DEVELOPMENT OF GREEN ADHESIVES FOR FIBREBOARD MANUFACTURING, USING TANNINS AND LIGNIN FROM PULP MILL RESIDUES

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In order to reduce formaldehyde emissions from wood panels and to develop green adhesives, natural phenolic polymers of tannins and lignin have been investigated as substitutes of petrol-based chemicals used in wood panels. The potential of several wood barks, obtained from pulp mills as industrial wastes, has been evaluated for tannin extraction and further for their adhesive properties. Aqueous extractions were carried on wood barks of five different tree species on a laboratory scale – Aleppo pine barks led to the highest yield (15%) compared to spruce, Douglas fir, maritime pine and eucalyptus. Urea and sulfite used as water-additives favoured the extraction of condensed tannins, especially for spruce and Douglas fir barks. Eucalyptus barks presented the lowest tannins contents. Pyr-GC/MS of the bark extracts showed that Douglas fir and Aleppo pine tannins were mainly constituted of phenol and catechol tannins. The adhesive potential of these tannins was also established. Cooking liquors from pulp mills are very rich in lignin. Lignin was isolated by acidification/precipitation of black liquors. The abilities of softwood and hardwood kraft liquors under several extraction conditions were compared. After glyoxylation, these lignins presented interesting adhesive properties. Furthermore, novel formulations of [tannin/hexamine + glyoxylated lignin] were tested for wood particleboard manufacturing. The internal bond strength of a panel manufactured with 60% tannin/40% lignin satisfied the value required by the European standard.

Keywords: lignin, tannin, pulping liquor, bark, adhesives, phenol, particleboard, panel, green chemical, wood, residues, sustainability, formaldehyde

INTRODUCTION

The production of European wood panels rose to ~50 million m^3 in 2004 (30% of the world production). France is the second largest productive country in Europe, with 6.7 million m^3 of fibre/particleboards manufactured in 2005.[1] The fibre/particle cohesion is generally provided by the addition of 5-12% (w/w) of adhesives. Phenolic and amino resins are widely used as binders in fibreboard and particleboard manufacturing. Amino resins are usually based on urea-formaldehyde or melamine-formaldehyde, whereas phenolic resins are produced by condensation of phenols and formaldehyde. Recently, formaldehyde has been classified as a probable human carcinogen and its use could be limited in the near future.[2] In order to reduce formaldehyde emissions from wood panels, new environmentally friendly adhesives need to be developed. The main natural resins used as wood panel binders are vegetal tannin adhesives, lignin adhesives and, more recently, soy protein adhesives.

Tannins, natural polyphenolic compounds, are present in large concentrations in wood barks. They are natural hydrophilic complexing agents. Wood adhesives from condensed flavonoid tannins have been developed, especially from acacia (Mimosa – *Acacia mearnsii* De Wild) and

quebracho (*Schinopsis lorentzii*) tannins.[3] *Pinus radiata*, a fast growing pine species from South America and Spain, contains tannins with a high degree of polymerisation, which are especially reactive,[4] suitable for economical industrial tannin production. The flavonoid units in such tannins present phloroglucinol or resorcinol A-rings and catechol B-rings (Fig. 1).

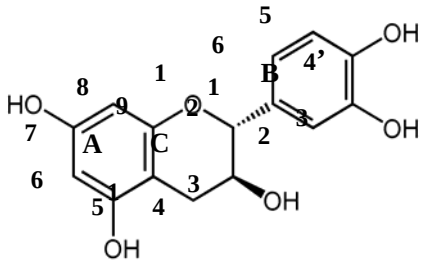

Figure 1: Phloroglucinol or resorcinol-type A ring and catechol-type B ring structure of condensed tannin

From the point of view of both molecular size and reactivity, phloroglucinolic tannins (i.e. mimosa bark extract) are less interesting than resorcinolic tannins (i.e. pine bark extract).[5] In order to develop industrial green wood-based adhesives, tannins need to be easily available and in large quantity. The addition of sulphite during aqueous bark extraction allows limiting the tannin auto-condensation and the formation of phlobaphenes. Also, sulphite leads to the breaking of interflavonoid links, making tannins more soluble.[6] Urea and ammonia allow the increase of the extraction yield and lead to better final adhesive properties, respectively.[6,7]

During pulping, lignin macromolecules are degraded and modified, its polymeric nature being however maintained. The phenolic character of lignin makes possible the substitution of of phenol by lignin in phenol-formaldehyde resins (PF)[8] Nevertheless, lignin addition is often limited to 20% of phenol to ensure adhesive properties. A higher percentage can be achieved only if the reactivity of lignin is chemically enhanced. Lignin can react with formaldehyde mainly through unsubstituted 5-position and form hydroxymethylated species in alkaline solution with glyoxal, leading to the polymerisation of lignin. This reaction is favoured especially with high molecular weight lignin.[9]

Bark wastes and cooking liquors from the pulp and paper industry represent huge quantities of suitable raw materials for tannin and lignin recovering. This study aims to investigate industrial bark samples from different European wood species for aqueous tannin extraction, and industrial cooking liquors from different pulping processes for lignin recovering.

EXPERIMENTAL

Tannin extraction

Two sets of experiments were carried out: first, experiments were performed on several barks on a laboratory scale, in order to optimize aqueous extraction and to select the most interesting bark samples, then, a large-scale study was carried out on several kilograms of industrial samples in order to produce sufficient quantity of tannin for adhesives preparations.

Laboratory aqueous extractions

Five different barks, from pulp mills were studied in the laboratory: spruce (*Picea abies*), maritime pine (*Pinus pinaster*), Aleppo pine (*Pinus halepensis*), Douglas fir (*Abies alba*) and eucalyptus (*Eucalyptus globulus*). They were air-dried and ground (particles Ø <3mm). 100 g of bark (expressed as oven-dried bark) were extracted by 500 mL of aqueous solution (ratio L/S of 5:1, as reported by Patel *et al*.[10] at 75 °C during 1 h, under reflux. The extract was filtrated on sintered glass N°1 before analysis. Four different aqueous solutions were tested: (1) aqueous solution: tap water, (2) urea solution containing 2% of urea, (3) urea/sulphite solution containing 2% urea and 2% sulphite (Na_2SO_3), (4) sulphite/carbonate solution with 2% sulphite and 0.5% carbonate ($NaHCO_3$).

Chemical characterization of tannins

Rapid spectrophotometric methods were applied to quantify phenolic compounds. Total phenolic substances were determined by the Folin-Ciocalteu (FC) method, using tannin acid as standard.[11,12] The total content of phenols was also quantified by UV measurement at 280 nm, as described by Antoine and Pizzi[13] using mimosa tannin as standard. Condensed tannins were determined by the butanol/HCl method,[13,14] using catechine and mimosa tannin as standards.

0.1 to 0.3 mg of dried bark extract was pyrolysed using a Pyrolab 2000, at 500 °C/4 s. GC/MS

pyrograms were recorded on an Agilent GC/MS equipped with HP1 column (30 m x 0.25 mm, film thickness – 0.25 µm), with a temperature programme as follows: 50 °C (1 min) – 5 °C/min – 300 °C.

Adhesive properties of tannins

The hardening reaction of a resin system or glue mixes can be evaluated by thermomechanical analysis (TMA), by the study of the rigidity of the wood–resin joint as a function of temperature. Thus, the different adhesive system tannins were thermomechanically analyzed under the same conditions. Samples of 45% tannin solution in water, to which 5% paraformaldehyde on tannin extract solids content had been added, were prepared. Triplicate samples of beech (*Fagus sylvatica*) wood alone, and of two beech wood plies, each 0.6 mm thick, bonded with each system, for a total samples dimension of 20×5×1.1 mm, were tested in non-isothermal mode between 25 °C and 250 °C, at a heating rate of 10 °C/min, 30 mg of resin, with a Mettler 40TMA apparatus in three-point bending, on a span of 18 mm, exercising a force cycle of 0.1/0.5 N on the specimens with each force cycle of 12 seconds (increase during 6 s and decrease during 6 s). The classical mechanics relation between force and deflection $E = [L3/(4bh3)]\ [\Delta F/(\Delta f)]$ allowed the calculation of Young's modulus E for each case tested. The deflection curves that allow MOE determination were obtained in the three-point bending TMA mode. The MOE of the wood joints bonded with different resin systems give a good indication of the final strength of the adhesive system tested and the possible end performance of the adhesive system tested.

Lignin recovering

Kraft pulping liquors

Black liquors from hardwood mix kraft pulping and softwood kraft pulping were studied. Lignin content was measured by the Klason method according to the standard method NF T 12-020, which allows quantifying the insoluble lignin in sulphuric acid. The soluble fraction was measured by a spectrophotometer at 280 nm.

Lignin precipitation

Different protocols of lignin precipitation were developed in this study. The more easily implemented were based on acidic precipitation. Black liquors at 35% solid content were acidified with 2% sulphuric acid under sharing at 300 rpm to reach different targeted pH – about 2 and 4. Another acidification protocol was based on gaseous CO_2 addition. In this case, CO_2 was introduced in the black liquor solution for 1 hour at constant flow under sharing to reach a constant pH. After precipitation, the solid precipitate was collected by centrifugation. Soluble residual chemicals and carbohydrates were removed by washing with 0.2% sulfuric solution. This step was repeated twice to purify the lignin extracted.

Wood panel adhesive application

Formulations

A tannin solution in water was prepared at 45% concentration, and its pH was adjusted to 10.4 with 33% NaOH water solution. A high pH was chosen as the hardener used performs best at such a pH. Hexamine was dissolved in water to form a 30% solution. It was added to the tannin extract solution on the basis of 5% hexamine solids on tannin extract solids. Glyoxylated lignin was added to the tannin/hexamine solution in order to get a tannin/lignin ratio of 60:40 (w/w). Hexamine hardener is now accepted by JIS A5908 as no formaldehyde source in the presence of a polyflavonoid condensed tannin. The total amount of natural material on dry resin solids was almost 94% and the thus prepared adhesive did not contain any synthetic resins.

Wood panel production and characteristics

Duplicate one-layer laboratory particleboards, with the dimension 350 mm × 310 mm × 14 mm, were prepared using a mixture of core particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) wood particles at 28 kg/cm^2 maximum pressure and 190-195 °C press temperature. Prior to resin addition, the wood particles had a moisture content of 2%. The resin solids load on dry wood was maintained at 10% of the total mix of tannin + glyoxylated lignin. The total pressing time was maintained at 7.5 minutes. All particleboards were tested for dry internal bond (IB) strength. The IB strength test, a relevant international standard test (EN 314-1 (1993) and EN 314-2 (2004)), is a tensile test perpendicular to the plane of the board and was done on five board specimens. Formaldehyde emissions were measured according to the European standard EN 717-3, by the flask method.

RESULTS AND DISSCUSION

Tannin characteristics of industrial bark extracts

Extraction yields and tannin contents

Extraction yields highly depended on the wood bark species (Fig. 2). Aleppo pine bark presented the highest extraction yield of all aqueous solutions tested, between 10% (aqueous solution) to 15% (urea/sulphite solution). This is slightly less than those mentioned for mimosa and *Pinus radiata* barks (i.e. 42.5% and 20%, respectively),[15,16] but high enough to foresee possible industrial exploitation. The extraction yield of Douglas fir barks was above 14% in case of urea/sulphite solution. Spruce, maritime pine and eucalyptus barks led to lower yields, especially eucalyptus.

Phenolic structures of tannin extracts

Phenolic tannins quantified by UV-280 nm (i.e. total tannins) were exceptionally high in all urea/sulphite extracts, representing 66% to 90% of the whole extract (Fig. 3).

Sulfite/carbonate solutions also led, in some cases, to high tannin contents in the extract, as noted for Aleppo pine, spruce and maritime pine barks. Urea, which reacts on C2 of the flavonoid heterocyclic ring on this ring opening,[6] thus inhibiting self-condensation and rearrangement to catechinic acid, would maintain open the tannin structure and then improve condensed tannin extraction. The determination of phenolics contents by FC method confirmed the high level of polyphenols in all Aleppo pine extracts. Sulfite/carbonate spruce bark extract and urea/sulfite Douglas fir bark also showed higher phenolic contents, compared to maritime pine and eucalyptus barks. By the BuOH/HCl method, urea/sulfite solution favours condensed tannin extraction, the highest content being obtained for Aleppo pine and Douglas fir barks.

Pyr-GC/MS allowed identifying aromatic structures constituting tannins, especially the nature of A and B rings.[17,18] The pyrograms of most softwood bark extracts were mainly constituted of phenol, methoxy-phenol, and to a lower extent, of catechol and methyl-catechol. Usually, water extracts present more impurities than urea, carbonate and urea+sulphite extracts. In the case of Douglas fir bark, the [urea+sulphite] extract presented especially high content of catechol B ring and a lower one of phenol-type A ring by-products. This observation confirmed previous results of high phenolic and condensed tannins in this extract. Aleppo pine bark extracts were particularly rich in phenol-type A ring and catechol-type B ring. In some cases, stilbene/terpene derivative compounds were found, particularly, in water extracts. The pyrograms of eucalyptus bark extracts presented only few aromatic peaks, with a lot of polysaccharide derivatives structures in the water extracts.

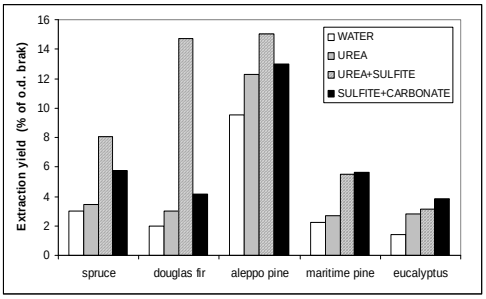

Figure 2: Aqueous extraction yields of industrial wood barks (in gram of dry extract per 100 g of eq. oven-dry bark)

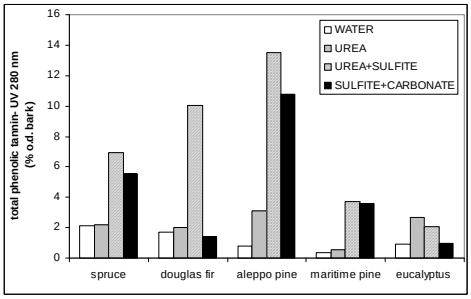

Figure 3: Total phenolic tannin contents of bark, expressed in equivalent mimosa tannin (in gram of dry extract per 100 g of eq. oven-dry bark)

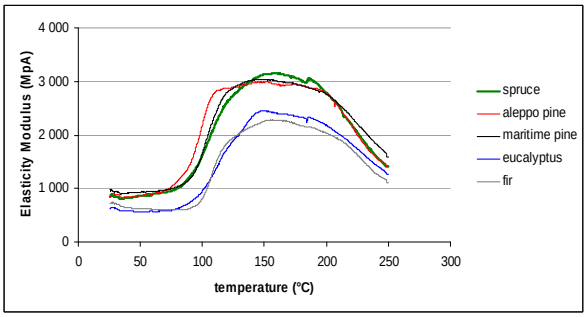

Figure 4: Thermomechanical analysis (TMA) of wood panels prepared with tannin-based adhesives: comparison of elasticity modulus (MOE, MPa) obtained for different laboratory-made wood bark extracts

Adhesive properties of bark extracts

TMA analysis consists in the measurement of elasticity modulus (MOE) of two particleboards bonded with adhesives. The TMA curves are characterised by the main starting point of the slope, and by the highest strength measured. A regular evolution of the MOE is also a good indication of the quality of the adhesive formulation tested. TMA showed similar MOE curves for Norway spruce, Aleppo pine and maritime pine bark extracts, with a high MOE of ~3000 MPa (Fig. 4). Douglas fir and eucalyptus bark extracts gave similar curves, but lower MOE (the highest MOE of 2200 MPa). Therefore, Norway spruce, Aleppo pine and maritime pine bark extracts led to acceptable properties of the adhesive system tested, which allow anticipating a good final performance.

Lignin recovering from industrial pulping liquor

Lignins were extracted from different industrial liquors. Precipitation was performed by acidification of the black liquor by different methods: by H_2SO_4 and by CO_2.

The solubility of lignin decreases with decreasing pH due to protonised phenolic groups. Sulfuric acid presents the advantage of being easy to handle in the mixing stage, but the sulphur balance in the mill will be affected. The use of CO_2 avoids the sulfur balance problem in a pulp mill, but the mixing is more complicated.

After precipitation, the solid fraction was washed to obtain a pure lignin precipitate. The best precipitation conditions are presented in Table 1. The lignin that presented the best characteristics in terms of purity was precipitated from softwood Kraft black liquor by the CO_2 process. This allowed obtaining a lignin precipitate with 89% of lignin content, with a low sulphur content and a low mineral content – of about 2.9%. This lignin will be used in the adhesive formulation.

Tannin/lignin adhesive formulation

Tannin/lignin adhesive formulations were developed with the different lignins produced and both with mimosa and *Pinus radiata* tannins (Figs. 5, 6). The best results were obtained for a mixture constituted by 60% of commercial mimosa tannins with hexamine and 40% of lignin extracted from softwood kraft black liquor and glyoxylated (CO_2/pH 7.8). A gel time of about 11'40'' was measured. The TMA analysis confirmed that this was the best formulation selected with a maximal strength value – of about 3300 MPa (Fig.4). The particleboard made presented an internal bond of 0.53 MPa. This value is higher than the requirement given by European standard EN314-2 (IB > 0.35 MPa). The formaldehyde emission was measured for the panels made with the new green adhesive formulation and compared to the emission of the panel boards made with conventional adhesives made with urea-formaldehyde (UF) or melamine-urea-formaldehyde (MUF) (Fig. 7).

The formaldehyde level in the panels made with the tannin and lignin formulations was below 1 mg of formaldehyde released in the air. The low formaldehyde release is due to the wood itself. If we compare the values obtained for synthetic adhesives (UF and MUF), a significant difference is noted, hence our objective to produce a green adhesive which would allow reducing the formaldehyde emission has been reached.

Table 1
Characterisation of extracted lignin from Kraft black liquors

	Initial pH	Reagent	Final pH	Lignin yield (%, w/w)[1]	Lignin purity (%, w/w)[2]	Mineral (%, w/w)
Softwood kraft black liquors	11.8	CO_2	7.8	35	89.4	2.9
		H_2SO_4	2.0	35	86.4	1.5
		H_2SO_4	4.0	35	85.6	3.8
Hardwood kraft black liquor	12.1	CO_2	8.8	28	80.0	7.5

[1] gram of dry extract per 100 g of eq. dry matter of black liquor,
[2] gram of [Klason lignin and acid soluble lignin] per 100 g of dry extract

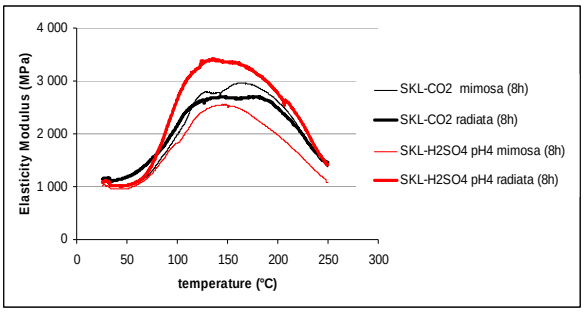

Figure 5: Adhesive properties of softwood kraft lignins (SKL): comparison of lignins precipitated with CO_2 and H_2SO_4,: comparison of the different lignins prepared and used in mimosa or *pinus radiata* tannin-based formulation after 8 h

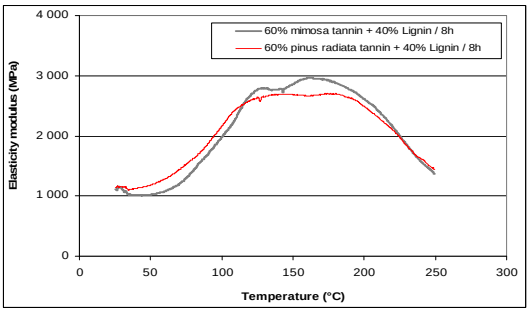

Figure 6: Adhesive properties of softwood kraft lignins precipitated with CO_2 (SKL-CO2): effect of mimosa and *pinus radiata* tannin-based formulation after 8 h

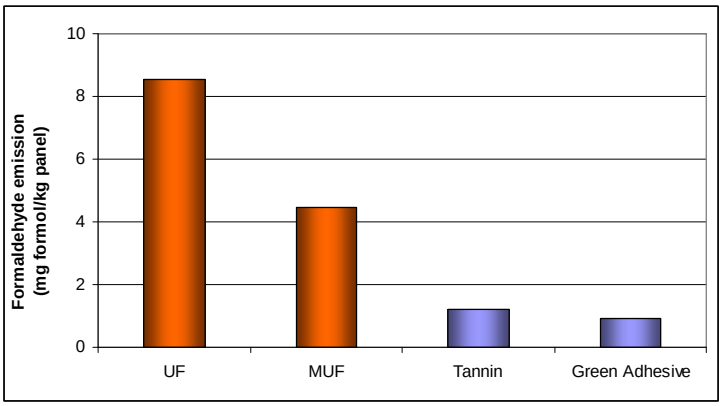

Figure 7: Formaldehyde emission measurement for panel boards

CONCLUSION

Industrial barks from the pulp and paper industry can be turned into valuable raw materials by tannin extraction. Aleppo pine bark was identified as the most promising one. Aleppo pine extract is mainly constituted of polyphenolic tannins, the samples analysed in this study presented a high condensed tannin concentration, ensuring further adhesive application. Douglas fir and spruce barks also led to interesting amounts of tannin in the sulphite/carbonate aqueous extract. Large laboratory scale extractions of the most promising wood barks (spruce, Douglas fir and Aleppo pine) have been performed by using urea/sulphite aqueous solution. The extraction yields of large quantities were even higher than the laboratory trials, and they confirmed Aleppo pine bark as being among the most promising, with an extraction yield of ~45%. Nevertheless, such polyphenolic structures need to be carefully handled, avoiding oxidation and recombination, to ensure good tannin quality.

High-quality lignin was obtained from softwood kraft black liquor precipitation with CO_2. This process seems to be easily adaptable to the pulp mill. From an economical perspective, CO_2 is the preferred source of hydrogen ions. The tannin/lignin adhesive formulation, constituted from 60% commercial mimosa tannins with hexamine and 40% glyoxylated softwood kraft lignin, gave the best particleboard characteristics, with an internal bond of 0.53 MPa. Furthermore, this green adhesive based on the lignin/tannin formulation reduced significantly the formaldehyde emission of the particleboards.

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