acids-grafted tannin, especially with lauric and palmitic acids is very low, in line with their increase in elasticity.

The other point of interest is the decrease of elasticity with the length of the fatty acid chain, the character of the tannin foams with added fatty acid-grafted tannin with oleic acid is near to that of a rigid foam (0.011 MPa) as the MOE of an unmodified rigid foam (0.010 MPa) is even lower than that of a rigid foam modified with same fatty acid (0.033MPa). The reasons for such behavior have been ascribed to the contribution of the superposed physical entanglement network formed by the fatty acid chains linked to both the phenolic part of the tannin extract and on the hemicellulos's, oligomer fragments in it.

In Fig.2.25, a comparison between unmodified, rigid, and flexible foams is shown. Actually, the semi-flexible foam rather than the rigid foam did not show a real yield or brittle point, and after several cycles of compression or a complete compression cycle, the foam keeps its shape and can return at 70% of its initial weight and dimension. A comparison between three fatty acid-grafted foams (rigid and flexible) has been registered and shown to prove the increase in rigidity with an increase in the length of the fatty acid chain used (Figs.25 and 26).

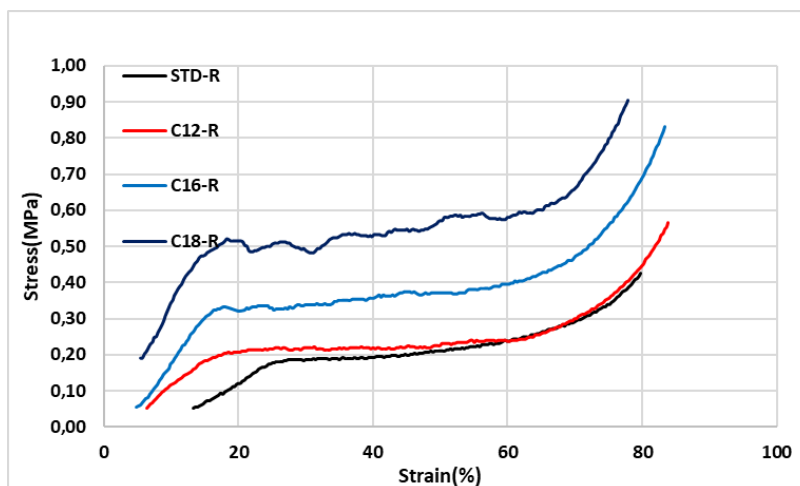


Figure.2. 24-Compression results of unmodified and rigid oil-grafted foams with three chains of fatty acid

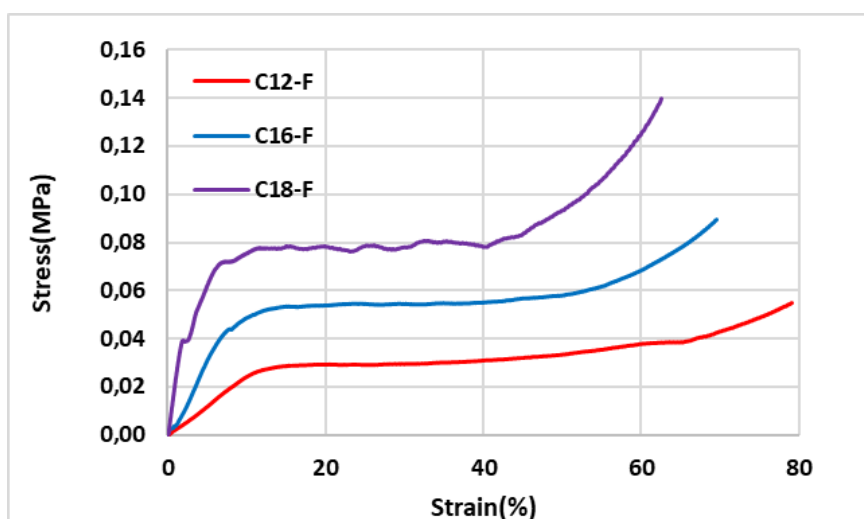


Figure.2. 25-Comparison between flexible fatty acid-grafted foams with three different fatty acid chains

Since the strain yield point in the rigid foams was observed to be around 10-15%, and less than 10% for the semi-flexible foams, compression and, stress-strain cycles were studied at 10%, 20%, and 40% strain to compare the effect of pressure on flexibility.

In the first step, the rigid foams like unmodified foam with or without glycerol (Fig.2.27) and rigid fatty acid-grafted foams were studied and the role of glycerol to increase flexibility has been shown (Fig.2.27). Afterwards, cyclic compression tests were carried out to observe the behavior of the flexible foams.

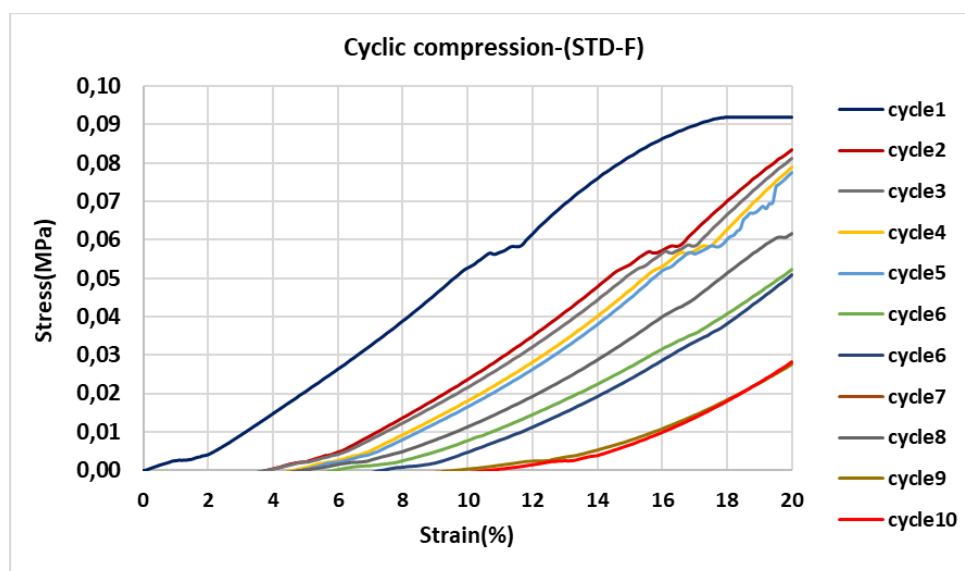
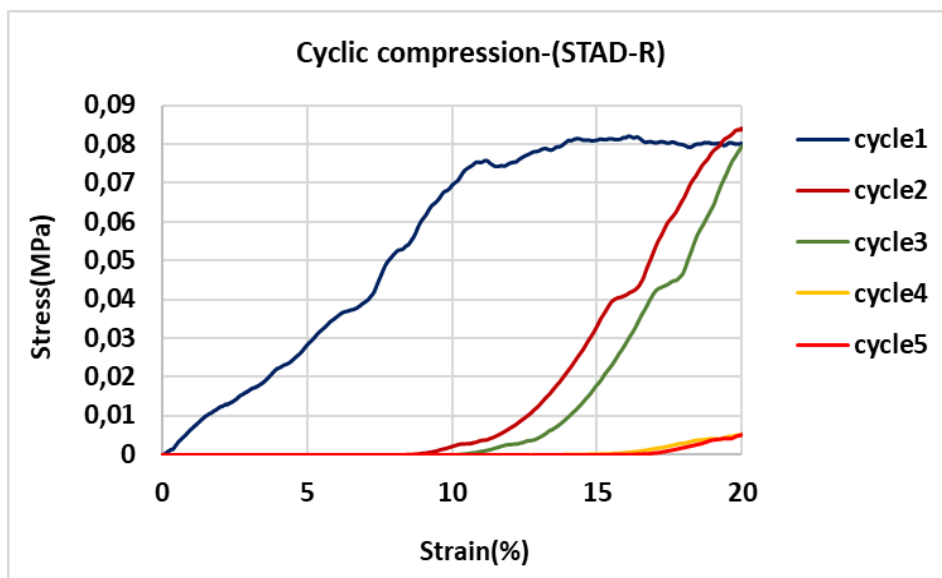


Figure.2. 26-Cyclic compression tests for the unmodified rigid foam (STD-R) without plasticizer and with glycerol plasticizer (STD-F).

The comparison between two rigid unmodified foams shows the increase in flexibility in the unmodified foam with glycerol, although this flexibility is even more remarkable in the semi-flexible oil-grafted foams. Glycerol is a so-called external plasticizer, in principle a plasticizer that does not react covalently with the covalent polymer network forming the foam cell walls. It interposes itself in the interspaces between polymer chains blocking or interrupting some of the covalent bonds and physical entanglements possible in the network during its forming stage. The fact that also some physical entanglement knots of the fatty acid chains can be prevented by the presence of glycerol can explain the improved flexibility of the esterified tannin extracts foams (Figure 2.26). From Figure.2.28 the polymer network structure is more open due to the

insertion of glycerol, this more open polymer network also contributing to the acquired flexibility of the foam.

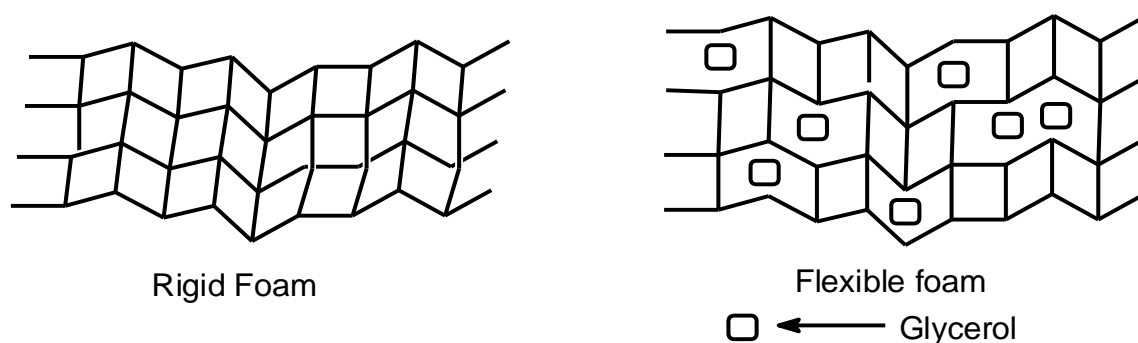


Figure.2. 27-Schematic differences at the level of the polymer network between rigid and flexible foams

The compression results of three oil-grafted foams were compared. The flexibility appears to decrease as a function of the increase of the fatty acid chain length. Thus, the foams with added oleic acid-grafted tannin (C18) showed lower flexibility compared to modified foams with lauric or palmitic acid. This only means that the oleic acid-based foam is still flexible but at a higher range of compression strength. It is in line with the higher compression strength observed the longer is the chain of fatty acid esterifying the tannin extract.

In the present work, the behavior of foams with added flexible lauric acid-grafted tannin have been studied. As a control the compression of a rigid foam with added lauric acid -grafted tannin have also been studied.

The compression test was carried out at 10, 20 and 40% strain (Figs.2.29-2.30- 2.31).

As the flexible foam with the added fatty acid-grafted tannin with chains of C12 and C16 showed, the cyclic compression results for the rigid and flexible foam added of the lauric acid-grafted tannin is the one shown in this report (Figs.2.9-2.30).

The oil-grafted foam with oleyl-grafted tannin has shown results different from the other flexible foams, the cyclic compression result in these foams even containing the plasticizer indicated an almost rigid behavior (Fig.2.31).

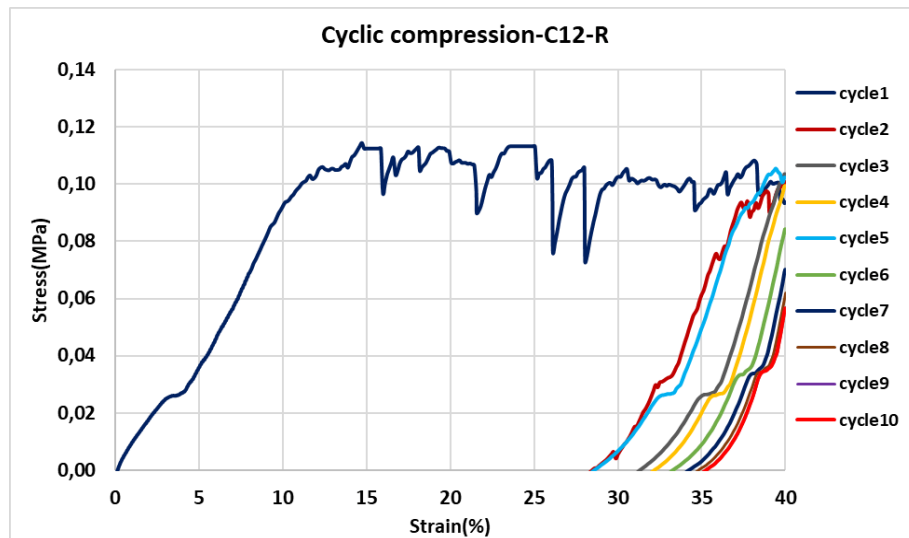
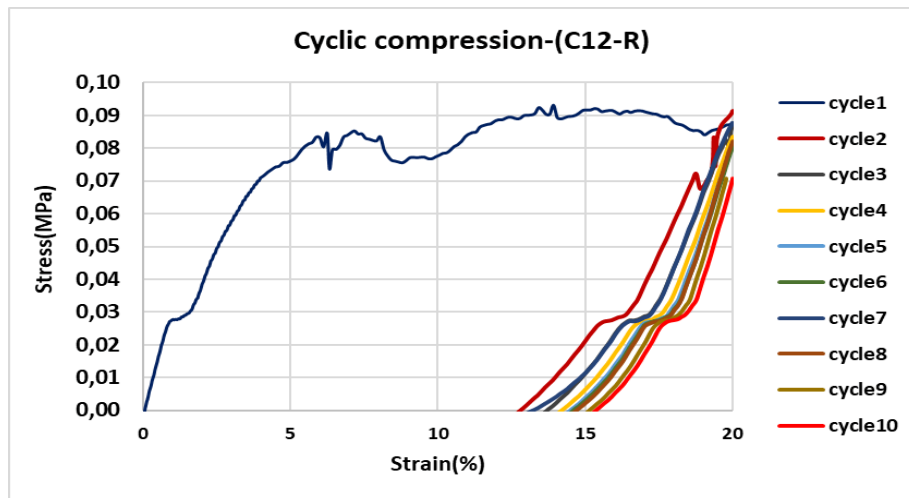
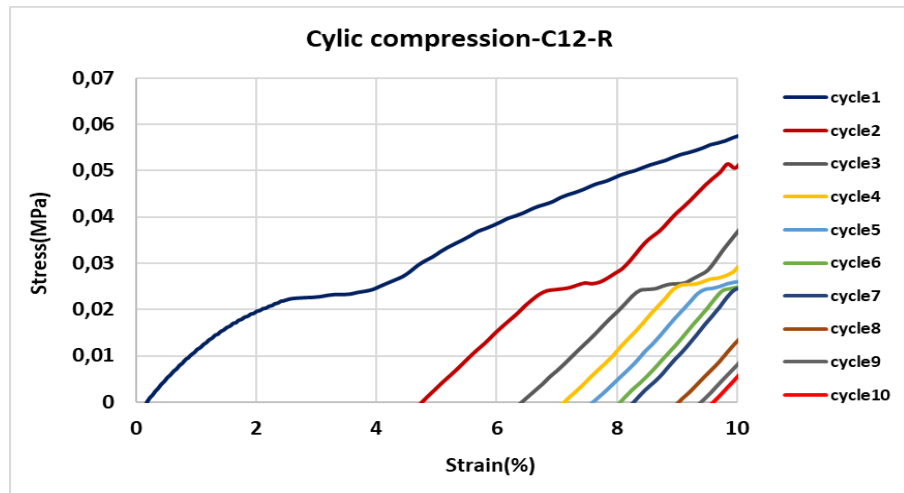


Figure.2. 28-Ten cycles strain-stress curves of rigid foams added with lauric acid -grafted tannin at 10, 20 and 40% strain

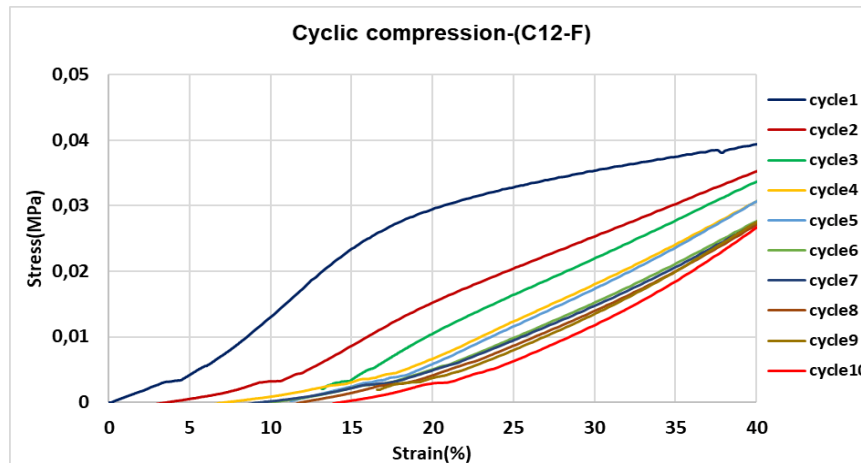
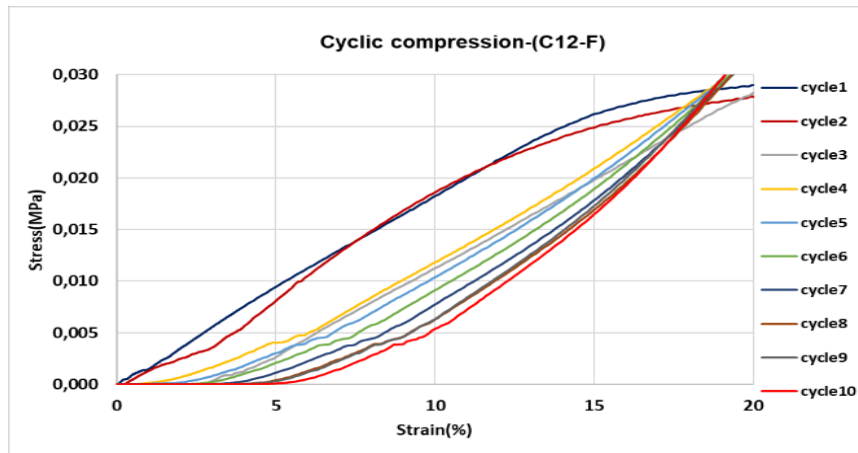
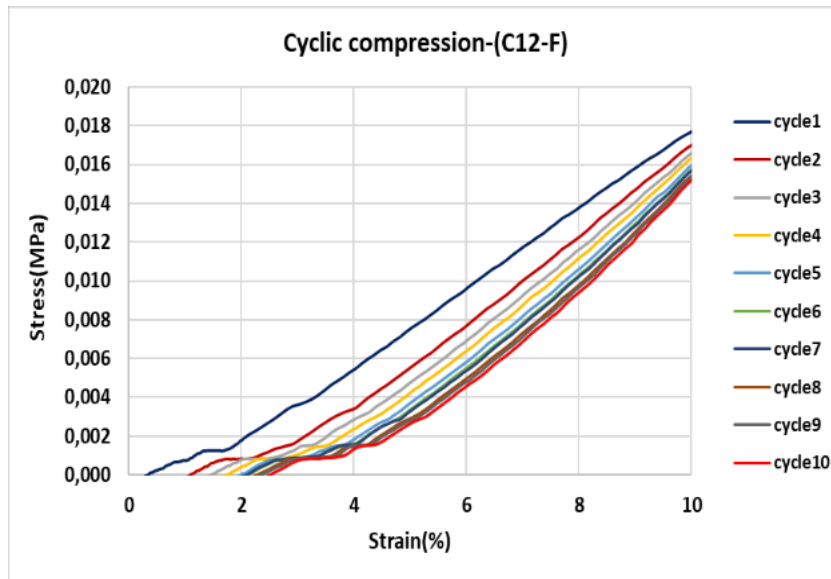


Figure.2. 29- 10 Cycles strain-stress of flexible foams with added lauric acid-grafted tannin at strains of 10, 20 and 40%



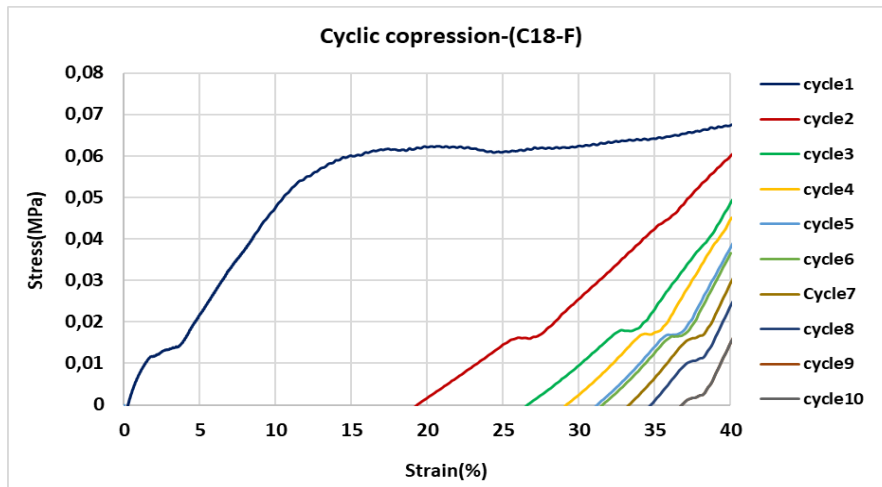
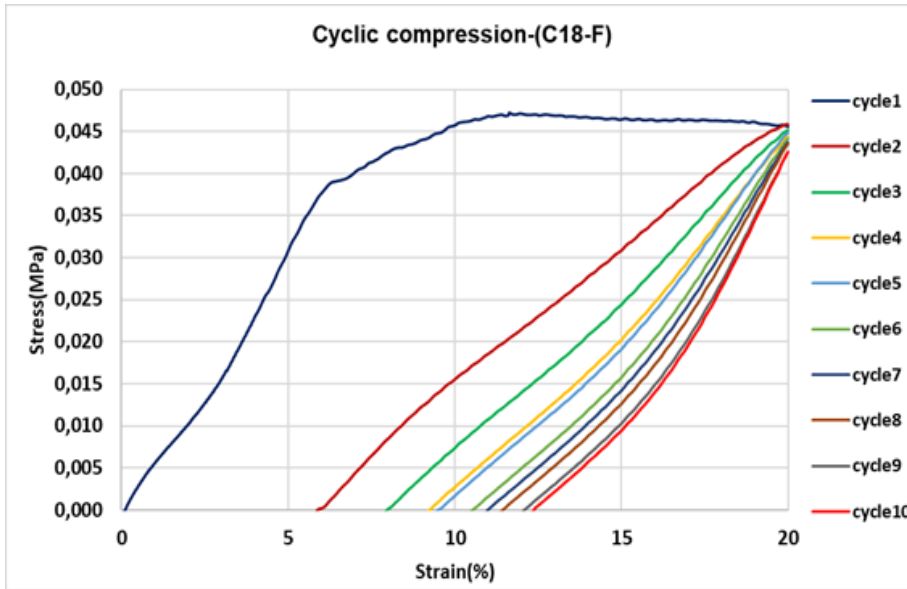
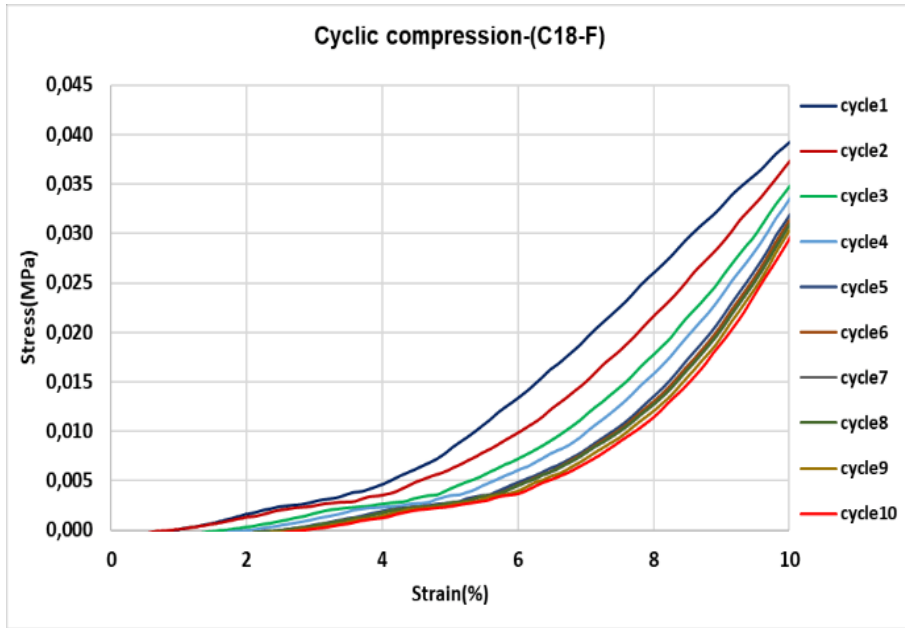


Figure.2. 30- Ten cycles strain -stress of flexible foams with added oleic acid-grafted tannin at strains of 10, 20 and 40%.

### 3.5-Contact angle measurement

The comparison of foam water repellence has been done by the sessile drop test method by measuring the difference in contact angle of three tannin foams modified by adding tannin grafted with fatty acids of three different chain lengths. The rigid foams added of lauric acid-grafted tannin and palmitic acid grafted tannin showed an initial water contact angle of  $120^\circ$ , stabilizing then after 180 seconds to around  $110^\circ$ . The rigid foams added of oleic acid-grafted tannin also showed a water contact angle of  $120^\circ$  but this decreased nearer to  $100^\circ$  in 180 seconds. This might be due to the larger cell size compared to the other foams. Nonetheless, all the three rigid foams added fatty acid-grafted tannin show both a much-improved water repellency, water contact angle, and better contact angle stability than the rigid unmodified foam control (Fig.2.32). This effect is due to two contributions, first by the water repellence imparted by the presence of the linked fatty acids and second by the decrease in hydrophilicity of the carbohydrate oligomers in the tannin extract as these too have been esterified with the fatty acid chains. The rigid unmodified foam shows an initial water contact angle of  $52^\circ$  decreasing rapidly down to around  $10^\circ$  after 180 seconds without appearing to stabilize.

The water contact angle measures for the flexible foams are shown in Fig.2.33. The results showed an initial water contact angle of  $120^\circ$  decreasing down to  $105^\circ$  and stabilizing. The flexible foam in which glycerol was added but that was not added of any fatty acid-grafted tannin, namely STD-F, presented a much lower water repellency presenting an initial water contact angle of  $79^\circ$  decreasing in 180 s down to  $50^\circ$  without apparently stabilizing. Both the results of the rigid and flexible foams indicate that is the addition of the tannin grafted of the fatty acid chains that is the reason for the water repellence of both these types of tannin-based foams, the glycerol contributing only the flexibility of the foams to which it has been added.

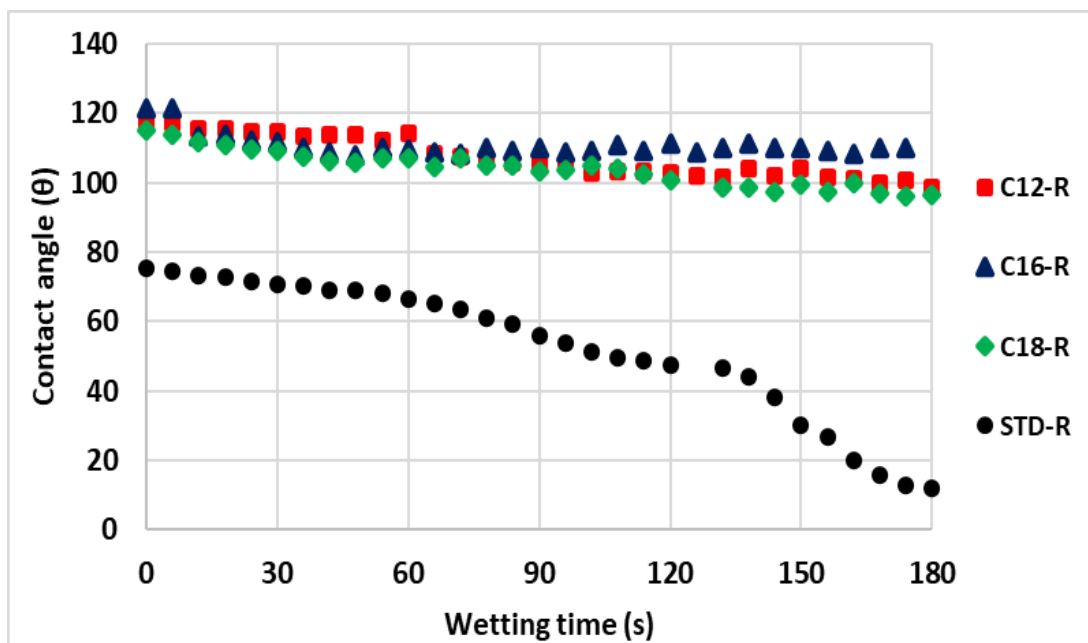


Figure.2. 31- Comparison of rigid standard foam and rigid foams added of fatty acid-grafted tannin different chain length.

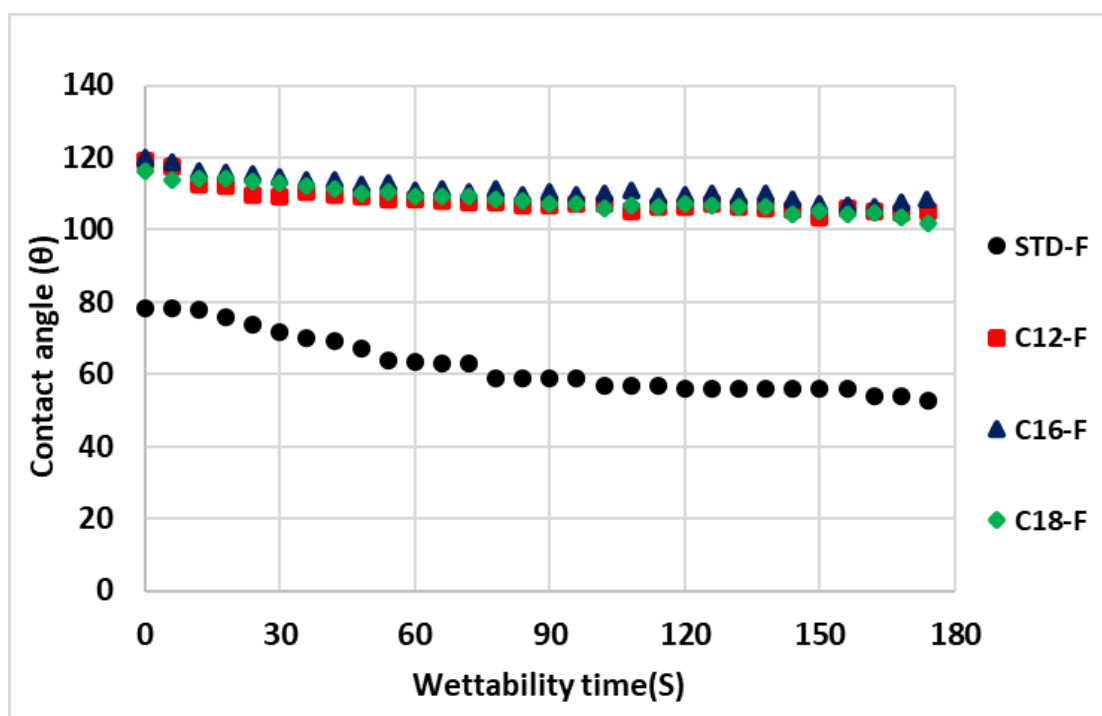


Figure.2. 32-Comparison between standard flexible foam and flexible foams added fatty acid-grafted tannin of different chain lengths.

### 3.6. Thermogravimetric Analysis (TGA)

To investigate the thermal stability of the fully cured series of resins thermogravimetric analysis (TGA) was carried out. The corresponding resulting TGA curves and particularly its first derivate (DTG) are shown in Figs.2.34 -35-36. From the DTG curves of the rigid foams in Fig.34 there appear to be several stages in the thermal degradation process, thus, in the 50 °C–125 °C, 175 °C–250 °C, and two zones between 280 °C -550 °C. For the first, in the lower temperature range, the weight loss can be attributed to the residual water evaporation and some small molecular impurities degradation [123], [198]. The second range corresponds to some degradation of the linkages between the tannin and the fatty acids portion of the foam. The series of degradation stages between 280°C °C and 550 °C correspond to the progressive degradation of the materials of the network formed, both first the complete degradation of the linkages between tannin and furanic oligomers and finally at the higher temperature the degradation of the tannin molecules. Condensed tannins degrade at high temperatures as generally they are used for improving the temperature resistance of resins and adhesives. Some more stable chemical bonds, such as C-C and C-O, are cleaved within this temperature range [123], [198].

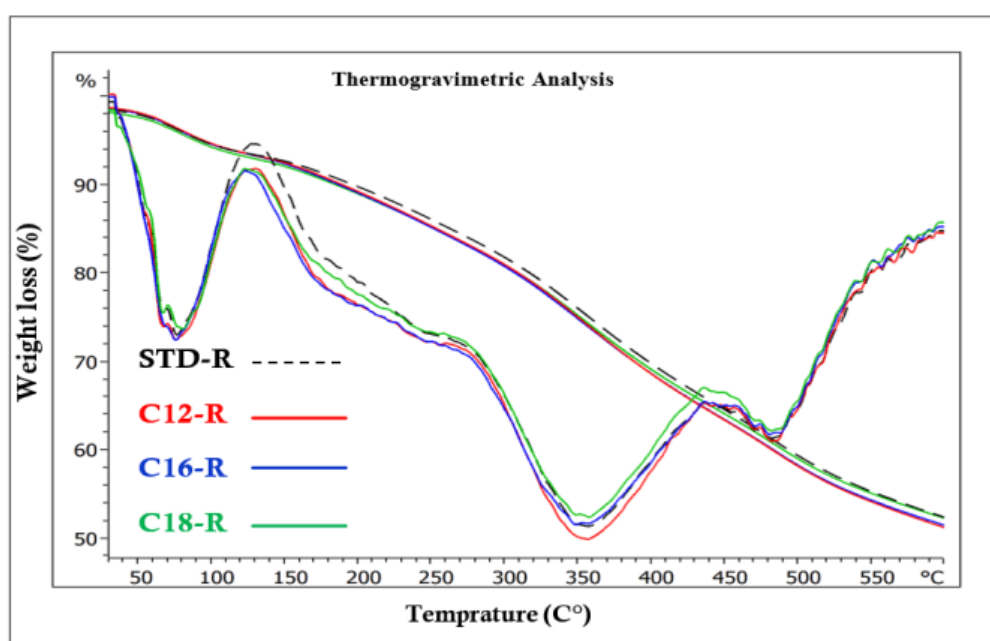


Figure.2. 33-Comparison of TGA and DTG weight curves as a function of time, between an unmodified rigid foam (STD-R) and rigid foams added of fatty acids-grafted tannin with fatty acid chains of three different kinds.

The DTG of the four foams with different fatty acids–grafted tannins added are very similar whatever the length of the fatty acid chain used.

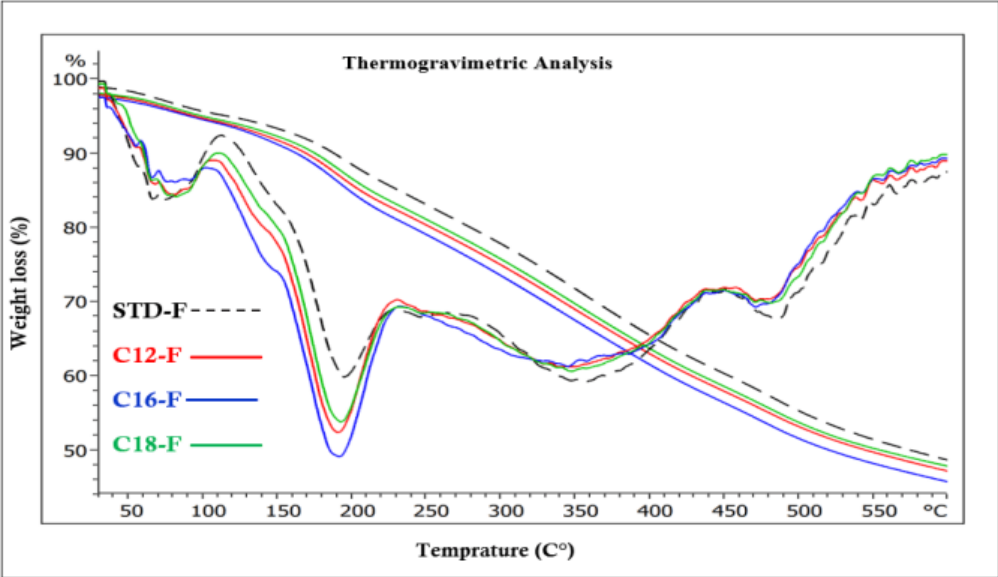


Figure.2. 34- Comparison of TGA and DTG curves weight curves as a function of time, between an unmodified flexible foam (STD-F) and rigid foams added of fatty acids-grafted tannin with fatty acid chains of three different kinds

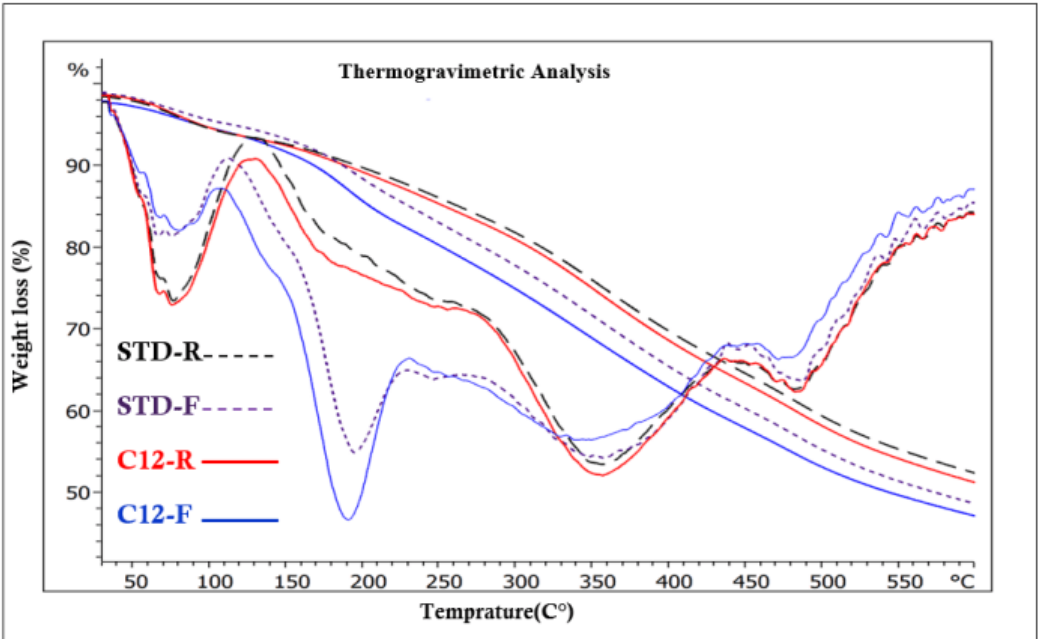


Figure.2. 35- Comparison of TGA and DTG between unmodified foams (STD-R, STD-F) and rigid (C12-R) and flexible(C12-F) lauric grafted-tannin foam

The behavior of the flexible foams with added different fatty acid-grafted chains (Fig. 2.35) also presents 5 zones of degradation. The first one is as for the rigid foams in the 50 °C–125 °C range, the reason for it being the same as for the rigid foams in Fig. 2.34. What changes mainly are the length of the second degradation stage that is markedly shorter, in the 125°C-230°C range (Fig. 2.35), with the first slope between 125°C and 150°C much shorter than the start of the degradation of the linkage between tannin and furanic oligomers observed for the rigid foams. The 125°C-150°C range corresponds to the start of the degradation of some tannin-fatty esters linkages, with the second portion namely the 150-230°C range corresponding to the degradation of the glycerol plasticizer present in the flexible foams. The fact that this zone peaks at 175°C which is the temperature of degradation of glycerol in the presence of oxygen [199] clearly indicates that this zone is the one representing the degradation of the glycerol in the flexible foams, explaining the absence of this peak in the rigid foams. In the 150°C-230°C stage degradation of the linkages of the fatty acids and between the tannin and the fatty acids portion of the foam still occurs, as shown by the slope in the rigid foams DTGA traces, and also exists in the flexible foams where it is masked by the more marked event of glycerol degradation. This stage is thus shifted to a slightly lower temperature range than for the rigid foams probably due to the influence of the presence of glycerol in the flexible foams. In this range of temperature, the standard flexible foam without fatty acids-modified tannin degrades relatively less than the ones modified with fatty-acid-esterified tannin added. This is an indication that the combination of glycerol and fatty acid-modified tannin accounts for a more evident degradation, with the C16 case appearing to be slightly more sensitive than the C12 and C18 cases (Fig. 2.35). The higher temperature stages appear to be like what observed for the rigid foams, for the same type of degradation.

The very different behavior in this temperature range between rigid and flexible foams is very much put into evidence in Fig. 2.36, where rigid and flexible lauric acid esterified foams are directly compared.

#### **4. Conclusions**

The flexible tannin-furanic bio foams developed by the addition of a small proportion of one or other type of three fatty acids-grafted tannins of chain length of respectively C12, C16, and C18 carbons, and glycerol have shown to be water repellent as their equivalent rigid foams without the glycerol plasticizer. It is the glycerol that imparted the flexible character to the structure of the tannin-furanic foam, but the small proportions of fatty-acid grafted tannins added yielded their water repellency. The use of acetaldehyde as a cross-linker rather than formaldehyde yielded an improved mechanical performance when the fatty acid-grafted tannins were added. The flexibility was determined by the decrease of the MOE of these foams under a 10 cycles compression test. Lauryl- and palmitoyl-esterified bio foams encourage similar mechanical properties. The oleyl-esterified bio foam instead showed a different compression behavior and morphology showing rigidity characteristics almost like rigid foam, and thus of much-decreased flexibility. The flexible foams appeared by SEM to present a somewhat lower proportion of holed cells with a smaller cell size than the rigid foams, and good instant as well as a function of time water repellency. Both types of foams presented much lower surface friability than non-esterified rigid foams.

#### 4. Discussion et conclusion

Ce chapitre est le fruit d'une étude approfondie sur la modification chimique du tannin condensé (mimosa) par voie d'estérification, à travers le couplage entre les groupes hydroxyles du tanin et les groupes carboxyles des chlorures d'acides. L'objectif était d'utiliser ce produit modifié pour concevoir des mousses à base de tannin furanique.

Tout d'abord, la modification du tannin par estérification avec des chlorures d'acides gras a été étudiée dans le but d'améliorer le caractère hydrophobe des matériaux dérivés du tanin, tels que les mousses tanin-furaniques. Cette modification a entraîné une augmentation de l'hydrophobicité des mousses, compensant ainsi la nature hydrophile du tannin. Cette caractéristique du tannin entraîne des limitations dans la production de matériaux tels que les mousses ou les colles à base de bois. L'amélioration de l'hydrophobicité des mousses en tant que matériaux d'isolation est très importante, car elle garantit des performances à long terme et une durabilité dans des environnements humides.

Pour confirmer le couplage et le succès de cette réaction, des analyses telles que l'infrarouge et la spectrométrie de masse MALDI-TOF ont été utilisées. Les résultats de l'infrarouge, en comparant les spectres du tannin, du chlorure d'acide gras et du produit greffé, ont confirmé le succès de la greffe et la formation de groupes esters. L'apparition d'un pic à  $1742\text{ cm}^{-1}$  confirme la présence de groupes esters dans le produit obtenu, qui correspond au tannin greffé par le chlorure d'acide gras. Le spectre du chlorure de palmitoyle montre un pic à  $1804\text{ cm}^{-1}$  correspondant à la bande d'étirement C=O pour les chlorures d'acides, et ce pic a disparu dans le produit greffé par l'acide gras.

Pour préparer une mousse hydrophobe, 8,3 % de tanin standard et non modifié ont été remplacés par les produits greffés. Les premières mousses conçues ne présentaient pas une grande résistance à l'absorption d'eau, et l'angle de contact était d'environ  $90\text{-}99^\circ$ . La densité des mousses modifiées par rapport à une mousse standard a augmenté, ce qui peut être attribué à une diminution de la hauteur des mousses. Un problème important observé était le rendement des mousses. En remplaçant du tannin standard par des tannins modifiés, la température de réaction a été augmentée, réduisant ainsi de moitié la taille des mousses. Ce phénomène était plus remarquable dans le cas de l'utilisation du produit greffé avec le chlorure d'acide oleyl.



Pour résoudre ce problème, deux solutions ont été proposées :

1. Remplacer l'eau par du glycérol pour atténuer la température de réaction.
2. Changer l'aldéhyde (formaldéhyde), qui joue le rôle d'agent de réticulation, par d'autres aldéhydes ayant un point d'ébullition plus élevé. Les structures des mousses ont commencé à s'améliorer lors de l'utilisation du glycérol.

Lors du changement d'aldéhyde, les résultats étaient plus intéressants, de telle manière que la structure des mousses était formée sans perte de matériau. Les mousses avec l'acétaldéhyde ont montré une très bonne résistance à l'humidité et une densité inférieure à celle des mousses avec le formaldéhyde. En revanche, les mousses avec le glutaraldéhyde ont démontré une densité très élevée.

Dans toutes les mousses modifiées, qu'elles soient rigides ou flexibles, on a observé une augmentation de l'hydrophobicité et de la mouillabilité. La densité de toutes les mousses est d'environ 0,10, avec une légère augmentation dans le cas de l'ajout de glycérol. L'ajout de glycérol a également augmenté le temps d'induction, qui correspond au temps nécessaire pour achever la formation des mousses, en raison de la réduction de la température. De plus, les mousses flexibles ont présenté une taille plus petite par rapport aux mousses rigides, ce qui peut être attribué à la diminution de la température et de l'énergie impliquée dans la formation des mousses.

Au niveau de l'analyse structurale (MEB), l'ajout de glycérol a un impact sur la formation de la structure cellulaire des mousses, influençant ainsi les propriétés et les caractéristiques des mousses rigides et flexibles. Les observations au microscope électronique permettent de visualiser et de comprendre les différences dans la structure des cellules et des pores, ce qui peut expliquer les variations de résistance à l'absorption d'eau entre les deux types de mousses.

La comparaison entre les mousses non modifiées rigides et flexibles révèle des changements significatifs dans la structure cellulaire. Dans le cas des mousses standard contenant du glycérol, les cellules apparaissent plus épaisses et les parois cellulaires sont plus solides. Cela suggère que l'ajout de glycérol a un effet sur la robustesse de la structure cellulaire de la mousse.

La partie importante qui distingue les mousses en deux groupes est leur caractérisation physique et mécanique. Une analyse de compression a été réalisée pour évaluer l'élasticité des mousses. Les mousses rigides et flexibles ont été comparées en termes de rupture et de comportement élastique. Les résultats de cette comparaison ont montré que la mousse rigide non modifiée,

utilisant l'acétaldéhyde, est plus flexible que la mousse rigide utilisant le formaldéhyde. Le module d'élasticité (MOE) des mousses rigides utilisant le formaldéhyde comme durcisseur est plus élevé que celui des mousses utilisant l'acétaldéhyde. La mousse non modifiée avec l'acétaldéhyde présente une composition structurelle et une résistance mécanique moins favorables. Cependant, en remplaçant seulement 8,33% du tannin par du tannin greffé à un acide gras, il est possible d'obtenir une mousse hydrofuge avec une meilleure structure cellulaire et une meilleure résistance mécanique.

Les mousses modifiées avec les trois chaînes d'acides gras ont montré une augmentation du module d'élasticité, et cette augmentation varie légèrement en fonction de la longueur de la chaîne. En particulier, les mousses rigides et flexibles modifiées avec le chlorure d'acide oléyl ont un module d'élasticité plus élevé que celles modifiées avec le chlorure d'acide lauryl ou palmitoyl. Les mousses modifiées avec le chlorure d'acide lauryl et palmitoyl présentent un module d'élasticité très faible, ce qui confirme leur flexibilité, en particulier dans le cas des mousses flexibles.

L'analyse de l'angle de contact des mousses permet d'évaluer leur hydrophobicité et leur capacité à repousser l'eau. Les mousses modifiées avec des tanins greffés d'acides gras ont montré une hydrophobicité remarquable, bien supérieure à celle des mousses non modifiées. Cela indique que l'ajout de tanins greffés joue un rôle clé dans la propriété d'imperméabilité à l'eau de ces mousses. Les résultats montrent que les mousses rigides modifiées ont initialement un angle de contact de  $120^\circ$ , ce qui signifie que l'eau forme une goutte sur leur surface plutôt que de s'étaler. En comparaison, la mousse rigide non modifiée présente un angle de contact plus bas, à  $65^\circ$ , indiquant une moindre capacité à repousser l'eau. Même la mousse non modifiée contenant du glycérol, qui est un additif utilisé pour apporter de la flexibilité, présente une hydrophobicité relativement stable malgré un angle de contact moins élevé. Les mousses flexibles, quant à elles, ont également montré un angle de contact initial de  $120^\circ$ , montrant leur capacité à repousser l'eau. Cependant, au bout de 180 secondes, l'angle de contact diminue légèrement à  $105^\circ$ , indiquant une légère perte d'hydrophobicité au fil du temps.

L'analyse thermogravimétrique a permis d'évaluer la stabilité thermique des mousses modifiées par rapport aux mousses non modifiées. Les résultats ont montré que les mousses modifiées ont une plus grande perte de masse, ce qui indique une plus grande susceptibilité à la dégradation thermique. De plus, les mousses flexibles ont montré une perte de masse plus élevée que les mousses rigides, ce qui suggère une plus grande sensibilité à la chaleur. Une observation intéressante est que la longueur de la chaîne d'acides gras n'a exercé qu'une faible influence sur

la perte de masse. Cependant, les mousses contenant du tanin modifié par le chlorure d'acide oléyle ont montré une meilleure résistance à la dégradation thermique par rapport à celles contenant du tanin modifié par le chlorure d'acide lauryl. Dans l'ensemble, les mousses modifiées ont montré une certaine sensibilité à la dégradation thermique, avec les mousses flexibles étant plus affectées que les mousses rigides. La longueur de la chaîne d'acides gras a eu peu d'impact sur la perte de masse, mais les propriétés thermiques ont été influencées par le type de modification du tanin. Ces résultats fournissent des informations importantes pour la conception et l'optimisation de mousses résistantes à la chaleur.

En conclusion, cette étude ouvre de nouvelles perspectives pour développer des matériaux résistants à l'eau et respectueux de l'environnement en utilisant des tanins modifiés pour concevoir des mousses hydrophobes. L'innovation dans le développement de matériaux respectueux de l'environnement est essentielle pour divers domaines industriels.



**Chapitre III- Synthèse et caractérisation  
de mousses d'isolation thermique bio-  
polyuréthane sans isocyanate à base de  
tanins hydrolysable**



**Ce chapitre a fait l'objet de deux articles :**

**Article. III : Azadeh, E.,** Chen, X., Pizzi, A., Gérardin, C., Gérardin, P., & Essawy, H. (2022). Self-blowing non-isocyanate polyurethane foams based on hydrolysable tannins. *Journal of Renewable Materials*, 10(12), 3217.

**Article.IV : Azadeh, E.,** Pizzi, A., Gerardin-Charbonnier, C., & Gerardin, P. (2022). Hydrolysable Chestnut Tannin Extract Chemical Complexity in Its Reactions for Non-Isocyanate Polyurethanes (NIPU) Foams. *Journal of Renewable Materials*.

## **1.Introduction générale**

Les tanins hydrolysables sont des composés phénoliques végétaux qui ont été peu étudiés dans la recherche sur les matériaux en raison de leur faible réactivité et de leur structure différente par rapport aux tanins condensés. Cependant, des études récentes ont mis en lumière leur potentiel dans la formation de liaisons uréthanes sans recourir aux isocyanates, ce qui les rend intéressants pour la fabrication de mousses NIPU et de colles sans isocyanates pour le bois.

Ce chapitre est consacré à la conception de mousses rigides de polyuréthane sans isocyanate, connues sous le nom de mousses NIPU, à partir de tanins hydrolysables, et il est divisé en deux parties principales :

La première partie, qui a fait l'objet de la publication dans l'article III, porte sur la conception de mousses isolantes thermiques en polyuréthane sans isocyanate (NIPU) à base de tanin hydrolysable, tel que le tanin extrait du châtaignier. Les résultats ont révélé des caractéristiques intéressantes en termes de densité, de résistance thermique et de comportement face à la flamme. Une observation majeure est que les mousses NIPU ont montré une densité plus élevée par rapport aux mousses à base de tanin-furanique, en raison de la formulation spécifique utilisée pour leur préparation.

Les analyses par spectroscopie infrarouge à transformée de Fourier (FTIR) ont permis de mettre en évidence la formation de liaisons uréthanes non isocyanates dans les mousses NIPU. Cette caractéristique est importante car elle confirme la nature chimique des liaisons formées dans le matériau et leur contribution à la stabilité thermique.

L'analyse thermogravimétrique a été effectuée pour d'étudier le comportement thermique des mousses NIPU.

En ce qui concerne la résistance à la compression, il a été constaté que celle-ci ne dépendait pas directement de la densité apparente de la mousse. Cela indique que d'autres facteurs, tels que la composition chimique et la structure de la mousse, ont un impact plus important sur cette propriété.

La deuxième partie, présentée dans l'article. IV, concerne la caractérisation des structures cellulaires des différentes mousses par microscopie électronique à balayage (MEB), dans le but de comprendre leur comportement mécanique. Une analyse approfondie par MALDI-ToF et RMN <sup>13</sup>C a également été réalisée sur la mousse présentant la meilleure structure cellulaire et la plus grande résistance à la compression. Enfin, cette étude aborde la manière dont les unités de glucose pentagalloylées sont liées, une question qui avait été traitée de manière contradictoire dans seulement deux articles.



En résumé, les mousses NIPU à base de tanin hydrolysable, extrait du châtaignier, présentent des propriétés intéressantes en termes de densité, de résistance thermique et de résistance à la flamme, en faisant des matériaux prometteurs pour les applications isolantes.

## **2. Self-Blowing Non-Isocyanate Polyurethane Foams Based on Hydrolysable Tanins (Publication. III)**

### **Abstract:**

Non-isocyanate polyurethane (NIPU) foams using a hydrolysable tannin, also vulgarly called tannic acid, namely here commercial chestnut wood tannin extract was prepared. Compression strength did not appear to depend on the foam's apparent density while the formulation composition of the NIPU foams has been shown to be more determinant. These NIPU foams appeared to be self-extinguishing once the high-temperature flame is removed. The ignition time gave encouraging results but for improved fire resistance the foams may need some fire-retardant addition. FTIR spectrometry showed the formation of non-isocyanate urethane linkages. Thermogravimetric analysis indicated a good thermal resistance of these foams, with thermal degradation following four phases. First in the interval 25°–120°C range, mainly evaporation of water occurs with a maximal loss of 10% weight. In the 150°C - 450°C temperature range foam mass loss is almost 70%. In particular, in the 125°C–275°C range occurs the degradation of some small molecular weight substances. In the 500 - 790 °C temperature range the foams do not present any further large degradation.

**Keywords:** Non-isocyanate bio polyurethanes (NIPU), bioforms, chestnut tannin, hydrolyzable tannins, self-extinguishing

## 1- Introduction

Vegetable tannins have been used for centuries as agents for transforming animal hides into leather. They can loosely be divided into two broad classes: condensed tannins and hydrolyzable tannins. While in the last decades, considerable research work for the preparation of new environment-friendly biomaterials has been focused on natural polyphenolics, in particular on lignin [200] and condensed tannins for a variety of uses, such as wood adhesives and rigid insulating foams [102], this has not really been the case for hydrolysable tannins. While the literature on hydrolyzable tannins for use in leather is extensive, the literature on their use for the preparation of renewable biomaterials is rather scant and limited to some rare papers on their use for wood adhesives [13], [201]. This is due to the lower reactivity of their aromatic nuclei towards aldehydes [197] and to their relatively higher cost.

Hydrolysable tannins, of which chestnut wood tannin extract is the most abundantly extracted commercial species, include also several other commercial tannin extracts such as sumach, tara, divi-divi, myrabolans, algarobilla, valonea, oak and several others. They are all composed of gallic and digallic acids esters with a sugar, mainly glucose. Pentagalloyl glucose monomers and oligomers (**I**) are the main species present but in the extract they share their importance with their rearrangements to other compounds such as castalagin (**II**), vescalagin, vescalin (**III**) and castalin [202], [203].

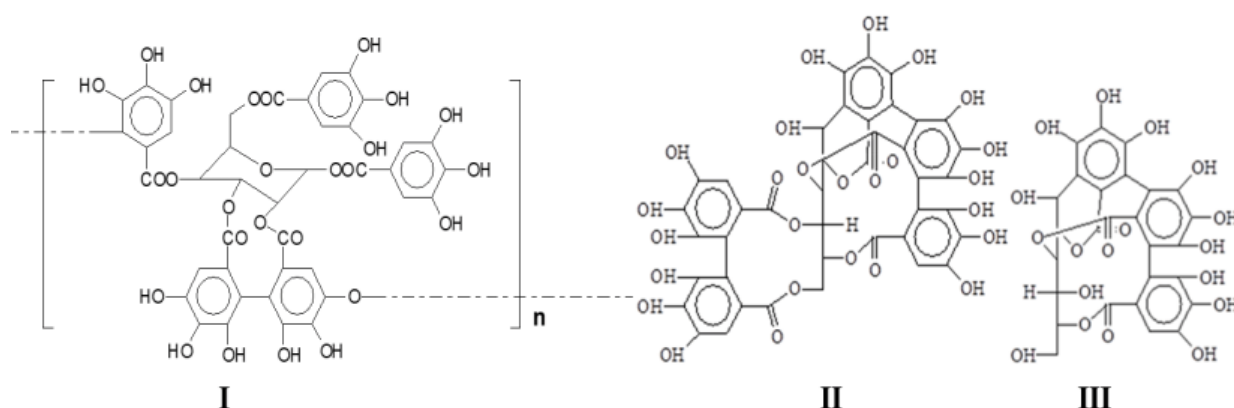


Figure.3. 1-Schematic structural formulas of oligomers of pentagalloyl glucose (I), and its rearrangements to castalagin (II), and vescalin (III).

More recently, due to their structural abundance in hydroxyl groups, hydrolysable tannins, namely chestnut tannin, were found to be ideally suited for the preparation of non-isocyanate bio polyurethane (NIPU) [126] as the reactions involved did not rely on their aromatic ring's

reactivity. More interestingly both their phenolic and carbohydrate fractions were found to contribute to forming bio-NIPUs [126]. In this previous work, the species formed were identified by both  $^{13}\text{C}$  NMR and by MALDI TOF mass spectrometry. It was shown that numerous species presenting urethane linkages between gallic acid units (**IV**) as well as species forming urethane linkages on glucose (**V**) formed and were identified, such as for example:

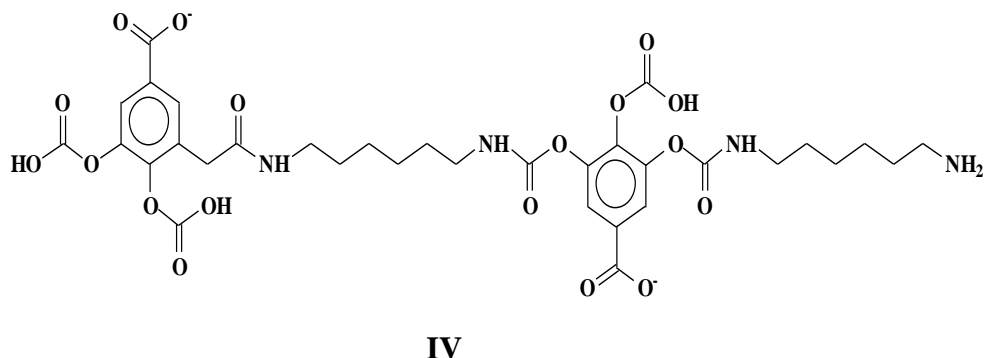


Figure.3. 2-Example of a urethane species isolated by reaction of carbonated gallic acid with hexamethylene diamine in chestnut tannin [8]

As the focus then shifted to condensed tannins NIPU and on their applications for adhesives and for fire-resistant foams [102], [155], [193], [197], [204] the work on, the application of hydrolysable tannins NIPU for the preparation of new useful biomaterials did not advance further. However, the presence of gallic acid as the hydrolysable tannins' basic structure linked to carbohydrates [202], [203], [205], [206] does instead identify them as an ideal raw material for the preparation of non-isocyanate polyurethanes, whatever their subsequent application. It is then pertinent to try to develop their use for the development of adequate biomaterials. The work presented here then focuses on the development of chestnut tannin-based non-isocyanate polyurethanes (NIPU) foams.

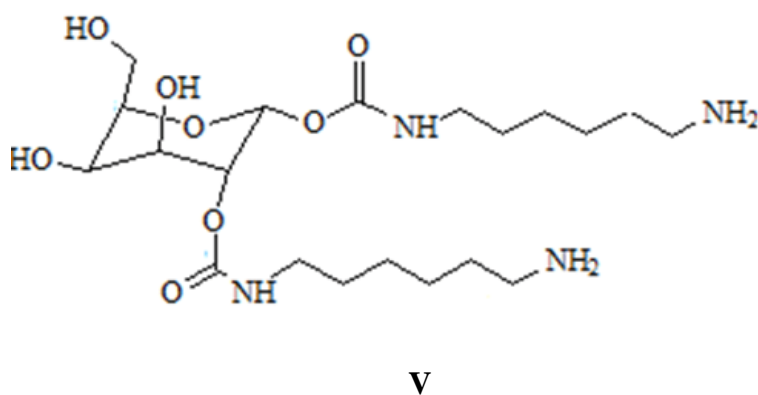


Figure.3. 3-Example of a urethane species formed by glucose present in chestnut extract after carbonation with dimethyl carbonate with hexamethylene diamine

## 2-- Materials and Methods

### 2.1- Materials

Commercial chestnut tannin extract was obtained from Silva Chimica (S.Michele Mondovi', Italy). Commercial products, including dimethyl carbonate (DMC, anhydrous,  $\geq 99\%$ ), hexamethylenediamine (HDMA, technical grade, 70% water solution), glutaraldehyde, citric acid and hexamethylene tetramine were obtained from Sigma-Aldrich (St.Louis, Missouri, USA). All raw materials in the experiments were employed directly without any pre-treatment.

### 2.2- Preparation of chestnut tannin extract non-isocyanate polyurethane (NIPU) resin and foams.

The NIPU foam preparation is based on three phases:

- A) Preparation of the NIPU resin
- B) Preparation of a flexible foam or a homogeneous mixture from the NIPU resin
- C) Heat to cure and harden the foam obtained.

Tannin-based NIPU resins were prepared by the same procedure used and reported previously [8]. Briefly, distilled water was charged into a three-neck round flask with magnetic stirrer and thermometer immersed in an oil bath condition. Then, chestnut tannin extract was added and sufficiently mixed till a homogenous mixture was obtained. Thereafter, DMC was added into the flask and the mixture heated to 65°C and kept at this temperature for 1h. Finally, HDMA was added under continuous mechanical stirring and maintained at 90°C for 2h. The reactions were tried by heating them either in an oil bath or without an oil bath. The resin so obtained was cooled down to room temperature and recorded as tannin NIPU. The relative proportions of the reactives used are shown in Table 3.1

Tableau.3. 1-Relative proportion of the proportions of materials used to prepare the chestnut tannin NIPU resin.

Formulation	Tannin (g)	Eau (g)	DMC (g)	HDMA (g)
Resin NIPU(NU)	10	8.4	6.8	17.7

Tableau.3. 2-Proportion of materials used to prepare the NIPU foams.

NIPU Foam	NIPU Resin (g)	Hexamine (g)	Citric acid (g)	Glutaraldehyde (g)
NU-1.1	10	2	9	3
NU-1.2	10	2	6	6
NU-1.3	10	2	6	7.5
NU-1.4	10	4	6	6
NU-1.5	10	4	6	7.5

Foams formulations were prepared using the amounts of reagents listed in Table 3.2. The foams were obtained by mixing several compounds. The first one is a homogeneous acid mixture, the composition of which consists of citric acid (50% in water solution) and glutaraldehyde (50% in water solution). The second compound is a homogeneous tannin NIPU resin, composed of the chestnut tannin based NIPU resin and hexamethylene tetramine (hexamine).

Briefly, difference proportions of tannin based NIPU resin and hexamine were mixed in glass beakers, and stirred rapidly, resulting in a homogeneous tannin resin, ready for application. The mixture of citric acid and glutaraldehyde was then weighed and placed into a foaming module, and the tannin-based NIPU resin and hexamine mix was added to it immediately, stirring manually for an optimal predetermined period of 10-15s. Subsequently the foams were left to grow at ambient temperature (25°C). When the self-blowing step was finished, a homogeneous dark and red liquid but self-supporting foam was obtained. This was then cured and hardened overnight in an oven at 70-80°C to obtain the final rigid foam. Finally, the hardened foam samples were conditioned for a minimum of 2 days at 25°C and 12% relative humidity before being characterized.

### 2.3 Apparent density determination

The determination of the apparent density for each foam sample was conducted according to the provisions of the standard GB/T 6342-2009 standard [207], [208]. The size of the prepared sample was measured, and the following formula was applied for calculating the apparent density:

$$\rho = (m/V) 10^6 \quad (1)$$

where, m is the mass of the sample (g); V is the volume of the sample (mm<sup>3</sup>); ρ is the apparent density (kg/m<sup>3</sup>), and the accuracy limit of the results is around 0.1 kg/m<sup>3</sup>.

## **2.4 -Compression Strength**

The compression strength of the foams in the direction parallel to that of the foam rise were determined under ambient conditions by using a universal testing machine (Instron 3300, Elancourt, France). The size of the samples was 25mm x 25mm x 25 mm, and the crosshead rate was fixed at 2.0 mm min<sup>-1</sup> for each sample. At least three samples were tested to determine the average value.

## **2.5 -Fourier transform Infrared spectrometry (FTIR)**

Samples of the hydrolysable chestnut tannin extract, of the NIPU resin 1 prepared in an oil bath before foaming it, of the NIPU resin 1 prepared without an oil bath before foaming it, and of the NIPU foam after curing, were placed into a diamond eye (1.8 mm) of the PerkinElmer Frontier ATR-FTMIR (PerkinElmer, Villebon-sur-Yvette, France) spectrometer. The scan results of each sample were recorded with 32 scans between the wave range of 600 and 4000 cm<sup>-1</sup>, with the scan resolution of 4 cm<sup>-1</sup>.

## **2.6- Thermogravimetric analysis (TGA)**

The thermal stability of tannin-based NIPU foams was investigated with a TGA 5500 analyzer (Mettler Toledo, Guyancourt, France). 5–8 mg of dried powder was put into a platinum pan, and heating was started on the sample to the desired temperature at a heating rate of 10°C/min, under nitrogen atmosphere with a flow rate of 50 mL/min in the temperature range from 50 to 700°C.

## **2.7- Ignition test**

The direct ignition test was carried out according to a method already described in the literature [123], [209]. Foam samples were made to specification size, 30 mm x 30 mm x 30 mm, and then were exposed facially to a stainless-steel frame preheated on a Bunsen burner (around 1000°C), making sure the samples were in the outer flame area of the Bunsen burner. The ignition time was calculated starting by when the samples were placed on the burner, until the sample strained burning. The Bunsen burner flame was then immediately extinguished and the time the sample either continued burning or self-extinguished was determined.

## **3. Results and Discussion**

### **3.1 -FTIR of Chestnut tannin**

The Chestnut tannin extract FTIR spectrum in (Figs. 3.4 ,3.5 and 3.6) shows the wide hydroxyl groups band between 3000 and 3500 cm<sup>-1</sup> as this tannin is particularly rich in –OH groups both

on the phenolic part and on its carbohydrate part. The Carboxylic group of the gallic acid and its sugar esters (**I**) characteristic of this tannin appears at  $1719\text{ cm}^{-1}$ . The band at  $1175\text{ cm}^{-1}$  belonging to the carbohydrate alcoholic  $-\text{OH}$  or to the ethers that are both abundantly present in the rearranged species castaline and vescaline. The  $1612\text{ cm}^{-1}$  band is assigned to antisymmetric stretching of  $\text{C}=\text{C}$  groups in the aromatic rings [210]. The band at  $1267\text{ cm}^{-1}$  is also assigned to the numerous ether bridges present in the rearranged species such as **II** and **III** in this tannin extract. The  $1089\text{ cm}^{-1}$  band is the asymmetric stretching of six rings ethers also present in castalagin (**II**) and vescalin (**III**). All the ethers presence being confirmed by the small band at  $807\text{ cm}^{-1}$ . The aromatic region. All the bands from  $870\text{ cm}^{-1}$  and lower, as well as the two relatively smaller bands around  $1500\text{ cm}^{-1}$  are assigned to the aromatic nuclei of the phenolic part of this tannin.

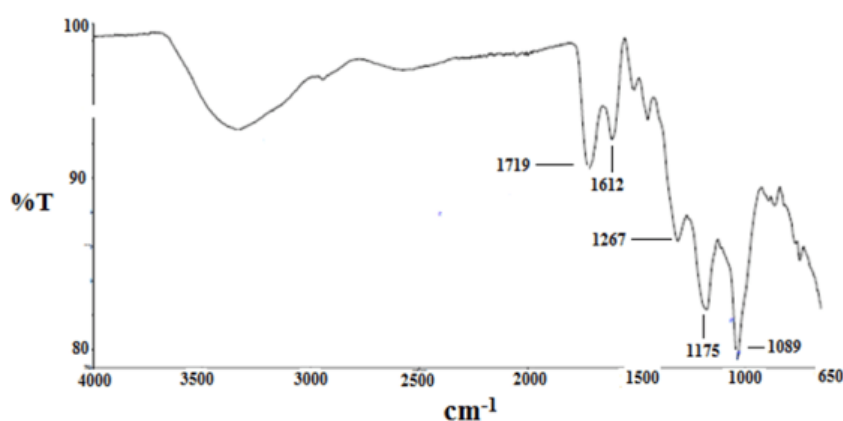


Figure.3. 4- FTIR spectrum of chestnut tannin extract.

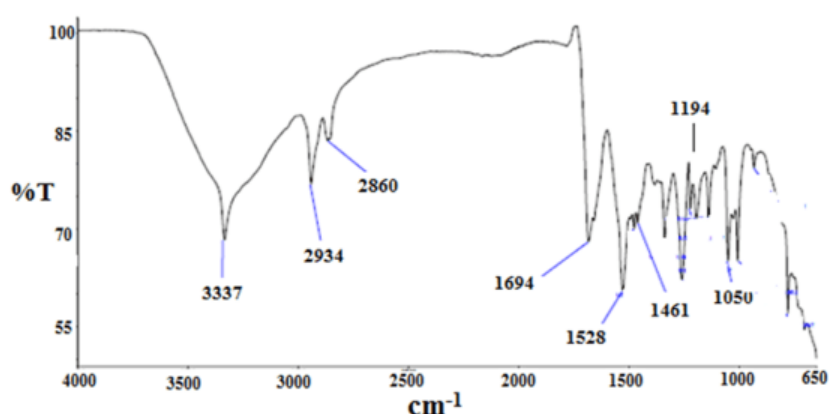


Figure.3. 5- FTIR spectrum of NIPU resin before foaming, Oil Bath reacted.



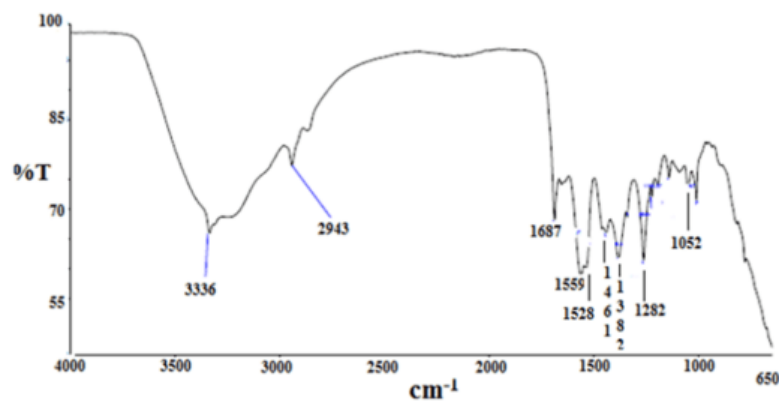


Figure.3. 6-FTIR spectrum of Hardened Foam after hardening it in the oven.

From the FTIR spectrum of the liquid NIPU resin prepared by heating in an oil bath many peaks more have appeared on the spectrum of the chestnut tannin extract alone (Fig. 3.5). Thus, from Fig. 1b the  $3337\text{cm}^{-1}$  is the asymmetric stretching of the amide bonds of urethane groups. All this shows that urethane linkages have formed. The marked intensity of this peak indicates that urethane linkages are in a relatively high proportion. However, comparing the spectra in Figs.3.4 and 3.5 and 1c, the sharpness of this band in Fig. 1b could indicate that the band belongs to carbamic acid ( $-\text{NH}-\text{COOH}$ ) groups formed by the reaction of DMC with hexamethylene diamine. The slight change of shift and intensity in (Fig. 3.6) indicating that further urethane linkages (thus  $-\text{NH}-\text{COO}-\text{R}$ , esters) have then formed afterwards, on curing. All this shows that urethane linkages and bridges have formed. This is supported in Fig. 1b by the peaks at  $1694\text{cm}^{-1}$ , and  $1687\text{cm}^{-1}$  (Fig. 3.6) characteristic of the carboxyl group of urethane bridges, as well as of the bands at  $1528\text{cm}^{-1}$  (also representative of the C-N of a urethane or an amide),  $1194\text{cm}^{-1}$ , and  $1050\text{cm}^{-1}$  (urethane C-O-C) all characteristic of urethane bridges. Equally the band at  $1282\text{cm}^{-1}$  in Fig. 3.6 confirm the presence of urethane bridges. The peaks at  $2934\text{cm}^{-1}$  and  $2860\text{cm}^{-1}$  are assigned to the  $-\text{CH}_2-$  groups of the hexamethylene diamine, with the  $2934\text{cm}^{-1}$  band being the C-H symmetric stretching and the  $2860\text{cm}^{-1}$  band being the C-H asymmetric stretching. These assignments are also supported by the asymmetric stretching bands at  $1461\text{cm}^{-1}$  of the alkane chain of the hexamethylene diamine. Conversely, the  $1333\text{cm}^{-1}$  band is characteristic of the stretching of the branched  $-\text{CH}-$  groups of the glucose chain in (I). The  $1382\text{cm}^{-1}$  band in Fig. 3.6 C confirm the presence of an aldehyde group from the glutaraldehyde. The spectrum in Fig. 3.5 is much clearer than the spectra being carried out without the oil bath, where urethanes are also formed but in a much lower yield. Once the foam is cured in an oven, the spectrum (Fig. 3.6) is less defined due to the formation of a cross-linked network, nonetheless that the fundamentally same peaks are in place. The urethane bands have

very slightly shifted, an indication that further urethane bridges, thus esters have been formed.

### 3.2 Thermogravimetric analysis (TGA)

To observe the foams thermal resistance, their characterization by TGA was carried out. Specific degradation up to a temperature at 790 °C was used. The thermal decomposition behavior of the series of chestnut tannin based NIPU foams was studied, and the corresponding thermograms as well as relevant DTG are collected in Figs. 3.7 and 3.8. A multi-stage response was encountered for the decomposition behavior as can be seen in all curves.

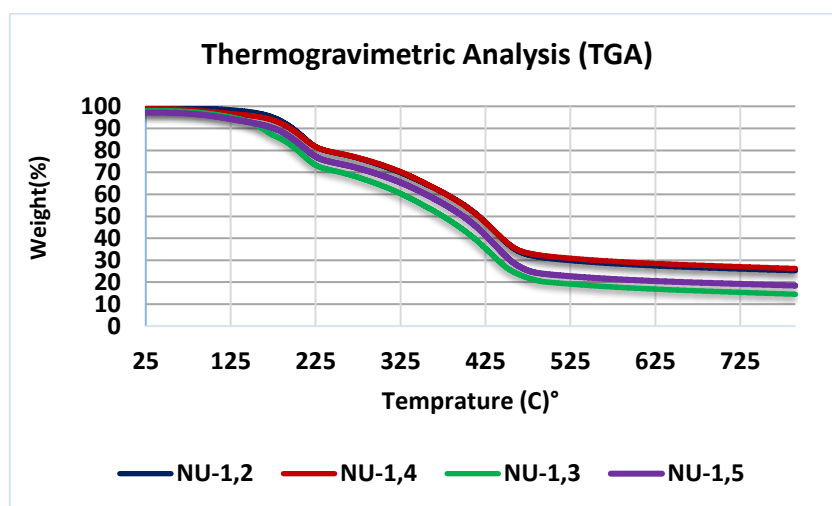


Figure.3. 7-Thermogravimetric Analysis (TGA) curves of the four chestnut tannin foams. To note that the curves are practically coincidental.

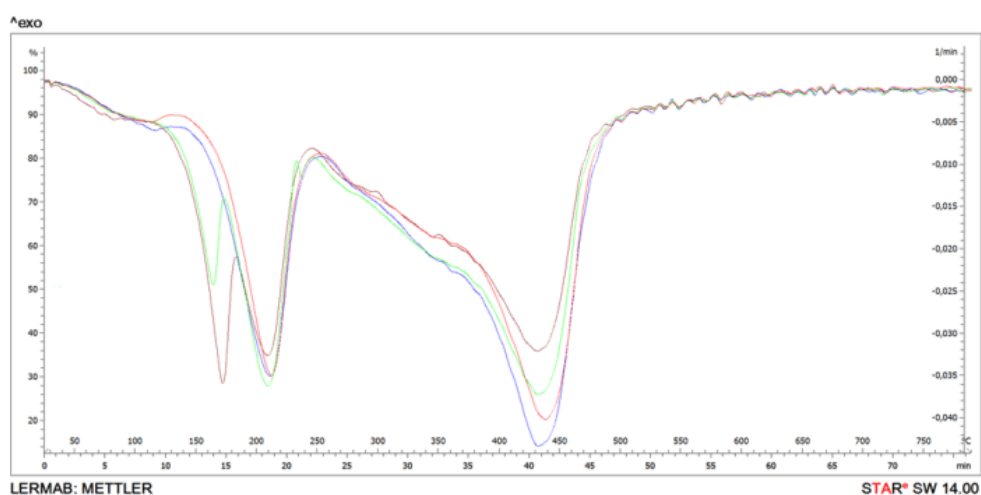


Figure.3. 8- Superimposed DTG curves for the four-chestnut tannin NIPU experimental foams  
NU-1.2; NU-1.3; NU-1.4; NU-1.5

The maximum temperatures are indicated by the peaks of the DTG curves at the different stages of pyrolysis.

Two types of curves are obtained, namely curves with two main DTG peaks (NU-1.2 and NU-1.3) and curves with three DTG peaks (NU-1.4 and NU 1.5). The three peaks' curves, and the DTG peak at 150-160°C is probably issued from the depolymerization of the excess of hexamine present in NU-1.4 and NU-1.5, and probably not due to the glutaraldehyde seen that a higher proportion of this is equally present in NU-1.3 (and this presents only two peaks) and NU-1.5 (with 3 peaks). However, the difference in the DTG 150-160°C peak intensity smaller in NU-1.4 than in NU-1.5 appears to indicate that the higher proportion of glutaraldehyde is synergic with the higher proportion of hexamine, thus an excess of hardeners liberating an excess of water as they react.

1) The first stage shows a small weight loss within the temperature interval 25°–120°C, which belongs to the evaporation of adsorbed water from the foams and with the loss of mass reaching up to 10%.

2) The second stage is between 150 and 450 °C including a loss of mass of the foam of almost 70%. The mass loss in the temperature range 125–275°C is assigned to the initial degradation of the samples, typically from some small molecular weight substances (saccharide present in the tannin extract) and unstable chemical linkages such as ether bonds [211]. In addition, the release of excess HDMA can also cause weight loss in this stage because its boiling point is around 190°C.

3) In the temperature range 500 - 790 °C the foams do not show any further large degradation.

4) At the temperature of 790 °C, only a maximum of 20% of the initial mass of the foam remains.

At the temperature of 185 °C, the mass loss reaches 10% for sample NU-1.2, while for NU-1.4, which has the same formulation but with twice as much hexamine, 10% mass loss is reached at 167 °C while a higher temperature is required for the first degradation. NU-1.3 with a higher proportion of glutaraldehyde than NU-1.2 showed the first degradation at 182°C. NU-1.5 which has a higher proportion of both hexamine and glutaraldehyde than NU-1.2 shows the lowest temperature for the first decomposition stage at 156 °C.

The second stage of weight loss appeared within the 275–425°C range due to the decomposition of the urethane groups [123]. This is the main degradation step, with the major part of the weight loss occurring in this stage. The second decomposition at the temperature 460°C showed that NU-1.2 lost 70% of its initial mass. The same mass loss occurred for NU-1.4 at the temperature

of 442 °C. The last weight loss stage occurs in the 425–525°C temperature range, which is attributed to covalent C–C bonds breaking. Some pyrolysis residual products coming from the previous few stages can also undergo further decomposition [123], [211], [212].

### 3.3 Compression test

The liquid flexible foams prepared need to be hardened by heating, which was necessary to obtain and measure stable physical properties. According to the relevant literatures [213] lower density foam samples have thinner cell walls, thus they can only provide a rather limited contribution to compression resistance [63]. Thus, to investigate whether any upgrading in mechanical properties is only attributed to the increasing density, or is due to the higher strength provided by the difference in formulation, the specific compressive strength of all foams was measured according to the literature [214]. The specific compressive strength of all foam samples is shown in Table 3.3. From Table 3.3 it appears that in the case of the chestnut tannin NIPU foams the rule that higher apparent density led to higher compression strength is not respected. This indicates that the differences in formulation, hence of reaction dependent from to relative proportions of the components have influenced quite strongly the compressive strength of the foams. For foams 1.2, 1.4 and 1.5 the compression strength differences are not significant seen the standard deviations obtained for them, showing however a certain structural heterogeneity considering the spread of their standard deviations. Foam 1.3 however, shows a very significantly different compression strength notwithstanding that its density is only rather slightly higher than that of the other three foams formulations. The main difference noted from Table 2 is its lower level of hexamine and higher level of glutaraldehyde. This infers that for these NIPU foams the relative strength of the cell walls is more upgraded by the reaction of glutaraldehyde than hexamine with the other foam components. Thus, the results show that the strength improvement of the mechanical properties of chestnut tannin NIPU foams is not exclusively attributed to their density alone, but related to the contribution of the cell wall and the influence of the relative proportions of the additives contributing to the reaction [214].

Tableau.3. 3-Compression tests compression

<b>Foam</b>	<b>Ave.Compression strength (MPa)</b>	<b>Apparent density(g/m<sup>3</sup>)</b>
<b>NU-1.2</b>	0.55±0.14	0.31-0.33
<b>NU-1.3</b>	0.91±0.03	0.35-0.37
<b>NU-1.4</b>	0.32±0.14	0.32-0.33
<b>NU-1.5</b>	0.37±0.05	0.33-0.35

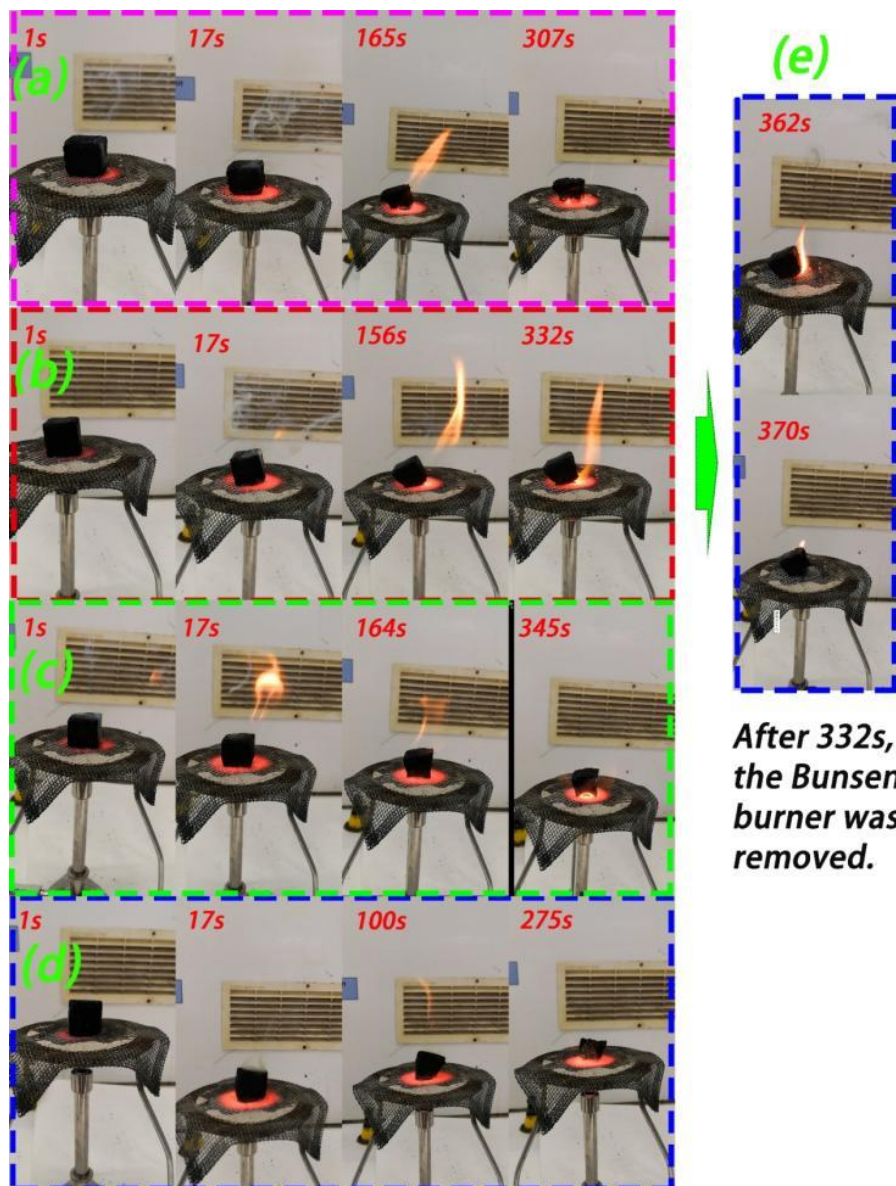
### 3.4 Ignition test

Although there are some limitations to the fire resistance evaluation of the ignition tests reported here, they can indicate to a certain extent the combustion resistance of the material. Therefore, this test was designed to investigate the flammability of foams 1.2, 1.3, 1.4 and 1.5. The ignition combustion tests were conducted on the foam samples directly. The results are shown in Table 3.4 and Figure.3.9.

The ignition times of the four foams were roughly comparable, with foam 1.5 taking a slightly shorter time to ignite and foam 1.4 presenting a slightly longer ignition time. Remarkably, foam 1.4 had the lower density of all the chestnut tannin NIPU foams. Foams 1.2, 1.4 and 1.5 self-extinguished immediately as the burner flame was removed. The only different behavior was presented by foam 1.3. While this had the second longest ignition time, possibly due to the difference in composition of its cell walls as shown by its higher compression strength, it was also the only foams that took 40 second to self-extinguish once the burner flame was removed. It is difficult to imagine why it behaved so, because while the density range of its samples was the highest of the four foams, while this might have contributed to the longest ignition time it did not appear to be determinant in causing a 40 second maintenance of burning after the direct burner flame was removed. It also indicates that while an interesting resistance to fire is shown, as already observed for foams obtained from mixed condensed tannin/glucose foams, they need the addition of some fire retardants for achieving an even better resistance to fire. An image of the ignition test for the 4 NIPU foams is shown in Fig.3.9, showing the encouraging behavior in fire of foams 1.2, 1.4 and 1.5, their instant self-extinguishing, and showing the short afterburning for foams 1.3. The performance of foams 1.4 and 1.5 are particularly impressive, with hardly any flame been present.

Tableau.3. 4- Ignition test comparison

Samples	Ignition time	Note
NU-1.2	307s	As the flame is removed the foam stops burning
NU-1.3	Around 332s	The flame was removed after 332s, but the foam kept burning strongly and released lot of dark smoke. The burning was maintained for 40 s after flame removal.
NU-1.4	Around 345s	As the flame is removed the foam stops burning
NU-1.5	Around 275s	As the flame is removed the foam stops burning



*After 332s,  
the Bunsen  
burner was  
removed.*

Figure.3. 9- Ignition test images with time scale in seconds for (a) foams 1.2, (b) foam 1.3, (c) foam 1.4, (d) foam 1.5. For foam 1.3 the afterburning before self-extension is shown.

#### 4 -Conclusions

The work presents the preparation of non-isocyanate polyurethane (NIPU) foams using a hydrolysable tannin, namely commercial chestnut wood tannin extract. While NIPU foams have been obtained using condensed flavonoid tannins this is the first time that a hydrolysable tannin extract, also vulgarly called tannic acid, has been used for NIPU foams application. The richness of this extract in phenolic hydroxyl groups and alcoholic hydroxyl groups from the skeletal glucose chain and the rearranged molecular species has shown that it is particularly suitable for NIPU resins and for their rigid foam applications. The formulation of the NIPU foams has shown to be determinant the apparent density and compression resistance of the

foams, rather independently from the foam density. The rigid foam prepared showed to have the interesting property of being self-extinguishing once the high temperature flame is removed. Ignition time was quite encouraging but indicated that for improved fire resistance the foams may need some small proportion of a fire retardant.





### **3.Hydrolysable Chestnut Tannin Extract Chemical Complexity in Its Reactions for Non-Isocyanate Polyurethanes (NIPU) Foams (Publication.IV)**

#### **Abstract**

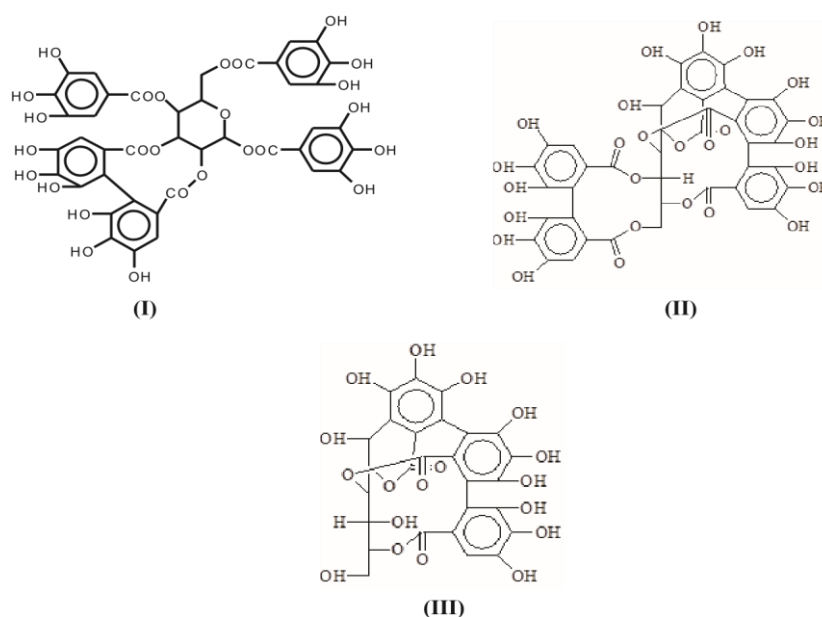
Non-isocyanate polyurethane (NIPU) foams from a commercial hydrolysable tannin extract, chestnut wood tannin extract, have been prepared to determine what chemical species and products are taking part in the reactions involved. This method is based on two main steps: the reaction with dimethyl carbonate and the formation of urethane bonds by further reaction of the carbonated tannin with a diamine-like hexamethylene diamine. The hydroxyl groups on the tannin polyphenols and on the carbohydrates intimately linked with it and part of a hydrolysable tannin are the groups involved in these reactions. The carbohydrate skeleton of the hydrolysable tannin is also able to participate through its hydroxyl groups to the same two reactions rendering the whole molecular complex able to react to form NIPUs. The analysis by Matrix-Assisted Laser Desorption Ionization (MALDI-TOF) mass spectrometry and <sup>13</sup>C Nuclear Magnetic Resonance (<sup>13</sup>C NMR) to further investigate the reaction mechanisms involved revealed the unsuspected complexity of chestnut hydrolysable tannin, with different fragments reacting in different manners forming a hardened network of considerable complexity. As the morphology and performance of these types of foams changes slightly with the change in the amount of glutaraldehyde and hexamine hardeners, the best performing foam formulation previously determined was scanned by SEM and analyzed chemically for the structures formed.

**Keywords:** Hydrolysable tannin; chestnut tannin ; non-isocyanate bio polyurethanes ; NIPU; MALDI-ToF; <sup>13</sup>C NMR; SEM; bio-based materials

## 1-Introduction

Hydrolysable tannins are phenolic organic compounds that have been used, although rarely, in materials development research because of their low reactivity and structure when compared to condensed tannins [13], [88], [206], [215]. While they are very valuable for leather tanning due to the low color they impart to the finished leather, they are nonetheless produced in a less than 10% proportion of the present commercial tannins market [216]. They are found in smaller quantities also in plants and secondary plant metabolites.

The structure of condensed tannin is phenolic, the hydrolysable tannins commercialized being, in general, a mixture of esters of sugar, mainly glucose, with simple phenols such as gallic and digallic acids and also with more complex structures such as ellagic acid[53], [205], [217]. Because of their different structure from condensed tannins, they have not been used with reactions with aldehydes in the same reactions as condensed tannins. They are composed mainly of pentagalloyl glucose (I) and its rearrangements forming castalagin (II) and castalin (III) [218].



One of the problems unresolved as regards their structure is how are enchainned the pentagalloyl glucose units in the tannin in their natural state and in their extracted from where they constitute at least 30% of the commercial extract [217], [219]. On this subject, only three articles exist in the literature [53], [205], [217].

Some carbohydrate chains in which several galloyl residues esterified on the carbohydrates have been lost in the extraction process also occur in commercial chestnut tannin extract, as well as

smaller molecular species [53], [205]. To take advantage of the potential of this type of tannin, with its abundance in hydroxyl groups, an approach such as the preparation of Non-Isocyanate Polyurethane (NIPU) has been used [102], [126], an approach being used also for other biomaterials [155], [220]. The application of this approach to prepare biomaterials based on hydrolysable tannins has made it possible to start using them in materials research such as for adhesives [2] and insulating foams and other polymers [140].

Recently, a kind of rigid thermal insulating foam has been prepared using chestnut tannin [140]. The technique of preparing tannin-furanic foams is not adapted to form a foam with hydrolysable tannins due to their phenolic sites' low reactivity. Thus, the non-isocyanate polyurethane approach based on their abundance in hydroxyl groups was used and the initial results of thermal and mechanical resistance were found to be acceptable [140].

Non-Isocyanate polyurethane foams from hydrolysable tannin with varying proportions of glutaraldehyde and citric acid and hexamine have been prepared (Table 3.5). The energy for foam expansion comes from the reaction between citric acid with the amino group of hexamethylene diamine with glutaraldehyde having the role of cross-linking agent [137], [140], [221]. FTIR characterization proved the existence and formation of urethane bonds.

Tableau.3. 5-The relative proportion of materials used to prepare the chestnut tannin NIPU resin.

Formulation	Tannin (g)	Water (g)	DMC (g)	HDMA (g)
NIPU resin	10	8.4	6.8	17.7

Based on these initial analyses, density and compressive strength appeared to be independent of each other for some foams. Coherence was supposed to exist between foam density and its mechanical strength. However, at almost the same densities for the different types of foam formulations, one of them showed instead a remarkably higher strength compared to the other foams. The present work presents (i) a scanning electron microscope (SEM) characterization of the different foams cell structures to explain their mechanical behavior. Furthermore (ii) an in-depth complementary analysis by MALDI ToF and <sup>13</sup>C NMR was carried out of the foam with the best cell structure and highest compressive strength, to explain the type of very complex oligomers mix formed and contributing to the hardened foam network, this being the first time this type of study is carried out on a finished hydrolysable tannin NIPU foam, and (iii) as the manner in which pentagalloyl glucose units are linked is not really explained in the literature

with only two articles [205], [217] addressing this problem drawing different conclusions this was also studied.

Commercial chestnut (*Castanea sativa*) wood tannin extract was obtained from Silva Chimica (S. Michele Mondovi, Italy). Retail products, including dimethyl carbonate (DMC, anhydrous,  $\geq 99\%$ ), hexamethylene diamine (HDMA, technical grade, 70% water solution), glutaraldehyde, citric acid, and hexamethylene tetramine were obtained from Sigma-Aldrich (St.Louis, Missouri, USA).

## **2. Materials and Methods**

### **2.1. Foam preparation**

Preparation of Chestnut Tannin Extract Non-Isocyanate Polyurethane (NIPU) Resin and Foams  
the NIPU foam preparation is based on three phases:

- A) Preparation of the NIPU resin.
- B) Preparation of a flexible foam or a homogeneous mixture from the NIPU resin.
- C) Heat to cure and harden the foam obtained.

Tannin-based NIPU resins were prepared by the same procedure used and reported previously [127], [137], [220], [221]. Briefly, distilled water was charged into a three-neck round flask with magnetic stirrer and thermometer immersed in an oil bath condition. Then, chestnut tannin extract was added and sufficiently mixed till a homogenous mixture was obtained. Thereafter, DMC was added into the flask and the mixture heated to 65°C and kept at this temperature for 1 h. Finally, HDMA was added under continuous mechanical stirring and maintained at 90°C for 2 h. The reactions were tried by heating them either in an oil bath or without an oil bath. The resin so obtained was cooled down to room temperature and recorded as tannin NIPU. The relative proportions of the reactive used are shown in Table 3.5.

To complete this study, four types of foam were prepared (Table 3.6). The formulations to prepare the resin and the foams come from recent research [52], [127]. In addition, initial observations such as density and compressive strength are mentioned to be able to distinguish foams by their physical characteristics.

Tableau.3. 6-The proportion of materials used to prepare the NIPU foams.

Foams	Tannin (g)	Hexamin(g)	Citric acid (g)	Apparent density(g/cm <sup>3</sup> )	Compression strength (MPa)
A	10	2	6	0.31 + 0.02	0.55 ± 0.14
B	10	2	6	0.35 ± 0.03	0.91 ± 0.03
C	10	4	6	0.32 + 0.02	0.32 ± 0.14
D	10	4	6	0.34 + 0.03	0.32 ± 0.14

## 2.2. Scanning Electron Microscopy (SEM)

The microscopy structure and morphology of the foams were examined using scanning electron microscopy (SEM, Hitachi TM-3000) (Milexia, Paris, France). The sample was cut into a 0.2 cm<sup>2</sup> cross-section. A thin metallic coating was sputtered on top of the foams.

Table 2: The proportion of materials used to prepare the NIPU foams.

## 2.3. Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF)

5 mg of sample powder was dissolved in 1 mL of a 50:50 v/v acetone/water solution. Then, 10 µL of a 2,5-dihydroxy benzoic acid (DHB) matrix was added to 10 mg of the sample solution. Furthermore, 2 µL of a NaCl solution 0.1 M in 2:1 v/v methanol/water was applied and pre-dried on the sample support plaque, followed by adding 1 µL of the sample solution. The plaque was then dried again. The standardization of the MALDI spectrometer was done with red phosphorous. The spectrometer was an Axima-Performance from Shimadzu Biotech (Kratos Analytical Shimadzu Europe, Ltd., Manchester, UK). The tuning mode was linear polarity positive. A total of 1000 transients for each sample were done, with two shots accumulated per profile. The spectrum precision is ±1 Da.

## 2.4. Solid State CP MAS 13C NMR

Solid state Cross Polarization-Magic Angle Spinning CP MAS 13C NMR was used to characterize the cured foam. As foam B showed the best physical results physique, it was chosen for this analysis. The spectrometer used was an AVANCE II 400 MHz spectrometer (Bruker, Billerica, MA, USA). Furthermore, 100.6 MHz was the frequency used at a 12-kHz sample spin, and the recycling delay was 1 s, depending on the 1H spin-lattice relaxation times (t<sub>1</sub>) estimated with the inversion-recovery pulse sequence and a contact time of 1 ms. The decoupling field was 78 kHz, with 15,000 being the number of transients. Tetramethyl silane

(TMS) was used as the shift control. The spectra precision was  $\pm 1$  ppm. Spinning sideband suppression was used.

### 3 -Results and Discussion

#### 3.1 Scanning Electron Microscopy (SEM) Analysis

The results of scanning electron microscopy are shown in Figs.3.10 and 3.11. Comparing foams A and B, which have the same formulation, but with the only difference being in the amount of glutaraldehyde, it is visible that the cell structure of foam B is more arranged, and the cells are better formed and more closed. Thus, the addition of glutaraldehyde appears to have improved cell formation yielding less perforated open cells when compared to foam A. As the foams with a higher amount of glutaraldehyde are much denser, it can be concluded that there is a reasonable reaction between tannin, and glutaraldehyde and that cross-linking is more completed. For this reason, formulation D while having the same amount of hexamine as C, has a higher amount of glutaraldehyde and its cells are thus less fractured.

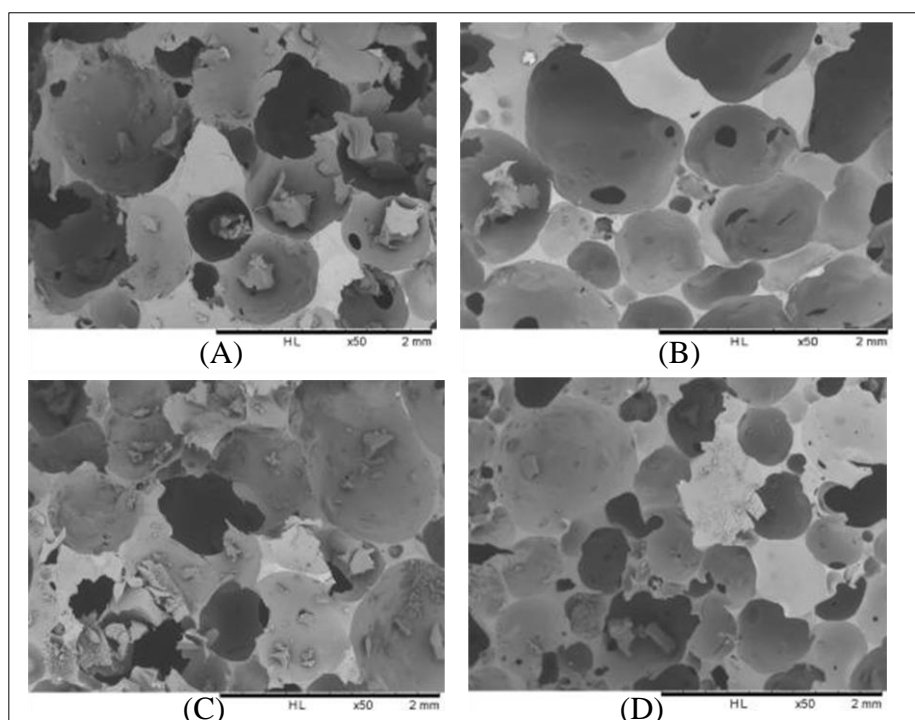


Figure.3. 10-SEM images of chestnut tannin extract-based non-isocyanate polyurethane (NIPU) bio-foam.

The addition of glutaraldehyde can increase the viscosity and speed-up foam formation, and for this reason, foams containing more glutaraldehyde are slightly denser and have higher molecular weights [15,16]. The addition of hexamine may accelerate foam formation, leading

to faster formation of foams C and D rather than for B. Still, a kind of cell fracture appeared, which can be attributed to the higher rate of reaction.

This excessive speed does not allow the cells to complete the formation of their structure or starts to break down the cell walls. Conversely, in formulation D, by increasing the amount of glutaraldehyde, the cross-linking has improved which can be attributed to a better-balanced rate of foam formation, and as it is visible in Fig.3.10 and 3.11, foam D is less fractured than foam C, its cells being less fractured. However, the addition of glutaraldehyde and hexamine has decreased the cells size and the rate of cells formation.

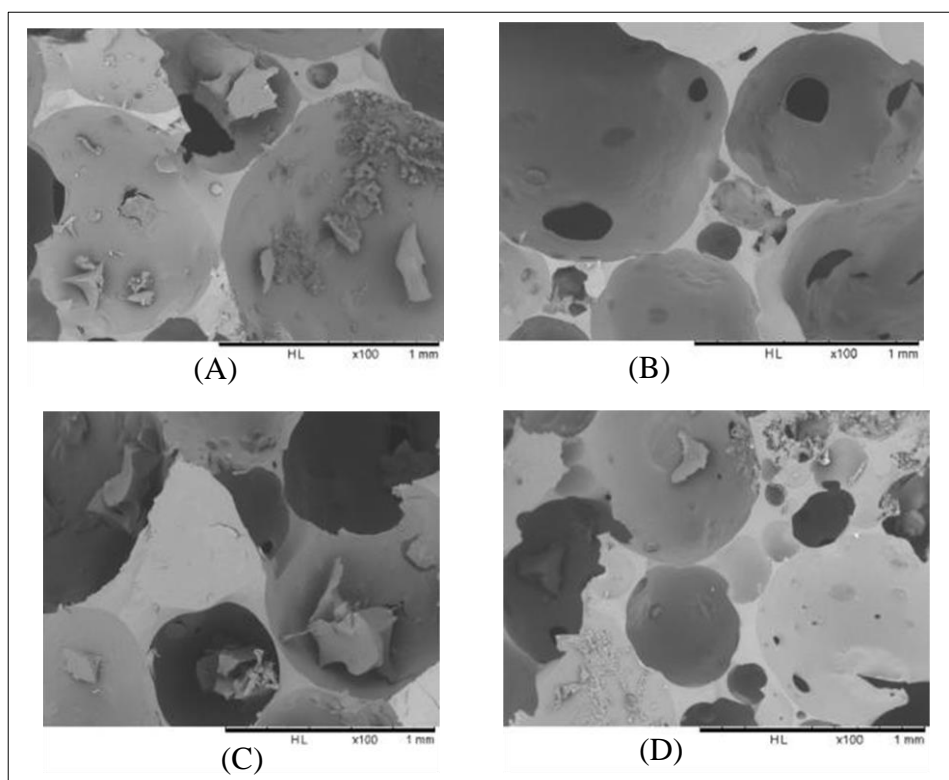


Figure.3. 11-SEM images of chestnut tannin extract-based non-isocyanate polyurethane (NIPU) bio-foams

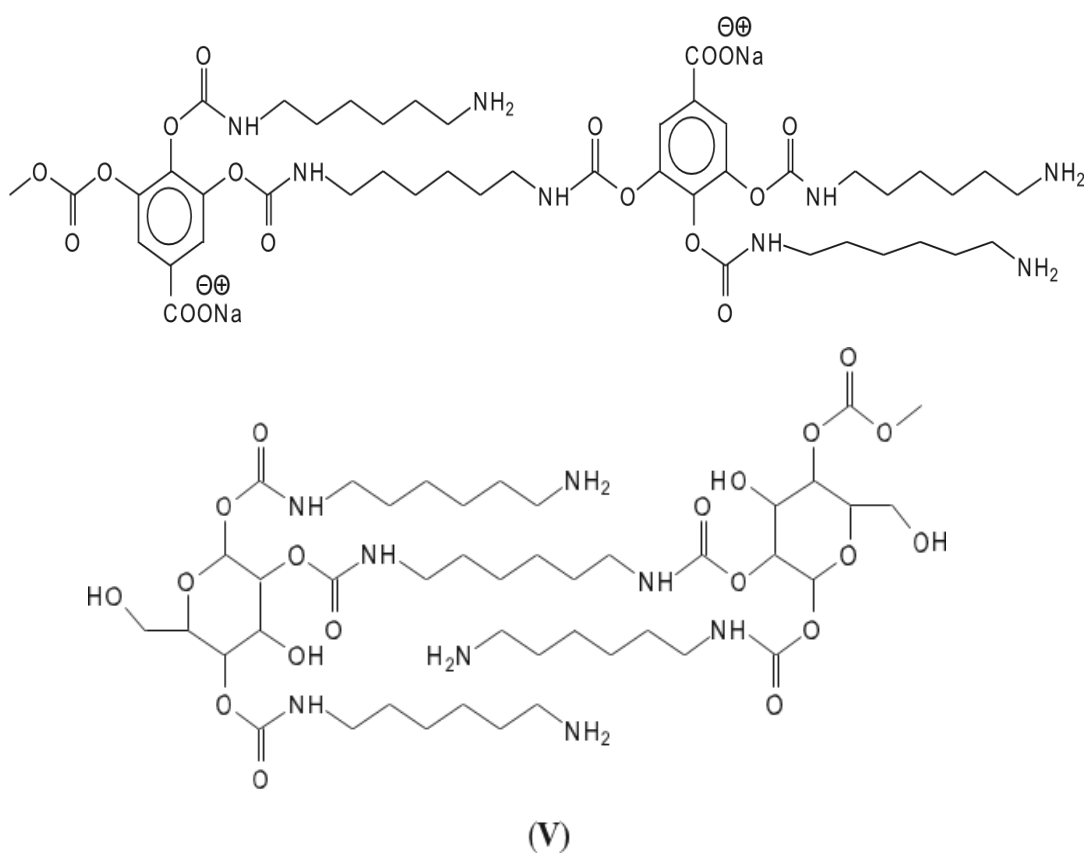
### 3.2 MALDI-TOF

The preparation of non-isocyanate urethane linkages, which is the essential reaction, comprises several processes.

The first step is the reaction between the gallic acid and/or ellagic acid groups of chestnut tannin with the dimethyl carbonate. The second step is the reaction of this mix of compounds formed in the previous reaction with a diamine, in our case with hexamethylene diamine: Because they are polyols, it is also probable that some of the carbohydrates that are intimately linked to the

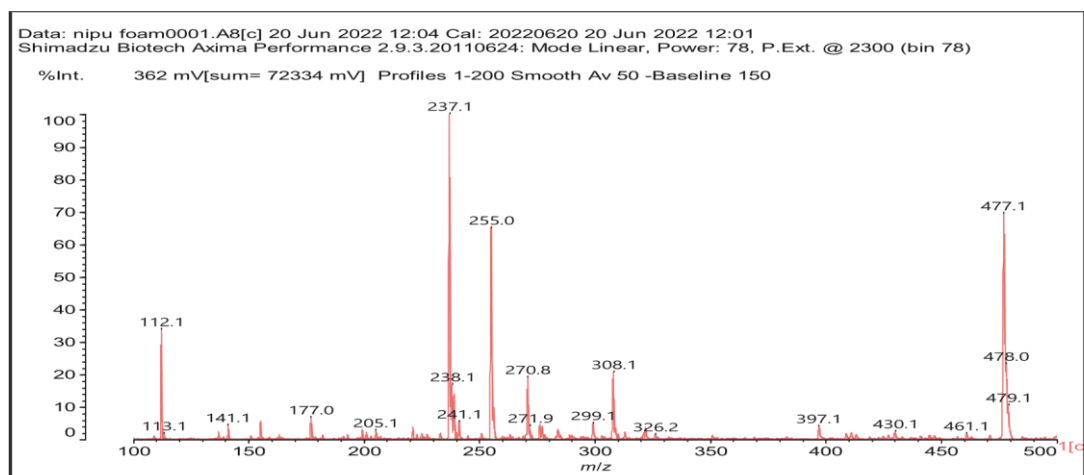
polyphenols in the tannin are affected by carbonation and thus participate to the formation of non-isocyanate polyurethanes once reacted as well with hexamethylene diamine. The MALDI ToF analysis of all the species formed by the reactions or already present in the tannin is shown in Table S1 in Appendix A.

This simplicity of reaction is only apparent as a complex series of reactions with several of the chemical species present are possible and many different products are hence formed. It must be considered that the extraction process of a tannin such as chestnut leads to the formation of all sorts of fragments of different molecular weight, rendering the environment rather complex. The first point to consider is to see if gallic acid moieties are carbonated by the dimethyl carbonate (DMC) and then if the reaction with the diamine occurs. That this does occur with ease is shown by all the species at 254, 309, 411, 447, and 475 Da (Fig. 3.12). The second point to see is if the carbonated gallic acid moieties do react with the hexamethylene diamine. Many species have been identified where this is the case, namely at 477, 529, 670, 731, 753, 817, 838, 896, 953, 1037 Da, such as the species at 1037 Da clearly demonstrating the participation of gallic acid residues to the NIPU formation (IV) (Fig. 3.12).

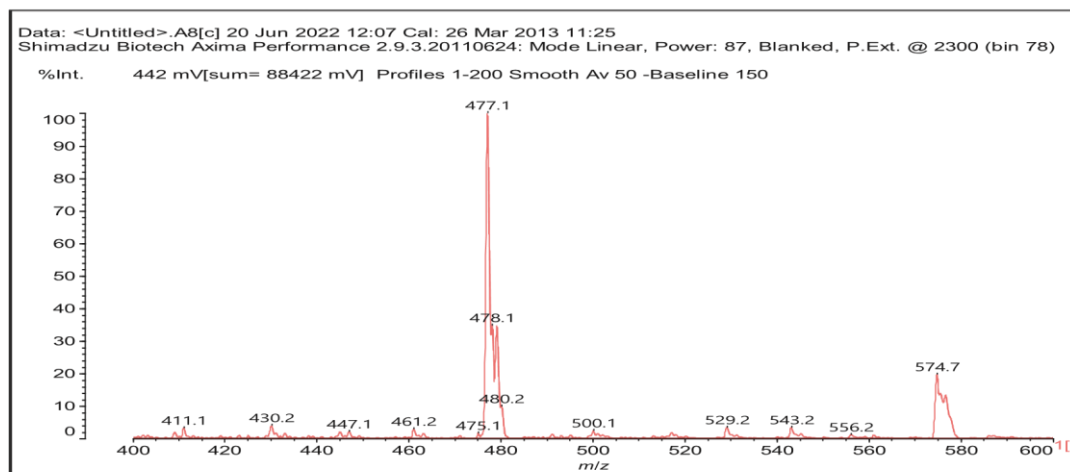




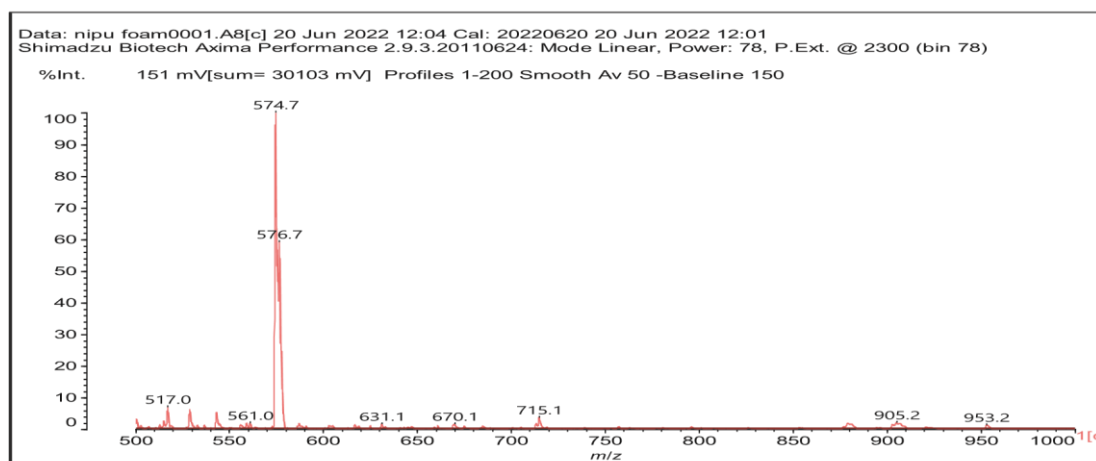
It must be equally pointed out that some of these peaks can be represented with NIPU being formed with the glucose residues that are inherent part of this tannin before and after extraction, namely the peaks at 529, 670, 810, 953, 1020 and 1037 Da (V) [127], [135]



(a)



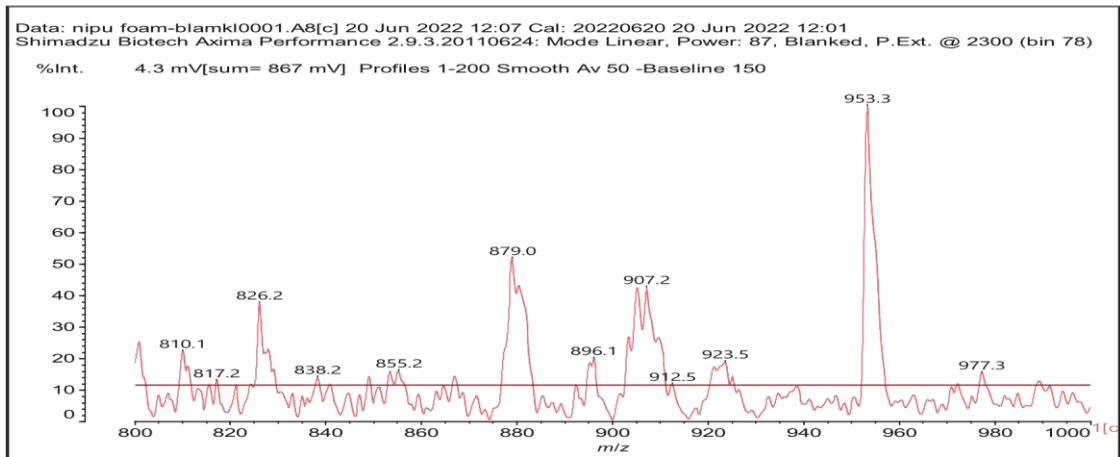
(b)



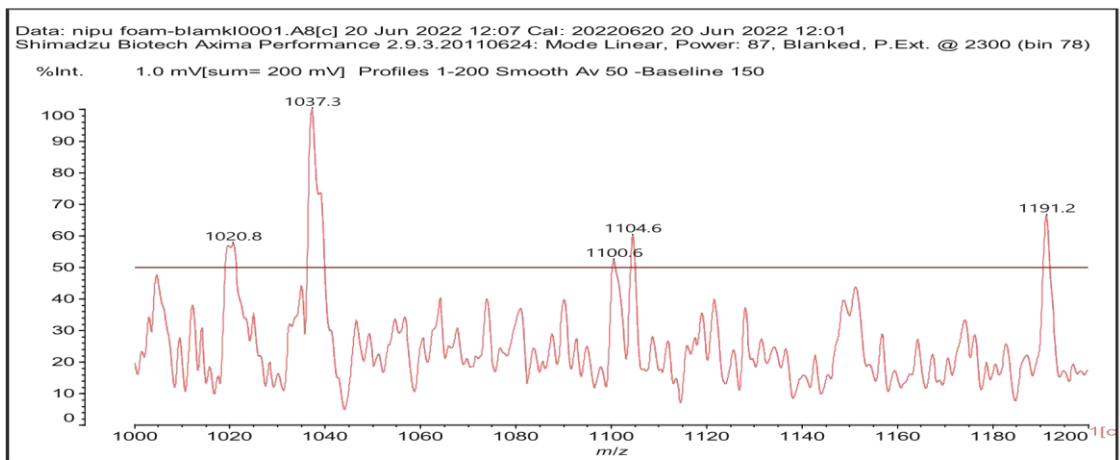
(c)

Figure.3. 12-(MALDI ToF spectra of chestnut tannin extract non-isocyanate polyurethane (NIPU) bio-foam

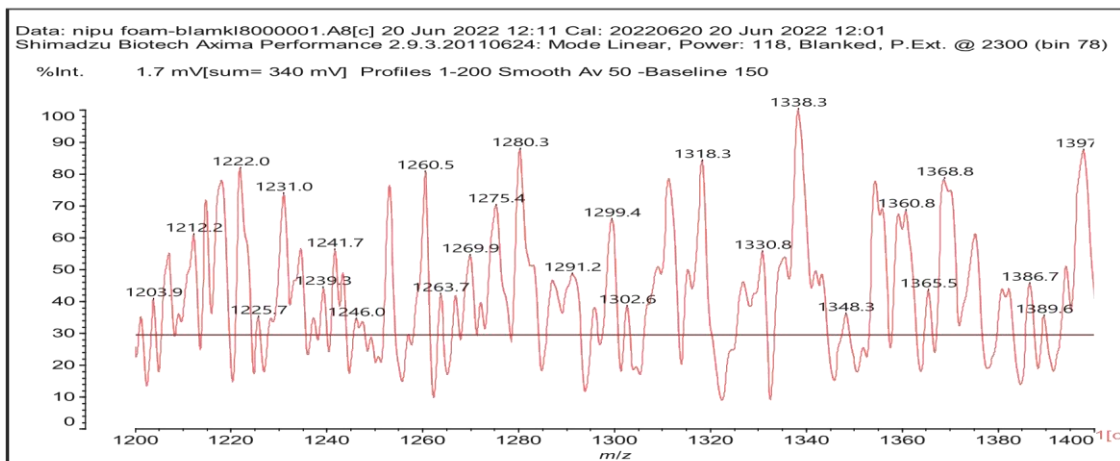
(a) 100–500 Da range, (b) 400–600 Da range, (c) 500–1000 Da range.



(d)



(e)



(f)

Figure.3. 13- (MALDI ToF spectra of chestnut tannin extract non-isocyanate polyurethane (NIPU) bio-foam

(d) 800–1000 Da range, (e) 1000– 1200 Da range, (f) 1200–1400 Da range, (g) 1600–2000 Da range, (h) 2000–250,000 Da range

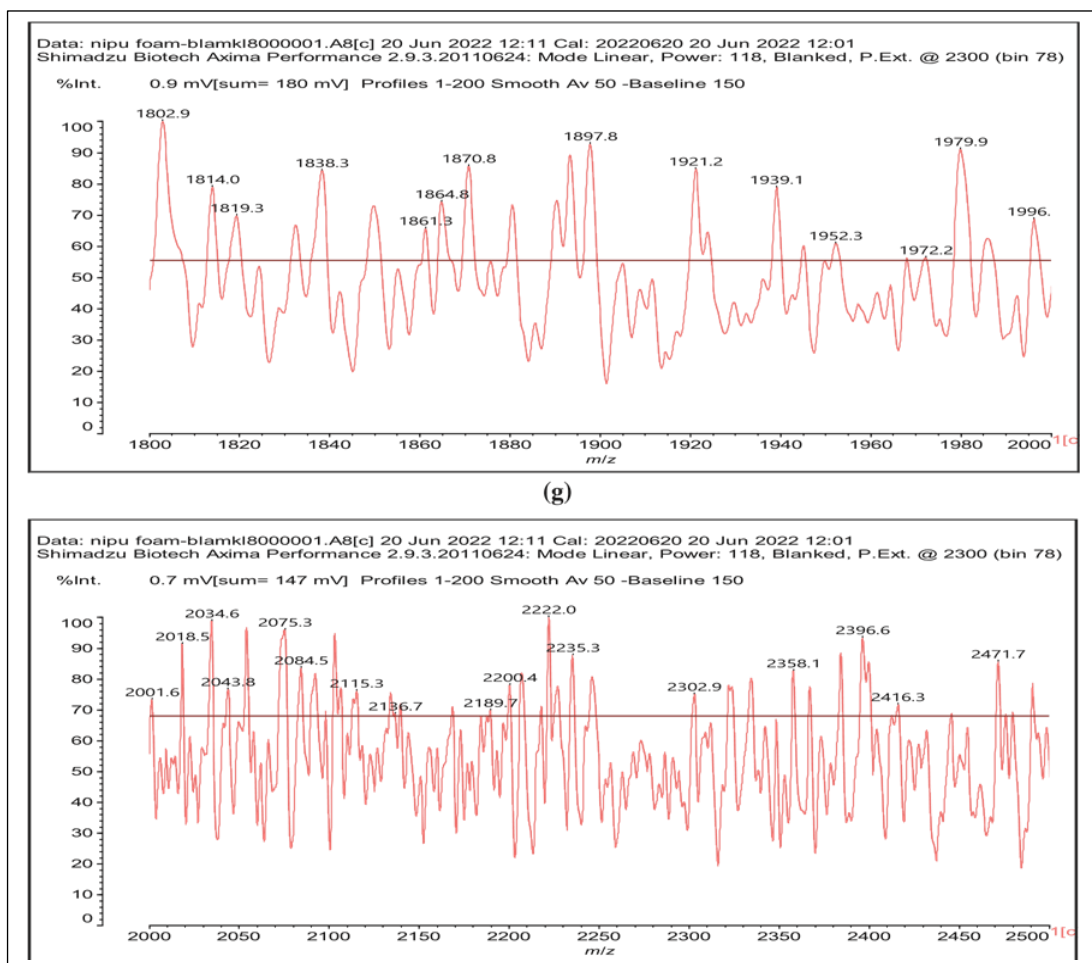
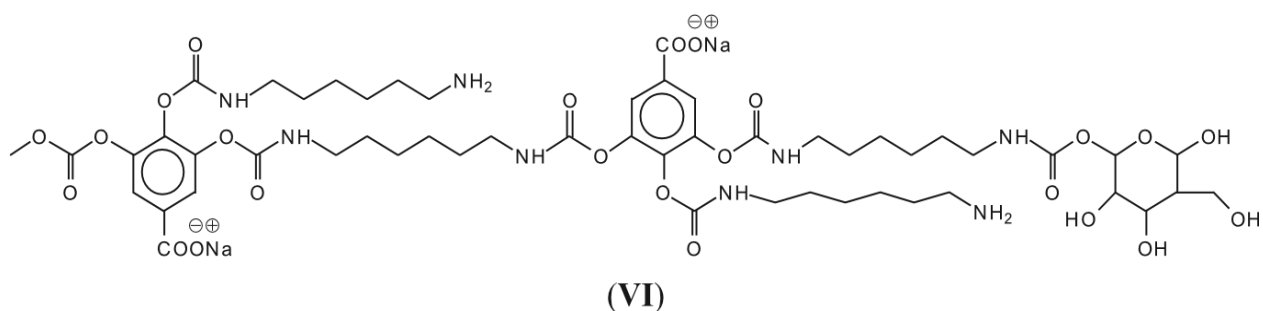


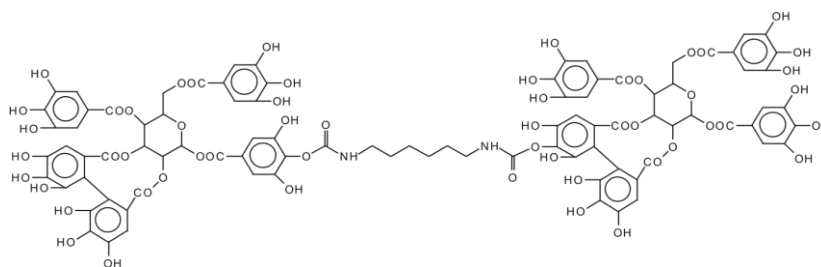
Figure.3. 14-(MALDI ToF spectra of chestnut tannin extract non-isocyanate polyurethane (NIPU) biofoam.(g) 1600–2000 Da range, (h) 2000–250,000 Da range

And moreover, mixed species in which both gallic acid and glucose participate in the non-isocyanate polyurethane formed also occur, such as those at 1242 and 1264 Da (Fig. 3.13), such as (VI).



Species I, II and III also show that DMC + hexamethylene diamine are able to form urethane cross-links between gallic acid residues, between glucoses and jointly between gallic acid and glucose residues.

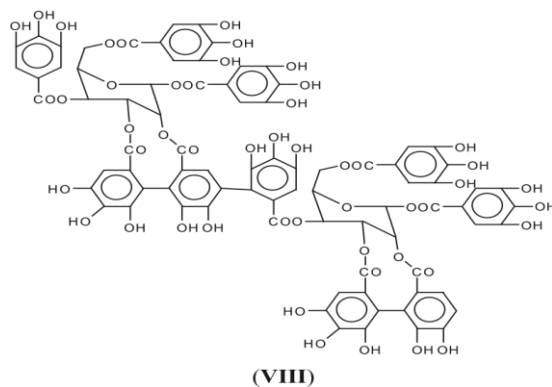
All these compounds are formed with small residues in the tannin extract, namely gallic acid and glucose that have been separated by the extraction process from the main structures of the tannin itself. Thus, it is essential to find out how the set of reactions to form NIPU do occur with big oligomers such as pentagalloyl glucose, the real repeating unit of the chestnut tannin polymer in nature. The reactions also occur with ease with pentagalloyl glucose, such as shown by the species peaks at 1275, 1299, 1524, 1635, 1712, 1747 Da and particularly 2044 Da, this last one showing cross-linking of two pentagalloyl glucose units by formation of two non-isocyanate polyurethane linkages by reaction with DMC and hexamethylene diamine (Fig. 3.14) (VII).



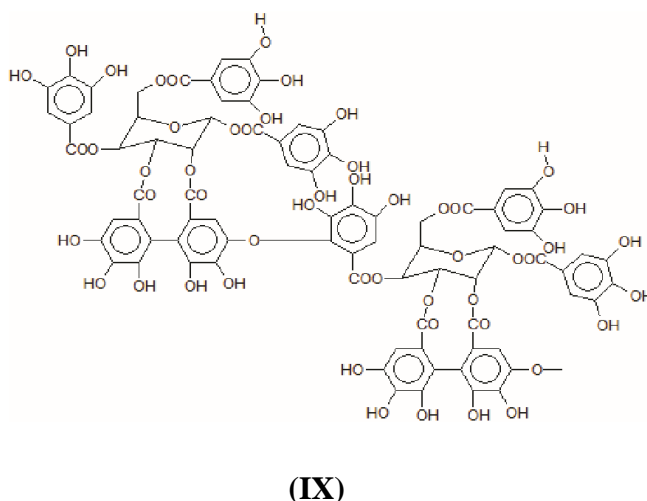
(VII)

To proceed further the structure of the polymer formed by just pentagalloyl glucose units is not really sure and is unreported in the literature. Only two early articles [53], [202] gave an explanation both of which could well be true as, while corresponding to the MALDI results obtained then, is possibly not the only type of linkages between the units, given the structural complexity of this tannin. There are several different ways that the pentagalloyl glucoses can be linked.

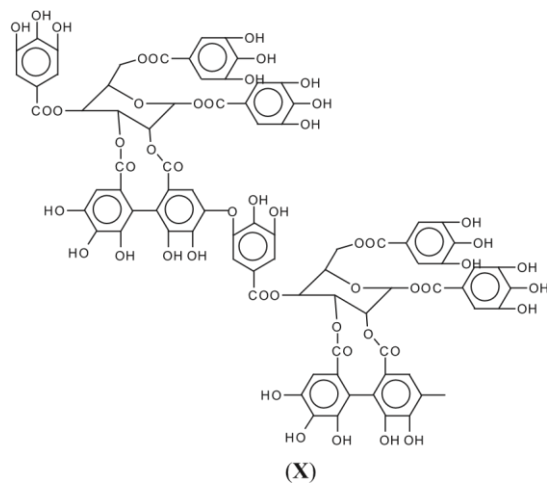
1. Through a linkage directly between aromatic rings through ArC-Car of the two units as for example as between gallic residues in ellagic acid (VIII).



2. Through a bridge ArC-O-CAr as in one of the only two articles on this subject [217], leaving all the  $3 \times \text{OHs}$  of the receiving gallic acid free so with the O bridge being formed between a -OH and the meta position of a gallic residue. This however at first sight seems unlikely as it would entail the elimination of just 2Hs, notwithstanding that in the article the MW of the trimer so formed corresponds to what expected from such a structure (IX).

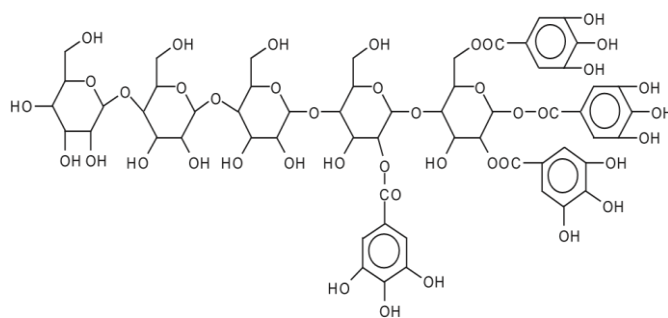


3. Third, and possibly more probable as a linkage ArC-O-CAr in which the -OH of the gallic acid donor and of the gallic acid receiver for such bridge are both involved by elimination of a  $\text{H}_2\text{O}$  molecule (X).



(X)

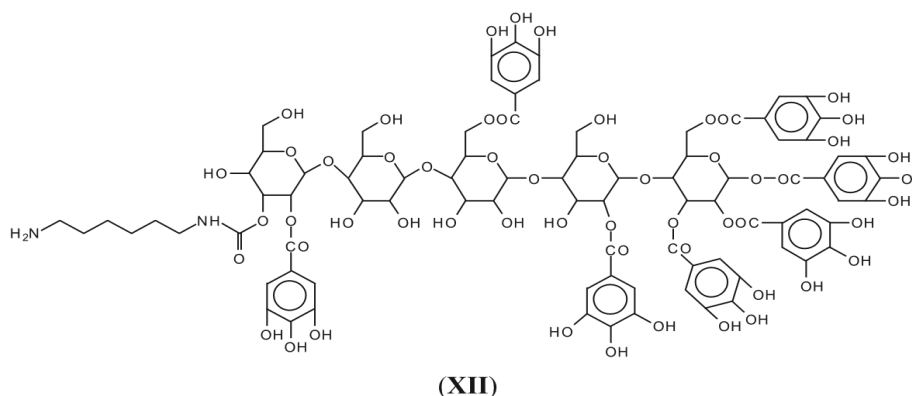
4. As can be seen from the long carbohydrate oligomer chains on which less or much less galloyl residues are linked, the possibility that in the commercial chestnut tannin extract the repeating units might not be pentagalloyl glucose but a lesser number of galloyl residues on glucose and that such units are linked by just glucose to glucose by glycosidic bridges. It may also be that such a configuration is generated by the extraction process. This type of configuration has already been shown to exist in commercial chestnut tannin extract [53], [205], as for example structure (XI) at 1437 Da (Fig. S1 in Appendix A), and all its isomers.



While of these four possibilities the first type of link exists in ellagic acid and the third is most logical for an enzymatic driven reaction in the native tannin, there is clear evidence that the other two are well present as well, adding to the complexity of chestnut tannin extract.

Thus, for the first linkage possibility, in the spectra present the peaks at 1861 and 2001 Da pertain to pentagalloyl glucose dimer alone and with a NIPU linkage. For the second possible link between units the peaks at 1898, 2018 and 2302 Da belong to it, pertaining to a pentagalloyl glucose dimer alone, with one NIPU linkage, and with 3 NIPU linkages, respectively. For the third possibility the peaks at 1898 and 2001 Da are also interpreted in the same manner as the

first type of possibility. Thus, it is not possible to distinguish between the first and the third type of linkage between the units. It is only possible to state that the type 2 does clearly exist [217], and that either the first or the third exist, or possibly both. The fourth type of inter-unit linkage definitely exists [53], [127], [135], [205] as shown in Fig. 3.15 by the peaks at 1231 Da (1 galloyl residue + 8 stripped glucose residues chain), 1365 Da (1 galloyl residue + 9 stripped glucose residues chain), 1437 Da (4 galloyl residues + 6 stripped glucoses chain), 1762 Da (1 galloyl residue + 12 stripped glucose residues chain), 1892 Da (7 galloyl residues + 5 glucose residues chain) (V), 2035 Da (7 galloyl residues + 5 glucose residues chain + 1 × NIPU) (XII).



A reaction scheme of what does occur with a kind of configuration can be better explained with the example given in Fig. 3.15 for one configuration of glucose chains linked by glycoside bridges with a variable number of galloyl residues linked to it between 0 and 4.

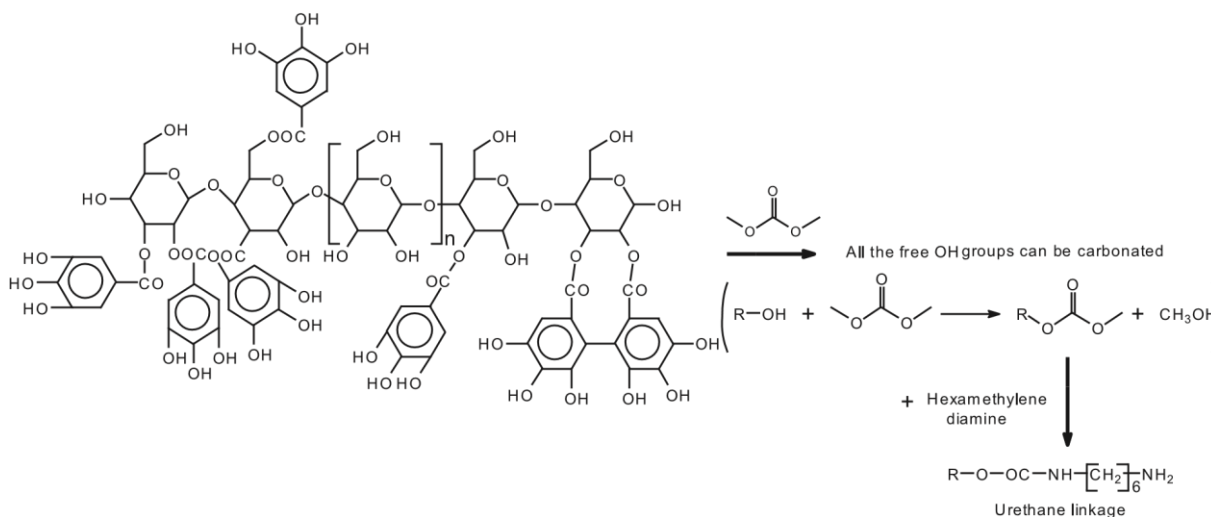


Figure.3. 15-Reaction scheme showing that all the free-OH groups in a glucose.

The reaction this schema has shown that chain with the glucoses linked by glycosidic linkages with on each glucose either no galloyl residue attached or with a variable number of galloyl

residues attached can be first carbonated and the carbonate group reacted with a diamine to form a urethane Linkage.

### 3.3 -CP-MAS $^{13}\text{C}$ NMR

Several peaks of significance are visible in the CP-MAS  $^{13}\text{C}$  NMR spectrum in Fig. 5 [20,21].

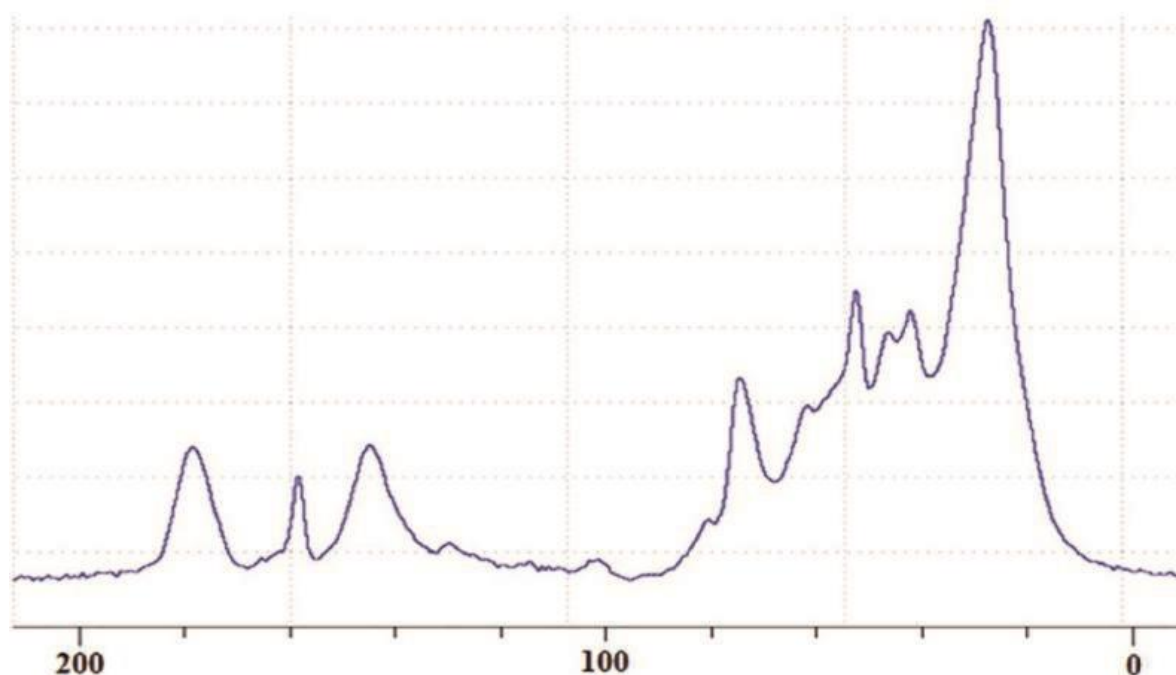


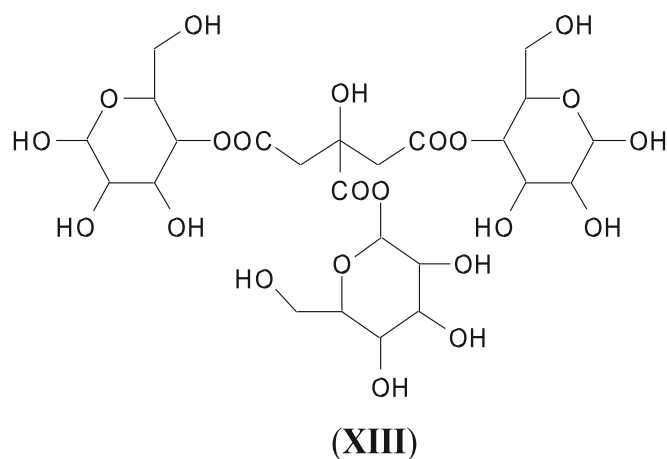
Figure.3. 16-CP-MAS  $^{13}\text{C}$  NMR of non-isocyanate polyurethane (NIPU) chestnut tannin extract bio-foam

Finally it is worth to notice that among all the types of oligomers observed in the foam there are a few more that have been observed in the system such as flavogallonic acid or valoneic acid[52][ linked to a pentagalloyl glucose, at respectively 1390 and 1426 Da, and glucose esters of citric acid Hardenberg such as the species at 699 Da (XIII).

First of all, the broad peak at 180 ppm is just due to overlap of carboxylic group from gallic acid and citric acid, this latter used as catalyst, and quinone structures due to oxidation of phenolic hydroxyls while the phenolic part of the hydrolysable tannin is undergoing the different reaction leading to the NIPU resin and finally the foam. The evident width of the majority peaks already indicates that the material in the foam is polymerized. The very small peak at 168 ppm is assigned to the free C=O of gallic acid. The more marked peak at 159 ppm is assigned to the C=O group of the NIPU hydroxy urethane linkages -NH-CO-O-R formed confirming that non-isocyanate urethane linkages have been formed. The wide peak at 144 ppm belongs to the aromatic carbons of the two non-vicinal phenolic hydroxyl groups of gallic acid



residues. The width of this peak also attests of the complexity of the variety of environments in which gallic acid finds itself as seen above by MALDI ToF analysis. The barely visible shoulder centered at 137 ppm central belongs to the aromatic carbon of the central hydroxyl group of gallic acid, thus the only one doubly vicinal of the other two hydroxyls. There is a very small peak at 120 ppm which belongs to the aromatic carbon attached to the C=O of gallic acid carboxyl group. The small but wide peak is composed of two shifts at 109 and 106 ppm and are assigned to the unsubstituted aromatic carbons of gallic and ellagic acids. The shift range between 50 and 90 ppm mainly belongs to carbohydrates groups. In this range the peak centered on 72 ppm and the peaks at 80 ppm, the shoulder at 90 ppm and the peak at 68 ppm are all assigned to the carbons of the pyranose heterocycle ring in pentagalloyl glucose confirming that a marked amount of the glucose is in its pyranose cycle form, thus belonging to pentagalloyl glucose and other galloyl glucoses rather than in the open sugar structure form present in rearrangement products such as castalagin or castalin. The 56-ppm shift while generally assigned in general to carbohydrates is really assigned to the presence of sugar chains linked by glycosidic bonds [184], [185], [222], [223] indicating a further manner in which galloyl glucoses with a different number of galloyl residues can be linked through the carbohydrate chain as well [7,8]. It reflects the reality of the MALDI ToF analysis peaks at 826, 977, 1231, 1365, 1437, 1762, 1819, and 1892 Da of long sugar chains oligomers with just very few galloyl residue linked to them [53], [205]. These are species where the galloyl residue esters to the carbohydrates have been cleaved with only very few of them remaining attached to the main, skeletal carbohydrate chain. The C-O- of the chestnut extract carbohydrates is represented by the peak at 40 ppm. The small peak at 45 ppm is assigned to the -CH<sub>2</sub> groups of citric acid. The dominant peak at 30 ppm is assigned to -CH- and -CH<sub>2</sub>- belonging to both open and ring carbohydrates and to the linear -CH<sub>2</sub>- groups of the diamine aliphatic chains in the NIPU urethanes formed, predominating in the NIPU resin linked to a pentagalloyl glucose, at respectively 1390 and 1426 Da, and glucose esters of citric acid hardener such as the species at 699 Da (XIII).



This confirms that, even under the reaction conditions of a bio-foam, citric acid is not only the catalyst of the foaming reaction but also cross-links the hydrolysable tannin, especially by reacting with the carbohydrate fraction linked to the polyphenolic part of the tannin extract. The reaction of citric acid with carbohydrates monomers and oligomers has already been studied in depth previously [224].

This shows the complex system in hydrolysable tannin extracts in which a tannin foams needed to be developed (Table S1 in Annex;5).

#### **4 -Conclusion**

The analysis work presented here shows the multitude of species initially present in commercial chestnut wood tannin extract the complex chemical species environment as well formed during the preparation of this hydrolysable tannin NIPU foams. The instrumental chemical analysis has shown that gallic acid and gallic acid residues linked to carbohydrates are cross-linked by the reaction with dimethyl carbonate and diamine, but that the same cross-linking occurs between the glucose residues which are an inherent part of the tannin itself, as well as mixed cross-linking of gallic acid residues and glucose residues. Such reactions occur both with the lower molecular weight species formed by cleavage of the tannin polymer during its extraction process, but more interestingly also between gallic acid esterified glucose chains and the glucoses of equivalent carbohydrate chains.

The analysis confirms the formation of non-isocyanate polyurethane bridges between all these species. It also confirms that citric acid is not only the catalyst of foaming, but that it reacts covalently and participate to the cross-linking of the total foam system by esterifying glucose residues in the hydrolysable tannin, and possibly also some of the phenolic material. As regards the way in which galloyl glucoses are linked to each other, all the 4-manner possible, including the two already mentioned in the literature, appears to occur but with the likely predominance

of long glucose chains linked by glycosidic bridges and with gallic acid and ellagic acid residues esterifying to different degrees the glucoses in the chain.

#### 4. Discussion et conclusion

Dans cette étude, des mousses de polyuréthane sans isocyanate (NIPU) ont été préparées en utilisant un extrait commercial de tannin de bois de châtaignier comme composant polyol.

Le tannin de châtaignier est un type de tannin hydrolysable qui contient des groupes phénoliques capables de réagir avec des composés d'hydroxyle.

La formulation des mousses de NIPU a été réalisée en mélangeant le tannin de châtaignier avec d'autres composants tels que le polyéthylène glycol (diol), l'hexaméthylène diamine (diamine) et le glutaraldéhyde (réticulant). Différentes proportions de ces composants ont été utilisées pour préparer des mousses avec des densités apparentes variables.

Les propriétés des mousses de NIPU ont été évaluées en termes de densité apparente, résistance à la compression, analyse infrarouge, caractérisation thermogravimétrique (TGA) et résistance au feu.

Les résultats ont montré que la densité apparente des mousses de NIPU variait en fonction de la formulation, mais cela n'était pas toujours directement lié à leur densité réelle. La résistance à la compression des mousses n'était pas uniquement déterminée par la densité, mais également par les proportions relatives des composants. Par exemple, une mousse avec une densité légèrement plus élevée mais une proportion plus élevée de glutaraldéhyde a montré une résistance à la compression différente des autres mousses.

L'analyse par spectrométrie infrarouge a confirmé la formation de liaisons uréthane et de ponts uréthane dans les mousses de NIPU. Cependant, des différences ont été observées entre les spectres de la résine de NIPU, de la mousse rigide et de la mousse durcie. Une bande d'étirement asymétrique plus faible a été observée dans le spectre de la mousse rigide, suggérant la présence de groupes acide carbamique (-NH-COOH) formés par la réaction entre le diméthylcarbonate (DMC) et la diamine d'hexaméthylène. D'autres bandes caractéristiques ont confirmé la présence de liaisons uréthane et de ponts uréthane dans les mousses de NIPU. Cependant, des techniques de caractérisation supplémentaires, telles que la spectrométrie de masse MALDI-TOF et la RMN C13, ont été utilisées pour une étude plus approfondie de la structure moléculaire et de la composition des mousses.

L'analyse MALDI-TOF a éclairé les réactions complexes qui se produisent lors de la formation des mousses de NIPU. Il a été observé que les groupes hydroxyle des polyphénols de tannins et des glucides participaient à la réaction avec le carbonate de diméthyle (DMC) et la diamine d'hexaméthylène. L'analyse a révélé la formation de divers composés et espèces, comme la

participation de fractions d'acide gallique, de résidus de glucose et d'espèces mixtes dans la formation des NIPU. De plus, l'analyse a montré que les réactions se produisaient avec de gros oligomères tels que le pentagalloyl glucose, qui est une unité répétitive du tannin de châtaignier.

Différents types de liaisons entre les unités, comme la liaison directe entre les cycles aromatiques, la formation de ponts et l'implication de ponts glycosidiques, ont été identifiés, ajoutant à la complexité de l'extrait de tannin de châtaignier.

L'analyse par RMN <sup>13</sup>C CP-MAS a confirmé la formation de liaisons uréthanes sans isocyanate dans les mousses NIPU. L'analyse a également fourni des informations sur la présence de divers composés, dont l'acide flavogallolique, l'acide valonéique et les esters de glucose de l'acide citrique Hardenberg. La large gamme de pics observés indiquait la polymérisation du matériau dans la mousse et la complexité de l'extrait de tannin.

Dans l'ensemble, la discussion met en évidence les effets du glutaraldéhyde et de l'hexamine sur la formation de la mousse et la structure des cellules. Elle souligne également la complexité des mécanismes de réaction impliqués dans la formation des NIPU à partir de l'extrait de tannin de châtaignier. Les analyses en MEB, MALDI-TOF et RMN <sup>13</sup>C fournissent des informations précieuses sur les espèces chimiques et les produits participant aux réactions ainsi que sur la variété de structures formées dans les mousses NIPU.

La caractérisation thermogravimétrique (TGA) a été utilisée pour évaluer la résistance thermique des mousses de NIPU. Les résultats ont montré que la dégradation des mousses se produisait en plusieurs étapes, avec une perte de poids significative dans la plage de température de 150 à 450 °C, principalement due à la décomposition des groupes uréthane. Cependant, des différences ont été observées dans les courbes de décomposition, indiquant que d'autres facteurs, tels que la proportion relative des composants, pouvaient influencer la dégradation thermique des mousses.

En termes de résistance au feu, les mousses de NIPU au tannin de châtaignier ont montré des performances améliorées par rapport aux mousses de polyuréthane traditionnelles. Cela est attribué à la présence de groupes phénoliques dans le tannin, qui peuvent se carboniser et former une barrière contre la propagation des flammes.

Il convient de noter que les résultats des tests d'allumabilité peuvent varier en fonction de plusieurs facteurs, tels que la formulation spécifique des mousses, les méthodes d'essai utilisées et les normes de référence appliquées. Sans des informations spécifiques sur les tests

d'allumabilité réalisés dans une étude particulière, il est difficile de fournir des détails précis sur les résultats obtenus.

En résumé, les mousses de polyuréthane sans isocyanate (NIPU) utilisant un tannin hydrolysable tel que le tannin de châtaignier offrent des propriétés intéressantes en termes de densité, résistance mécanique, résistance thermique et résistance au feu. Ces matériaux peuvent potentiellement être utilisés dans diverses applications, telles que l'isolation thermique, l'emballage et les matériaux de construction, en offrant une alternative plus écologique aux mousses de polyuréthane traditionnelles.

# **Chapitre IV : Conception de composites bois/tanin/alcool furfurylique**





Ce chapitre se concentre sur la préparation de résine à partir de tanin pour la création de composites en bois, ainsi que sur l'amélioration des propriétés et de la durabilité biologique de ces composites. Les résultats de ce chapitre ont été présentés lors de conférences internationales et sont en cours de préparation en vue de leur publication.

1. La première partie est axée sur l'effet de la proportion de tanin et d'alcool furfurylique sur l'amélioration de la durabilité et les propriétés chimiques et physiques du bois.
2. La deuxième partie est concentrée sur l'ajout de tanin modifié pour observer l'impact de cette modification sur l'amélioration de la durabilité biologique et l'hydrophobicité.

## 1.Introduction générale

Le bois est un composite naturel qui joue un rôle essentiel dans de nombreuses industries, notamment la construction, l'ameublement et l'emballage, Cependant, il présente certaines limitations en termes de propriétés physiques et chimiques, qui peuvent être surmontées grâce à des modifications chimiques.

Le risque biologique des matériaux bois est généralement classé en cinq catégories, en fonction de leur utilisation en intérieur ou en extérieur et de l'exposition à l'humidité [141].

Les classes d'emplois du bois en France sont présentées ci-dessous.

**Classe 1** : Intérieur : bois hors du contact du sol, utilisé à l'intérieur, le risque est constitué par les insectes.

**Classe 2** : Bois hors contact du sol pouvant occasionnellement être humidifié : charpente.

Risques : insectes et champignons.

**Classe 3** : Extérieur (menuiseries extérieures) : humidification temporaire (pluie).

Risques : insectes et champignons.

**Classe 4** : Extérieur (bois au contact du sol). Risques : insectes, y compris termites dans les zones infectées.

**Classe 5** : Bois au contact de l'eau de mer : risques térébrants marins.

Pour améliorer la durabilité du bois et prolonger sa durée de vie, il est souvent recommandé d'appliquer un traitement de préservation, surtout lorsque le matériau est exposé à des conditions environnementales défavorables, telles que les précipitations ou encore l'exposition à des organismes biologiques comme les insectes et les champignons. Ces traitements aident à protéger le bois et à prévenir sa dégradation prématurée, assurant ainsi une meilleure performance et une plus grande résistance aux agressions extérieures.

La plupart des méthodes de préservation du bois utilisaient jusqu'à ces dernières années souvent des traitements biocides nocifs pour l'homme et l'environnement. Ces traitements sont maintenant prohibés en Europe (loi Biocides, loi sur l'air). Les réglementations environnementales ont joué un rôle clé dans la promotion de traitements alternatifs respectueux de l'environnement pour la préservation du bois. Le traitement thermique et la modification chimique du bois sont des méthodes de préservation du bois plus respectueuses de l'environnement car elles permettent d'éviter l'utilisation de biocides.

Ces alternatives offrent une protection du matériau similaire à celle des produits conventionnels tout en réduisant l'impact sur l'environnement et la santé humaine [225].

Cependant, il est important de noter que l'utilisation de ces produits alternatifs n'est pas sans risques environnementaux, Bien que leur impact soit généralement moindre que celui des produits conventionnels, des précautions doivent être prises lors de leur utilisation, Des restrictions strictes et des réglementations fédérales ont été mises en place pour encadrer leur utilisation et leur élimination, afin de minimiser les risques environnementaux associés [226], [227].

Il est donc essentiel de respecter scrupuleusement ces réglementations et de tenir compte des recommandations spécifiques liées à l'utilisation des traitements alternatifs, Cela garantira une utilisation responsable de ces produits, réduisant ainsi leur impact sur l'environnement et assurant une préservation durable du bois.

Dans ce contexte, les méthodes de préservation impliquant des modifications chimiques permettant à obtenir des biopolymères dérivés du bois suscitent de plus en plus d'intérêt dans la littérature scientifique. Ces biopolymères, issus de matières premières renouvelables et non toxiques, présentent un potentiel prometteur pour remplacer les produits chimiques traditionnels utilisés dans les traitements de préservation du bois. Ils offrent une alternative plus respectueuse de l'environnement tout en préservant leurs propriétés protectrices contre les attaques fongiques.

Les résultats préliminaires sont encourageants, montrant que les biopolymères dérivés du bois peuvent constituer une option viable et écologique pour la préservation du bois [228], [229].

Cependant, il est essentiel de noter que ces méthodes de préservation alternatives sont encore en phase de développement et doivent faire l'objet d'essais approfondis pour évaluer leur efficacité et leur durabilité sur le long terme. De plus, il est nécessaire d'établir des réglementations et des normes strictes afin de garantir à la fois la sécurité et l'efficacité de ces nouvelles méthodes de préservation.

Parmi les méthodes de modification chimique du bois, l'acétylation et l'estérification avec des acides gras, permettent d'améliorer les propriétés du bois. L'acétylation implique la réaction du bois avec de l'anhydride acétique pour améliorer sa stabilité dimensionnelle et sa résistance aux intempéries.

Le mécanisme d'estérification du bois avec des acides gras, utilisé depuis longtemps, implique la réaction d'un groupe acide carboxylique (-COOH) de l'acide gras avec un groupe hydroxyle (-OH) du bois, ce qui entraîne la formation d'une liaison ester (-COO-) et la libération d'une molécule d'eau (H<sub>2</sub>O). Cette réaction est catalysée par un catalyseur acide [142], [230].

Ces méthodes de modification chimique sont respectueuses de l'environnement, car elles utilisent des réactifs moins toxiques et renouvelables.

La furfurylation du bois est également une méthode utilisée depuis des années pour la modification du bois et est connue comme une méthode peu toxique. La furfurylation est un processus chimique dans lequel le bois est traité avec de l'alcool furfurylique, Cette réaction chimique permet à l'alcool furfurylique de pénétrer dans la structure cellulaire du bois, où il polymérise et forme des liaisons chimiques avec les constituants du bois, tels que la cellulose et l'hémicellulose, Cela conduit à une augmentation de la stabilité dimensionnelle, de la résistance à l'humidité et de la durabilité du bois,

Dans le contexte de la modification du bois, les tanins sont utilisés en combinaison avec certains réticulant, réactifs ou additifs chimiques pour améliorer les propriétés du bois, Parmi ces substances, on retrouve l'alcool furfurylique, l'hexamine, le formaldéhyde, l'anhydride maléique, le glyoxal, le furfural, le caprolactame et l'acide lactique [230], [231], Ces composés chimiques peuvent réagir avec les tanins présents dans le bois pour former des liaisons chimiques supplémentaires, ce qui entraîne la création de polymères réticulés.

Récemment, de nouvelles méthodes de modification du bois qui utilisent des matériaux végétaux tels que le tanin en combinaison avec l'alcool furfurylique se révèlent être une approche prometteuse pour la préservation du bois. Une étude récente a été menée pour imprégner le bois en utilisant une solution combinée de tanin de mimosa et d'alcool furfurylique, et elle a montré des résultats positifs en termes de stabilité dimensionnelle et de résistance aux attaques fongiques [148], [225]. Cette réaction permet de créer un matériau appelé tanin-furanique.

Les matériaux tanin-furaniques sont des matériaux polymères qui peuvent être créés par la réaction des tanins avec un composé furanique tel que le furfural ou l'alcool furfurylique, Ces matériaux présentent des propriétés intéressantes, telles que la résistance mécanique, la résistance à la chaleur, la résistance à la corrosion et la faible densité, De plus, ils sont peu toxiques et respectueux de l'environnement, ce qui en fait des candidats prometteurs pour remplacer les matériaux synthétiques [232]. Dans ces formulations, l'utilisation de catalyseurs notamment acide est un facteur important, car il joue un rôle crucial dans l'efficacité de la modification du bois [233].

Les tanins, en tant que polyphénols, sont des composés naturels présents dans de nombreux végétaux, Ils sont caractérisés par leur structure chimique contenant plusieurs groupes phénoliques, Ces composés ont été largement utilisés dans différents domaines, tels que

l'industrie des adhésifs, des composites, des produits pharmaceutiques, médicaux, alimentaires et des boissons [150], Leur utilisation dans la modification du bois est également répandue en raison de leur faible réactivité chimique avec ce matériau.

Cette approche de modification du bois à l'aide de tanins offre des perspectives intéressantes, En créant des liaisons polymériques supplémentaires, il est possible d'améliorer certaines propriétés du bois telles que la résistance mécanique, la durabilité, la stabilité dimensionnelle et la résistance à la dégradation biologique, De plus, l'utilisation de tanins comme alternative aux réactifs chimiques conventionnels peut contribuer à des traitements plus respectueux de l'environnement et durables pour la transformation du bois.

Ces méthodes ouvrent également de nouvelles perspectives d'application pour le bois dans des domaines tels que la construction, le mobilier et les revêtements, en offrant des performances améliorées et une durabilité accrue, L'amélioration de la stabilité dimensionnelle et de la résistance aux intempéries rend le bois plus adapté aux environnements extérieurs, tandis que la résistance accrue à la dégradation biologique permet une plus grande longévité du matériau, De plus, les propriétés hydrophobes confèrent une protection contre l'humidité, ce qui peut contribuer à prévenir la pourriture et la dégradation du bois [144], [234], [235].

Les résultats de cette étude contribueront à une meilleure compréhension des possibilités offertes par l'utilisation du tanin condensé en association avec d'autres biopolymères pour la préservation du bois, Cela pourrait ouvrir la voie à de nouvelles formulations respectueuses de l'environnement, offrant une protection efficace contre les agents biologiques tout en réduisant les risques pour la santé humaine et l'environnement.

Dans cette partie du projet, l'étude s'est concentrée sur la capacité des tanins à concevoir des composites bois-tanin. L'objectif était d'effectuer plusieurs séries d'imprégnation afin d'explorer cette possibilité.

Ce projet a été initié à la suite d'une recherche antérieure menée au sein du laboratoire LERMAB [147], [236]. L'étude précédente visait à évaluer la capacité et le potentiel des tanins condensés, notamment ceux issus du mimosa, pour la conception de composites bois-tanin. Pour atteindre cet objectif, différentes séries d'imprégnation ont été réalisées :

**1. Groupe A :** Trois solutions ont été préparées pour l'imprégnation afin d'obtenir un composite bois-tanin-alcool furfurylique, avec des concentrations de 10 %, 25 % et 50 %. Les échantillons traités ont été soumis à des tests de lessivage et à des essais biologiques pour déterminer la meilleure formulation. Ensuite, à partir de la concentration sélectionnée,

des solutions contenant différentes quantités de tanin et d'alcool furfurylique ont été préparées. L'objectif de cette partie du projet était de comparer les propriétés des composites thermodurcissables à différentes concentrations et d'observer l'effet de la quantité de tanin afin de trouver la formulation appropriée pour la suite du projet.

- 2. Groupe B :** La deuxième partie du projet avait pour objectif de substituer une faible quantité de tanin par du tanin modifié (estérifié) afin d'étudier l'impact de ce tanin modifié sur l'amélioration de certaines propriétés telles que la résistance au lessivage, la durabilité biologique et la stabilité dimensionnelle.

Dans la première partie de ce chapitre (Groupe A), différentes concentrations et proportions de tanin et d'alcool furfurylique ont été testées pour trouver la meilleure formulation permettant l'imprégnation du bois. Deux types de solutions ont été utilisés, avec des proportions de tanin et d'alcool furfurylique de 1 :1 et 2 :1, en présence d'un catalyseur acide tel que l'acide maléique.

Dans la deuxième étape de cette partie de l'étude, des proportions variables de tanin et d'alcool furfurylique ont été testées pour observer l'effet de l'augmentation de la quantité de tanin sur les résultats de l'imprégnation. Les résultats ont montré une diminution progressive de la quantité d'alcool furfurylique de 45,45 % à 0 %, tandis que la quantité de tanin augmentait de 0 % à 45,45 %.

Dans la deuxième partie de ce chapitre (Groupe B), une faible quantité de tanin utilisée pour obtenir le composite bois-tanin-alcool furfurylique a été remplacée par des tanins modifiés à l'aide de chlorure d'acide lauryl, palmitoyl et oléyl, obtenus dans le premier chapitre.

Les échantillons traités et non traités ont été soumis à des tests tels que le tamisage, l'analyse infrarouge, la dégradation biologique et l'analyse de dégradation thermique, etc., afin d'observer l'efficacité des formulations.

## **2.Optimizing Furfuryl Alcohol/Tannin Concentration and Ratio for Enhanced Biosourced Thermoset Resins in Wood Protection**

### **Abstract:**

This project aimed to contribute to sustainable development by utilizing by-products of the wood industry, particularly tannins, for the purpose of wood preservation without the need for biocides. The objective was to design copolymers based on furfuryl alcohol and condensed tannins, building upon the project that utilized tannins as cross-linkers during wood furfurylation. In this study, we explore the use of tannins as both cross-linking agents and co-monomers to reduce the reliance on furfuryl alcohol.

The chemical modification of wood was carried out using different formulations with varying proportions of tannins and furfuryl alcohol (1:1 and 2:1) in the presence of an acidic catalyst (maleic acid), at different water concentrations (90%, 75%, and 50%). The characterization of the modified wood samples, including leaching tests and decay durability evaluations, was performed to determine the effect of concentration and identify the optimal formulation.

Based on the results, a concentration of 50% was selected for further investigation. Subsequently, aqueous formulations were prepared with decreasing proportion of furfuryl alcohol (from 45.45% to 0%) and increasing amounts of tannin (from 0% to 45.45%), along with 4.54% of maleic acid. The modified or treated wood samples were characterized through leaching tests, decay durability assessments, and thermal stability analysis.

The utilization of tannins not only as cross-linking agents but also as co-monomers has shown promising results in improving wood durability while reducing the reliance on furfuryl alcohol. Wood samples modified with tannin/furfuryl alcohol solutions exhibited enhanced decay durability, particularly against *Coniophora puteana*, regardless of the concentration used. These positive outcomes provide encouragement to further this study.

Regarding the variation in the tannin/furfuryl alcohol ratio, the results indicate that partial substitution of furfuryl alcohol with condensed tannins yields comparable outcomes to those achieved with furfuryl alcohol alone. However, complete substitution of furfuryl alcohol does not provide a treatment resistant to leaching and decay. Thermal analysis demonstrates that treatments involving tannin, furfuryl alcohol, or a combination of both chemicals enhance the thermal resistance of the treated wood compared to untreated wood.

## 1. Introduction

Wood preservation research has increasingly focused on the development of non-toxic, bio-sourced chemicals with low environmental impact. However, only a few methods based on thermal or chemical modification have been successfully commercialized [237].

Preservation treatments often involve the impregnation of biocidal substances into wood, but the toxicity of many preservatives has led to their ban in recent years. In response to directives such as the Biocide Directive and Air Act, it is urgent to find alternative wood protection methods, especially for outdoor use, as regulations are likely to further restrict the use of authorized molecules.

These methods aim to modify the chemical structure of wood cell wall polymers to enhance resistance against decay, insects, dimensional instability, and thermal degradation. This can be achieved through various conditions, including thermal degradation reactions via mild pyrolysis or chemical modification techniques like acetylation and furfurylation [144], [238].

In this study, we explored an alternative approach: developing a hydrophobic wood-polymer composite using the formulation of tannin-furanic foams but without the foaming effect, thus, eliminating the need for biocides. Furfurylation was chosen as the principal method due to the importance of furfuryl alcohol, a key component in this approach. Furfurylation is a well-established industrial-scale wood modification technology [144], [238], [239].

The combination of these bio-sourced compounds aimed to enhance the fixation and retention of the polymer in wood, leveraging on the already reticulated tannins [230]. Furthermore, the objective was to increase the tannin percentage, as they can be directly extracted from wood without requiring transformation, unlike furfuryl alcohol. While the reaction between furfuryl alcohol and tannins has been studied for various applications, its use for modifying solid wood is still limited.

Furfurylation is a specific type of chemical modification that occurs when furfuryl alcohol is impregnated into wood and undergoes *in situ* reactions within the wood structure under acid catalysis. The polymerization of furfuryl alcohol forms a polyfurfuryl alcohol polymer, which may or may not react with the wood polymers. Furfurylated wood exhibits improved dimensional stability, reduced water affinity, and increased resistance to decay and insect degradation. Furfurylation also enhances the wood's thermal resistance, reducing susceptibility to high-temperature degradation. In contrast, tannins, natural polyphenols found in tree bark, leaves, and seeds [150], can create thermoset resins through electrophilic aromatic



substitutions, serving as replacements for phenol. Recent research has demonstrated that condensed tannins can modify wood's chemical composition when reacted with furfuryl alcohol [147], [236]. The reaction between condensed tannins and furfuryl alcohol, facilitated by an acidic catalyst, leads to the creation of resins within wood cell walls [142], [230].

This reaction results in the formation of a composite that enhances wood properties. The aromatic and crosslinked structure of the furfuryl alcohol/tannins composite exhibits excellent thermal stability [232], [240].

This study aimed to evaluate the possibility of partially or totally replacing furfuryl alcohol with tannins to develop bio-sourced thermoset resins without using formaldehyde. By avoiding toxic substances and incorporating sustainable components, this research contributes to the development of environmentally friendly wood protection methods in line with sustainable development principles and the pursuit of non-toxic preservation techniques in the wood industry.

In conclusion, this study focused on exploring the use of tannins as a partial replacement for furfuryl alcohol in the development of bio-sourced thermoset resins for wood preservation. By avoiding toxic substances and incorporating sustainable components, this research contributes to the development of environmentally friendly wood protection methods aligned with the principles of sustainable development and the pursuit of non-toxic preservation techniques in the wood industry.

## **2. Materials and Methods**

### **2.1. Material preparation**

Defect-free European beech (*Fagus sylvatica*) with a dried density of approximately 687 kg/m<sup>3</sup> was utilized in this study. Prior to sample cutting, the wood was conditioned at room temperature (20°C) and a relative humidity of 60%. The samples were labelled as R, T, and L, and the specific details regarding their cutting are presented in the table.

Technical-grade furfuryl alcohol (FA) and laboratory-grade maleic acid (MA) were procured from Sigma Aldrich. Additionally, active tannin powder extract (Tan) was generously provided by Sylvateam, Italy. The catalyst, maleic acid, was also purchased from Sigma Aldrich.

Tableau.4. 1-Sample dimension and their corresponding characterization

<b>Samples size</b>	<b>Caracterisation</b>	
20 mm × 20 mm × 5 mm	During the impregnation process	Solution Uptake
20 mm × 20 mm × 5 mm	After the impregnation process	WPG, leaching test (water up-teke, leaching), decay durability TGA, FTIR
20 mm × 20 mm × 10 mm	During the impregnation process	Solution up-take, swelling
20 mm × 20 mm × 10 mm	After the impregnation process	Bulking, ASE

It is important to note that the initial part of this study focused on investigating the effects of different concentrations and proportions of Tan/FA. The analyses of leaching and decay durability were conducted for this purpose. In the case of the formulation with a 50% water concentration and different ratios of Tan/FA, additional characterizations such as FTIR and TGA were also performed.

## 2.2. Formulation of impregnating solution

The impregnating solution was prepared based on the formulation provided in Table 4.1 for the resins with three concentrations (F1). The solutions were prepared in two different ratios of Tan/AF: 1 :1 (A, B, C) and 2:1 (D, E, F).

The impregnating solutions with varying ratios of tannin and furfuryl alcohol at a 50% concentration in water (F2) are also presented in Table 4.2.

Tableau.4. 2-Formulation of the applied impregnating solution (F1)

<b>Formulation</b>	<b>Tannin (Tan)</b>	<b>Furfuryl alcohol (FA)</b>	<b>Solution Concentration</b>
<b>F1. A</b>	1	1	90%
<b>F1. B</b>	1	1	75%
<b>F1. C</b>	1	1	50%
<b>F1. D</b>	1	0.5	90%
<b>F1. E</b>	1	0.5	75%
<b>F1. F</b>	1	0.5	50%

**F1.A, B, C** : the ratio of tanin et furfuryl alcohol is 1/1

**F1.D, E, F** : the ratio of tanin et furfuryl alcohol is 1/0.5

For the second group (F2), varied solutions of tannin and furfuryl alcohol were prepared with a 50% concentration in water. The pH of all the solutions was observed to be within the range of 3.2 to 4.4

The quantity of furfuryl alcohol was decreased from 100% to 0% while increasing the amount of tannin from 0% to 100%. It should be noted that the quantity of maleic acid remained constant at approximately 4.54% of the solution.

Tableau.4. 3-Formulation of the applied impregnating solution (F2)

<b>Formulation</b>	<b>Tannin (Tan)%</b>	<b>Furfuryl alcohol (FA)%</b>
<b>F2. A</b>	0	100
<b>F2. B</b>	25	75
<b>F2. C</b>	50	50
<b>F2. E</b>	75	25
<b>F2. F</b>	100	0

### **2.3. Wood modification**

The wood samples were dried at 103°C for 48 hours and weighed (m0) and measured (V0). Subsequently, the samples were placed in a beaker covered with glass beads within a desiccator equipped with a two-way tap. Vacuum pressure (100 mbar) was applied for 15 minutes. Following that, the impregnation solution was introduced by suction until it completely covered the wood samples, and atmospheric pressure was restored. The samples were kept at atmospheric pressure for 24 hours.

Afterwards, the samples were removed from the solution, quickly drained, and weighed to determine their wet mass (m1). They were also measured to calculate their wet volume (V1). Subsequently, the samples were dried at 103°C for 72 hours, with the first 48 hours wrapped in aluminum foil and the remaining 24 hours without wrapping. They were then weighed again (m2) and measured to calculate their dry volume (V2).

Several parameters were calculated using the following formulas: solution uptake (SU), swelling after impregnation (S), weight percent gain before leaching (WPG1), and bulking coefficient (B).

During the wood modification process described above, the solution uptake (SU) and swelling caused by the impregnating solution were calculated using the following formulas (Equation.1) (Equation.2) :

Solution Uptake (SU) :

$$\text{Equation (1)}-SU (\%) = 100 \times (m_1 - m_0) / m_0$$

Where:  $m_1$  is the wet mass of the wood sample after impregnation and  $m_0$  is the initial mass of the wood sample before impregnation.

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

After the curing and drying process, the weight percent gain (WPG) and bulking coefficient (B) were calculated using the following formulas:

Weight Percent Gain (WPG):

$$\text{Equation (2)}-WPG_1 (\%) = 100 \times (m_2 - m_0) / m_0$$

Where  $WPG_1$ : is the weight percentage gain before leaching process.  $m_2$  :is the final mass of the wood sample after curing and drying  $m_0$  is the initial mass of the oven-dry wood at 103°C.

B the bulking value,  $m_2$  and  $V_2$  are the mass and volume of impregnated wood sample after curing process.

### **3. Characterizations**

#### **3.1. Leaching test**

Leaching Test according to NF X 41-568 [241] (2014) for Characterization of Wood Samples In this study, wood samples measuring 5 mm × 20 mm × 20 mm (L, T, R) were utilized. The sample size ranged from  $n = 12$  to 15 and included both treated and untreated wood. The samples were submerged in distilled water contained in separate chambers based on their treatment groups. The volume of water used was at least five times greater than the volume of the wood sample.

A dynamic leaching test was conducted, employing a shaking force of 100 linear shakes per minute. At specific time intervals (1, 2, 4, 8, 16, and 48 hours), the leaching water (leachate) was replaced, and the collected leachate was measured. Between the 4-hour and 8-hour periods, the wood samples were kept without water for 16 hours before continuing with the subsequent leaching period. The pH value and volume of leachate from each period were recorded.

After the completion of the leaching periods, each water-saturated (wet) wood sample was weighed ( $m_3$ ) and subsequently dried at room temperature for 2 hours and at 103°C for 48

hours( $m_4$ ). Using the results obtained from the leaching test, the leaching value and acidity of the total leachates were calculated as follows:

$$\text{Equation (3)-WPG}_2 (\%) = 100 \times (m_4 - m_0) / m_0$$

$$\text{Equation (4)-WU (\%)} = 100 \times (m_3 - m_2) / m_2$$

$$\text{Equation (5)-WL\%} = 100 \times (m_4 - m_2) / (m_2)$$

$$\text{Equation (6)-L (\%)} = 100 \times (m_2 - m_4) / (m_2 - m_0)$$

Where  $\text{WPG}_2$  is the weight percentage gain after leaching process,  $m_4$  oven-dry mass of sample after leaching.

WU: Water Uptake after Leaching Process, WL Weight Loss after Leaching and L: is Leaching Value.

### **3.2. Fourier transform infrared (FTIR) spectroscopy**

The FTIR spectra of the polymers, untreated wood, and wood modified with the polymer were recorded using an ATR-FTIR Perkin Elmer Spectrum 2000 instrument. Each measurement consisted of 16 scans within the range of 4000 – 600  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$ . Subsequently, the spectra were baseline corrected and normalized (3%) using IR Spectrum software. This analysis was conducted on both untreated wood samples and wood samples treated with the solution from Group (F2) in order to observe the effects of increased tannin content on the structure of the modified wood.

### **3.3. Thermogravimetric analysis (TGA)**

TGA was performed by TGA/DSC1 84Xe instrument from Mettler Toledo equipped with STARe v.11 fir System program. Ten milligrams ( $\pm 1.00$  mg) of dried powder were put into a platinum crucible and heated from 25 to 700°C with a heating rate of 10°C/min, under a nitrogen atmosphere with a flow rate of 50 mL/min. Thermal degradation was observed between 30°C and 600°C. This analysis was conducted on both untreated wood samples and wood samples treated with the solution from Group (F2) in order to observe the effects of increased tannin content on the structure of the modified wood.

### **3.4. Decay resistance properties**

Decay durability against (*Trametes versicolor*) (white-rot), (*Coniophora puteana*) (brown-rot) was performed using a modified method EN 113 (1996). Further, a durability class referred to EN 350 (2016).

A culture medium was prepared under sterile conditions using 40 g of malt, 25 g of agar, and 1L of distilled water. The culture medium was placed in the 9 cm diameter Petri dishes under

sterile conditions and left for a reasonable time for jellification. A small piece of mycelium of a freshly grown pure culture of (*Trametes versicolor*) Quélet (TV) and *Coniophora puteana* (CP) was placed in the middle of each dish and Petri dishes incubated for 2 weeks at  $22 \pm 2^\circ\text{C}$  and  $70 \pm 5\%$  RH to allow full coverage of the medium by the mycelium. Wood samples (2 treated and 1untreated) were placed under sterile conditions near a flame in each Petri dish and incubated for a period of 12 weeks at  $22 \pm 2^\circ\text{C}$  temperature and  $70 \pm 5\%$  relative humidity. After 12 weeks, the samples were cleaned from the mycelium and weighed to determine their wet weight ( $m_5$ ) before being dried at  $103^\circ\text{C}$  for 48 hours and then weighed again ( $m_6$ ). Weight loss due to decay was calculated by the following equation:

$$\text{Equation (11)-MC (\%)} = 100 \times (m_5 - m_6)/m_6$$

$$\text{Equation (12)-WLD (\%)} = 100 \times (m_3 - m_6)/m_3$$

where MC is the percentage of moisture content of wood sample just after decay test before drying,  $WLD$  the weight loss percentage of the wood sample due to decay,  $m_5$  the humid mass of wood sample just after decay test before drying,  $m_6$  the dry mass of wood sample after decay test.

## 4. Results and Discussion

### 4.1. Leaching test results

The two groups of wood/tannin/furfuryl alcohol composites, designated as F1 and F2, were subjected to a leaching test to evaluate the effectiveness of the quantity of tannin and the proportion of tannin/furfuryl alcohol in reducing the leaching rate and improving the wood properties against this effect.

The results of Group F1 are presented in Table 4.4 and Figure 4.1. The results of Group F2 are presented in Table.4.5 and Figure 4.2.

Tableau.4. 4-The results of leaching process (F1)

Formulation	Solution Uptake (%)	WPG <sub>1</sub> (%)	WPG <sub>2</sub> (%)	Water Uptake (%)	WL (%)	L (%)
F1. A	89,20	23,89	17,21	49,16	3,70	44,07
F1. B	92,54	30,45	23,22	42,13	4,84	21,65
F1. C	106,80	56,86	42,18	30,34	2,34	9,79
F1. D	84,04	17,23	10,22	48,45	6,94	42,50
F1. E	100,86	28,12	21,03	44,39	6,02	26,77
F1. F	100,39	36,99	29,32	38,07	4,90	21,06

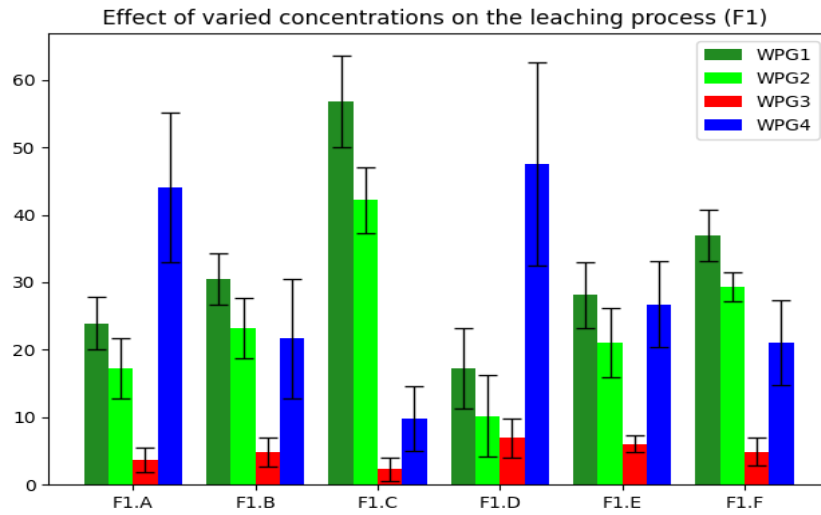


Figure.4. 1- Results of the effect of different concentration of solution on the leaching Process (GroupF1)

Tableau.4. 5-The results of leaching process (F2)

Formulation	Solution Uptake (%)	WPG <sub>1</sub> (%)	WPG <sub>2</sub> (%)	Water Uptake (%)	WL (%)	L (%)
F2. A	139,89	48,53	44,97	20,61	2,84	8,47
F2. B	133,01	48,48	42,77	27,22	3,86	12,08
F2. C	123,19	45,58	41,39	39,40	3,06	10,38
F2. D	122,40	41,84	36,48	45,65	3,80	12,90
F2. E	129,62	41,01	21,25	52,50	13,99	48,3
Untreated	0	0,0	0,0	79,50	2,1	0,7

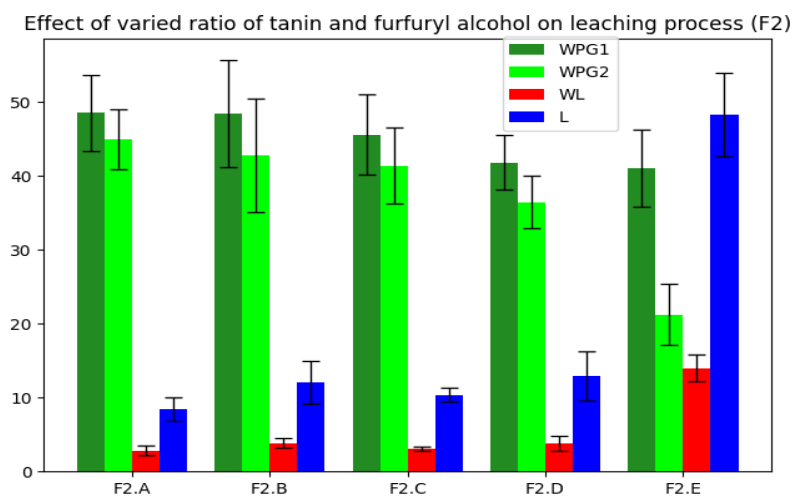


Figure.4. 2- Results of the effect of different ratio of TAN/FA Ratios on the leaching Process (GroupF2)

According to the results indicated and presented in Figure 4.1, concentration has a direct effect on improving the properties of the treated samples. The weight percent gain (WPG) before and after leaching increased in the first part, which includes three solutions with concentrations of 10, 25, and 50% with an equal proportion of tannin and furfuryl alcohol. This increase in weight gain influenced the decrease in leaching rate and mass loss during the leaching process.

The second part, composed of three solutions with concentrations of 10, 25, and 50% with a tannin to furfuryl alcohol ratio of 2 :1, showed less favorable results. The weight percent gain before and after leaching, compared to the solutions containing an equal proportion of tannin and furfuryl alcohol, is lower, and the leaching rate also increased for solutions with concentrations of 10 and 25%. The solutions with a concentration of 50% showed a higher difference, where solution F1.C, containing an equal proportion of TAN/FA, showed a rate of 9%, while solution F1.F, containing a TAN/FA ratio of 2 :1, showed a rate of 21%.

The leaching rate for the solution with a 25% concentration is 26%, and for the solution with a 50% concentration, it is 21%. This difference may be due to the viscosity of the solution, which reduces the penetration rate into the wood. This means that when the amount of furfuryl alcohol decreases, a concentration higher than 25% or 30% does not really influence the decrease in the leaching rate.

In summary, these results suggest that a higher concentration of tannin and furfuryl alcohol with an equal proportion promotes better mass retention and a decrease in the leaching rate in the treated samples. However, an increase in the proportion of tannin compared to furfuryl alcohol can lead to less favorable results, possibly due to the increase in solution viscosity.

Regarding the F2 group, where the quantity of tannin gradually reduces, as indicated in Table 4.5 and Figure 4.2, the leaching rate from F2.A to F2.D is almost the same or shows a similar variation. However, the removal of furfuryl alcohol (F2.E) has significantly decreased this value, confirming the important role of furfuryl alcohol in creating polymeric bonds.

In fact, these wood/tannin : furfuryl alcohol composites involve several reactions that lead to the formation of a well-crosslinked polymer network.



### A. Condensation reaction between tannin and furfuryl alcohol

Furfuryl alcohol (FA) can react with the phenolic groups of tannin to form covalent bonds in a process called condensation reaction. This reaction is catalyzed by maleic acid. The condensation reaction between FA and tannin can lead to the formation of C-C and C-O-C bonds, thus generating a three-dimensional network of polymers [19].

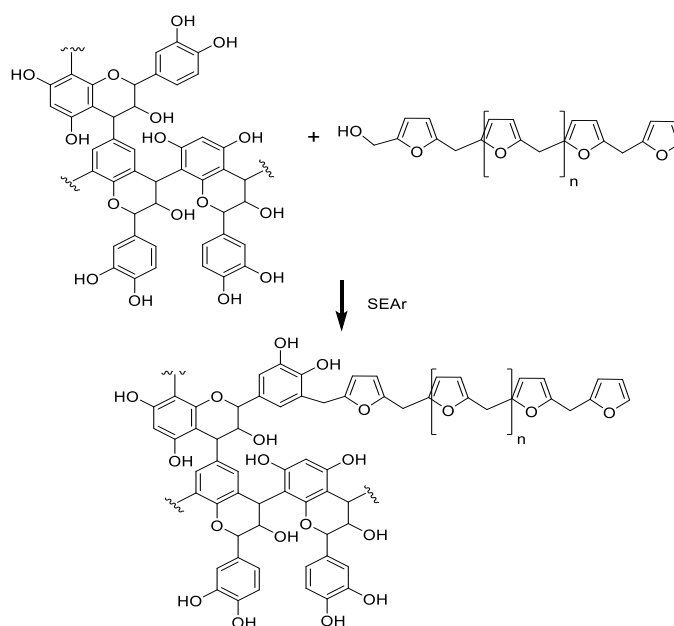


Figure.4. 3-The reaction between the polyphenolic groups and furfuryl alcohol

### B. Autocondensation of furfuryl alcohol

Furfuryl alcohol is a molecule that possesses a reactive alcohol group. Under certain conditions, these alcohol groups can react with each other through autocondensation to form polymeric structures. This autocondensation reaction of furfuryl alcohol plays a key role in the formation of furfuryl prepolymers, which are important components in the preparation of thermosetting polymers using tannin, furfuryl alcohol, and maleic acid.

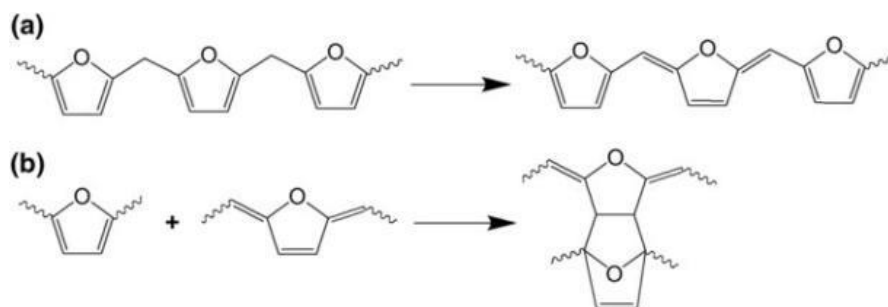


Figure.4. 4-Mechanism of crosslinking in the polycondensation of furfuryl alcohol: a) Conjugation of structure and b) Diels-Alder cycloaddition of different chains [11]

### C. Reaction between furfuryl alcohol and maleic acid

Maleic acid reacts with the alcohol groups present in furfuryl alcohol to form covalent bonds. This reaction can lead to the formation of additional chemical bridges in the polymer network[19], [142], [242] .

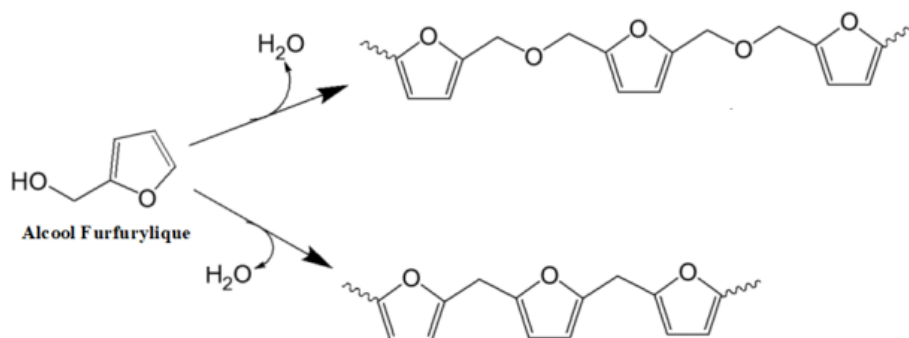


Figure.4. 5- Autocondensations of furfuryl alcohol under acid conditions [242].

### D. Autocondensation of tannin

Tannin is a natural polyphenol that contains multiple reactive phenolic groups. These groups can participate in autocondensation reactions, meaning they can react with each other to form covalent bonds. This reaction is catalyzed by factors such as temperature, pH, and the presence of catalysts. The autocondensation of tannin allows the formation of larger polymeric structures, which can enhance the properties of the final polymer[19].

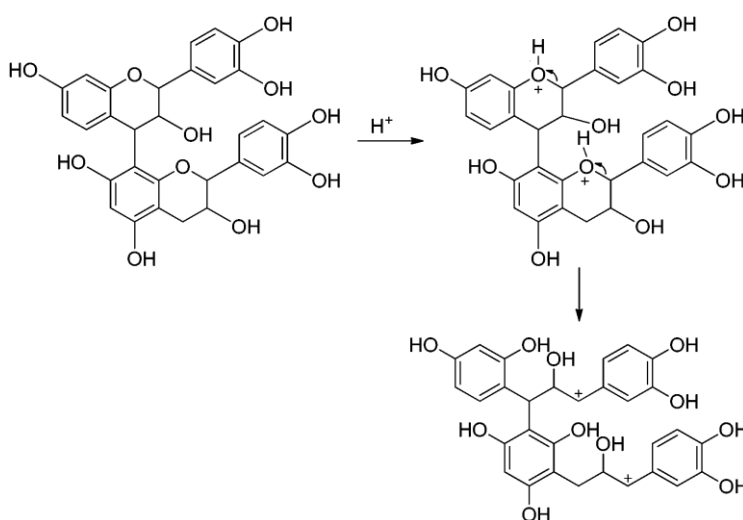


Figure.4. 6- Autocondensation of condensed tannin under acidic conditions through the hydrolysis of flavonoids heterocycles

## 4.2. Fourier Transform Infrared Spectroscopy (FTIR) Spectroscopy

The polymers and impregnated samples of group(F2) were subjected to infrared analysis to observe the differences between the various formulations. At first, the spectra of untreated wood and Mimosa tannin were compared (Fig.4.8)

For Group F2, the spectra of the polymerized solutions are presented in Figure (4.9-4.10), and the comparison between the impregnated and untreated samples is shown in Figure (4.11).

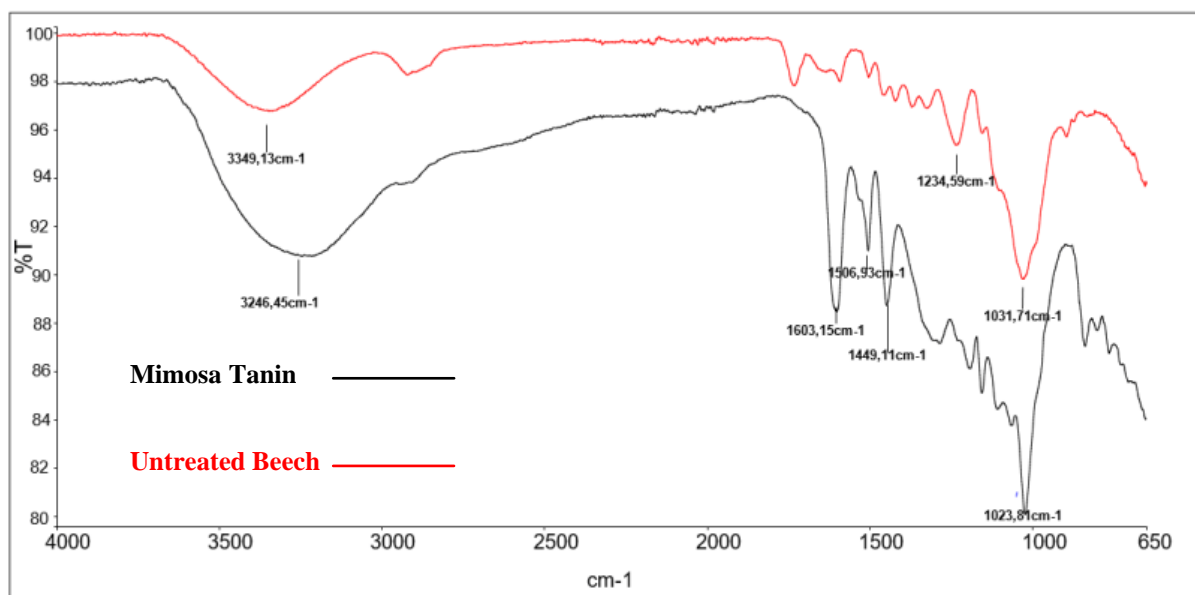


Figure.4. 7-Infrared spectroscopy of untreated beech wood and mimosa tannin.

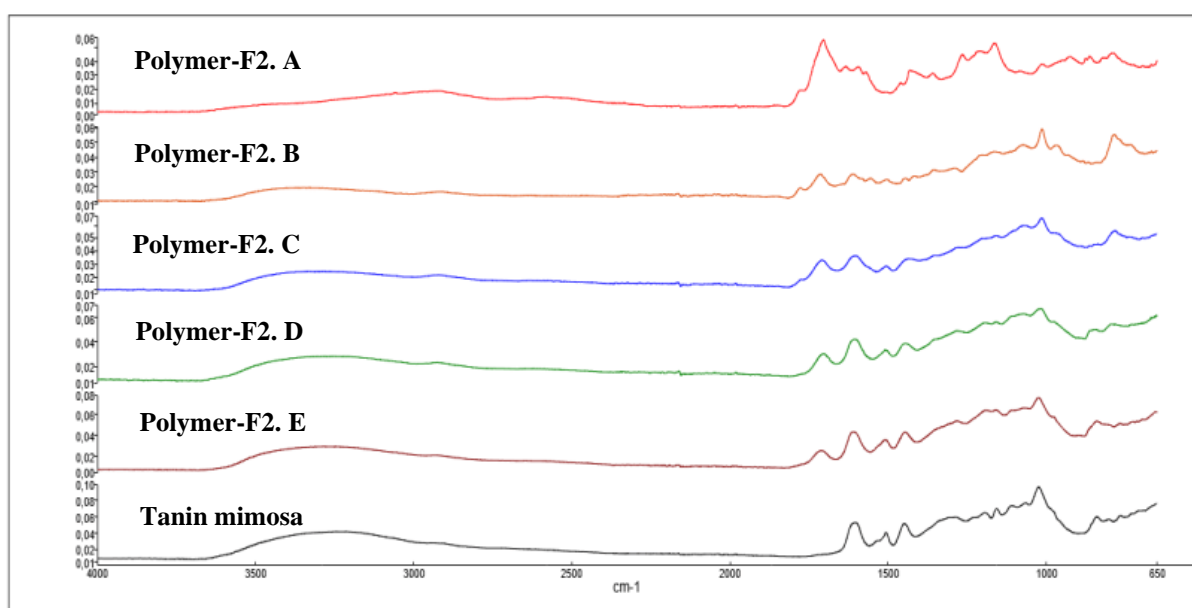


Figure.4. 8-Infrared spectroscopy of different polymerized solutions with varied ratios of Tan/FA

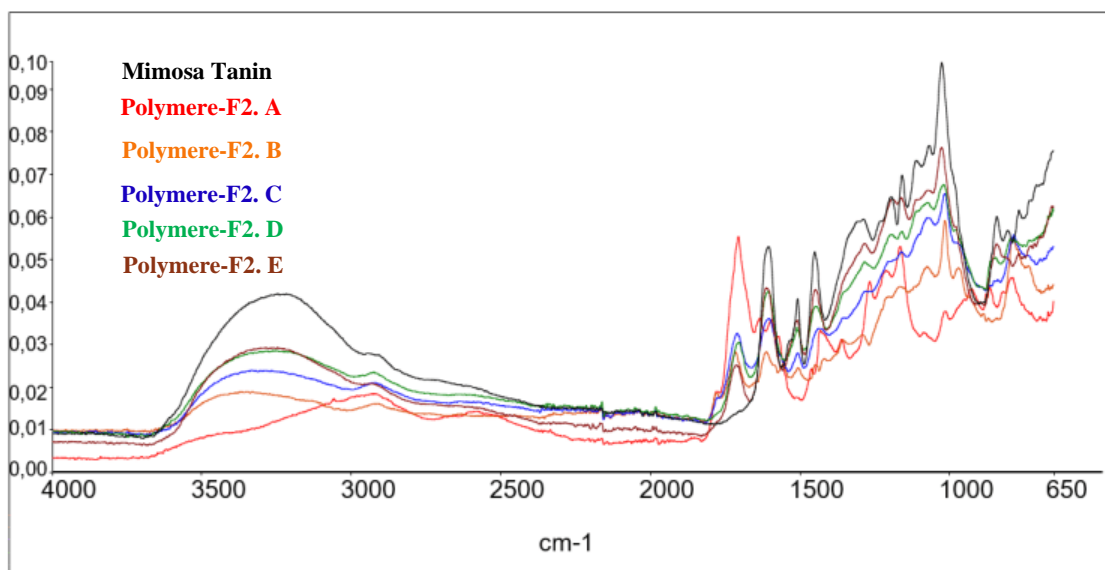


Figure.4. 9-Infrared spectroscopy of different polymerized solutions with varied ratios of Tan/FA.

The Figure (4.8 and 4.9) presents a comparison of the spectra of mimosa tannin and polymers obtained from different proportions of tannin and furfuryl alcohol.

The peak located between 3000 and 3500  $\text{cm}^{-1}$ , attributed to the vibrations of hydroxyl groups in tannin, shows an increasing intensity from F2.A to F2.E. The polymer F2.E samples respectively contain only tannin and acid catalyst. The peak at 3120  $\text{cm}^{-1}$ , corresponding to the stretching of the =CH- group in the furan ring of dihydroxyfuran, is absent in the polymers containing tannin (Szczurek et al., 2016).

The intensity of the peak at 1710  $\text{cm}^{-1}$ , attributed to the  $\gamma$ -diketone formed by the hydrolytic opening of the furan ring of certain furan groups during the polycondensation of fumaric acid (FA) in an acidic medium [142] is reduced in the polymers containing tannin, likely due to cross-linking with tannin. As shown in the Figure (4.9), this peak is not present in the spectrum of mimosa tannin.

Furthermore, the carbonyl group at 1710  $\text{cm}^{-1}$ , attributed to the  $\gamma$ -diketone formed by the hydrolytic opening of the furan ring of certain furan groups during the polycondensation of fumaric acid (FA) in an acidic medium, is observed.

The spectra exhibit the following peaks :

- The peak at 1610  $\text{cm}^{-1}$  is attributed to the stretching of the C=C bond in an aromatic structure as well as the flavonoid group.

- The peak at 1505 cm<sup>-1</sup> is attributed to the asymmetric stretching of the C=C-H bond in aromatic structures as well as furanic compounds.
- The peak at 1450 cm<sup>-1</sup> corresponds to the asymmetric bending of the C-H bond in an aromatic structure.
- The peak at 1290 cm<sup>-1</sup> is attributed to the stretching of the C-O bond in an aromatic structure as well as the B-ring of a flavonoid.
- The peak at 1160 cm<sup>-1</sup> is attributed to the stretching of the C-O bond in an aromatic structure as well as furanic compounds, the A-ring of a flavonoid, and the H-C-C bending of the B-ring.
- Stretching vibration of the C=O bond in cellulose, hemicelluloses, and lignin.
- The peak at 780 cm<sup>-1</sup> corresponds to the bending of the C-H bond in a plane perpendicular to the aromatic structure, typical of conjugated furanic compounds.
- The peak at 730 cm<sup>-1</sup> corresponds to the symmetric bending of the C-C-C ring and the symmetric bending of the C-H bond in a plane perpendicular to the aromatic structure, also characteristic of furanic compounds [147], [243].

In the second step, a comparison between untreated beech samples, treated samples, and polymerized solutions was studied (Fig.4.11).

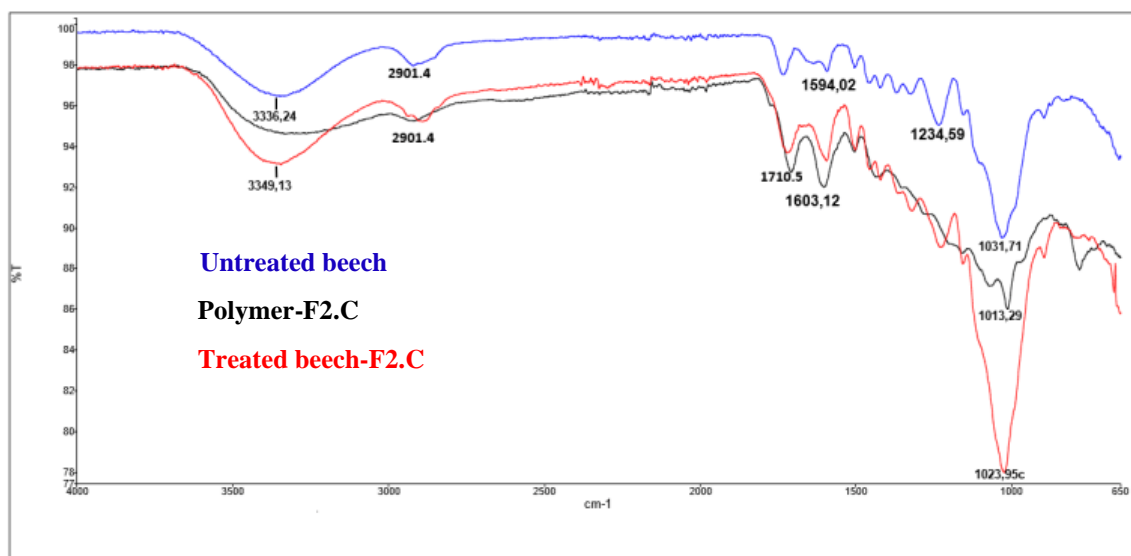


Figure.4. 10-FTIR spectra of untreated beech vs tannin-furanic polymer vs tannin-furanic-treated beech

Regarding the treated samples, not all modified spectra are presented here. Formulation F2.C, which has equal proportions of tannin and furfuryl alcohol, was selected for comparison with untreated beech wood and cross-linked polymer.

Untreated beech wood exhibits a broad and intense band in the 3200-3600 cm<sup>-1</sup> region, attributed to the stretching of hydroxyl (OH) groups present in the cellulose, hemicellulose, and lignin of wood. In the impregnated beech sample (F2.C), this band has been broadened, particularly the peak at 3349 cm<sup>-1</sup>.

The mimosa tannin used in the impregnation solution contains hydroxyl groups. When beech wood is impregnated with this solution, an interaction occurs between the hydroxyl groups of tannin and those present in the cellulose and hemicellulose of wood. This interaction can enhance the vibrations of hydroxyl groups, leading to an increase in the intensity of the corresponding band in the infrared spectrum. This increase can also increase water absorption. Therefore, in the third part of this study, a small amount of tannin was replaced with esterified tannin to improve the hydrophilic nature of wood.

The 2800-3000 cm<sup>-1</sup> region in the beech wood spectrum is attributed to C-H bonds. These bands are generally more intense in the aliphatic region of wood. The observed band around 2901 cm<sup>-1</sup>, corresponding to the stretching of aliphatic C-H bonds, becomes more intense in the modified wood. Several reasons can explain this increase, such as the presence of furfuryl alcohol. The peak at 1710 cm<sup>-1</sup> is attributed to the carbonyl group C=O in the wood structure. This band indicates the presence of esters in cellulose. The mimosa tannin used in the impregnation solution contains carbonyl groups (C=O). When beech wood is impregnated with this solution, there may be an interaction between the carbonyl groups of tannin and the functional groups present in wood, which enhances the vibrations of C=O groups in the 1710 cm<sup>-1</sup> region.

The formation of ester bonds can also contribute to this increase. During wood impregnation with the impregnation solution, there can be chemical reactions between the hydroxyl groups of tannin and the alcohol groups of furfuryl alcohol in the presence of the acid catalyst. These reactions can lead to the formation of ester bonds, which may be associated with a C=O stretching peak in the 1710 cm<sup>-1</sup> region.

Even like in the formulation F2. A which does not contain tannin, the intensity of the carbonyl group band was increased, which can be attributed to the presence of furfuryl alcohol. This increase in intensity may be due to the presence of  $\gamma$ -diketone formed by the hydrolytic opening of the furan ring of certain furan groups during the polycondensation of fumaric acid (FA) in an acidic medium [142], [147], [243].

### 4.3. Decay durability

The biological durability of treated and untreated samples against brown rot (*Coniophora puteana*) and white rot (*Trametes versicolor*) was evaluated for the group. F1 and F2, and the results were recorded and presented in Figure (4.12 and 4.13).

In each culture box, two impregnated and leached samples were placed. Additionally, an untreated control sample was added to the same culture box. A culture box containing untreated samples was also subjected to the biological effect to compare the mass loss results of the untreated samples with that of the unmodified sample placed with the modified samples.

Tableau.4. 6.The results of decay durability against brown-rot (CP)for the group(F1)

Formulation	Leaching rate (%)	Humidity (%)	WL <sub>D</sub> (CP)	Durability Class
F1. A	44.07	55,35	22,18	Moyen durable
F1. B	21.65	46,98	16,46	Moyen durable
F1.C	9,79	44,68	6,43	Durable
F1. D	50,53	68,55	18,69	Moyen durable
F1. E	26,77	48,55	9,44	Durable
F1. F	21,06	37,10	6,99	Durable
Untreated	0,7	79,50	40,67	Non durable

F1.A, B, C: The Ratio of Tannin to Furfuryl Alcohol at 1:1 in Various Water Concentrations (90%, 75%, and 50%)

Tableau.4. 7.The results of decay durability against White-rot (CP) for the group (F1)

Formulation	Leaching rate (%)	Humidity (%)	WL <sub>D</sub> (CP)	Durability Class
F1. A	44.07	61,16	16,93	Moyen durable
F1. B	21.65	49,96	9,34	durable
F1.C	9,79	52,93	4,53	Durable
F1. D	42,50	53,55	17,40	Moyen durable
F1. E	26,77	53,81	9,61	Durable
F1. F	21,06	37,37	6,80	Durable
Untreated	0,7	79,50	51,84	Non durable

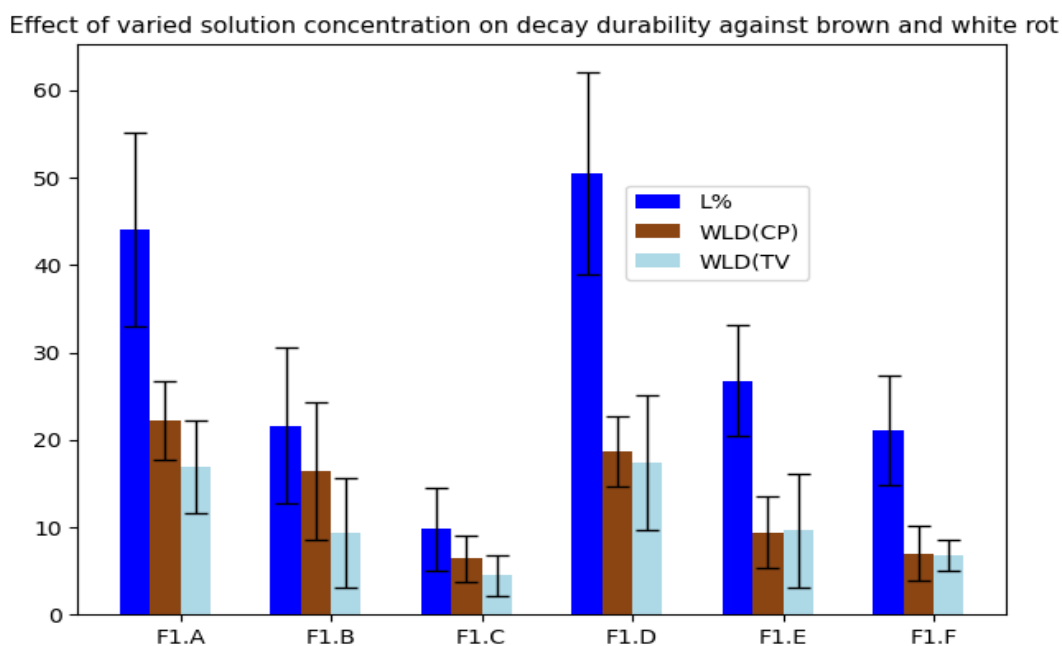


Figure.4. 11-Effect of varied concentration on decay durability for the group(F1) against white-rot and Brown-rot

The weight loss for the first part of F1 samples with a Tan: AF ratio of 1 :1 at three concentrations is presented in the figure.4.11.

As shown in Figure (Fig.4.12), the weight loss in samples treated with a 50% solution exhibits a significant decrease compared to the other concentrations.

The untreated samples, within the same culture box, experienced a lower mass loss than the untreated samples that were not in contact with the treated samples. This confirms the effect of the treatment even on the unmodified samples placed next to the impregnated samples.

For instance, the mass loss of an untreated sample in contact with samples impregnated with the (F1.C-50%) formulation under the influence of brown rot (*Coniophora puteana*) is 22.63%. In contrast, the mass loss for the untreated wood placed in a culture box without contact with impregnated samples is approximately 40.67%.

The mass loss due to biological degradation for the second series of Group.F1 with a Tan: AF ratio of 2:1 is presented in Figure (4.13) and for despite the decrease in the amount of furfuryl alcohol, the mass loss is reduced for both brown and white rot compared to untreated samples. Furthermore, the formulation (F1.D-10%) showed improved biological resistance compared to the formulation (F1.A-10%), which contains twice the amount of furfuryl alcohol. This confirms the role of tannins in increasing resistance against rot.



Firstly, tannins are phenolic compounds that can improve antifungal and antibacterial properties. They can interfere with the enzymatic activities of micro-organisms responsible for wood degradation, such as lignolytic fungi. Tannins can inhibit the activity of cellulase and lignase enzymes, which are essential for the decomposition of wood. By disrupting these enzymes, tannins limit the ability of microorganism to degrade wood, leading to increased biological durability. Furthermore, the polymerization of tannin by furfuryl alcohol can form polymeric bonds with the wood structure, creating insoluble polymers. These polymers strengthen the wood structure and decrease its susceptibility to biological degradation.

On the other hand, the results of decay durability for Group F2 have also been recorded and presented in Table 4. Additionally, Figure 4 illustrates the corresponding findings.

Tableau.4. 8- The decay durability of untreated and tannin-furanic treated samples with varied ratios of Tan / FA against white rot (*Coriolus versicolor*).

Formulation	Leaching rate (%)	Humidity (%)	WL <sub>D</sub> (%)	Durability Class
F2. A	8.47	23.17	2.66	Durable
F2. B	12.08	23.67	3.98	Durable
F2.C	10.38	28.54	4.29	Durable
F2. D	12,90	31.73	5.16	Durable
F2. E	48.38	43.18	18.18	Moyen durable
Untreated	0.7	79.50	43.03	Non durable

Tableau.4. 9- The decay durability of untreated and tannin-furanic treated samples with varied ratios of Tan / FA against brown rot (*Coniophora puteana*).

Formulation	Leaching rate (%)	Humidity (%)	WL <sub>D</sub> (%)	Durability Class
F2. A	8.47	27.10	2.45	Durable
F2. B	12.08	21.01	2.91	Durable
F2.C	10.38	27.91	4.22	Durable
F2. D	12.90	32.72	5.01	Durable
F2. E	48.38	43.30	15.55	Moyen Durable
Untreated	1.5	85.80	48.34	Non Durable

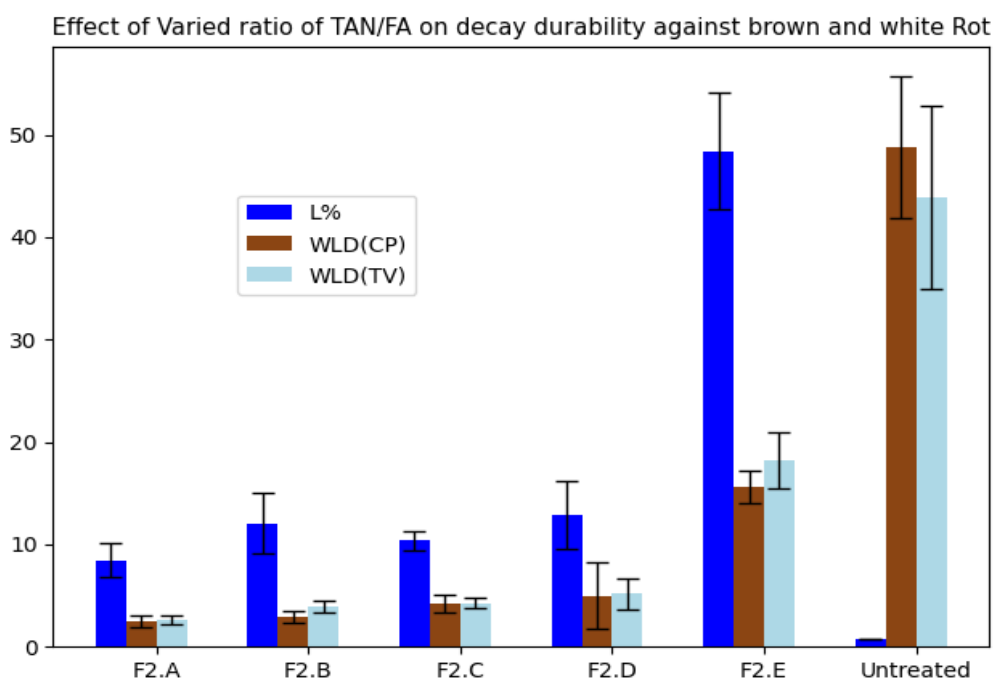


Figure.4. 12-Illustration of Decay Durability: Comparison of untreated and treated samples with varied ratios of Tan/FA against whiter rot and brown rot, including leaching rate

As presented in Figure (4.14), the leaching rate is almost similar in all formulations, except for F2.E, which does not contain furfuryl alcohol. The mass loss due to biological degradation is very similar in formulations containing furfuryl alcohol, even at low quantities. In contrast, formulation F2.E, which only contains tannin and the catalyst but no furfuryl alcohol, showed a higher mass loss but lower than that of untreated samples.

The comparison between the five formulations containing the impregnated samples and the untreated samples confirms the effectiveness of tannin and furfuryl alcohol in improving biological resistance. Furthermore, the results, particularly those of F2.E which does not contain furfuryl alcohol and formulation F2.D with a low quantity of furfuryl alcohol, confirm the important role of tannin in enhancing wood durability.

The tannins present a crucial role in plant protection against biological attacks such as fungi and insects. Tannins disrupt the metabolism of fungi, limiting their ability to decompose wood. This inhibitory interaction between tannins and fungi strengthens the biological resistance of wood and plants against decomposers.

Thermo-polymerization treatment appears to disrupt enzymatic activities involved in wood degradation, resulting in low weight loss even in impregnated and polymerized samples at high

temperatures, including cases where furfuryl alcohol is absent (F2.E). Despite a high leaching rate in this formulation, the mass loss is significantly reduced compared to untreated wood.

Condensed tannins may likely block or hinder the activity of cellulase and lignase enzymes after thermal modification [244].

#### 4.4. Thermogravimetric Analysis (TGA)

The results of Thermogravimetric analysis (TGA) for the untreated and treated samples with varied proportions of tannin and furfuryl alcohol are recorded and presented in Figures 4.15 and 4.16.

Figure (4.15) presents the thermal degradation of untreated samples, samples modified with tannin-furanic or furfuryl alcohol alone solutions, and a solution without furfuryl alcohol containing only tannin(F2).

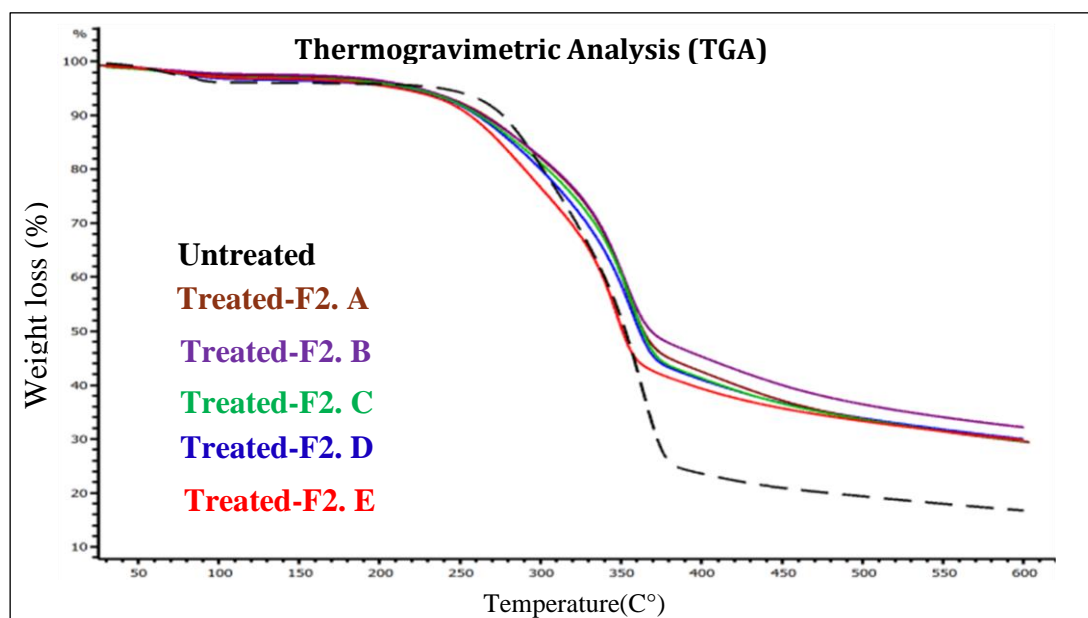


Figure.4. 13-Thermogravimetric Analysis (TGA) of Untreated and Treated Samples with Varied Solution (F2)

The mass loss in all treated samples was reduced compared to untreated wood. Particularly noteworthy is the mass loss in sample F2.B, which contains 11.36% tannin compared to the F2.A formulation containing only furfuryl alcohol. This confirms that the addition of a small amount of tannin is effective in enhancing thermal resistance.

In fact,TGA analysis indicated that all treated samples, independently of the percentage of furfuryl alcohol or tannin, presented higher thermal stability than untreated beech. This higher

stability could be associated to the higher stability of aromatic moieties present in tannins or furfuryl alcohol.

Increasing the amount of tannin up to 22.72% and 34.09% also showed results similar to furfurylation, but the removal of furfuryl alcohol resulted in a significant mass loss.

The optimal formulation could be F2.B with 11.36% tannin and 34.09% furfuryl alcohol. This suggests that the thermal stability of tannin-furanic polymers is slightly higher compared to a furanic-based polymer solution (F2.A). However, it should be noted that the specific proportion of tannin and furfuryl alcohol can have an impact on these results, and further investigation is required to draw definitive conclusions.

The addition of tannin in the correct proportion (lower than the amount of furfuryl alcohol) is capable of forming strong cross-linking with FA, which can also influence mass loss, leaching rate, and thermal stability.

On the other hand, increasing the amount of tannin beyond the amount of furfuryl alcohol can decrease the intensity of the polymer matrix, increase leaching rate, moisture absorption, and reduce thermal stability.

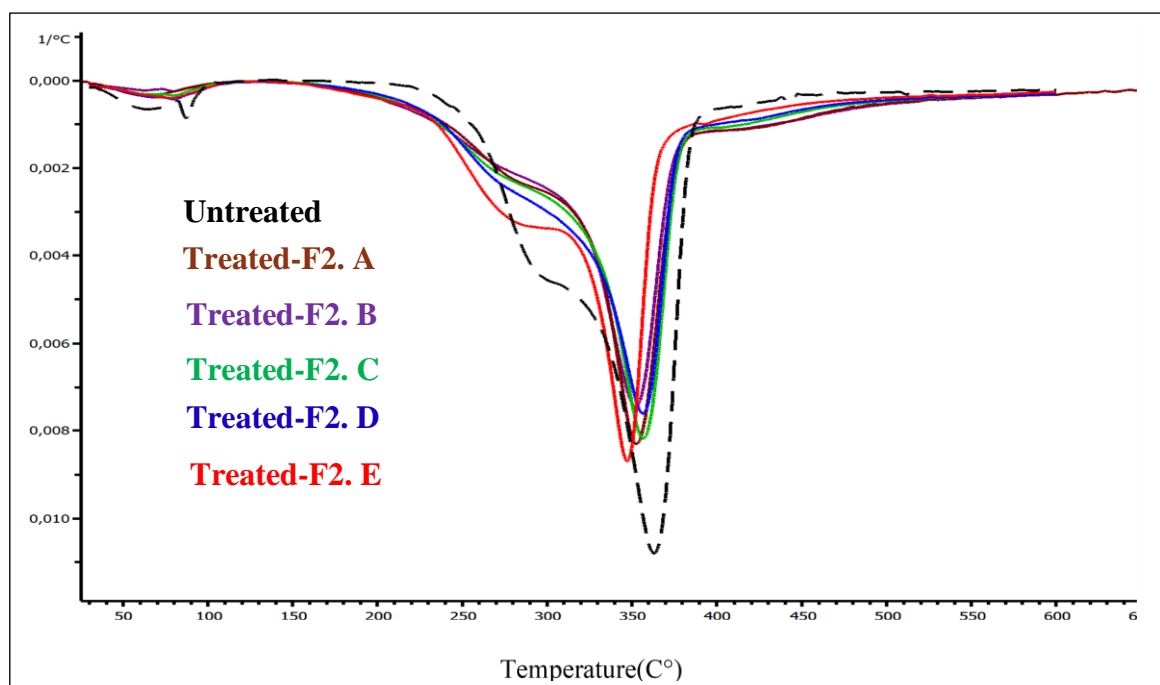


Figure.4. 14-Thermogravimetric Analysis (DTG) of Untreated and Treated Samples with Varied Solution (F2).

The central points of the curves were compared, especially for the results of Derivative Thermogravimetric Analysis (DTG). The unmodified wood reaches the midpoint of mass loss at a higher temperature than the other samples. This can be attributed to the presence of volatile components and an excess of tannin.

Overall, all samples modified with furanic, tannin-furanic, or tannic solutions showed higher thermal stability than untreated wood. Weight percent gain (WPG) also plays an important role in thermal stability, as the WPG after treatment for formulations B. I and B.II before and after leaching is very similar, while the WPG of the B.V formulation after leaching is half of the other treated samples. Therefore, thermal stability is also lower for this formulation.

Thermal stability comparison : Untreated beech wood < Beech-B. V < Beech-B. IV = Beech-B.III < Beech-B. I < Beech-B. II.

By comparing the untreated sample with the samples treated with furfuryl alcohol (F2.A), furanic tannin formulations (F2.B, C, D), and tannin alone (F2.E) in the presence of a dicarboxylic acid catalyst, the mass loss regions can be divided into three significant parts.

The first part of mass loss occurs between 30°C and 150°C, with a peak around 70°C. At this temperature, there is an initial mass loss due to the evaporation of moisture present in the material. This mass loss may vary depending on the initial moisture content of the wood [245]. The second zone ranges from 150°C to 300°C or 310°C : this region of mass loss can be attributed to the degradation of volatile organic compounds, evaporation of water, formation of CO<sub>2</sub> through dehydration and decarboxylation processes, degradation of extractives, initial degradation of carbohydrates, particularly hemicellulose and a portion of cellulose, as well as lignin. Non-reactive materials in the reaction, degradation of the acid catalyst, and release of CO gas can also contribute to this mass loss. A significant amount of furfuryl alcohol and tannin can decompose at this temperature.

Tannin decomposition typically occurs between 160°C and 275°C, and within this temperature range, tannin loses approximately half of its initial mass. This confirms that samples treated with solutions containing a high amount of tannin exhibited higher mass loss than untreated wood in this temperature range.

The third zone is observed between 330°C and 370°C, with a peak at around 350°C. In this region, there is a deep depolymerization of organic components such as cellulose and a portion of lignin. This can lead to a remarkable decrease in the initial mass [147], [246].

From 400°C to 500°C, mass loss can generally be attributed to the opening or breaking of carbon-carbon bonds in lignin, the release of flammable volatile components, and the formation of non-volatile charcoal residue at the end [246].

## **Conclusion**

The study aimed to investigate the potential use of tannins as both cross-linking agents and comonomers in wood preservation, with the objective of reducing reliance on furfuryl alcohol. The results obtained from the experiments shed light on the effectiveness of tannins in enhancing wood properties, particularly dimensional stability and decay durability.

In the first part of the study (Group F1), the concentration of tannin and furfuryl alcohol was varied to assess their impact on the treated wood samples. The results revealed that higher concentrations of tannin and furfuryl alcohol, in equal proportions, led to better mass retention and a decrease in the leaching rate. This indicates that the combination of tannin and furfuryl alcohol improves the properties of the treated wood by forming covalent bonds through a condensation reaction. However, increasing the proportion of tannin compared to furfuryl alcohol resulted in less favorable outcomes, possibly due to increased solution viscosity.

In the second part of the study (Group F2), the quantity of tannin was gradually reduced while keeping furfuryl alcohol constant. The results demonstrated that removing furfuryl alcohol significantly decreased the leaching rate, highlighting its crucial role in forming polymeric bonds. The wood/tannin/furfuryl alcohol composites underwent various reactions, including the autocondensation reaction between tannin and furfuryl alcohol, as well as the autocondensation reactions of furfuryl alcohol itself. These reactions resulted in the formation of a well-crosslinked polymer network, thereby enhancing the properties of the treated wood.

The leaching tests revealed that the concentration of tannin and furfuryl alcohol directly influenced the improvement of the properties of the treated wood samples. Higher concentrations resulted in increased weight percent gain (WPG) before and after leaching, leading to a decreased leaching rate and mass loss. However, an increase in the proportion of tannin compared to furfuryl alcohol showed less favorable results, likely due to increased solution viscosity and a deficiency of cross-linkers. Furfuryl alcohol acts as both a comonomer and a cross-linker for the tannin.

The decay durability tests demonstrated that the treated wood samples exhibited improved resistance against brown rot (*Coniophora puteana*) and white rot (*Trametes versicolor*)

compared to untreated wood. Tannins, with their antifungal and antibacterial properties, can disrupt the enzymatic activities of microorganisms responsible for wood degradation. The polymerization of tannin by furfuryl alcohol forms insoluble polymers that strengthen the wood structure, reducing its susceptibility to biological degradation.

In conclusion, this study successfully demonstrated the potential of utilizing tannins as cross-linking agents and co-monomers in wood preservation. The combination of tannin and furfuryl alcohol showed promising results in improving the dimensional stability and decay durability of the treated wood. Higher concentrations of tannin and furfuryl alcohol, in equal proportions, resulted in better mass retention and a decreased leaching rate. The presence of furfuryl alcohol was crucial in creating polymeric bonds and enhancing the wood's resistance to biological degradation. The impregnation process, incorporating tannin, furfuryl alcohol, and maleic acid, modified the wood's structure and composition, leading to improved stability properties.

This research opens up possibilities for utilizing impregnated wood in various applications where dimensional stability and resistance to biological degradation are crucial. Further investigations can focus on optimizing the tannin/furfuryl alcohol ratio, exploring different wood species, and evaluating the long-term performance of the treated wood. By utilizing tannins as sustainable alternatives to traditional biocides, this study contributes to the development of environmentally friendly wood preservation methods.

### **3.Optimizing Esterified Tannins and Fatty Acids to Enhance European Beech Properties**

#### **Abstract**

In the current research, wood composites based on tannin, furfuryl alcohol, and tannin modified by fatty acids of various chain lengths, including C12, C16, and C18, have been studied. The solutions, 50% in water (STD), were prepared with mimosa tannin (TAN) and furfuryl alcohol (FA) in the presence of maleic acid (MA) as a catalyst. In the second step, the tannin at 2.2% and 4.75% was substituted with modified tannins. The chemical modification of tannin was realized via esterification using three fatty acid chains: lauryl chloride, palmitoyl, and oleyl. The proportion of tannin and furfuryl alcohol was equal (1:1).

The purpose of this substitution was the increasing the hydrophobic character of the wood. Using modified tannin in small quantities (2.2%, 7%, and 4.75%) has shown a decrease in the leaching effect and improved the biological durability of wood against white and brown rot. even with half the amount of alcohol compared to the tannin, the leaching rate and resistance biologic improved.

Based on leaching results, the treated simples containing modified tannins have shown less weight loss and leaching value compared to the treated simples without modified tannins. This improvement was observed in the samples modified with all three chains, but the woods containing C12 and C16 modified tannin showed better data than those containing C18 modified tannin, although this difference was not significant.

The biological durability results showed increased resistance to degradation compared to control samples and slightly compared to those treated without modified tannin. All the modified woods were in the category of very durable, but the samples containing C12 and C16 modified tannin showed slightly higher durability than those treated with C18 modified tannin. The treatment with a lower quantity of furfuryl alcohol also demonstrated favorable resistance against fungi degradation.

Contact angle measurement was performed to observe the effect of modified tannin on the hydrophobic character of the wood, and the results confirmed an increase in contact angle compared with untreated wood and treated wood without modified tannin. The contact angle for the samples containing C18 modified tannin was slightly less than the other modified woods, but it was still over 90°, confirming an increase in the hydrophobic character of the wood compared to unmodified or treated wood without modified tannin.

TGA analysis showed a slight weight loss in the treated samples containing modified tannin compared to the treatments without esterified tannin, but the resistance to thermal degradation



compared to solid wood was very high. Weight loss was slightly less in the samples treated with C12 modified tannin compared to the other chains.

## 1. Introduction

Wood is an important natural composite material in many industrial applications, such as construction, furniture, and packaging. However, wood has limited physical and chemical properties, which can be improved by chemical modification. Most chemical modification methods often use toxic organic materials, expensive catalysts, and environmentally harmful reagents. Environmental methods of wood chemical modification are to avoid the use of toxic organic and replace them with renewable and non-toxic compounds.

The new chemical modification methods like acetylation, furfurylation, and esterification with fatty acid refer to the wood chemical treatment to improve its properties or to create new composites with specific characteristics. These environmental modification methods can be used to improve the dimensional stability, durability, and decay resistance of wood, as well as to enhance its mechanical properties and impart new functions, such as fire retardancy, water repellency, or biocidal activity [144], [234], [235].

The mechanism of wood esterification with fatty acids which is used for a long time ago, involves the reaction of a carboxylic acid group (-COOH) of the fatty acid with a hydroxyl group (-OH) of the wood, resulting in the formation of an ester bond (-COO-) and the release of a water molecule (H<sub>2</sub>O). This reaction is catalyzed by an acid catalyst [60], [230]. Another method of chemical modification is furfurylation, which involves the impregnation of wood with furfuryl alcohol and its polymerization thermoset.

wood furfurylation is the reaction between wood cell wall components with furfuryl alcohol (FA) under acidic conditions. In fact, the furfuryl cation reacts with the hydroxyl groups of the wood cell wall components, resulting in the formation of covalent bonds between the furfuryl alcohol and the wood. This leads to the formation of a three-dimensional network structure with high mechanical and thermal stability [144], [235].

Tannin is an extractible material of wood. Tannins are phenolic compounds with complex chemical structures. The tannins are the phenolic aromatic biomolecule and have a structure like the phenol synthetic derivative of fossil resources. It's for this reason, can be an alternative vegetal for the elaboration of chemicals, and building blocks to develop polymers and materials [19].

The tannins, having nucleophilic sites due to the phenol groups can participate in the reaction of electrophilic aromatic substitutions. In fact, due to the aromatic structure, the coupling reaction can also occur with carboxylic acid and aldehydes. Tannin can react easily with furfuryl alcohol to create a three-dimensional network at the 103°C. This reaction can be stronger in the presence of acid-catalyzed [2], [19], [142].

The tannin-furanic materials are polymeric materials that can be created by the reaction of tannins with a furanic compound as furfural or furfuryl alcohol. These materials have interesting properties, such as mechanical strength, heat resistance, corrosion resistance, and low density. In addition, they are biodegradable, low-toxic, and environmentally friendly, making them promising candidates to replace traditional synthetic materials [232], [243].

Recently, the potential of this reaction to create the polymeric bond between the phenolic group of tannin and the furanic ring of furfuryl alcohol has given an idea to realize a chemical wood modification [147], [236]. However, tannins have poor water resistance, which limits their use in many fields. The derivatives of tannin have been shown to have poor hydrophobicity. To overcome these problems, methods of chemical modification of tannins have been developed.

In order to modify the tannin properties, some methods as acetylation or esterification by fatty acids have been proposed and shown promising results [19], [68].

As esterified tannin by the fatty acids has shown a strong effect on the improvement of the hydrophobic character of tannin-derived materials [70], [165] in this research, the addition or substitution of a small quantity of tannin by modified tannin has been proposed in order to improve the hydrophobicity of wood.

## **2. Materials and Methods**

### **2.1. Material preparation**

#### **2.1.1. preparation of modified tannin (oil grafted tannin)**

The method to synthesize the chemical modified tannin via the esterification with fatty acid is from the literature by Azadeh, E et al [71].

5 g of commercial mimosa tannin with 3.75 g of palmitoyl chloride with the 80 ml was mixed. To begin, mimosa tannin extract was weighed and transferred into a 250 mL round bottom flask. Then, the chloroform was added and followed by the addition of the fatty acid (dodecanoyl chloride, palmitoyl and oleyl chloride). The reaction mixture was stirred for at least 16 h. This

reaction can give the same results in the shorter time(4h) just with the addition of temperature (55C°). modified tannins has been analyzed by the capacitation of spectroscopy analysis (FTIR) and (MALDI-TOF) (Chapiter II).

### 2.1.2. Materials and sample preparation

Defect-free European beech (*Fagus sylvatica*) with a dried density of approximately 687 kg/m<sup>3</sup> was utilized in this study. Prior to sample cutting, the wood was conditioned at room temperature (20°C) and a relative humidity of 60%. The samples were labeled as R, T, and L, and the specific details regarding their cutting are presented in the table.

Technical-grade furfuryl alcohol (FA) and laboratory-grade maleic acid (MA) were procured from Sigma Aldrich. Additionally, active tannin powder extract (Tan) was generously provided by Sylvateam, Italy. The catalyst, maleic acid, was also purchased from Sigma Aldrich.

Tableau.4. 10-Sample dimensions and their corresponding characterization

Échantillon	Caractérisation	
20 mm × 20 mm × 5 mm	During the impregnation process	Solution Uptake
20 mm × 20 mm × 5 mm	After the impregnation process	WPG, leaching test (water up-teke, leaching), decay durability TGA, FTIR
20 mm × 20 mm × 10 mm	During the impregnation process	Solution up-take, swelling
20 mm × 20 mm × 10 mm	After the impregnation process	Bulking, ASE

### 2.2. Formulation of impregnating solution

The impregnating solution was prepared based on the formulation provided in Table 4.9, using three types of oil-grafted tannin chloride: lauryl, palmitoyl, and oleyl. Specifically, 2.7% and 4.54% of unmodified tannin were replaced with esterified tannin. The remaining composition of the formulation consisted of furfuryl alcohol and maleic acid as a catalyst. The formulations are presented in the Table.4.10.

Tableau.4. 11The formulations of the impregnation solutions with proportion equal (TAN: FA) (1:1)

Formulation	TAN (%)	Modified tannin (%)	FA (%)	MA (%)	Solvent (Water) (%)
STD	22.72	0	22.72	4.54	50
C12-1	20.45	2.27	22.72	4.54	50
C12-2	18.18	4.54	22.72	4.54	50
C16-1	20.45	2.27	22.72	4.54	50
C16-2	18.18	4.54	22.72	4.54	50
C18-1	20.45	2.27	22.72	4.54	50
C18-2	18.18	4.54	22.72	4.54	50

### 2.3. Wood modification

The wood samples were dried at 103°C for 48 hours and weighed ( $m_0$ ) and measured ( $V_0$ ). Subsequently, the samples were placed in a beaker covered with glass beads within a desiccator equipped with a two-way tap. Vacuum pressure (100 mbar) was applied for 15 minutes. Following that, the impregnation solution was introduced by suction until it completely covered the wood samples, and atmospheric pressure was restored. The samples were kept at atmospheric pressure for 24 hours.

Afterwards, the samples were removed from the solution, quickly drained, and weighed to determine their wet mass ( $m_1$ ). They were also measured to calculate their wet volume ( $V_1$ ). Subsequently, the samples were dried at 103°C for 72 hours, with the first 48 hours wrapped in aluminum foil and the remaining 24 hours without wrapping. They were then weighed again ( $m_2$ ) and measured to calculate their dry volume ( $V_2$ ).

Several parameters were calculated using the following formulas: solution uptake (SU), swelling after impregnation (S), weight percent gain before leaching (WPG1), and bulking coefficient (B).

During the wood modification process described above, the solution uptake (SU) and swelling caused by the impregnating solution were calculated using the following formulas (Eq.4.1) (Eq.4.2):

Solution Uptake (SU) :

$$\text{Equation (13) -SU (\%)} = 100 \times (m_1 - m_0) / m_0$$

Where:  $m_1$  is the wet mass of the wood sample after impregnation and  $m_0$  is the initial mass of the wood sample before impregnation.

Swelling (S) rate also was calculated for the group(F2)

$$\text{Equation (14)- S (\%)} = 100 \times (v_1 - v_0)/v_0$$

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

After the curing and drying process, the weight percent gain (WPG) and bulking coefficient (B) were calculated using the following formulas:

Weight Percent Gain (WPG):

$$\text{Equation (15)-WPG}_1 (\%) = 100 \times (m_2 - m_0) / m_0$$

Where  $\text{WPG}_1$ : is the weight percentage gain before leaching process.  $m_2$  :is the final mass of the wood sample after curing and drying  $m_0$  is the initial mass of the oven-dry wood at 103°C.

### 3.Results and Discussion

All the characterization are the same as the characterizations that were performed in the first part of this chapter. However, an additional analysis of contact angle was conducted to observe the hydrophobicity of the samples. For this reason, only the results of this analysis are presented and studied.

#### 3.1. Leaching test results

The leaching test results for the samples modified with a solution containing modified tannin by fatty acid are presented in the Table.4.9 and Figure.4.16.

Tableau.4. 12-Results of Leaching Test Following Modification Process

Formulation	Solution Uptake (%)	WPG <sub>1</sub> (%)	WPG (%)	WL (%)	Water Uptake (%)	L (%)	PH
STD	123,19	49,08	44,63	2,98	39,6	10,84	3,28
C12-I	123,07	48,31	46,37	1,30	35,77	3,99	3,41
C12-II	121,67	47,84	45,76	1,41	34,67	4,24	3,62
C16-I	115,10	50,39	48,91	1,56	38,24	4,29	3,22
C16-II	122,99	52,12	50,54	1,54	35,28	4,58	3,49
C18-I	117,20	53,26	50,58	1,83	33,75	4,96	3,52
C18-II	118,71	55,56	50,34	1,49	33,40	4,51	3,51
Untreated	0	0	0	2,10	89,60	1,89	4,90

C12.I. II: The solution with 2.27 and 4.54% of modified tannin with chlorid lauryl.

C16.I. II: The solution with 2.27 and 4.54% of modified tannin with chlorid Palmitoyl.

C18.I. II: The solution with 2.27 and 4.54% of modified tannin with chlorid Oleyl.

As is indicated in the Table (4.10) and the figure (4.17), the addition of modified tannin had a positive effect on improving the leaching results. In the standard formulation (STD), which contains furfuryl alcohol, tannin, and maleic acid as catalysts, the leaching rate is approximately 10%. However, replacing 8% and 16% of the tannin with modified tannin decreased the leaching rate to 4%. Additionally, the mass loss caused by leaching was also reduced, although the rate of mass gain or water absorption did not exhibit a significant difference.

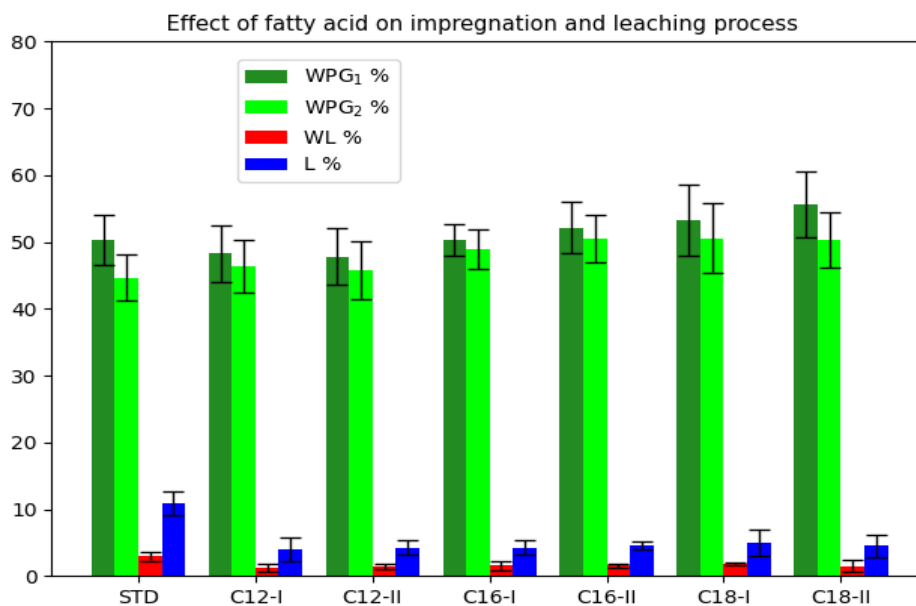


Figure.4. 15-Comparison of Leaching Values and Mass Gain Results

In comparison to impregnation without modified tannin, incorporating esterified modified tannin into the impregnation solution improved the wood's capacity to retain compounds and diminish their release during the leaching process. This modification had a positive impact on the durability and performance of the treated wood, enhancing its resistance to environmental conditions and degrading agents. Moreover, the water absorption rate after the leaching procedure in wood composites containing modified tannin was slightly lower than that in a solution without modified tannin. This suggests that modified tannin contributes to reducing water absorption, which can be advantageous for enhancing dimensional stability and moisture resistance of the wood.

### 3.2. The Fourier Transform Infrared Spectroscopy (FTIR)

In this section of the wood preservation study, we examined the impact of tannin esterification with fatty acid chains on the properties of beech wood. The findings from the infrared analysis of tannin modified with fatty acid chains were outlined in Chapter II. As a reference, one of the spectra is displayed in this chapter. The corresponding results are presented in Figure.4.18.

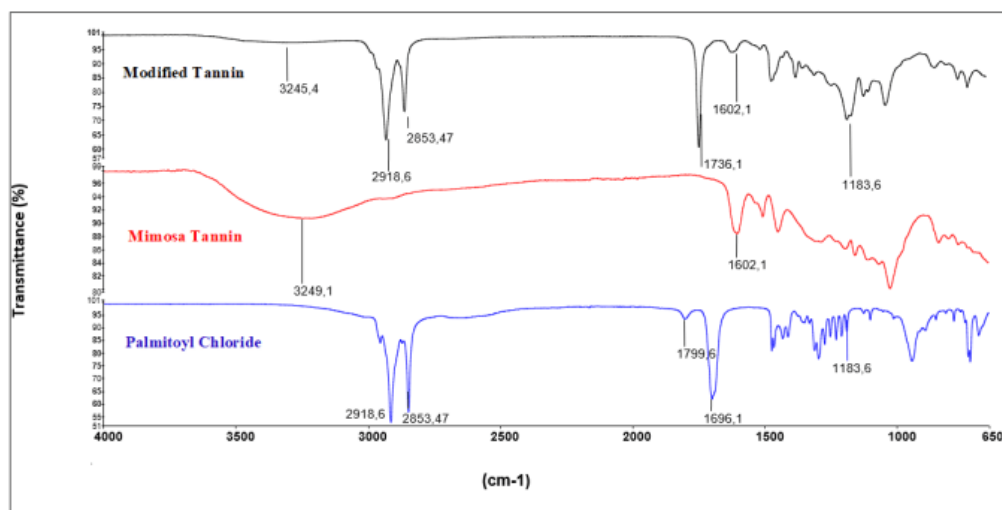


Figure.4. 16-The Comparison between Unmodified Tannin and Modified Tannin

Figure (4.18) displays the FTIR spectra of mimosa tannin, palmitoyl chloride, and the tannin or modified product obtained using palmitoyl chloride. In the spectrum of the mimosa tannin extract, a broad band between 3000 and 3500  $\text{cm}^{-1}$ , centered at 3245  $\text{cm}^{-1}$ , corresponding to hydroxyl groups, is observed. This band is also present in the modified mimosa extract, albeit with much lower intensity. This suggests a reduction in the number of hydroxyl groups in the obtained product after the esterification process.

In the modified tannin extract, a band at 2918  $\text{cm}^{-1}$  appears, distinguishing it from the original tannins. Notably, a band at 2920  $\text{cm}^{-1}$  is observed, potentially indicating the grafting of an aliphatic chain. In the FTIR spectra of esterified tannin, a strong peak emerges at 1742  $\text{cm}^{-1}$ , confirming the presence of ester groups resulting from the grafting of the tannin with the oil. The intense peak at 1799.6  $\text{cm}^{-1}$  in the palmitoyl chloride spectrum corresponds to the C=O stretching band of acid chlorides.

This peak disappears when palmitoyl chloride is used for the esterification of mimosa tannin. The absorption band at 1616.12  $\text{cm}^{-1}$  in the tannin spectrum is attributed to the C-H vibration in the aromatic ring of mimosa tannin.

In the second step, a comparison was made between the solution polymerized without modified tannin (STD) and with two percentages of modified tannin (C18.I and C18.II). This study is presented in Figure.4.19.

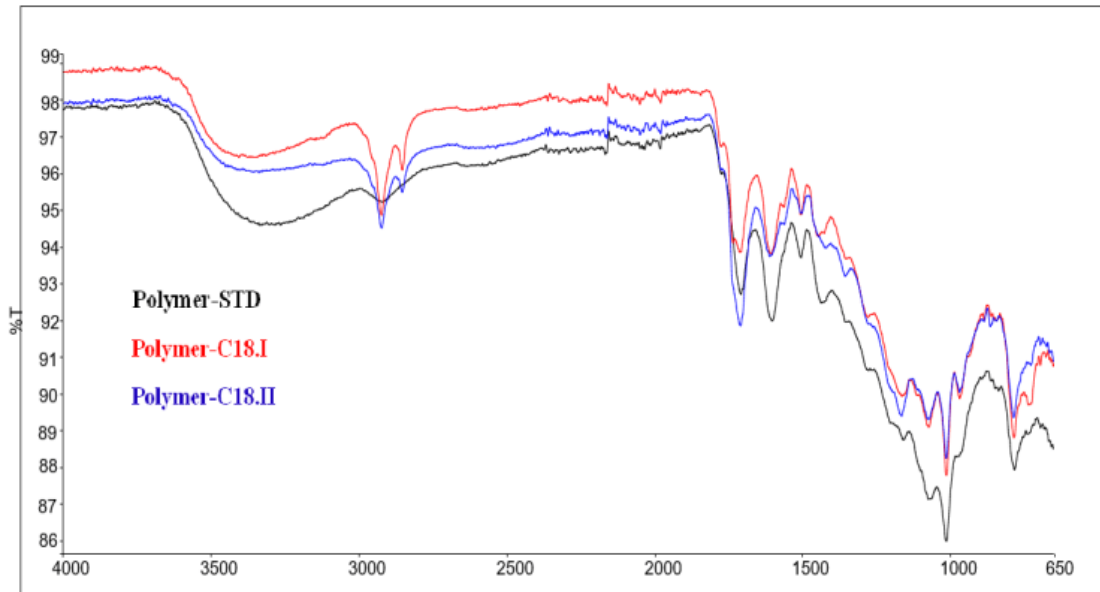


Figure.4. 17-FTIR spectroscopy of the polymers for the polymers:STD, C18,I, and C18,II

As shown, a decrease in the intensity of the bands corresponding to hydroxyl groups between 3000 and 3500 cm<sup>-1</sup> can be observed in the C18.I and C18.II formulations. This confirms the effectiveness of tannin esterification in increasing the hydrophobicity of the treated wood.

The range between 3000 and 3500 cm<sup>-1</sup> in the impregnated wood samples was widened due to the increased presence of hydroxyl groups. Impregnated wood contains substances such as tannin, which is abundant in hydroxyl groups. Hydroxyl groups exhibit stretching vibrations in this specific region of the infrared spectrum.

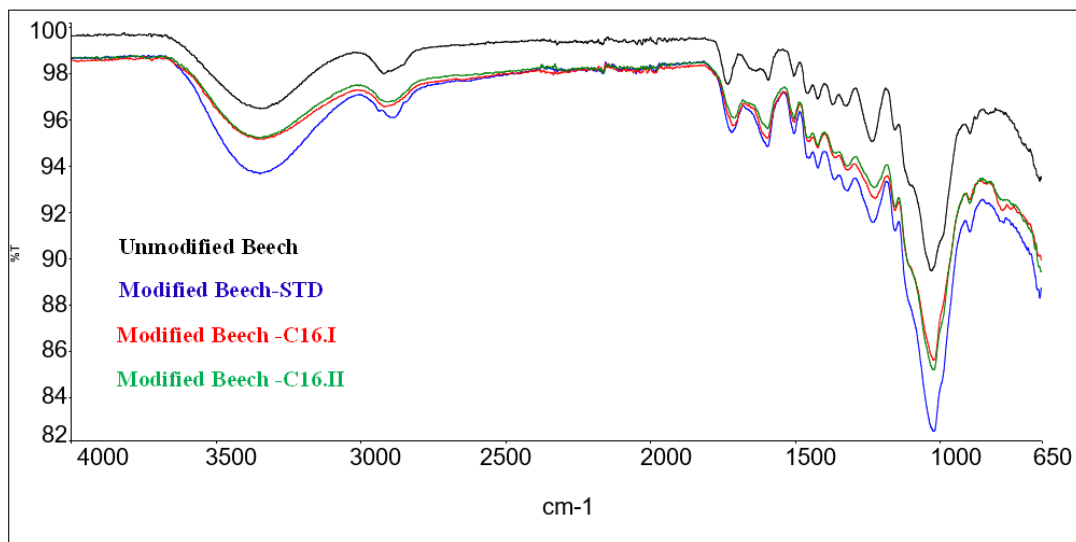


Figure.4. 18-Comparison FTIR spectroscopy of impregnated samples (STD, C16.I, and C16.II) with Unmodified Beech Wood.



When wood is impregnated with substances containing hydroxyl groups, such as tannin, the concentration of these hydroxyl groups increases within the material. This leads to an intensified and broader band in the infrared spectrum between 3000 and 3500 cm<sup>-1</sup>.

However, it is noteworthy that this band was reduced in samples containing fatty acid chains, confirming an enhancement in the wood's hydrophobicity.

In the case of samples with a lower content of esterified tannin (C16.I and C16.II), the less pronounced broadening of the band may indicate a decrease in the number of hydroxyl groups compared to samples impregnated with a higher amount of tannin.

### 3.3. Decay durability

The unmodified sample and samples modified without esterified tannin (STD) were subjected to decay durability analysis to observe the effect of esterified tannin on the increase of biological resistance. Additionally, treated samples with esterified tannin using three chains of fatty acids were included in the analysis. The results of this study are presented in Table-4.11 and Figure.4.21. Furthermore, the leaching value and humidity of the samples are also provided.

Tableau.4. 13-Biological durability of treated and untreated samples against brown and white rot

Formulation	Leaching (%)	Humidity (%)	WLD <sub>TV</sub> (%)	WLD <sub>ep</sub> (%)	Durability class
STD	10,80	36,02	4,56	5,38	<b>Very durable</b>
C12-I	3,99	30,31	3,73	3,49	<b>Very durable</b>
C12-II	4,24	31,59	2,96	4,85	<b>Very durable</b>
C16-I	4,29	28,31	3,65	3,99	<b>Very durable</b>
C16-II	4,58	31,77	3,90	3,19	<b>Very durable</b>
C18-I	4,96	29,97	4,15	4,48	<b>Very durable</b>
C18-II	4,51	26,68	4,02	4,87	<b>Very durable</b>
Untreated	1,89	80,30	43,03	52,68	<b>Non durable</b>

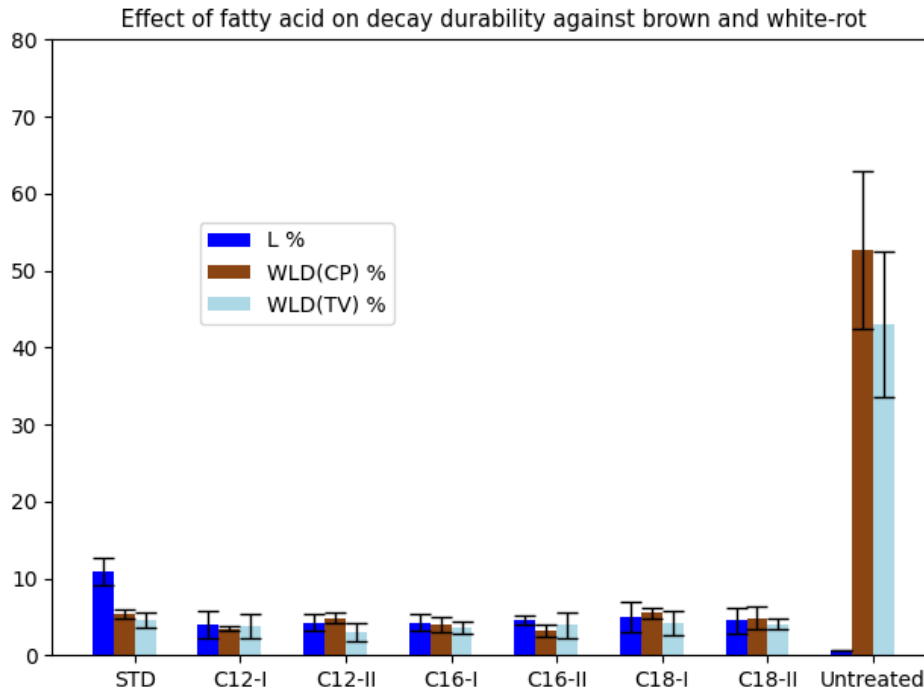


Figure.4. 19-Results of biological durability under the influence of white and brown rot.

As is indicated in Figure 4.21, the leaching rate was reduced in the modified samples containing tannin esterified with fatty acid chlorides compared to the standard formulation consisting of tannin and furfuryl alcohol.

The presence of tannin esterified with fatty acid chlorides can positively impact wood modification by enhancing its physical and chemical properties. Esterification of tannin with fatty acid chlorides facilitates the formation of covalent bonds between tannin and wood components, resulting in more effective cross-linking and fixation of tannin within the wood structure.

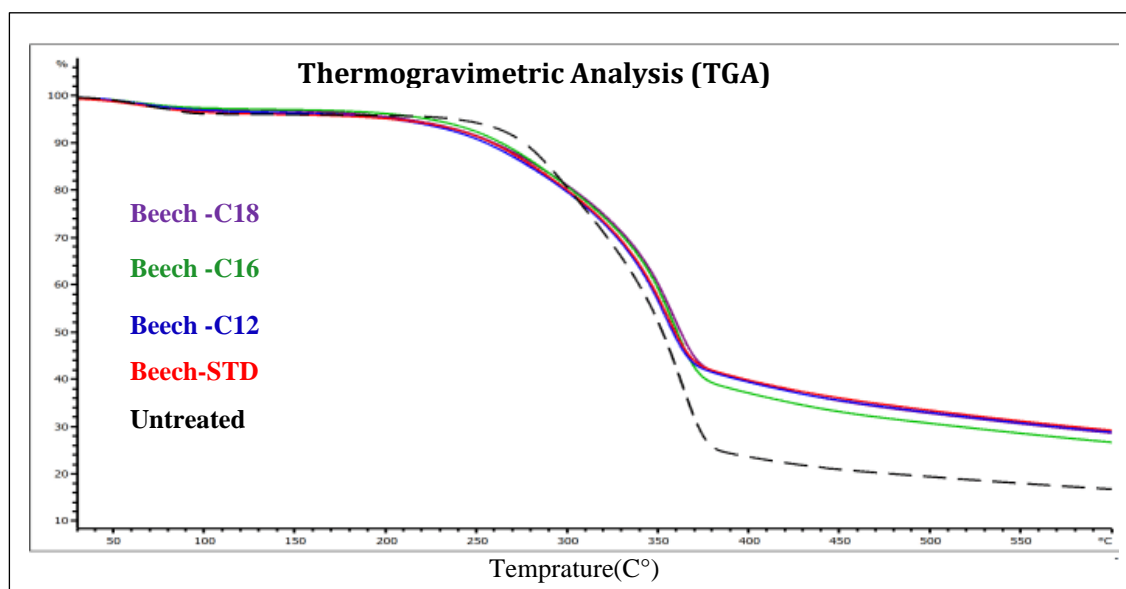
Additionally, the esterification of tannin with fatty acid chlorides significantly affects the hydrophobicity of wood. When tannin is esterified with fatty acid chlorides and impregnated into wood, it forms a hydrophobic barrier on the material's surface. This barrier reduces the wood's water absorption capacity, thereby decreasing its sensitivity to moisture variations.

Comparing treated samples with and without esterified tannin suggests that even a small amount of tannin grafted with various fatty acid chains can improve wood durability. However, the polymeric reaction between phenolic groups and furan groups in these formulations plays a more significant role in enhancing wood resistance against degradation agents.

Moreover, the comparison between samples containing tannin modified with lauryl, palmityl, and oleyl acid chloride chains did not reveal significant differences. The results for all three chains were very similar, indicating that these samples can be classified as durable woods.

### 3.4. Thermogravimetric Analysis (TGA)

In this part of the study, the thermogravimetric analysis, the effect of adding tannin modified with acid chloride chains in the wood modification or impregnation formulation was investigated. The addition of a small amount of modified tannin showed improvements in the leaching rate and a reduction in mass loss due to leaching, as well as enhanced biological durability against white and brown rot. The comparison between the untreated sample, treated with furfuryl tannin solution (STD), and solutions containing tannins modified with different acid chloride chains is presented in Figure 4.22.



Beech-C12 : The formulation containing tannin modified with lauryl acid chlorid.

Beech-C16 : The formulation containing tannin modified with Palmitoyl acid chlorid.

Beech-C18 : The formulation containing tannin modified with Oleyl acid chlorid.

Beech-STD : The formulation with furfuryl tannin without modified tannin.

The results show that the thermal stability of all the modified samples has been improved compared to untreated beech wood. This conclusion is confirmed by comparing the DTG curves (Fig.4.23).

The results presented in this part of the study are almost the same as the results of the first part of this chapter, which involved varying the proportion of tannin and furfuryl alcohol.

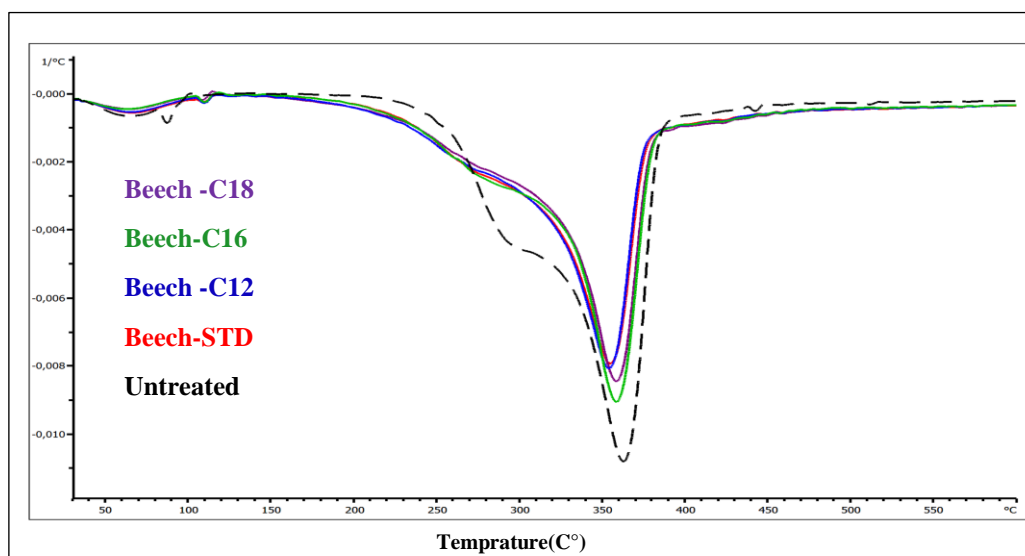


Figure.4. 21-Thermogravimetric analysis (DTG) of treated and control samples.

The first part of mass loss occurs between 30°C and 150°C, with a peak around 70°C. At this temperature, there is an initial mass loss due to the evaporation of moisture present in the material. This mass loss may vary depending on the initial moisture content of the wood [245].

The second zone ranges from 150°C to 300°C or 310°C : this region of mass loss can be attributed to the degradation of volatile organic compounds, evaporation of water, formation of CO<sub>2</sub> through dehydration and decarboxylation processes, degradation of extractives, initial degradation of carbohydrates, particularly hemicellulose and a portion of cellulose, as well as lignin. Non-reactive materials in the reaction, degradation of the acid catalyst, and release of CO gas can also contribute to this mass loss. A significant amount of furfuryl alcohol and tannin can decompose at this temperature. Tannin decomposition typically occurs between 160°C and 275°C, and within this temperature range, tannin loses approximately half of its initial mass. This confirms that samples treated with solutions containing a high amount of tannin exhibited higher mass loss than untreated wood in this temperature range.

The third zone is observed between 330°C and 370°C, with a peak at around 350°C. In this region, there is a deep depolymerization of organic components such as cellulose and a portion of lignin. This can lead to a remarkable decrease in the initial mass [147], [246].

From 400°C to 500°C, mass loss can generally be attributed to the opening or breaking of carbon-carbon bonds in lignin, the release of flammable volatile components, and the formation of non-volatile charcoal residue at the end [246].

No significant difference in mass loss was observed between the samples containing C12, C16, and C18 chains and the STD sample. The midpoint of mass loss in the unmodified wood is slightly

higher than in the other samples, which could be attributed to the presence of volatile components. The STD sample exhibits higher stability compared to the samples containing tannin modified by fatty acid. This could be attributed to the lower temperature at which the fatty acid chlorides decompose. Fatty acid chlorides generally decompose at temperatures around 200 °C, and they completely decompose at 270 °C [247] .

### 3.5. Analysis of contact angle (Wettability)

This analysis was used to measure the surface properties of samples modified with solutions containing tannin modified by acid chlorides, particularly their ability to be wetted by water. A goniometer was used to perform this measurement. The results of wetting behavior and water absorption resistance are presented in Figure (4.24).

The analysis of the contact angle for water to measure the wettability of the treated and untreated samples was performed with a system from Krüss Gmb(Villebon-sur-Yvettes France) equipped with a high-resolution CCD camera. A water droplet of 20 microlitres was placed on the wood surface using a micropipette to always obtain the same size droplet.

The drop shapes on the surface of the wood surface were captured by the CCD camera and measured for a period of 180 s. Image J 1.46 software with DropSnake plugin analysis was used to measure the contact angle for both the left and the right side of the individual image of the droplet. The values obtained were then averaged. In total, 60 images were taken for each recorded drop to obtain a curve of contact angle versus wetting time.

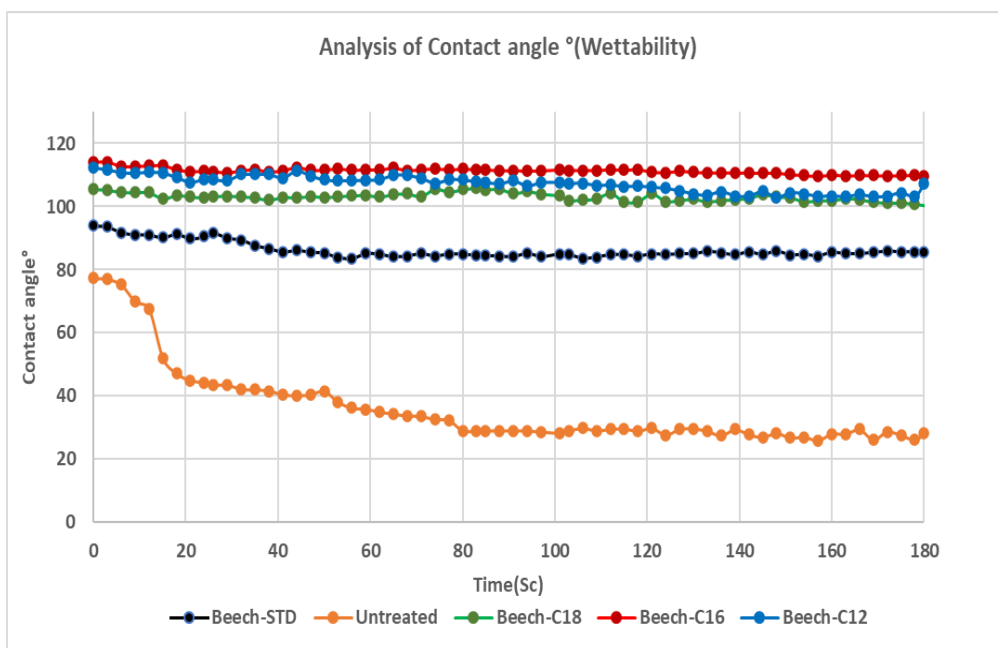


Figure.4. 22-Wettability results of untreated samples, treated Samples without modified Tannin (STD), and modified Tannin (Beech-C12, C16, C18)

Firstly, the contact angle of the untreated sample was observed, and the results showed low resistance in maintaining the water droplet. In fact, the water droplet quickly dispersed. The contact angle started at 80° and decreased to less than 20° within 180seconds.

In contrast, the contact angle of the sample treated with furfuryl tannin solution (STD) showed improved water absorption resistance and maintained droplet stability. The contact angle value started at 98° and remained stable for 60 seconds or longer. The contact angle results of the samples treated with furfuryl tannin solution containing tannin modified with fatty acid chloride chains demonstrated better resistance and contact angle values starting at 100° and 120°, remaining stable until the removal of the water droplet.

It is evident that the use of tannin modified with fatty acid chains helped reduce the presence of free hydroxyl groups in the polymer matrix of the composite wood, designed through the polymerization of tannin and furfuryl alcohol. Additionally, it is possible that the addition or substitution of a small amount of modified tannin strengthened the polymeric bonds in the furfuryl tannin matrix. Moreover, treatment with modified tannin solutions can reduce the number of active sites present on the wood surface, responsible for water absorption. This reduces the availability of absorption sites and thus the amount of absorbed water. As a result, the modified samples exhibit improved water absorption resistance and greater droplet stability, indicating an enhancement in their surface properties.

## **Conclusion**

The aim of this research was to investigate the effectiveness of modified tannins in enhancing the performance of biosourced thermoset resins for wood protection. The study focused on wood composites consisting of tannin, furfuryl alcohol, and tannin modified with fatty acids of different chain lengths (C12, C16, and C18).

The conducted leaching tests revealed a significant reduction in the leaching rate when modified tannins were incorporated into the impregnation solution, as compared to the standard formulation without modified tannin. By replacing a portion of the tannin with modified tannin (8% and 16%), the leaching rate decreased from approximately 10% to 4%. This improvement suggests that modified tannin enhances the wood's capacity to retain compounds and reduces their release during the leaching process.

Additionally, the treated wood samples containing modified tannins exhibited lower weight loss and leaching values compared to those treated without modified tannins. This improvement in leaching performance indicates that modified tannins contribute to the durability and performance

of the treated wood, enhancing its resistance to environmental conditions and degrading agents. Moreover, wood composites containing modified tannin demonstrated slightly lower water absorption rates after leaching, implying that modified tannin reduces water absorption and enhances the dimensional stability and moisture resistance of the wood.

The biological durability tests demonstrated that the incorporation of modified tannins improves the wood's resistance against white and brown rot when compared to control samples and samples treated without modified tannin. All the modified woods exhibited a high level of durability, with the samples containing C12 and C16 modified tannins showing slightly higher durability than those treated with C18 modified tannin. This suggests that even with half the amount of furfuryl alcohol compared to tannin, the presence of modified tannin contributes to improved resistance against fungal degradation.

The contact angle measurements confirmed that modified tannins increase the hydrophobic character of the wood compared to untreated wood and wood treated without modified tannin. Although the contact angle for the samples containing C18 modified tannin was slightly lower than that of the other modified woods, it still exceeded 90°, indicating an increase in the wood's hydrophobicity.

TGA analysis showed a slight weight loss in the treated samples containing modified tannin compared to those treated without esterified tannin. However, the treated samples exhibited high resistance to thermal degradation compared to solid wood. Among the different chains, the samples treated with C12 modified tannin demonstrated slightly less weight loss compared to the other chains.

In conclusion, this study demonstrates the effectiveness of incorporating modified tannins into biosourced thermoset resins for wood protection. The substitution of a portion of tannin with modified tannin results in improved leaching performance, reduced water absorption, enhanced resistance against fungal degradation, and increased hydrophobicity of the treated wood. The esterification of tannin with fatty acids of various chain lengths facilitates the formation of covalent bonds and improves the fixation of tannin within the wood structure. These results suggest that even small amounts of tannin modified with fatty acid chlorides can significantly enhance the durability and performance of wood.

Overall, this study highlights the potential of modified tannins as effective additives in biosourced thermoset resins for improving wood protection, thus opening opportunities for the development of eco-friendly and durable wood products.

#### **4. Discussion et conclusion**

Dans cette partie du projet, nous avons exploré la capacité des tanins à concevoir des composites bois-tanin en effectuant plusieurs séries d'imprégnation. Notre objectif était de trouver la meilleure formulation pour l'imprégnation du bois en utilisant des concentrations variables de tanin et d'alcool furfurylique. Nous avons également étudié l'effet de l'ajout de tanins modifiés sur les propriétés des composites. Les résultats obtenus fournissent des informations précieuses sur l'utilisation des tanins comme agents de réticulation et co-monomères dans la préservation du bois.

Dans la première partie de l'étude (groupe A), nous avons varié les concentrations de tanin et d'alcool furfurylique pour observer leur impact sur les propriétés des échantillons de bois traités. Les résultats ont montré que des concentrations plus élevées de tanin et d'alcool furfurylique, avec une proportion équilibrée, conduisaient à une meilleure rétention de masse et à une diminution du taux de lixiviation. Cela suggère que la combinaison de tanin et d'alcool furfurylique améliore les propriétés du bois traité en formant des liaisons covalentes par une réaction de condensation. Cependant, lorsque la proportion de tanin par rapport à l'alcool furfurylique augmentait, les résultats étaient moins favorables en raison de l'augmentation de la viscosité de la solution, ce qui rendait l'imprégnation plus difficile et entraînait une distribution moins homogène des composés chimiques dans le bois.

Dans la deuxième partie de l'étude (groupe B), nous avons introduit des tanins modifiés en remplacement d'une petite quantité de tanin non modifié pour évaluer leur impact sur les propriétés des composites bois-tanin. Les composites contenant des tanins modifiés ont montré une amélioration significative de la résistance à la lixiviation par rapport aux composites contenant uniquement du tanin non modifié. Cela suggère que la modification chimique des tanins a renforcé leur capacité à se lier au bois, améliorant ainsi la stabilité du composite. De plus, les composites contenant des tanins modifiés ont également présenté une meilleure durabilité biologique, avec une résistance accrue à la dégradation par des microorganismes. Les tanins modifiés possèdent des propriétés antifongiques et antibactériennes qui peuvent inhiber les activités enzymatiques responsables de la dégradation du bois, ce qui contribue à la préservation de sa structure.

Les réactions de condensation entre le tanin et l'alcool furfurylique, ainsi que les réactions d'autocondensation de ces deux composés, ont été identifiées comme des mécanismes clés dans la formation de réseaux polymériques réticulés. Ces réseaux polymériques renforcent la structure du bois, réduisant ainsi sa sensibilité à la dégradation biologique. De plus, les tanins possèdent des propriétés antifongiques et antibactériennes qui peuvent perturber les activités enzymatiques des



microorganismes responsables de la dégradation du bois. Par conséquent, l'utilisation de tanins dans les composites bois-tanin-alcool furfurylique offre un potentiel prometteur pour améliorer la stabilité dimensionnelle et la durabilité du bois traité.

En ce qui concerne la stabilité dimensionnelle, les composites bois-tanin-alcool furfurylique ont montré une meilleure stabilité par rapport au bois non traité. La réticulation des composés chimiques dans le bois a renforcé sa structure, réduisant ainsi les variations dimensionnelles dues aux variations d'humidité. Cette amélioration de la stabilité dimensionnelle est cruciale pour de nombreuses applications du bois, notamment dans la construction et le mobilier, où des variations excessives de taille peuvent entraîner des problèmes structurels et esthétiques.

Cette étude ouvre des perspectives intéressantes pour l'utilisation de composites bois-tanin dans diverses applications où la stabilité dimensionnelle et la résistance à la dégradation biologique sont essentielles. Les résultats suggèrent que des concentrations plus élevées de tanin et d'alcool furfurylique, avec une proportion équilibrée, peuvent conduire à une meilleure performance des composites. Cependant, il est important de noter que l'augmentation de la proportion de tanin par rapport à l'alcool furfurylique peut entraîner une augmentation de la viscosité de la solution, ce qui peut affecter négativement les résultats. Des investigations supplémentaires peuvent être envisagées pour optimiser le rapport tanin/alcool furfurylique, explorer l'utilisation de différentes espèces de bois et évaluer la durabilité à long terme des composites bois-tanin-alcool furfurylique. Ces études permettront de mieux comprendre les mécanismes de formation des composites et d'optimiser les propriétés des matériaux pour des applications spécifiques.

En conclusion, cette étude a démontré le potentiel des tanins en tant qu'agents de réticulation et co-monomères dans la préservation du bois. Les composites bois-tanin-alcool furfurylique ont montré des améliorations significatives en termes de stabilité dimensionnelle et de durabilité contre la dégradation biologique. La présence d'alcool furfurylique était cruciale pour la création de liaisons polymériques et l'amélioration des propriétés du bois traité. Le processus d'imprégnation, intégrant le tanin, l'alcool furfurylique et l'acide maléique, a modifié la structure et la composition du bois, conduisant ainsi à l'amélioration des propriétés de stabilité. Ces résultats fournissent une base solide pour la poursuite de la recherche sur l'utilisation des tanins dans la conception de composites bois-tanin pour des applications durables.

# **Conclusion Générale**



## **Conclusion Générale**

Dans cette étude, des ressources de biomasse telles que les tanins condensés, comme le mimosa, et les tanins hydrolysables, tels que le châtaignier, ont été utilisées.

L'objectif était de concevoir des matériaux biosourcés, notamment des mousses d'isolation, en améliorant leur caractère hydrophobe, et de développer des composites bois-tanin pour prolonger la durée de vie et préserver le bois.

### **1. Modification chimique de tanins condensés**

L'objectif de cette étude était d'améliorer les propriétés hydrophobes des matériaux dérivés du tanin, tels que les mousses tanin-furaniques, en utilisant la modification chimique du tanin condensé (mimosa) par estérification avec des chlorures d'acides gras.

Différents protocoles ont été testés afin de trouver les meilleures conditions de réaction pour obtenir un haut rendement de greffage. Les facteurs tels que la proportion de tanin et de chlorures d'acides gras, le temps et la température de réaction ont été soigneusement examinés. Les meilleures performances ont été obtenues en utilisant des proportions équivalentes de tanin et de chlorures d'acides gras à température ambiante.

Également, les conditions de réaction ont été simplifiées en éliminant les agents de couplage et les catalyseurs tels que la triéthylamine (Et<sub>3</sub>N) et la 4-diméthylaminopyridine (DMAP). De plus, l'étape de lavage a été supprimée, ce qui a permis d'augmenter le rendement massique du produit modifié.

L'efficacité de la réaction de greffage a été vérifiée en utilisant l'analyse infrarouge. Les résultats ont confirmé la greffe et la formation de groupes esters, avec l'apparition d'un pic correspondant au tanin greffé par les chlorures d'acides gras. L'analyse de masse MALDI-TOF a également été utilisée pour confirmer la réussite de la réaction de greffage.

En résumé, cette étude démontre la faisabilité et l'efficacité de la modification chimique du tanin condensé (mimosa) par estérification avec des chlorures d'acides gras, dans le but d'améliorer les propriétés hydrophobes des matériaux dérivés du tanin. Ces résultats ouvrent de nouvelles perspectives pour l'utilisation de ces matériaux dans des applications telles que les mousses d'isolation.

## **2. Conception des mousses tanin-furaniques avec le caractère hydrophobe**

L'objectif de la modification chimique du tanin condensé était de créer des matériaux présentant des propriétés hydrophobes. Pour atteindre cet objectif, le tanin condensé a été modifié par réaction de couplage avec des chlorures d'acides gras dans un milieu de solvants organiques.

Cette modification visait à améliorer les propriétés hydrophobes des matériaux dérivés du tanin, tels que les mousses tanin-furaniques. En effet, la nature hydrophile du tanin limite l'utilisation de ces matériaux dans des applications telles que les mousses et les colles à base de bois. En augmentant le caractère hydrophobe des mousses, il était possible de garantir des performances durables et une longue durée de vie, même dans des environnements humides.

Dans le cadre de cette recherche, la formulation classique des mousses de tanin-furanique a été examinée. Cette formulation implique la réaction du tanin avec l'alcool furfurique, l'utilisation d'un aldéhyde comme agent de réticulation, d'un catalyseur acide et d'un agent d'expansion. Cependant, une petite quantité de tanin a été remplacée par du tanin modifié pour améliorer le caractère hydrophobe des mousses. Au départ, l'hydrophobicité des mousses a été améliorée, mais des recherches plus approfondies ont été entreprises pour obtenir de meilleurs résultats tout en évitant la dégradation de la structure des mousses due à la température élevée de réaction. D'autres solutions ont été explorées, telles que le remplacement de l'eau par du glycérol ou le changement de l'aldéhyde utilisé comme agent de réticulation.

Ces solutions ont donné des résultats prometteurs, ce qui a encouragé des recherches plus approfondies. En remplaçant le formaldéhyde par l'acétaldéhyde comme agent de réticulation, une mousse légère, hydrophobe et flexible a été obtenue. Cette avancée a été le point central des études ultérieures. La fragilité des mousses rigides a été considérablement réduite et leur résistance à l'absorption d'eau a été significativement augmentée.

## **3. Conception de mousses flexibles et hydrophobes à base de tanins furaniques de mimosa**

À la suite de recherches antérieures, la formulation des mousses a été modifiée en remplaçant l'agent de réticulation à base de formaldéhyde par de l'acétal aldéhyde, et en utilisant du glycérol à la place de l'eau. Cette nouvelle formulation a permis d'obtenir des mousses flexibles et hydrophobes à partir de tanin mimosa.

Étant donné les nombreuses applications des mousses flexibles dans la vie quotidienne et l'industrie, cette étude s'est concentrée sur l'analyse des propriétés mécaniques pour évaluer leur résistance à la déformation et confirmer leur flexibilité.

Des analyses supplémentaires, telles que l'imagerie des structures cellulaires au microscope électronique à balayage (MEB), ont été réalisées pour examiner la structure des mousses et étudier leur composition. Ces analyses ont permis de mieux comprendre les caractéristiques des mousses flexibles et de vérifier si elles répondaient aux critères de flexibilité et d'hydrophobicité recherchés.

Les résultats et observations de cette étude mettent en évidence l'impact significatif de l'ajout de tanin modifié par des acides gras sur la formation et les propriétés des mousses. Deux types de mousses ont été fabriqués à partir de tanin mimosa : des mousses rigides et des mousses flexibles.

L'ajout de tanin estérifié a considérablement amélioré l'hydrophobicité des mousses par rapport à la mousse standard non modifiée. De plus, l'ajout de glycérol a permis la formation de mousses flexibles. Dans toutes les mousses modifiées, on a observé une augmentation de l'hydrophobicité et de la mouillabilité.

Les mousses rigides et flexibles contenant du tanin modifié ont montré une structure cellulaire légèrement différente. L'ajout de glycérol a également influencé la formation de la structure cellulaire des mousses, en rendant les cellules plus épaisses et les parois cellulaires plus solides. Les mousses rigides ont des pores plus ouverts, ce qui contribue à leur résistance à l'absorption d'eau.

En conclusion, l'utilisation de l'acétal aldéhyde comme agent de réticulation et du glycérol comme substitut de l'eau a permis de concevoir des mousses flexibles et hydrophobes à partir de tanin mimosa. Les mousses modifiées ont présenté des améliorations significatives en termes d'hydrophobicité, de structure cellulaire, de résistance à l'eau et de propriétés mécaniques. Ces résultats ouvrent de nouvelles perspectives pour l'utilisation de ces mousses dans diverses applications industrielles.

#### **4. Conception de mousses rigides à partir de tanins hydrolysables de châtaignier**

Dans cette partie du projet, la conception de mousses rigides à partir de tanin de châtaignier, un tanin hydrolysable commercialisé, a fait l'objet d'une vaste recherche. Étant donné que les formulations classiques connues comme tanin-furanique n'ont pas réussi à produire une mousse, la méthode de bio polyuréthane sans isocyanate a été examinée afin de concevoir des mousses rigides.

Dans cette étude, les mousses de polyuréthane sans isocyanate (NIPU) ont été préparées en utilisant un extrait commercial de tanin de bois de châtaignier comme composant polyol. Le tanin

de châtaignier est un type de tanin hydrolysable contenant des groupes phénoliques qui peuvent réagir avec des composés d'hydroxyle.

La formulation des mousses de NIPU consistait à mélanger le tanin de châtaignier avec d'autres composants tels que le polyéthylène glycol (diol), l'hexaméthylène diamine (diamine) et le glutaraldéhyde (réticulant). Différentes proportions de ces composants ont été utilisées pour obtenir des mousses avec des densités apparentes variables.

L'analyse par spectrométrie infrarouge a confirmé la formation de liaisons uréthane et de ponts uréthane dans les mousses de NIPU. Des différences ont été observées entre les spectres de la résine de NIPU, de la mousse rigide et de la mousse durcie, suggérant la présence de groupes acide carbamique (-NH-COOH) formés par la réaction entre le diméthyl carbonate (DMC) et la diamine d'hexaméthylène. D'autres analyses ont été réalisées pour étudier plus en détail la structure moléculaire et la composition des mousses.

Les résultats ont montré que la densité apparente des mousses de NIPU variait en fonction de la formulation, mais cela n'était pas directement lié à leur densité réelle. La résistance à la compression des mousses dépendait non seulement de la densité, mais également des proportions relatives des composants. Par exemple, une mousse avec une densité légèrement plus élevée mais une proportion plus élevée de glutaraldéhyde présentait une résistance à la compression différente des autres mousses.

En termes de résistance au feu, les mousses de NIPU contenant du tanin de châtaignier ont montré de meilleures performances que les mousses de polyuréthane traditionnelles. Cela est dû à la présence de groupes phénoliques dans le tanin, qui peuvent se carboniser et former une barrière contre la propagation des flammes.

En conclusion, l'utilisation du tanin de châtaignier dans la formulation des mousses de polyuréthane sans isocyanate (NIPU) a permis d'obtenir des mousses rigides avec des propriétés intéressantes. Les mousses de NIPU présentent des densités variables en fonction de la formulation, et leur résistance à la compression dépend des proportions des composants utilisés.

## **5. Approfondissement de l'étude sur la caractérisation des mousses (NIPU) conçues par le tanin de châtaignier**

À la suite de l'étude sur la conception de mousses d'isolation thermique à partir du tanin de châtaignier avec la méthode de bio-polyuréthane sans isocyanate (NIPU), une recherche approfondie a été menée. Cette recherche comprenait l'utilisation de la microscopie électronique à balayage (MEB) pour examiner la structure cellulaire des mousses et l'impact des différentes

formulations sur la formation des cellules. De plus, une analyse de spectrométrie de masse (MALDI-TOF) et de résonance magnétique nucléaire du carbone-13 ( $C^{13}$  NMR) a été réalisée pour étudier les liaisons formées lors de la réaction de préparation des mousses.

Les résultats initiaux de cette étude ont montré que l'ajout de glutaraldéhyde avait un effet positif sur la structure et la densité des mousses. L'analyse en MEB a révélé que les mousses contenant une plus grande quantité de glutaraldéhyde présentaient une meilleure formation des cellules et moins de fractures. En revanche, l'ajout d'hexamine accélérât la formation de la mousse mais rendait les cellules plus fragiles en raison de la réaction plus rapide. Cependant, en augmentant la quantité de glutaraldéhyde, la réticulation s'améliorait et les fractures étaient réduites.

L'analyse MALDI-TOF a permis de comprendre les réactions complexes qui se produisent lors de la formation des mousses NIPU. Les tanins et les glucides présents dans l'extrait de tanin de châtaignier réagissaient avec le carbonate de diméthyle et la diamine d'hexaméthylène, formant ainsi divers composés. Différents types de liaisons, tels que les liaisons directes, les ponts et les ponts glycosidiques, ont été identifiés, ce qui ajoute à la complexité de l'extrait de tanin.

L'analyse RMN  $^{13}C$  CP-MAS a confirmé la formation de liaisons uréthanes sans isocyanate dans les mousses NIPU. Elle a également révélé la présence d'autres composés tels que l'acide flavogallolique, l'acide valonéique et des esters de glucose de l'acide citrique Hardenberg. La diversité des pics observés indique la polymérisation du matériau dans la mousse et la complexité de l'extrait de tanin.

En résumé, cette étude a permis de préparer et de caractériser des mousses NIPU à base d'extraits de tanins de châtaignier. Les résultats ont montré que l'ajout de glutaraldéhyde et d'hexamine avait des effets significatifs sur la structure et les propriétés des mousses. Les analyses en MEB, MALDI-TOF et RMN  $^{13}C$  ont fourni des informations importantes sur les réactions chimiques et les structures présentes dans les mousses NIPU. Ces avancées contribuent à une meilleure compréhension des mécanismes de réaction et ouvrent la voie au développement de matériaux polyuréthanes durables et respectueux de l'environnement. Des recherches futures pourront se concentrer sur l'optimisation des formulations afin d'améliorer encore les propriétés des mousses NIPU.

## **6. Conception de composites bois/tanins/alcool furfurylique**

Cette partie de la thèse porte sur la création de composites de bois et la préservation du bois de hêtre en utilisant des solutions contenant du tanin condensé et de l'alcool furfurylique.



Dans la première étape de l'étude, différentes conditions ont été testées pour trouver les meilleures conditions de réaction. Trois solutions ont été préparées avec des concentrations de tanin et d'alcool furfurylique de 10 %, 25 % et 50 %, en proportions égales.

La deuxième étape consistait à préparer des composites thermodurcissables en variant les proportions de tanin et d'alcool furfurylique. Les résultats ont montré qu'une concentration plus élevée de tanin et d'alcool furfurylique, en proportions égales, améliorait la rétention de masse et réduisait le taux de lessivage. Cependant, une augmentation de la proportion de tanin par rapport à l'alcool furfurylique avait des résultats moins favorables en raison de l'augmentation de la viscosité de la solution. Supprimer l'alcool furfurylique a également augmenté le taux de lessivage.

Les tests de durabilité biologique ont démontré que les échantillons de bois traité présentaient une meilleure résistance à la pourriture brune et blanche par rapport au bois non traité. Les tanins ont des propriétés antifongiques et antibactériennes qui perturbent l'activité des microorganismes responsables de la dégradation du bois. La polymérisation du tanin par l'alcool furfurylique renforce la structure du bois et le rend moins susceptible à la dégradation biologique.

En conclusion, cette étude a montré le potentiel d'utilisation des tanins comme agents de réticulation et co-monomères pour la préservation du bois. Une concentration plus élevée de tanin et d'alcool furfurylique, en proportions égales, a amélioré la stabilité dimensionnelle et la durabilité du bois traité. L'alcool furfurylique joue un rôle crucial dans la création de liaisons polymériques et la résistance du bois à la dégradation biologique. Des recherches supplémentaires peuvent se concentrer sur l'optimisation du rapport tanin/alcool furfurylique, l'utilisation de différentes essences de bois et l'évaluation à long terme des propriétés du bois traité. Cette étude contribue au développement de méthodes respectueuses de l'environnement pour la préservation du bois en utilisant les tanins comme alternatives durables aux produits chimiques traditionnels.

## **7. Optimisation de l'effet du tanin modifié par estérification pour l'amélioration des propriétés des composites bois/tanin/alcool furfurylique.**

Dans cette partie, l'objectif était d'étudier si les tanins modifiés peuvent améliorer les résines thermodurcissables biosourcées utilisées pour protéger le bois. Les composites de bois étaient composés de tanin, d'alcool furfurylique et de tanin modifié avec des acides gras de différentes longueurs de chaîne (C12, C16 et C18).

Les tests de lessivage ont montré que l'incorporation de tanins modifiés dans la solution d'imprégnation réduisait significativement le taux de lessivage par rapport à la formulation standard sans tanin modifié. En remplaçant une partie du tanin par du tanin modifié (8% et 16%),

le taux de lessivage est passé de 10% à 4%. Cela indique que le tanin modifié permet au bois de mieux retenir les composés et de les libérer moins lors du lessivage.

De plus, les échantillons de bois traités avec des tanins modifiés ont montré une perte de poids et un taux de lessivage plus faibles que ceux traités sans tanin modifié. Cela suggère que les tanins modifiés améliorent la durabilité et les performances du bois traité, le rendant plus résistant aux conditions environnementales et aux agents de dégradation. De plus, les composites de bois contenant du tanin modifié ont présenté une absorption d'eau légèrement plus faible après le lessivage, ce qui améliore la stabilité dimensionnelle et la résistance à l'humidité du bois.

Les tests de durabilité biologique ont montré que l'incorporation de tanins modifiés améliore la résistance du bois à la pourriture blanche et brune par rapport aux échantillons non traités et aux échantillons traités sans tanin modifié. Tous les bois modifiés ont montré une durabilité élevée, avec les échantillons contenant des tanins modifiés C12 et C16 montrant une légèrement meilleure durabilité que ceux traités avec du tanin modifié C18. Cela suggère que même avec une quantité réduite d'alcool furfurylique par rapport au tanin, la présence de tanin modifié contribue à une meilleure résistance à la dégradation fongique.

Les mesures de l'angle de contact ont confirmé que les tanins modifiés rendent le bois plus hydrophobe par rapport au bois non traité et au bois traité sans tanin modifié. Même si l'angle de contact pour les échantillons contenant du tanin modifié C18 était légèrement inférieur à celui des autres tanins modifiés, il dépassait toujours  $90^\circ$ , ce qui indique une augmentation de l'hydrophobicité du bois.

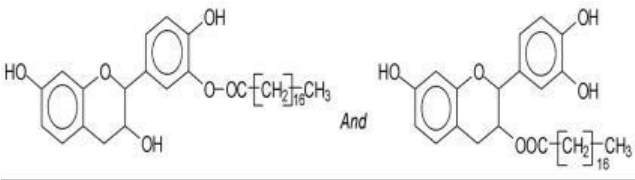
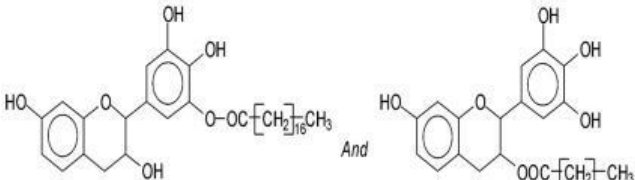
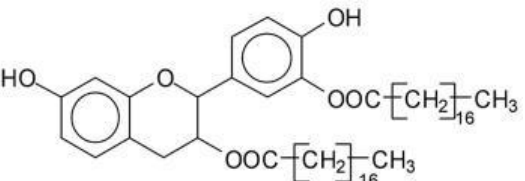
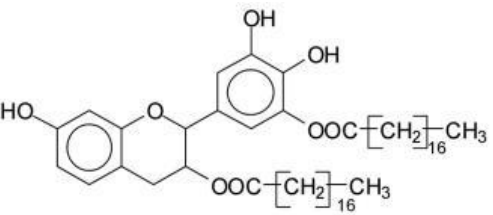
En conclusion, cette étude démontre que l'incorporation de tanins modifiés dans les résines thermodurcissables biosourcées améliore les performances de protection du bois. Le remplacement d'une partie du tanin par du tanin modifié entraîne une meilleure résistance au lessivage, une absorption d'eau réduite, une meilleure résistance à la dégradation fongique et une augmentation de l'hydrophobicité du bois traité. L'estérification du tanin avec des acides gras permet la formation de liaisons covalentes et renforce la fixation du tanin dans la structure du bois. Ces résultats suggèrent que même de petites quantités de tanin modifié avec des acides gras peuvent considérablement améliorer la durabilité et les performances du bois.

En résumé, cette étude prouve le potentiel des tanins modifiés en tant qu'additifs efficaces dans les résines thermodurcissables biosourcées pour améliorer la protection du bois, ouvrant ainsi des opportunités pour le développement de produits en bois respectueux de l'environnement et durables.

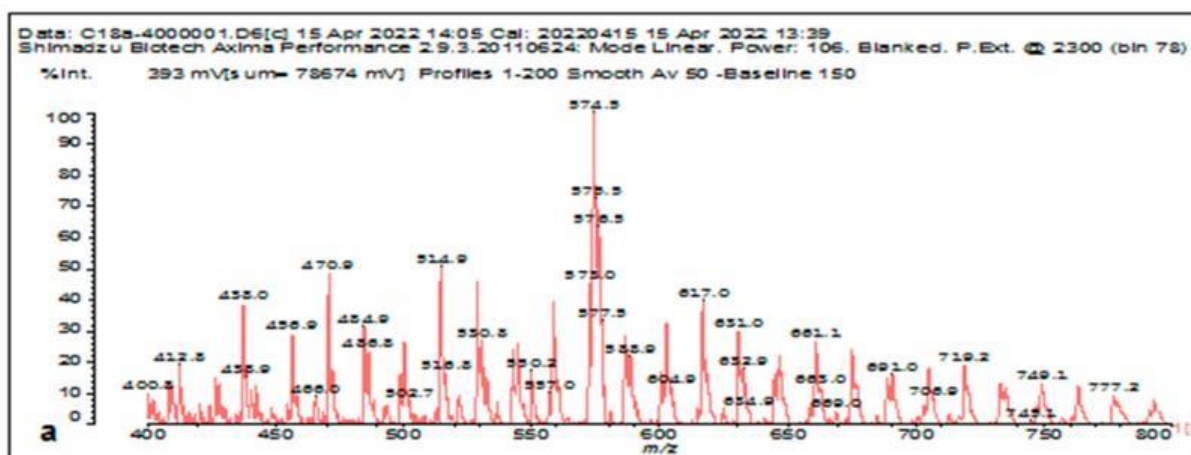


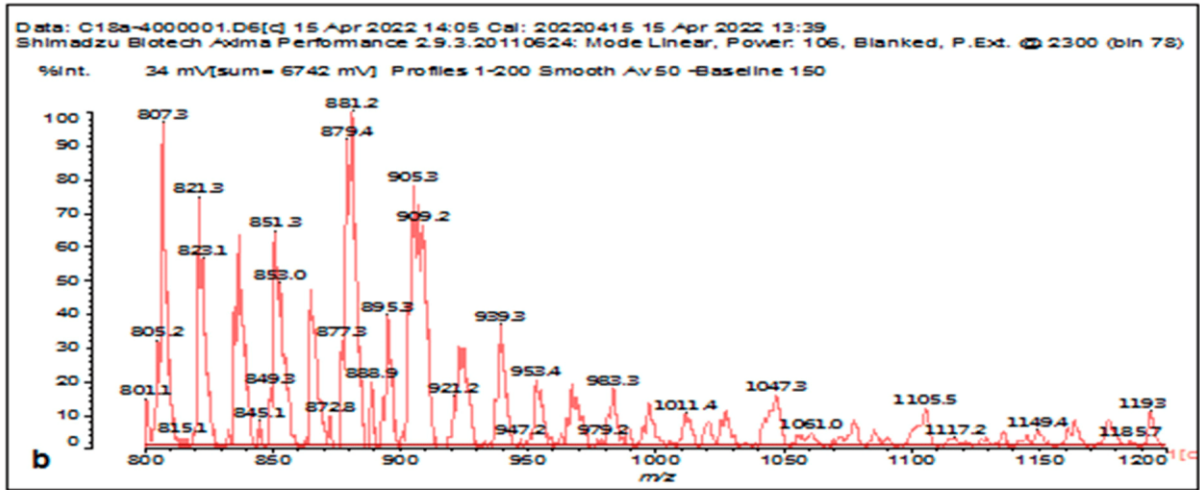
## Annexes

### Annex. 1-Characterization of oil-grafted tanin with oleoyl chloride by MALDI-TOF

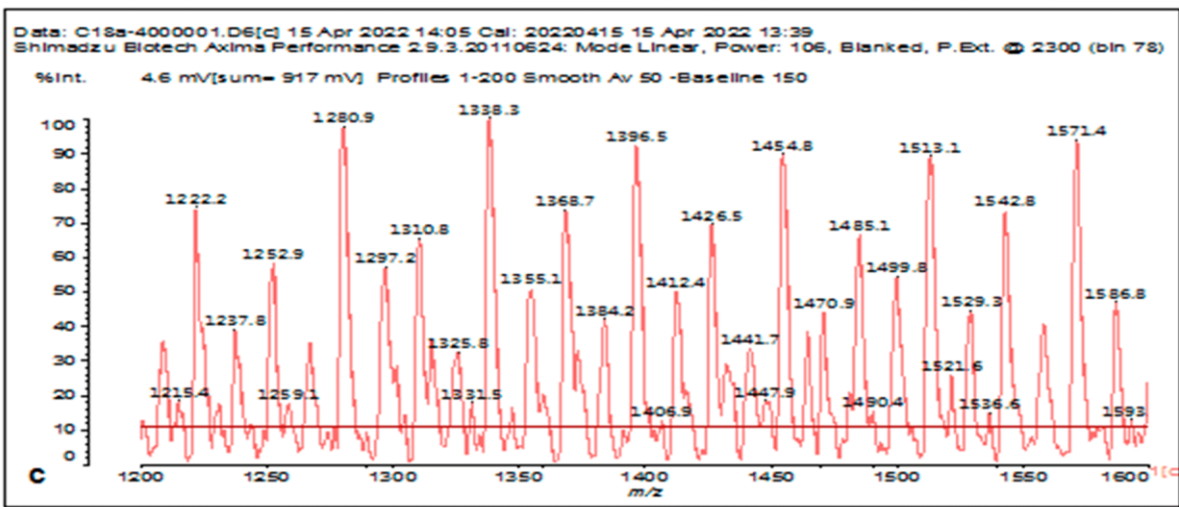
Molecules	Peak Experimental	Peak Calculated
 <p>Fisetinidin-oleate + Na<sup>+</sup></p>	561 Da	561 Da
<p>Robinetinidin-oleate, OR robinetinidin-robinetinidin dimer, no Na<sup>+</sup>, deprotonated</p> 	575-577 Da	575-577 Da
<p>Fisetinidin- (oleate)<sub>2</sub> no Na<sup>+</sup></p> 	801 Da	801 Da
<p>Robinetinidin- (oleate)<sub>2</sub> with Na<sup>+</sup></p> 	841 Da	841 Da
<p>(robinetinidin)<sub>2</sub>-gallocatechin trimer, no Na<sup>+</sup></p>	879-881 Da	881 Da
<p>(gallocatechin)<sub>2</sub>-robinetinidin trimer, no Na<sup>+</sup></p>	895 Da	895 Da
<p>gallocatechin)<sub>2</sub>-robinetinidin trimer, with Na<sup>+</sup></p>	909 Da	910 Da
<p>Robinetinidin-(oleate)<sub>3</sub> with Na<sup>+</sup></p>	1105 Da	1105 Da

$\text{CH} \left[ \text{H}_2\text{C} \right]_{16} \text{COO} \text{---} \text{C}_6\text{H}_3 \text{---} \text{O} \text{---} \text{C}(\text{OH}) \text{---} \text{C}_6\text{H}_2(\text{OH})_2 \text{---} \text{OOC} \left[ \text{CH}_2 \right]_{16} \text{CH}_3$ $\text{OOC} \left[ \text{CH}_2 \right]_{16} \text{CH}_3$		
robinetinidin-galocatechin-(oleate) <sub>2</sub> no Na <sup>+</sup> , protonated	1149 Da	1146 Da
fisetinidin-(oleate) <sub>4</sub> , protonated	1331 Da no Na <sup>+</sup> 1355 Da with Na <sup>+</sup>	1330 Da 1354 Da
(fisetinidin) <sub>2</sub> -(oleate) <sub>3</sub> no Na <sup>+</sup>	1338 Da	1338 Da
$\text{CH}_3 \left[ \text{CH}_2 \right]_{16} \text{COO} \text{---} \text{C}_6\text{H}_3 \text{---} \text{C}_6\text{H}_2(\text{OH})_2 \text{---} \text{O} \text{---} \text{C}_6\text{H}_2(\text{OH})_2 \text{---} \text{OOC} \left[ \text{CH}_2 \right]_{16} \text{CH}_3$ $\text{OOC} \left[ \text{CH}_2 \right]_{16} \text{CH}_3$ $\text{OOC} \left[ \text{CH}_2 \right]_{16} \text{CH}_3$		
glucose-(fisetinidin) <sub>2</sub> -(oleate) <sub>3</sub> , no Na <sup>+</sup>	1500 Da no Na <sup>+</sup>	1500 Da
(fisetinidin) <sub>2</sub> -(oleate) <sub>4</sub>	1601 Da no Na <sup>+</sup>	1601 Da
robinetinidin-(oleate) <sub>5</sub> , deprotonated	1609 Da no Na <sup>+</sup> 1630 Da with Na <sup>+</sup>	1609 Da 1631 Da
(galocatechin) <sub>2</sub> -(oleate) <sub>4</sub> , deprotonated	1688 Da with Na <sup>+</sup>	1688 Da

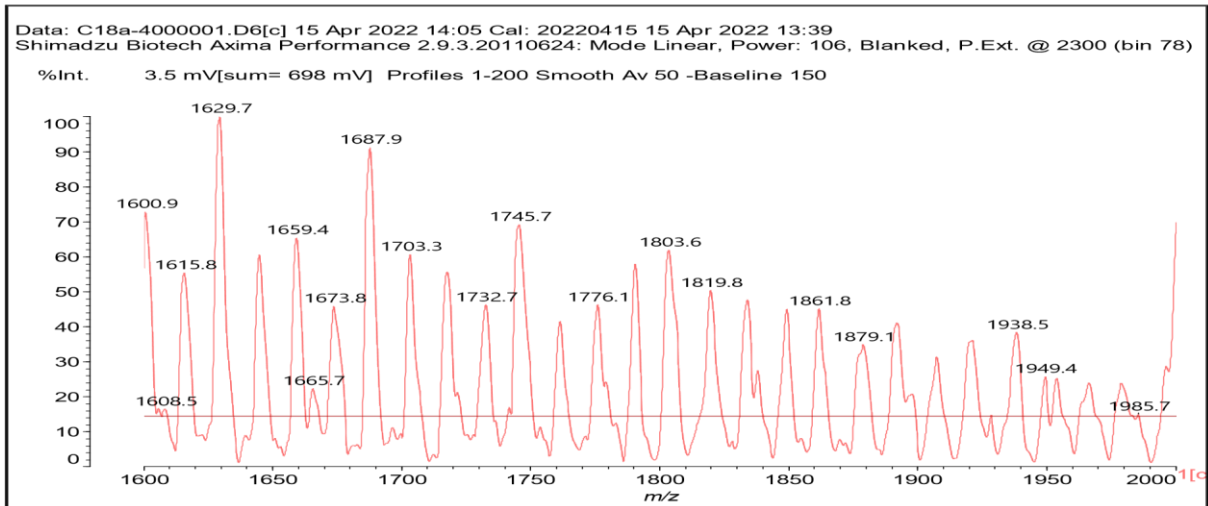




b

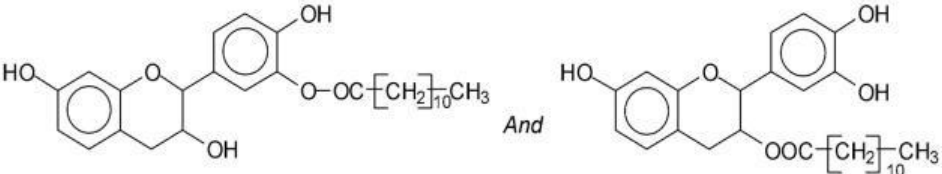
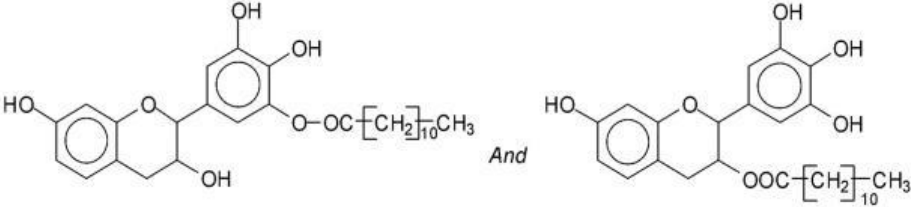
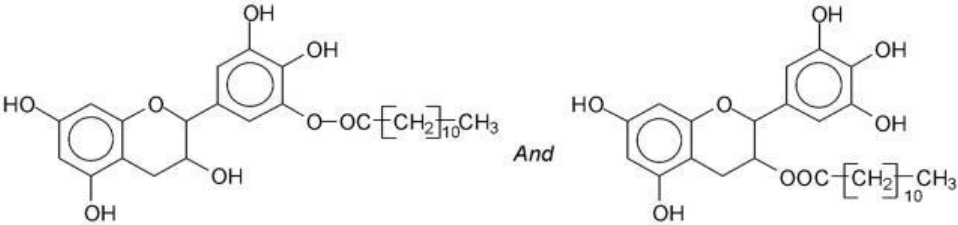


c



Annex. 2. MALDI-TOF mass spectrum of oil-grafted tannin with oleoyl chloride (a) from 400 Da to 800 Da, (b) from 800 Da to 1200Da,(c) from 1200 Da to 1600 Da , (d)from 1600 Da to 2400 D

Annex. 3-Characterization of oil-grafted tanin with lauryl chloride by MALDI-TOF

Molecules	Peak Experimental	Peak Calculated
 <p>Fisetinidin-laurate, protonated</p>	457 Da no Na <sup>+</sup>	457 Da
 <p>Robinetinidin-laurate</p>	471 Da no Na <sup>+</sup>	472 Da
 <p>Gallocatechin-laurate</p>	487 Da no Na <sup>+</sup>	488 Da
robinetinidin-robinetinidin dimer, deprotonated	575-577 Da no Na <sup>+</sup>	576-577 Da
fisetinidin-robinetinidin, protonated	587 Da with Na <sup>+</sup>	586 Da
gallocatechin-robinetinidin	617 Da with Na <sup>+</sup>	617 Da
(gallocatechin) <sub>2</sub>	633 Da with Na <sup>+</sup>	633 Da

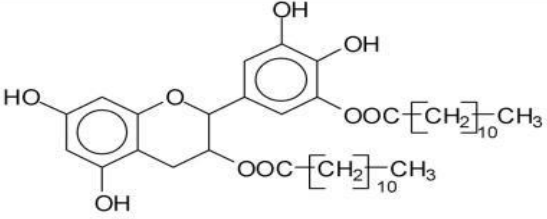
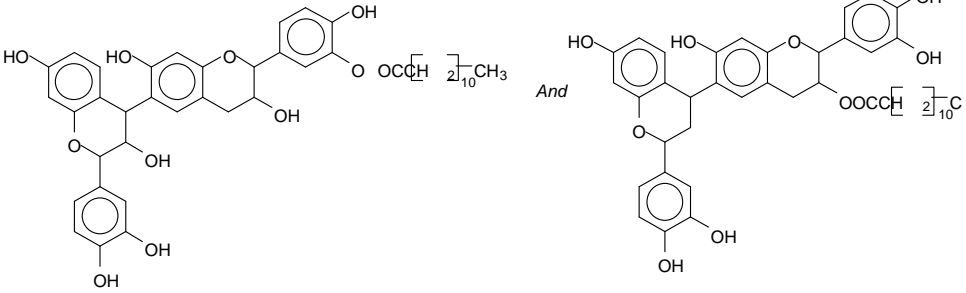
<p>Fisetinidin-(laurate)<sub>2</sub> + Na<sup>+</sup></p>	661 Da with Na <sup>+</sup>	661 Da
<p>Robinetinidin-(laurate)<sub>2</sub> + Na<sup>+</sup></p>	675-677 Da with Na <sup>+</sup>	677 Da
Gallocatechin-(laurate) <sub>2</sub> + Na <sup>+</sup>	691 Da with Na <sup>+</sup>	691 Da

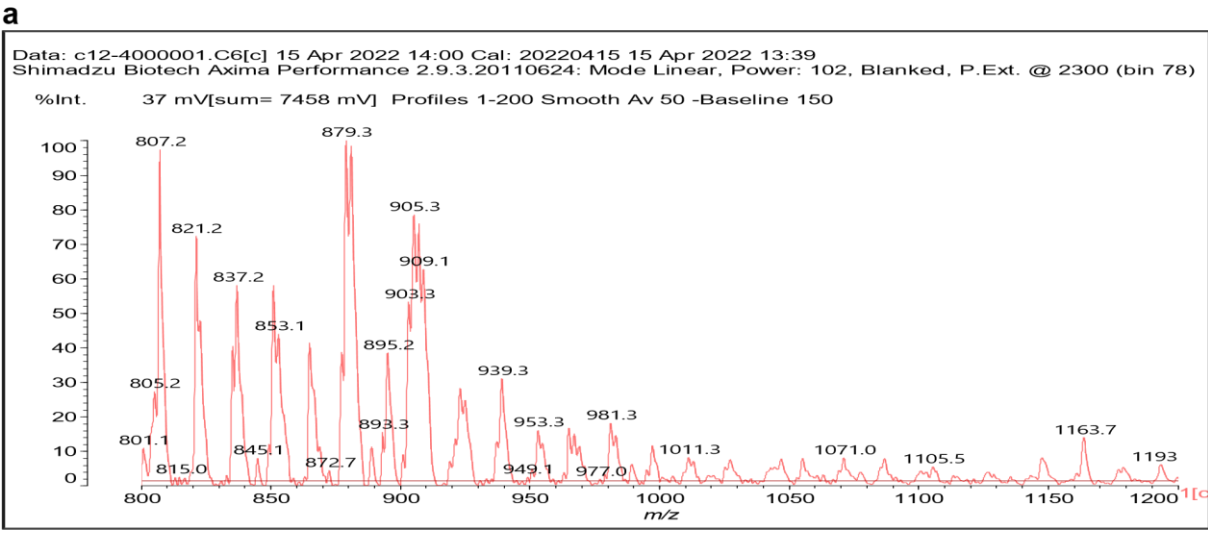
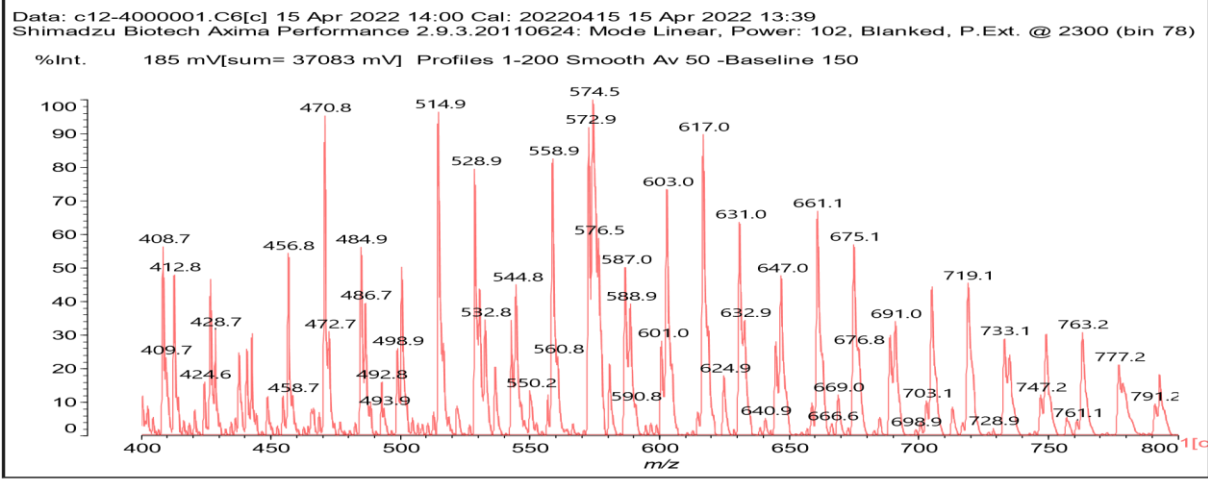
<p>(fisetinidin)<sub>2</sub>-laurate</p>	747 Da with Na <sup>+</sup>	750

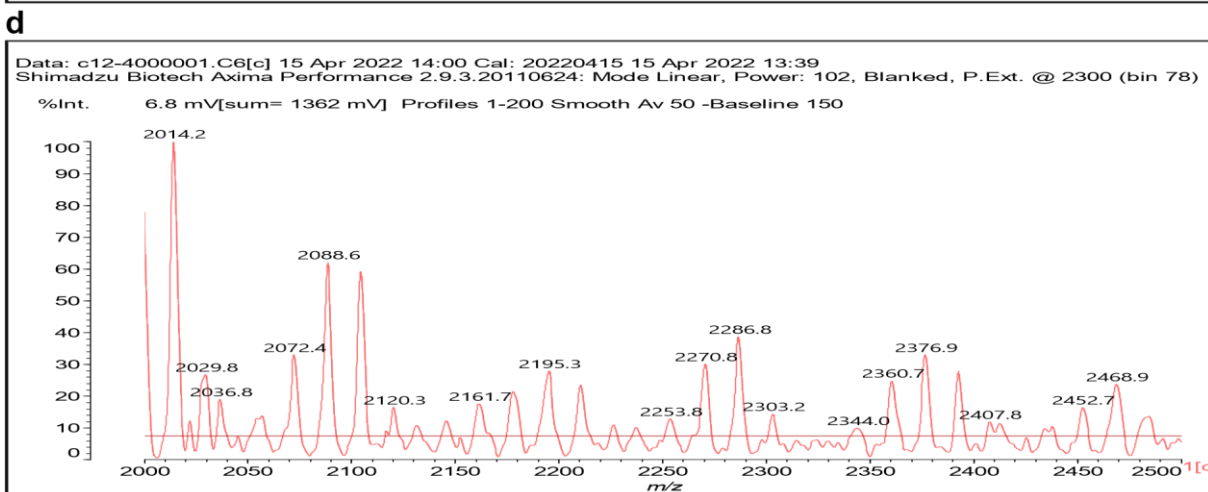
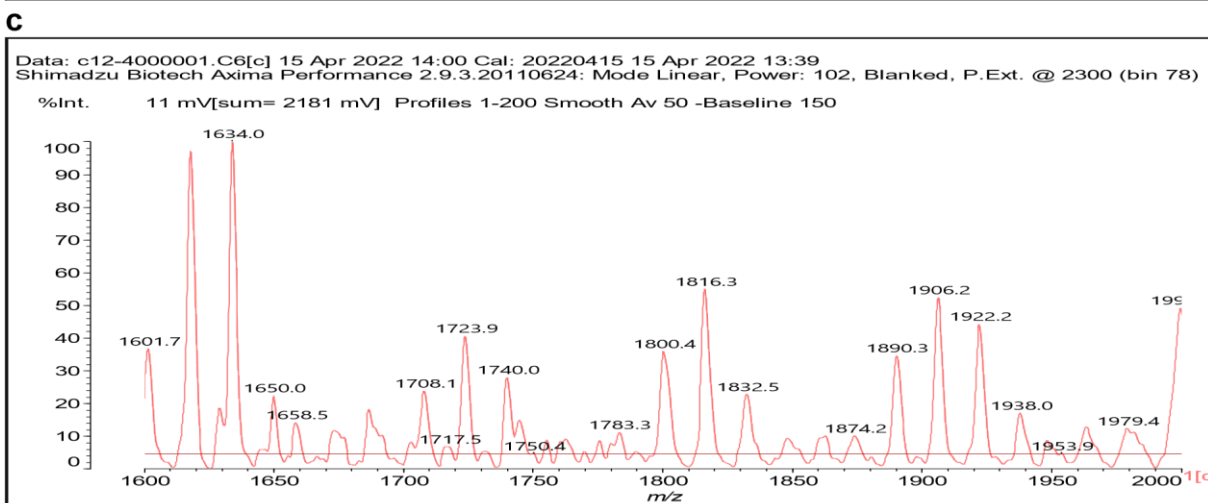
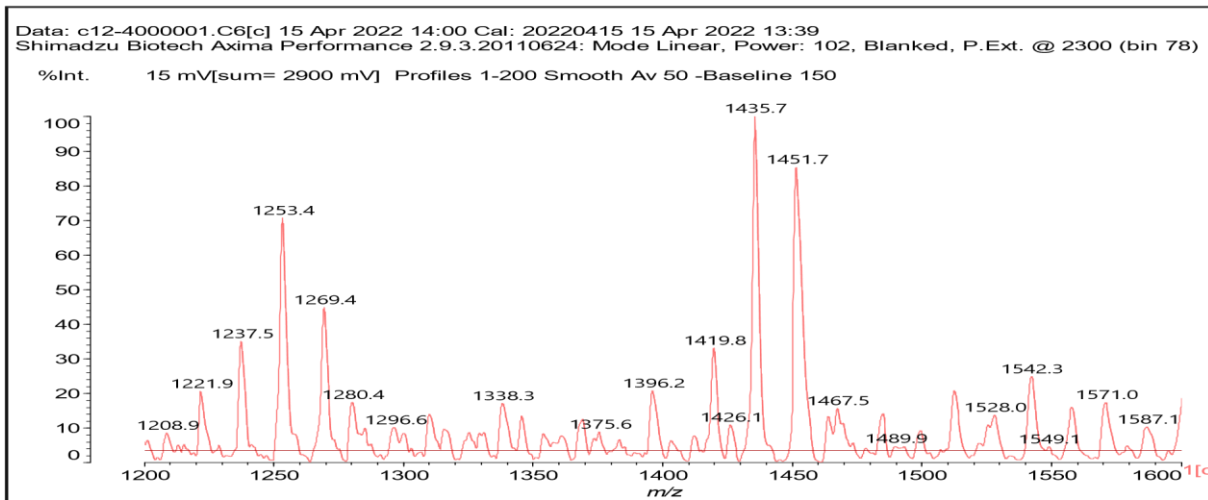


- (robinetinidin) <sub>2</sub> -laurate, protonated	761 Da no Na <sup>+</sup>	760 Da
- robinetinidin-galocatechin-laurate, protonated	777 Da no Na <sup>+</sup>	776 Da
- (galocatechin) <sub>2</sub> -laurate	815 Da with Na <sup>+</sup>	815 Da
-(robinetinidin) <sub>2</sub> -galocatechin trimer, deprotonated	879 Da no Na <sup>+</sup>	880 Da
- (galocatechin) <sub>2</sub> -robinetinidin trimer, no Na <sup>+</sup> , deprotonated	895 Da no Na <sup>+</sup>	896 Da
- fisetinidin-robinetinidin-(laurate) <sub>2</sub>	949-953 Da	949 Da
- robinetinidin-galocatechin-(laurate) <sub>2</sub>	with Na <sup>+</sup>	981 Da
- (galocatechin) <sub>2</sub> -(laurate) <sub>2</sub>	981 Da with Na <sup>+</sup>	997 Da
- glucose-(robinetinidin) <sub>2</sub> -fisetinidin	997 Da with Na <sup>+</sup>	1011 Da
- galocatechin-robinetinidin-(laurate) <sub>3</sub>	1011 Da, no Na <sup>+</sup>	1163 Da
- (galocatechin) <sub>2</sub> -(laurate) <sub>3</sub>	1163 Da with	1179 Da
- Glucose-(robinetinidin) <sub>2</sub> -fisetinidin-laurate	Na <sup>+</sup>	1193 Da
- (fisetinidin) <sub>2</sub> -robinetinidin-(laurate) <sub>2</sub>	1179 Da with	1221 Da
- (robinetinidin) <sub>2</sub> -fisetinidin-(laurate) <sub>2</sub>	Na <sup>+</sup>	1237 Da
- (robinetinidin) <sub>3</sub> -(laurate) <sub>2</sub> with Na <sup>+</sup>	1193 Da no Na <sup>+</sup>	1253 Da
- (robinetinidin) <sub>2</sub> -galocatechin-(laurate) <sub>2</sub>	1221 Da with	1269 Da
- fisetinidin-robinetinidin-(laurate) <sub>4</sub>	Na <sup>+</sup>	1317 Da
- (galocatechin) <sub>2</sub> -(laurate) <sub>4</sub>	1237 Da with	1338 Da
- (galocatechin) <sub>2</sub> -(laurate) <sub>4</sub>	Na <sup>+</sup>	1361 Da
- galocatechin-robinetinidin-(laurate) <sub>4</sub>	1253 Da with	1344 Da
- Glucose-(robinetinidin) <sub>2</sub> -fisetinidin-(laurate) <sub>2</sub>	Na <sup>+</sup>	1375 Da
- (robinetinidin) <sub>2</sub> -fisetinidin-(laurate) <sub>3</sub>	1269 Da with	1419 Da
- (robinetinidin) <sub>3</sub> -(laurate) <sub>3</sub>	Na <sup>+</sup>	1435 Da
- (robinetinidin) <sub>2</sub> -galocatechin-(laurate) <sub>3</sub>	1317 Da with	1451 Da
- robinetinidin-(galocatechin) <sub>2</sub> -(laurate) <sub>3</sub>	Na <sup>+</sup>	1467 Da
- fisetinidin-robinetinidin-(laurate) <sub>5</sub>	1338 Da no Na <sup>+</sup>	1499 Da
- robinetinidin-galocatechin-(laurate) <sub>5</sub>	1361 Da with	1526 Da
- (galocatechin) <sub>2</sub> -(laurate) <sub>5</sub>	Na <sup>+</sup>	1543 Da
- Glucose-(robinetinidin) <sub>2</sub> -fisetinidin-(laurate) <sub>3</sub>	1344 Da with	1557 Da
- fisetinidin-robinetinidin-(laurate) <sub>6</sub>	Na <sup>+</sup>	1681 Da
- robinetinidin-galocatechin-(laurate) <sub>5</sub> - (galocatechin) <sub>2</sub> -	1375 Da no Na <sup>+</sup>	1708 Da
(laurate) <sub>6</sub>	1419 Da with	1724 Da
- Glucose-(robinetinidin) <sub>2</sub> -fisetinidin-(laurate) <sub>4</sub>	Na <sup>+</sup>	1740 Da
- fisetinidin-robinetinidin-(laurate) <sub>7</sub>	1435 Da with	1863 Da
	Na <sup>+</sup>	
	1451 Da with	
	Na <sup>+</sup>	
	1467 Da with	
	Na <sup>+</sup>	
	1499 Da with	
	Na <sup>+</sup>	
	1526 Da with	
	Na <sup>+</sup>	
	1543 Da with	
	Na <sup>+</sup>	
	1557 Da no Na <sup>+</sup>	
	1681 Da with	
	Na <sup>+</sup>	

	1708 Da with Na <sup>+</sup> 1724 Da with Na <sup>+</sup> 1740 Da no Na <sup>+</sup> 1863 Da with Na <sup>+</sup>	
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<p>(fisetinidin)<sub>2</sub>-laurate</p> 	747 Da with Na <sup>+</sup>	750

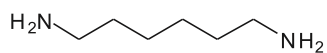




Annex. 4-MALDI-TOF mass spectrum of oil-grafted tannin with lauryl chloride (a) from 400 Da to 800 Da, (b) from 800 Da to 1200 Da, (c) from 1200 Da to 1600 Da, (d) from 1600 Da to 2000 Da, (e) from 2000 Da to 2500 Da

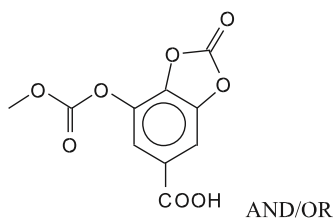
Annex. 5-Species assignments of MALDI ToF analysis for a chestnut tanin extract non-isocyanate polyurethane (NIPU) foam

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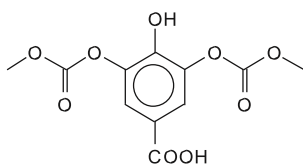


113 Da = no Na<sup>+</sup>, deprotonated

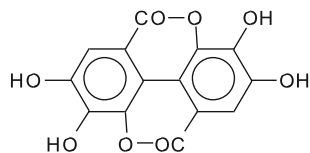
254 Da = no Na<sup>+</sup>, and 277 Da (small) with Na<sup>+</sup>



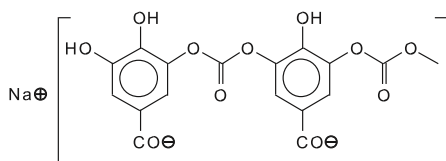
309 Da with Na<sup>+</sup>



326 Da = Ellagic Acid with Na<sup>+</sup>, calc. 325 Da



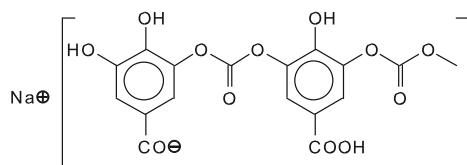
411 Da = with Na<sup>+</sup>



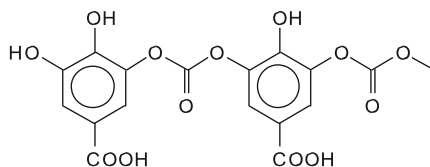
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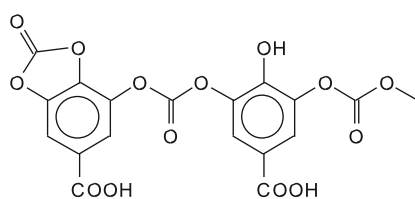
430 Da = with Na<sup>+</sup>



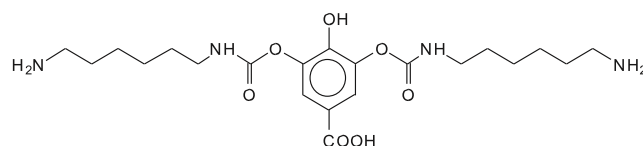
447 Da = with Na<sup>+</sup>



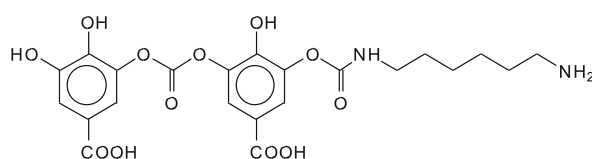
475 Da = with Na<sup>+</sup>



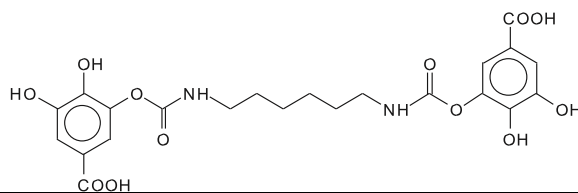
477 Da = with Na<sup>+</sup>



529 Da = with Na<sup>+</sup>, deprotonated, calc. 530 Da

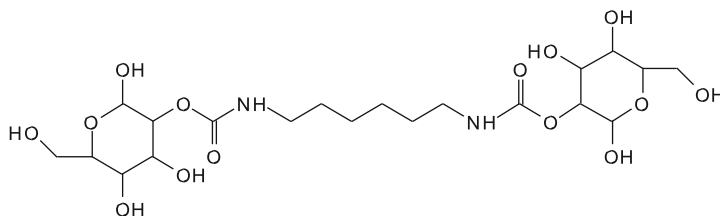


AND, with Na<sup>+</sup>

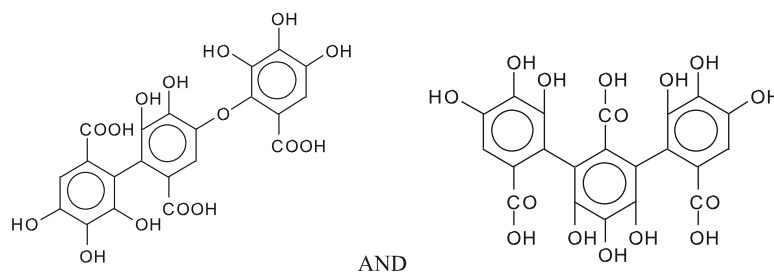


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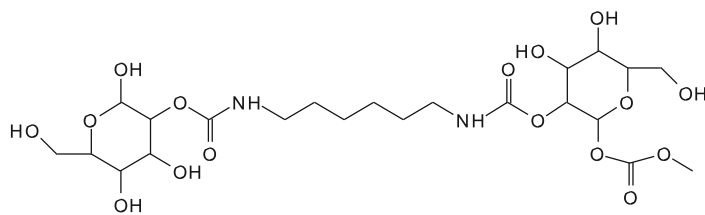
AND, no Na<sup>+</sup>, glucose, calc. 529 Da



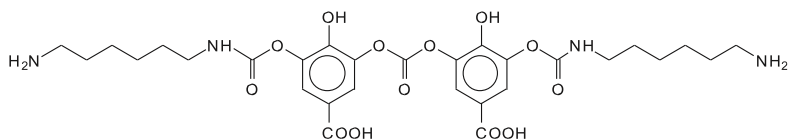
529 Da = Valoneic acid, and/or nonahydroxytriphenoic acid, with Na<sup>+</sup>,



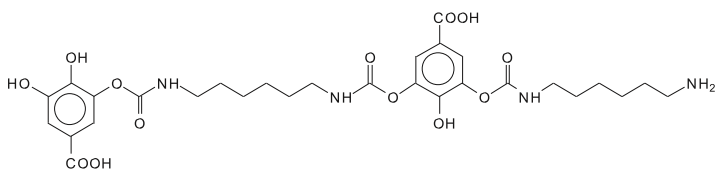
632 Da = 2 × Na<sup>+</sup>, deprotonated, glucose, calc. 631 Da



670 Da = with  $\text{Na}^+$ , deprotonated, calc. 671 Da

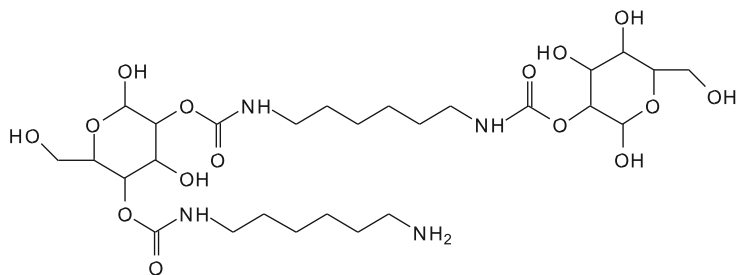


AND, calc. 672 Da, with  $\text{Na}^+$

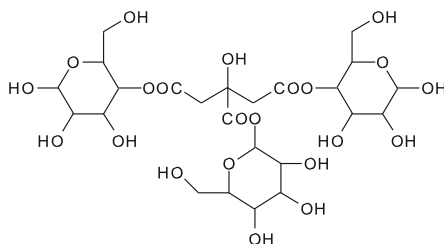


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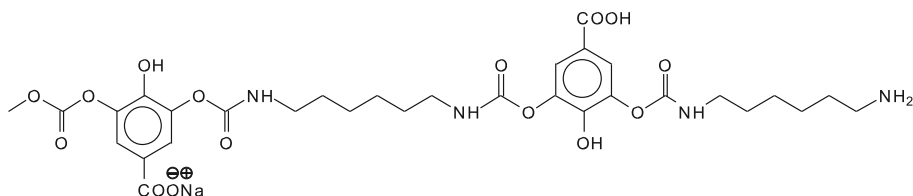
AND, Glucose, no  $\text{Na}^+$



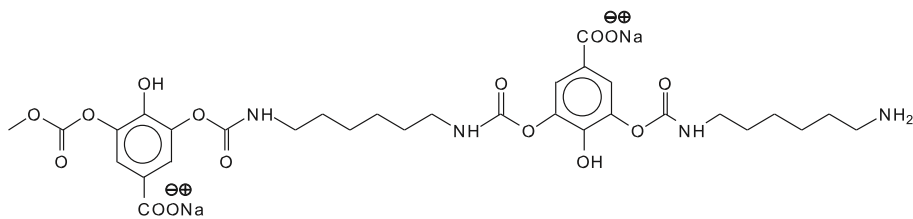
699 Da = with  $\text{Na}^+$ , 3 glucoses reacted on citric acid (small), deprotonated, calc. 699 Da



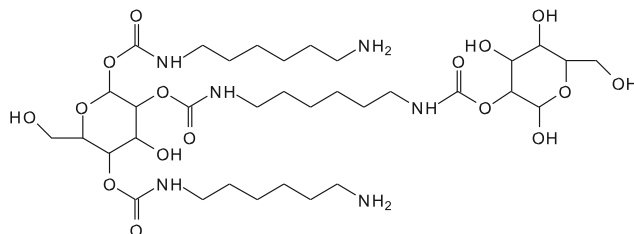
731 Da = with  $1 \times \text{Na}^+$



753 Da = with  $2 \times \text{Na}^+$ , calc. 753 Da<sup>+</sup>



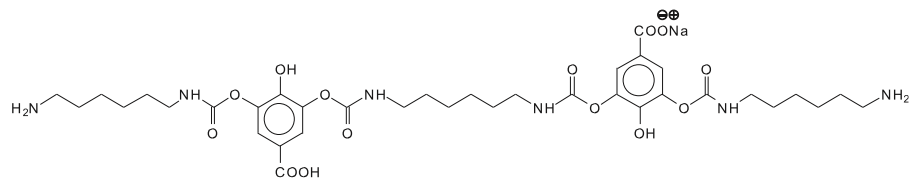
810 Da = no Na<sup>+</sup>, glucose, deprotonated, calc. 811 Da



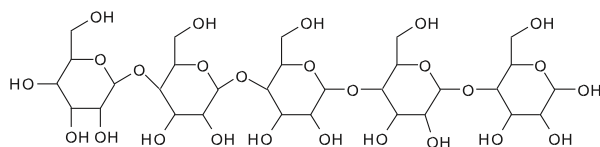
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AND/OR Tetragalloylglucose with Na<sup>+</sup>, calc. 809 Da, experimental 809 Da

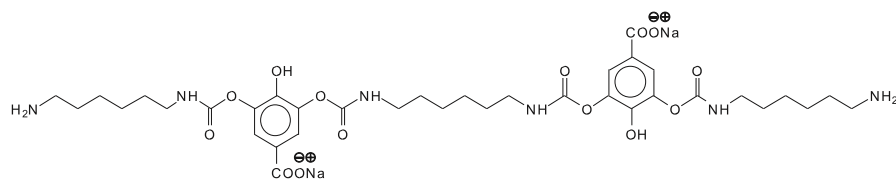
817 Da = with 1 × Na<sup>+</sup>, protonated, calc. 816 Da



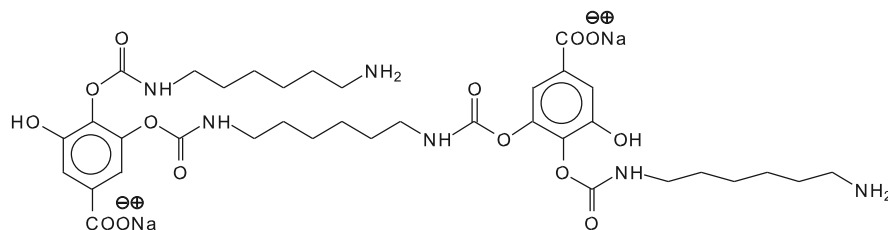
826 Da = no Na<sup>+</sup>, deprotonated, calc. 827 Da



838 Da = with 2 × Na<sup>+</sup>, calc. 838 Da

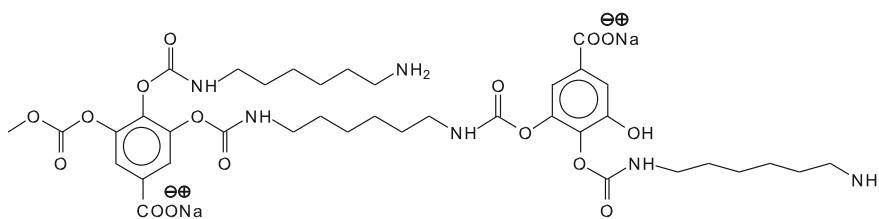


And equivalent isomers such as



896 Da = with 2 × Na<sup>+</sup>, protonated, calc. 895 Da



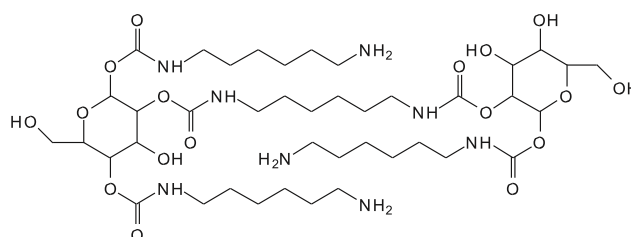


923 Da = Tetragalloyl glucose with 1 NIPU link with Na<sup>+</sup>, protonated calc. 922 Da

938 Da = pentagalloyl glucose, or castalagin no Na<sup>+</sup>

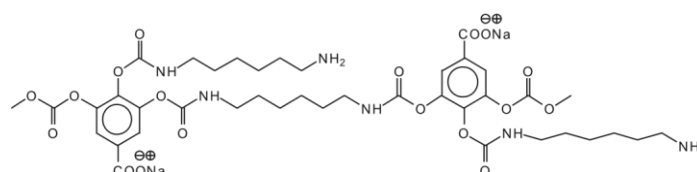
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953 Da = no Na<sup>+</sup>, deprotonated, glucose, calc. 953

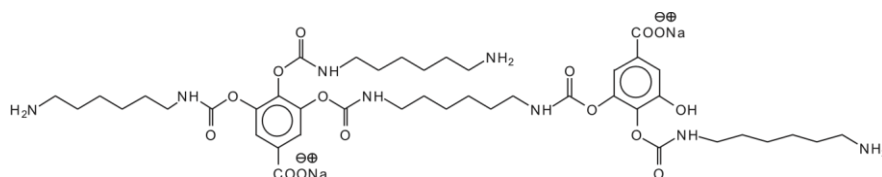


AND

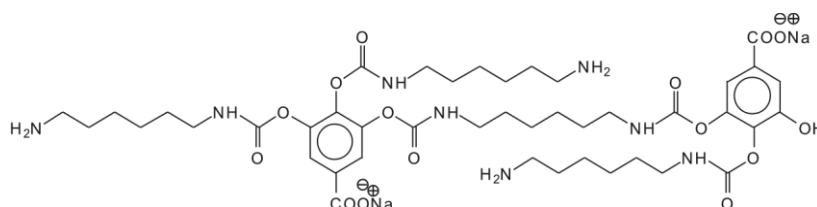
953 Da, Calc 953 Da, with 2 × Na



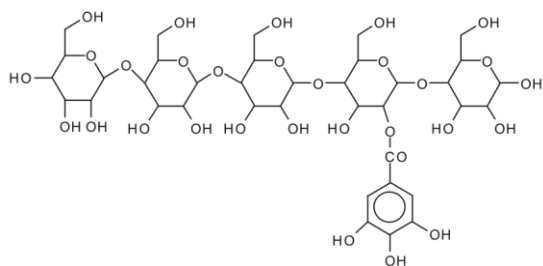
977 Da = with 2 × Na<sup>+</sup>, deprotonated, calc. 977 Da



AND

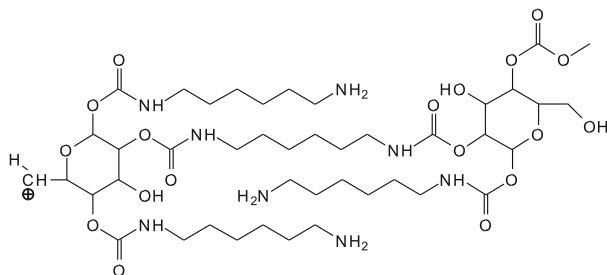


977 Da = no Na<sup>+</sup>, calc. 979 Da

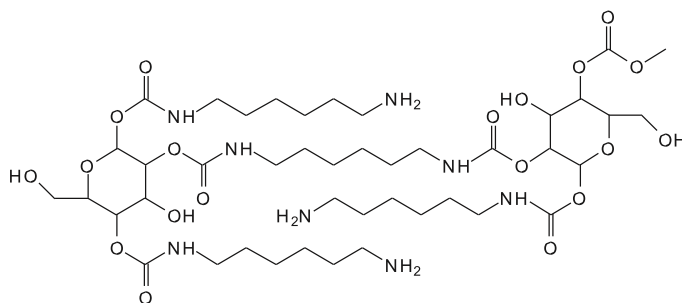


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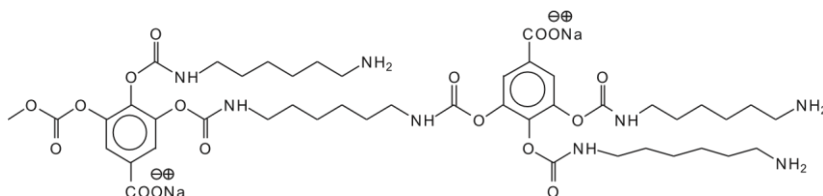
1020 Da = with Na<sup>+</sup>, glucose



1037 Da = with Na<sup>+</sup>, glucose, protonated, calc. 1037 Da

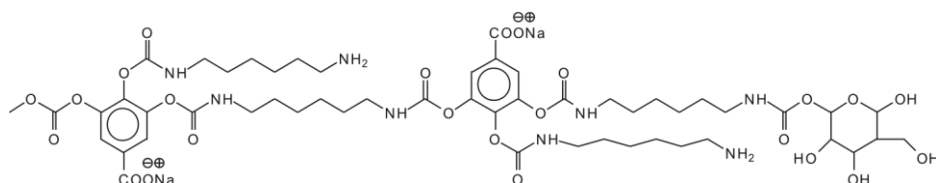


AND 1037 Da with 2 × Na<sup>+</sup>



1231 Da = 1 Galloyl residue + 8 stripped glucose residues = octamer [PIZZI 2009 JAPS]

1242 Da = 2 × Na<sup>+</sup> on gallic acid, demonstrate glucose and gallic moieties participate equally to NIPU, and 1264 Da with 1 more Na<sup>+</sup> on glucose



1260 Da = Tetragalloyl glucose with Na<sup>+</sup>, with 4 NIPU, protonated calc. 1258 Da

1275 Da = Pentagalloyl glucose, 3 × NIPUS, protonated, calc. 1275 Da, no Na<sup>+</sup>

1299 Da = Pentagalloyl glucose, protonated, 3 NIPUs calc. 1298 Da, with Na<sup>+</sup>

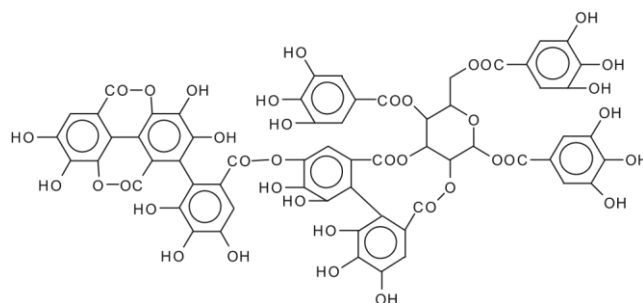
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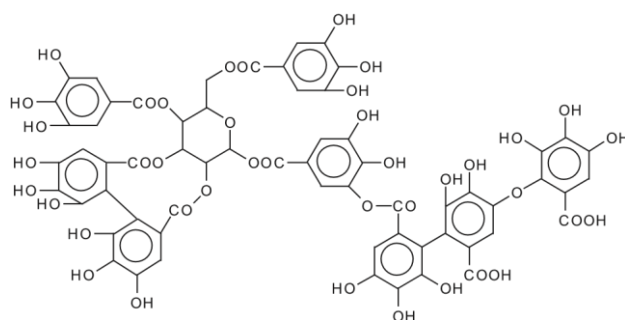
1348 Da = Tetragalloyl glucose with Na<sup>+</sup>, with 5 NIPU, protonated calc. 1346 Da

1365 Da = 1 Galloyl residue + 9 stripped glucose residues = nonamer [Pizzi2009 JAPS]

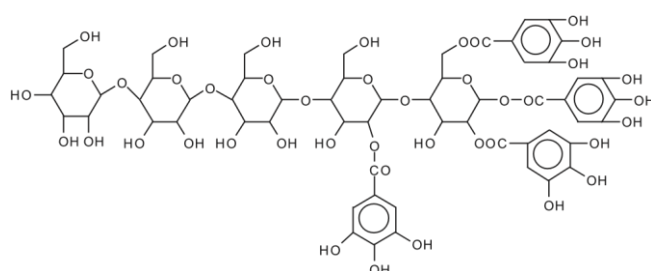
1390 Da = Pentagalloyl glucose (or castalagin) ester linked to flavogallonic acid, no Na<sup>+</sup>,  
and 1413 Da with Na<sup>+</sup>



1426 Da = Pentagalloyl glucose (or castalagin) ester linked to either valoneic acid or nonahydroxytriphenoic acid, for example



1437 Da = no Na<sup>+</sup>, calc. 1437 Da



1524 Da = Pentagalloyl glucose, protonated, 5 NIPUs calc. 1524 Da, with Na<sup>+</sup>

1558 Da = 1390 Da + 1 gallic acid (170 Da) linked directly (-2 Da), no Na<sup>+</sup>

1595 Da = 1426 Da + 1 gallic acid (170 Da) linked directly (-2 Da), with Na<sup>+</sup>

1635 Da = Pentagalloyl glucose, 6 × NIPUs calc. 1635 Da, with Na<sup>+</sup>

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(Continued)

1690 Da = 1390 Da + 1 ellagic acid (302 Da), linked directly (-2 Da), no Na<sup>+</sup>, and 1713 Da with Na<sup>+</sup>

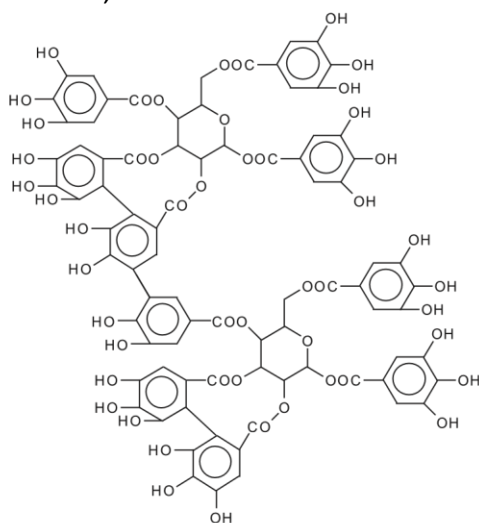
1712 Da = 1426 + 2 × NIPUs, protonated with Na<sup>+</sup>, calc. 1711 Da

1747 Da = Pentagalloyl glucose, 6 × NIPUs calc. 1747 Da, with Na<sup>+</sup>

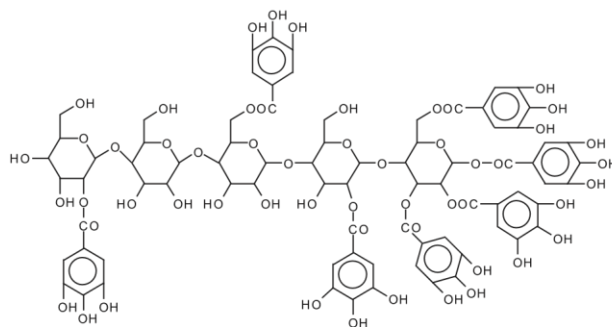
1762 Da = 1 Galloyl residue + 12 stripped glucose residues = dodecamer [Pizzi 2009 JAPS]

1819 Da = 1762 + 1 × Carbonate, deprotonated

1861 Da = Dipentagalloyl glucose, no Na<sup>+</sup>, no NIPUs, protonated calc. 1859 Da, no NIPUs, calculated according to structure VIII, see text



1892 Da = no Na<sup>+</sup>, galloylglucoses with stripped galoyl residues, as for structure XI, see text



+

2001 Da = Dipentagalloyl glucose, deprotonated, no Na<sup>+</sup>, 1 × NIPUs, calc. 2003 as structure VIII, see text

2044 Da = 1 Galloyl residue + 12 stripped glucose residues + 2 × NIPUs

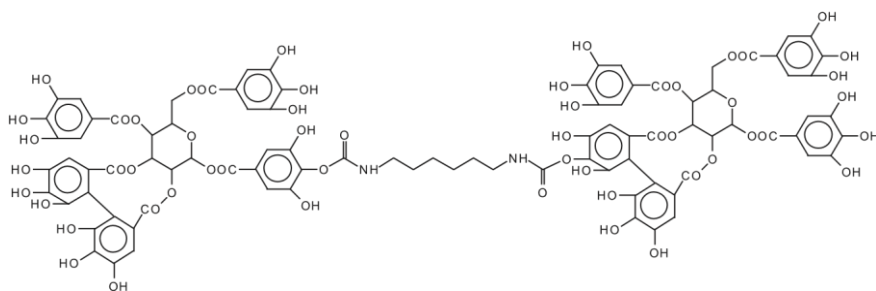
1898 Da = Dipentagalloyl glucose, with Na<sup>+</sup>, no NIPUs, intense peak, as for structure IX, see text

2018 Da = Dipentagalloyl glucose, with Na<sup>+</sup>, 1 × NIPU, deprotonated, calc. 2017, as for structure IX, see text

2044 Da = PentagalloylG-NIPU-Pentagalloyl glucose, no Na<sup>+</sup>, as for structure VII, see text

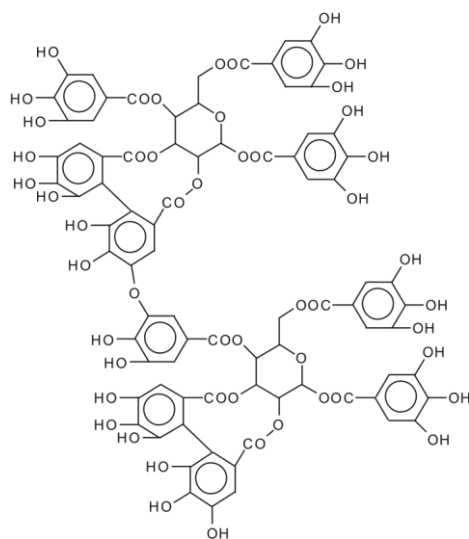
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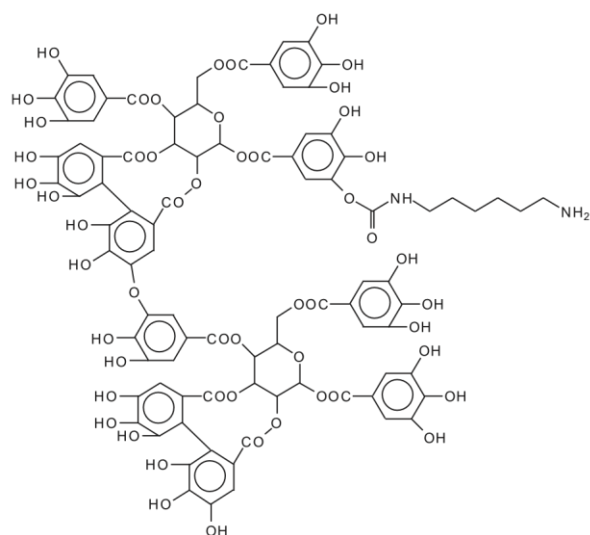


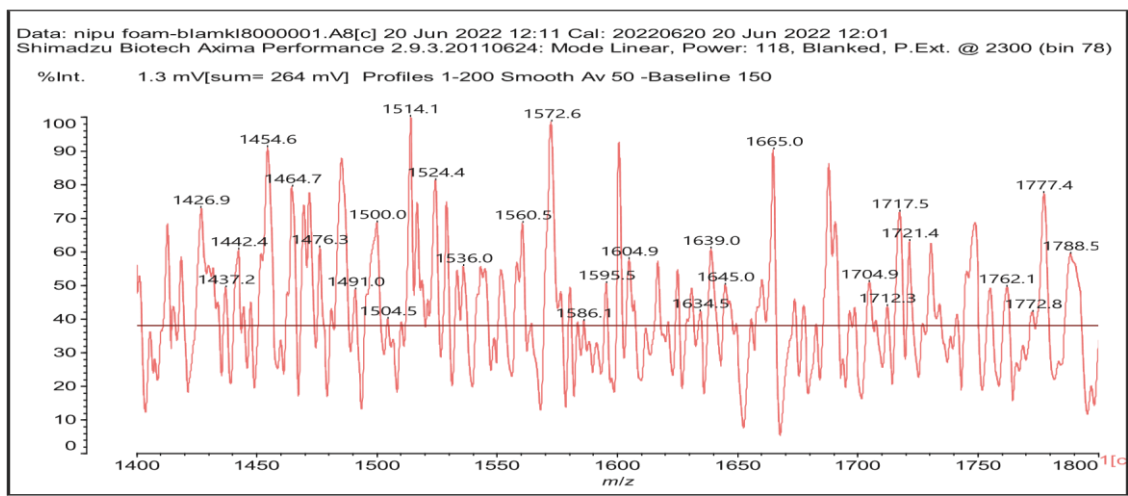
2302 Da = Dipentagalloylglucose, with  $\text{Na}^+$ ,  $3 \times \text{NIPU}$ , calc. 2301 Da, as for structure IX series, see text Third option

1858–1859 Da = Dipentagalloyl glucose, no  $\text{Na}^+$ , no NIPUs, protonated. as for structure X, see text



2001.6 Da = Dipentagalloyl glucose, deprotonated, no  $\text{Na}^+$ ,  $1 \times \text{NIPUs}$ , calc. 2001.6 Da, as for structure X series, see text





Annex. 6-MALDI ToF Spectra of chestnut tanin extract non-isocyanate polyurethane (NIPU) bio-foam in the 1400–1800 Da range

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## Résumé

La transition vers une économie plus durable et respectueuse de l'environnement a suscité un vif intérêt pour le développement de matériaux biosourcés issus de ressources renouvelables. Parmi ces matériaux, ceux dérivés du tanin, un composé phénolique naturellement présent dans de nombreuses plantes, ont attiré une attention croissante en raison de leurs propriétés uniques et de leur potentiel d'application dans différents domaines.

Les matériaux biosourcés dérivés du tanin offrent de nombreux avantages par rapport aux matériaux traditionnels issus de ressources fossiles. Tout d'abord, ils sont renouvelables et leur production ne contribue pas à l'épuisement des ressources non renouvelables. De plus, ils présentent souvent une empreinte environnementale réduite, car ils peuvent être obtenus à partir de déchets de l'industrie agroalimentaire ou de plantes cultivées spécifiquement à cet effet.

Les tanins, en tant que précurseurs de matériaux biosourcés, possèdent des caractéristiques intéressantes telles que leur capacité à former des liaisons chimiques, leur biocompatibilité et leur résistance aux UV. Ces propriétés permettent d'envisager leur utilisation dans des domaines tels que la chimie des polymères, la fabrication des matériaux d'isolation, les adhésifs, les composites.

L'objectif de cette étude est d'explorer les possibilités offertes par les matériaux dérivés du tanin dans le domaine des matériaux biosourcés, tels que les mousses d'isolation et les composites en bois. Nous examinerons les différentes méthodes de modification et de transformation des tanins pour améliorer leurs performances et leurs applications. Nous analyserons également les propriétés physico-chimiques des matériaux obtenus et évaluerons leur potentiel pour remplacer les matériaux synthétiques dérivés des ressources fossiles.

En résumé, les matériaux biosourcés dérivés du tanin offrent une alternative prometteuse et durable aux matériaux traditionnels issus de ressources non renouvelables. Leur utilisation permet de réduire notre dépendance aux ressources fossiles et de contribuer à la transition vers une économie circulaire et respectueuse de l'environnement. Cette étude vise à approfondir notre compréhension de ces matériaux et à explorer leur potentiel pour des applications innovantes dans divers secteurs industriels.

## **Abstract**

The transition to a more sustainable and environmentally friendly economy has generated a strong interest in the development of biobased materials from renewable resources. Among these materials, those derived from tanin, a phenolic compound naturally present in many plants, have attracted increasing attention due to its unique properties and its potential for application in various fields.

Bio-based materials derived from tanin offer many advantages over traditional materials from fossil resources. First, they are renewable, and their production does not contribute to the depletion of non-renewable resources. Moreover, they often have a reduced environmental footprint, as they can be obtained from waste from the food industry or plants grown specifically for this purpose.

Tanins, as precursors of bio-based materials, have characteristics interesting such as their ability to form chemical bonds, their biocompatibility, and their UV resistance. These properties make it possible to envisage their use in fields such as polymer chemistry, manufacturing insulation materials, adhesives, and composites.

The objective of this study is to explore the possibilities offered by materials derived from tanin in the field of biobased materials. It looks at the different methods of modification and transformation of tanins to improve their performance and their applications. It will also analyze the physio-chemical properties of the materials obtained and evaluate their potential to replace synthetic materials derived from fossil resources.

In summary, bio-based materials derived from tanin offer a promising and sustainable alternative to traditional materials from non-renewable resources. Their use would reduce the dependence on fossil resources and contribute to the transition to a circular economy that respects the environment. This study aims to deepen our understanding of these materials and to explore their potential for innovative applications in various industrial sectors.