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Preparation, processing and properties of lignosulfonate-flax composite boards

Edwige Privas¹, Patrick Navard*, 1

Mines ParisTech, CEMEF – Centre de Mise en Forme des Matériaux, CNRS UMR 7635, BP 207, 1 rue Claude Daunesse, 06904 Sophia Antipolis Cedex, France

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ABSTRACT

Hemp, hay, straw for animal litters, raffia and sisal stems, abaca and jute bleached pulp fibres, miscanthus stems and flax fibres were mixed to lignosulfonate at 70% filler concentration and compressed in the form of 5 cm-thick boards. Flax was found to give the best mechanical properties measured in bending mode and used for all tests. Several methods able to improve adhesion between matrix and flax fibres were studied. A treatment of flax fibres with NaOH–water was found to decrease the mechanical properties of composites. Ethanol or dichloromethane solvents that are known to dewax flax fibre surfaces improve the mechanical properties of final board. The addition of pectin to the lignosulfonate matrix was found to improve the mechanical properties in the same order of magnitude as with the ethanol treatment. Both methods improve the flexural strength by 60% while keeping the elastic modulus constant. Mechanical improvement shows that these two methods are increasing the lignosulfonate/flax fibre interfacial adhesion. The best compositions have mechanical properties above the normalized minimum required for wood-based boards.

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1. Introduction

Lignin is one of the major components of plants and one of the most abundant organic polymers on Earth. Lignin is mainly positioned in the middle lamella, giving mechanical strength to the cell wall and to the whole plant. Lignin is also present in the cell wall between cellulose, hemicellulose, and pectin components where it is covalently linked to hemicelluloses in the secondary wall. Lignin hydrophobicity is helping wood and plants to maintain water flowing in them (Sarkanen & Ludwig, 1971). Lignin is a complex polymer composed of three monolignols: p-hydroxyphenyl, guaiacyl, and syringyl units. Each class of plants, grasses, softwoods and hardwoods produces lignin with different amount of monolignols (for example Norway spruce is almost entirely composed of guaiacyl unit). In addition to this variation of composition with the source, lignin depends also on the method of extraction (Lora & Glasser, 2002). Research on how to use lignin to manufacture materials is very active due to the need to find ways to prepare biomass-based products not coming from arable land intended to be used for food. However, variation in lignin composition is hampering its utilisation explaining why lignin is mainly burned. Only a few percent of the total lignin or lignin derivatives is used in applications where the quality of lignin is not of primary importance such as vanillin production, concrete admixtures or animal feed (Hu, 2002). Many potential applications of lignin-based products have been looked at like the preparation of phenolic and epoxy resins or thermoplastic-lignin blends (Stewart, 2008; Lora & Glasser, 2002). One of the possible applications is in the preparation of wood-based panels which are widely used all over the world in the building construction. Despite the production of wood-based panels slowed down due to the economic crisis started in 2008 (FAO, 2010), it is still a very important industrial activity. However, wood-based panels like softwood, plywood, flakes and oriented strand board (OSB) are containing resins like urea-formaldehyde, phenol-formaldehyde and various other resins containing phenolics, melamines or isocyanates. These common resin binders are slowly releasing formaldehyde in the indoor environment. Since 2011, formaldehyde is considered as a known human carcinogen by the US Department of Health and Human Services. The use of formaldehyde will face tough emission standards that will be implemented in US and Europe in the coming years. This drove research to substitute formaldehyde-based resins by safer products, lignin being one of the candidates. Lignin and derivatives have the right chemistry to be used as binding agents in composites because of their small particle size, hydrophobicity and their ability to form stable mixtures (Parka, Doherty, & Halley, 2008). However, one of the disadvantages of lignin-based resins compared to formaldehyde-based resins is their weaker adhesion properties and they also tend to have a high degree of variability in adhesion performance (Cyr & Ritchie, 1989). The partial replacement of phenol by lignin in phenol-formaldehyde resins has been studied since the 1980s (Çetin & Özmen, 2002; Etün & Zmen, 2003; Kazayawoko,

^{*} Corresponding author. Tel.: +33 0 493957466; fax: +33 0 492389752. E-mail address: patrick.navard@mines-paristech.fr (P. Navard).

¹ Member of the European Polysaccharide Network of Excellence (www.epnoe.eu).

Riedl, Poliquin, Barry, & Matuana, 1992; Olivares, Guzmán, Natho, & Saavedra, 1988; Roy, Sardar, & Sen, 1989). The full substitution of formaldehyde by lignin (El Mansouri & Pizzi, 2007; Glasser, Saraf, & Newman, 1982; Mathiasson & Kubát, 1994; Tejado, Kortaberria, Peña, & Labidi, 2007), tannin (Pizzi et al., 2009) or soy derivatives (Pizzi, 2006) was also studied. Another possibility is to use the lignin already present in plant cell walls to produce binderless boards (Anglès, Ferrando, Farriol, & Salvadó, 2001; Van Dam, van den Oever, Teunissen, Keijsers, & Peralta, 2004; Van Dam, van den Oever, Teunissen, Keijsers, & Peralta, 2006).

The preparation of lignin-based composite boards can be done by mixing particles from wood or annual plants. Wood-based fibres like beech treated with laccase enzyme were mixed with dioxane extractable lignin to reach comparable strength to conventional urea-formaldehyde resin (Felby, Hassingboe, & Lund, 2002). Bagasse fibres were mixed with phenolic or lignophenolic matrix, bagasse fibres been treated by mercerization or esterification (Paiva & Frollini, 2002) or oxidation with chlorine dioxide and treatment with furfuryl alcohol (Hoareau et al., 2006). Steam exploded softwood (Anglès et al., 2001) and miscanthus stems (Velásquez, Ferrando, & Salvadó, 2003) have been mixed with commercial lignin (lignosulfonate and kraft lignin) to prepare composites.

As for all composite materials, physical or chemical interactions between the various components are key parameters. These interactions must provide a good stress transfer between the components when the composite is subjected to mechanical loading, resulting in a highest strength. This means that physical or chemical bondings are necessary to have a strong interphase with a good wetting between the components. The reason behind the use of lignin as such a binder for wood chips of plant fibres lies in the fact that lignin is already present in these lignocellulosic materials. Lignin interacts with other polysaccharides leading to the formation of chemical bonding, a phenomenon that researchers are taking advantage of when using lignin as glue for lignocellulosic materials. It has been suggested that covalent bonds such as benzyl ether, benzyl ester, glycoside and acetal types can be formed between lignin and carbohydrates (Koshijima & Watanabe, 2003; Smock, 2002). Due to this property, lignin has been used to compatibilize natural fibres with natural matrices like soy-oil based resins (Thielemans & Wool, 2005) or resol-type phenolic thermosetting resins (Megiatto, Silva, Rosa, & Frollini, 2008). Dynamic Fourier Transform Infra-Red spectroscopy indicates that strong interactions between lignin, protein and pectins in primary cell wall exist while the main interactions in the secondary layer are cellulose with glucomannan and lignin with xylan (Salmen & Patterson, 1995; Westermark, Samuelson, Simonson, & Pihl, 1887). Interfacial interactions between matrix and fibres depend a lot on surface area and affinity between fillers and matrix. A lot of work has been carried out in the area of natural fibre-polymers in order to increase the interactions between matrix and fibres. Many different treatments were tried like mercerization (Gopalakrisnan, Saiah, Gattin, & Saiter, 2008) or chemical peeling (Reich, El Sabbagh, & Steuernagel, 2008) with some success. One of the actions that such chemical treatments are doing is to remove the outside layer of the fibre surface. Natural fibres, such as flax, are covered by cuticular wax. This outside layer protects internal plant tissues against microbial attack or moisture loss. The main constituents of the cuticular wax are aldehydes, alcohols, alkanes, esters and ketones derived from very long chain aliphatic lipids associated with other components like terpenoids or sterols (Holser & Akin, 2008; Kunst & Samuels, 2003).

Although a lot of work has been done for preparing fully bio-based boards with lignin-based binders, there is not yet a material able to offer good properties and simple preparation. The aim of the present study is to explore the possibility to use flax

Table 1Calcium lignosulfonate properties.

Dry matter (DM)	95%	
Mw	30 000 Da	
Mn	3000 Da	
Sulphur degree	0.6	
OH phenol	1.8% of dry matter	
Acid group	7% of dry matter	
Methoxy	9% of dry matter	
Calcium	6% of dry matter	
Ash	10% of dry matter	

mixed with lignosulfonate (a by-product of the sulfite pulping) to prepare boards. The use of lignosulfonate and not lignin will bring differences in the interactions with cellulose, hemicellulose and pectin. Upon light sulfonation, the lignin–pectin interactions were found to be weaker (Srndovic, 2008). The first part of the work was to choose the best fibre to produce fibreboards, which turned out to be flax. The second part of the work was the preparation of flax–lignosulfonate boards, with a focus on the evaluation of the usefulness of (i) various simple chemical treatments of the fibres and (ii) the addition of pectins to the lignosulfonate matrix on the improvement of the mechanical properties of boards.

2. Materials and methods

2.1. Materials

Nine different natural fibres or stem debris were used. Hemp, hay and straw used for animal litters, sun dry raffia without chemical treatment and sisal were supplied in local markets. Abaca and jute fibres were cellulose bleached pulps of equatorial abaca and jute provided by Celesa (Spain). Miscanthus stems was kindly given by Phytorestore (France) and used as received. Flax fibres were provided by Dehondt (France) from the variety Drakkar harvested in 2010 and retting during 28 days, classical scotching and no heckling. Their properties are given by the manufacturer as length: 9 mm, elastic modulus: 30 GPa, strength: 500 MPa and elongation at break: 2% (norm XPT 25 501-2). Calcium lignosulfonate was kindly provided by Borregaard (Sarpsborg, Norway) as a brown powder. Composition given by the manufacturer is given in Table 1. Pectin with a low degree of esterification (36.3%) was provided by CP Kelco (Denmark). Ethanol, dichloromethane and sodium hydroxide were purchased from Sigma-Aldrich and used without further purification.

2.2. Treatments of flax fibres

Flax fibres were treated with NaOH-water, ethanol or dichloromethane. For the mercerization (NaOH-water) treatment, flax fibres were placed in a NaOH solution (5% or 10%) for 2 h at room temperature. The fibres were then washed with distilled water until total alkali elimination and dried at 80 °C under vacuum over night (Gassan & Bledzki, 1999). Ethanol and dichloromethane treatments were performed using a laboratory reflux apparatus. Around 40 g of flax fibres and 750 mL of ethanol or dichloromethane were placed in a vessel connected to a condenser. The vessel was heated up at 80 °C for ethanol and 35 °C for dichloromethane treatments under continuous stirring. Samples were treated two times with fresh solvent, first 5 min for the first extraction then 15 min for the second extraction. At the end of the treatments, fibres were filtered and washed three times with distilled water, then dried over night at 80 °C under vacuum (Holser & Akin, 2008; Sala, 2000). For the all ethanol and dichloromethane treatments, extracts were evaporated to collect extractives.

2.3. Composite preparation

All fibres and stems except flax fibres were cut with a mixer during 45 s to obtain length fibres of around 20 mm. Fibres or stems were left in the preparation room several hours before composite preparation. 70% (w/w) of untreated or treated fibres and stems were mixed with 30% (w/w) of lignosulfonate powder. When pectin was used, addition took place in the lignosulfonate powder as 2% weight loading replacement, the composition of the first mixture being 70% of fibres/stems, 28% of lignosulfonate and 2% of pectins. In all cases, 10% by weight of water was added to the mixture. The final preparations were mixed manually before compression. After this step, the mixture was placed in a mould of dimensions $150\times50\times5$ cm³ and then compressed with a Darragon hydraulic hot moulding press. The compression process took place in three stages following (Velásquez et al., 2003), with a total process time of 11 min:

- (1) Compression for 5 min at 160 °C and at a pressure of 8 MPa.
- (2) Complete release of pressure during 1 min at 160 °C. This allowed releasing steam and avoiding bubbles formation that can negatively affect mechanical properties.
- (3) Compression for 5 min at 160 °C and at a pressure of 8 MPa.

2.4. Physical and mechanical characterization

Composite boards were characterised by their density, elastic modulus in bending and flexural strength. Mechanical properties were obtained using a three-point bending test in accordance with EN 310 norm. The flexural test measures the force required to bend a beam under three point loading conditions. Elastic modulus in bending (Em) and flexural strength (fm) are calculated respectively with Eqs. (1) and (2) taken into account board dimensions and applied forces.

$$Em = \frac{l_1^3(F_2 - F_1)}{4bt^3(a_2 - a_1)} \tag{1}$$

$$fm = \frac{3F_{\text{max}}l_1}{2hr^2} \tag{2}$$

with l_1 : support span (mm); b: width of test board (mm); t: depth of test board (mm); $F_2 - F_1$: gradient of forces in the straight line portion (F_2 is around 40% of F_{max} and F_1 is around 10% of F_{max}); $a_2 - a_1$: displacement corresponding to F_2 and F_1 (mm); F_{max} : force at rupture (N).

Scanning electron imaging was used to study the fibre surface of untreated and treated fibres as well as the fractured surfaces after bending tests with a SEM-FEG (Field Emission Gun) ZEISS Supra 40 at acceleration voltage of 3 or 7 kV. To avoid charging effects, a thin layer of gold–palladium was deposited by sputtering onto the surface of samples.

Moisture content was calculated with the difference in weight between sample obtained after processing and same sample dry in a vacuum oven according to EN 322 standard. Density was measured in a board cut in $50 \times 50 \times 5$ mm³ shape. Density presented in this paper is an average of two specimens.

3. Results and discussion

3.1. Influence of the fibre/stem source on mechanical properties

Composites were prepared with the nine different natural fibres or stem parts. The first goal was to choose the plant-based filler giving the best mechanical properties without special interface treatments. To this purpose, composites with fillers of different botanical origins were prepared and the elastic modulus in bending

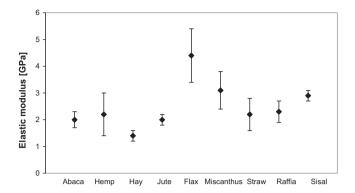


Fig. 1. Elastic modulus of the composites prepared with different types of fibres or stem parts.

was measured for all of them. Elastic modulus is primary a function of the intrinsic properties of each component and of the orientation of the reinforcing material. Composites were made by placing filler in a random manner, such as orientation is not significantly affecting the values of the elastic modulus. The results are given in Fig. 1. Over the nine materials tested, flax fibres, miscanthus stems and sisal fibres have the highest elastic modulus. These results do not seem to correspond to the classical ranking based on the mechanical properties of these fillers, where the elastic modulus is known to be higher in jute than in sisal (Bledzki & Gassan, 1999). It has to be noted that miscanthus stem debris are performing very well despite the cellulose fibres were not extracted from the stems. Considering the results of Fig. 1, flax will be used in the following parts of this study.

3.2. Effect of treating flax fibres with ethanol, dichloromethane and NaOH–water

Flax fibres were chemically treated as detailed above (Section 2.2). Visually, no change is observed for ethanol and dichloromethane treated fibres as the fibres conserve their initial light brown colour and their fibre structure. Differences are observed after the mercerization treatment with NaOH-water since fibres become brown-green and agglomerate. Observed by scanning electron microscopy, the thin cuticle layer that is surrounding the flax fibre bundle with a size larger than 200 µm (Fig. 2a) is destroyed by ethanol (Fig. 2b) and dichloromethane (Fig. 2c) peeling treatments, giving macrofibres of size around 50 µm and more individualized fibres. When observed by SEM, flax fibres treated with NaOH 5%-water solution have a similar appearance as the ones treated with ethanol and dichloromethane (Fig. 2d) But when flax is treated with NaOH 10%-water, fibres have a modified physical surface aspect, surfaces becomes very rough compared to the preceding cases. An underlining morphology of small fibres of size around 1 μm is clearly visible (Fig. 2e). The flax macrofibres loose their rigidity, as seen in Fig. 2f. The effect of NaOH treatments varies upon concentration and includes removing parts of lignin, hemicelluloses and low molar mass substances as well as changing the internal organisation of the fibres, like inducing a crystalline reorganisation. Typically, aqueous NaOH solution of a concentration ${\sim}10\,\text{wt.}\%$ causes the crystalline transformation of cellulose I into cellulose II (Dinand, Vignon, Chanzy, & Heux, 2002; El Oudiani, Chaabouni, Msahli, & Sakli, 2011; Zugenmaier, 2001).

3.3. Properties of composites prepared with flax fibres treated with ethanol, dichloromethane and NaOH–water

The moisture content (EN 322), density (EN 323) and mechanical properties (EN 310) of the composites were studied. Moisture

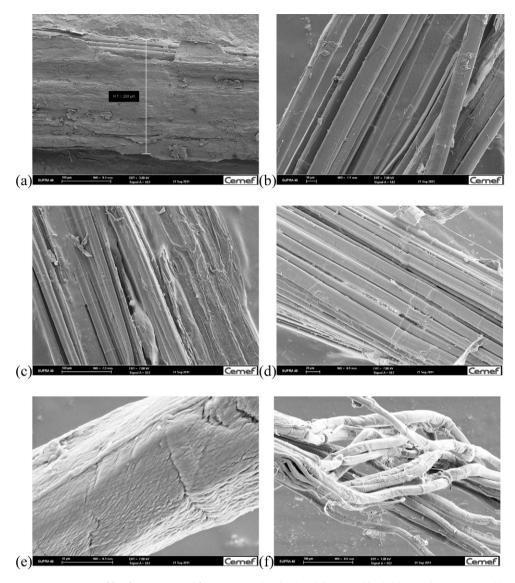


Fig. 2. Scanning electron microscopy pictures of flax fibres. Untreated fibre (a); treated with ethanol (b); treated by dichloromethane (c); treated by NaOH 10% (e, f).

content is not changed by a treatment of the fibre with ethanol, dichloromethane and NaOH 5% with moisture content around $7.4 \pm 0.2\%$. The moisture content of composites prepared with flax treated with NaOH 10% has a higher moisture content of $8.3 \pm 0.2\%$. These results are the direct consequence of the morphologies shown in Fig. 2. The moisture content is due in small part to the matrix and in a large part to water contained in the flax fibres. Water can be present in lignocellulosic cell walls in several states, depending on its location. In our case, the very high temperature of composite processing is eliminating all un-bound water. The ethanol, dichloromethane and NaOH 5% are giving the same overall morphologies. They are probably removing pectins and hemicellulose, in amounts depending on the type of treatment. However, these treatments do not seem to affect results and the same accessibility of flax to water was found for these three treatments. On the contrary, the stronger NaOH 10% treatment is removing all pectins and large parts of lignin and hemicellulose from the fibres, changing drastically the internal morphology of the fibres, and leaving space for a larger water intake. This gives higher final moisture content. The fact that this excess of water is not removed under the high temperatures experienced during processing is suggesting that a lot of tiny holes are formed during the NaOH 10% treatment, allowing trapping bonded water.

The composite densities for the different treatment are $1400\,\mathrm{kg/m^3}$ for the untreated and NaOH 5% treated flax composites, $1460\,\mathrm{kg/m^3}$ for NaOH 10% and $1500\,\mathrm{kg/m^3}$ for the ethanol and dichloromethane treatments. It is difficult to find a rational explanation behind these variations but all fibreboards prepared are in the standard requirement of density, higher than $800\,\mathrm{kg/m^3}$ according to EN 622 norm.

Elastic modulus and strength results obtained under three-point bending test are given in Fig. 3. Results are an average of two different preparations and range from 3.3 GPa to 8.4 GPa and from 24.1 MPa to 39.6 MPa for elastic modulus and strength respectively. As far as the elastic modulus is concerned, there no effect of an ethanol or dichloromethane treatment while treatments with NaOH have negative effects. This is more pronounced when increasing NaOH concentration. These results can be interpreted as follows. Ethanol and dichloromethane treatments are only affecting surfaces that are not playing a major role in the modulus of microfibres, thus not changing anything on this mechanical property of the prepared composites. Mercerisation is changing deeply

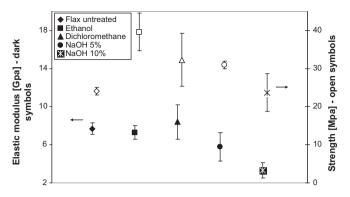


Fig. 3. Elastic modulus and strength of the composites for the different chemical treatment. Pressing temperature: $160\,^{\circ}$ C, pressure: 8 MPa. The position on the *X*-axis corresponds to the various treatments describe in Section 2.2.

the composition and structure of fibres and it affects negatively the properties of the composites, especially for the harsher treatment at 10% NaOH, where fibres are becoming more porous (Fig. 2 and moisture content results). On the other hand, strength, which is strongly linked to the anchoring of the matrix on the fibres, is increased whatever the treatment is. Similar results have been classically obtained for flax or other natural fibres in different matrices (Reich et al., 2008). In all our cases, the removal of a hydrophobic layer is favouring interactions with the hydrophilic lignosulfonate matrix. However, ethanol and dichloromethane treatments are more efficient than NaOH. This may be due to the removal of components like pectins that are playing a positive role in the lignin–cellulose interactions, as will be seen later. A large increase of composite strength after mercerisation treatments has been reported (Gopalakrisnan et al., 2008), an effect not seen here.

3.4. Properties of composites prepared with the addition of pectins in the lignosulfonate matrix

Pectin, a complex polysaccharide, is one of the constituents of plants, located mainly in the middle lamella, where it helps to bind cells together and in the primary cell wall where it is thought to allow cell growth. Its role in ligno-cellulosic organisms seems also to be linked to the way lignin is formed and polymerized. It is known that in vitro, pectin and lignin can form complexes and that the polymerization of synthetic lignin within a mat of pure cellulose is greatly enhanced in terms of dispersion if pectin is present (Touzel, Chabbert, Monties, Debeire, & Cathala, 2003). However, the exact structuration of the mixtures of lignin, cellulose and pectin in plants is still unresolved. Since interactions between these three components exist in natural assemblies, and since

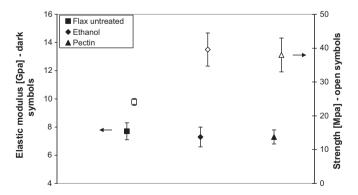


Fig. 4. Elastic modulus and strength of composite with no treatment, ethanol treatment and pectin formulation. The position on the *X*-axis corresponds to the untreated and treated by ethanol and pectin composites.

Table 2Elastic modulus and flexural strength of composites. (a) Without treatment, (b) with pectin addition, (c) ethanol treatment, (d) pectin addition plus ethanol treatment.

Sample	Elastic modulus in bending (GPa)	Flexural strength (MPa)
(a) Without treatment	7.7 ± 0.6	24.1 ± 1.0
(b) With pectin addition	7.3 ± 0.1	38.0 ± 5.0
(c) Ethanol treatment	7.3 ± 0.7	39.6 ± 4.9
(d) Pectin addition plus ethanol treatment	2.4 ± 0.1	23.0 ± 0.1

sulfonation seems to weaken but not suppress interactions between lignin and pectin (Srndovic, 2008), adding pectin in the lignosulfonate matrix was used with the hope it would improve the interfacial adhesion between flax fibre and matrix. Addition of pectin to lignosulfonate with one part of pectin for 14 parts of lignosulfonate was used as the matrix for preparing composites, keeping all process parameters equal to the ones used in the preceding tests (Section 2.3). Results are given in Table 2. Both modulus and strength are clearly increased with pectin addition. However, when coupling the two treatments, with both the ethanol treatment of the fibres and the addition of pectins in the lignosulfonate matrix, the results show a clear degradation of mechanical properties (Table 2). We can suggest the following explanation for interpreting these results, considering the role of pectins. During biosynthesis, it is suggested that pectin is forming a gel which contains the precursors of lignin. Through a dewatering process, lignin will polymerize and form the middle lamella, gluing cellulose reinforcement fibres to the ones of other cells. This lignin-pectin layer will then protect the cell wall against water loss and will help to resist to pathogenic agents (Lairez et al., 2005). Despite that the complexation and structuration of this layer is not really understood, it is known that pectin-lignin and pectin-lignin-polysaccharide complexes exist (Helm, 2000; Koshijima & Watanabe, 2003). When adding pectins in the matrix, we can thus suggest that this will have two effects. One effect is the increase of matrix strength through lignin moiety-pectin bonding, even if much less opportunities for bonding exist due to sulfonation. The second one is the increase in interaction between matrix, which is composed of lignosulfonate and pectin, and the pectin-polysaccharides present in the fibre. These two mechanisms will participate in the increase of the strength of the total composite. Chemical peeling is strongly inhibiting the effect of pectin addition. Thus, the major mechanism in the increase of strength is mainly due to the interfacial linkage obtained by pectin addition. It is usually considered that the polysaccharides bonding with pectins are hemicelluloses, themselves closely associated with cellulose. As it has been shown, some of the alkali-soluble hemicelluloses such as the ones having a backbone of xylose residues with a β -(1 \rightarrow 4)-linkage branched mainly through arabinofuranosyl units can be fractionated by ethanolwater mixtures (Peng et al., 2010). We can thus suggest that the ethanol treatment is not only removing the waxy layer (Holser, 2008), but is also removing part of the hemicelluloses that will not be able to bind with the pectin added. Such an explanation is very tentative and will need further investigations to be proved.

4. Conclusion

It is possible to prepare in a simple manner composite board made of 30% plant fibres or stems of various origins in 70% of lignosulfonate matrix. Without any specific treatments of the filler, most prepared composite boards have properties below the normalized minima for wood-based boards (elastic modulus higher than 3 GPa, EN 622 norm) (Fig. 2). However, three fillers have good properties, flax fibres, miscanthus stems and sisal fibres. It is remarkable that

miscanthus stem debris do perform well, having an elastic modulus of 3 GPa. Composites with flax fibres have the highest elastic modulus but a low flexural strength of 24.1 MPa (Table 2), lower than the minimum value in the specifications for wood based boards (40 MPa). A series of chemical treatments of the flax fibres were tested in order to improve the matrix-filler adhesion, and thus the strength. The best treatments we found is with ethanol, which does not change the elastic modulus (7.3 GPa), but strongly increases the flexural modulus from 24.1 MPa to about 40 MPa. Such a performance can be compared to Kraft lignin composites with miscanthus fibres pulped from the energy-intensive stream explosion method (Velásquez et al., 2003), where the elastic modulus was 4.9 GPa and the flexural strength 42 MPa. The same effect is found when pectin is added to the lignosulfonate matrix. The exact mechanism linking pectin-lignosulfonate and cellulose is not known. Calcium ions, known to form complexes with low methoxylated pectins, resulting in pectin gelation, could be one of these mechanisms (Fraeye, Duvetter, Doungla, Van Loey, & Hendreickx, 2010). Adding pectin is much easier and less costly than treating with ethanol and seems to be a convenient method for preparing flax-lignosulfonate boards with good properties (Fig. 4). In the present case, the type of pectin was not chosen specifically, but preliminary experiments not reported here show that varying pectin source is changing the effect on the mechanical properties, an effect that we intend to study in future. Another point of great practical importance is the sensitivity of these boards to humidity, a factor not considered here.

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References

- Anglès, M. N., Ferrando, F., Farriol, X., & Salvadó, J. (2001). Suitability of steam exploded residual softwood for the production of binderless panels. Effect of the pre-treatment severity and lignin addition. *Biomass and Bioenergy*, 21, 211–224.
- Bledzki, A. K., & Gassan, J. (1999). Composites reinforced with cellulose fibres. Progress in Polymer Science, 24(2), 221-274.
- Çetin, N. S., & Özmen, N. (2002). Use of organosolv lignin in phenol-formaldehyde resins for particleboard production: I. Organosolv lignin modified resins. *Inter*national Journal of Adhesion and Adhesives, 2(6), 477–480.
- Cyr, N., & Ritchie, R. G. (1989). Estimating the adhesive quality of lignins for internal bond strength. ACS Symposium Series, 397(Lignin: Properties and Materials), 372.
- Dinand, E., Vignon, M., Chanzy, H., & Heux, L. (2002). Mercerization of primary wall cellulose and its implication for the conversion of cellulose $I \rightarrow$ cellulose II. *Cellulose*, 9, 7–18.
- El Mansouri, N.-E., & Pizzi, A. (2007). Lignin-based polycondensation resins for wood adhesives. *Journal of Applied Polymer Science*, 103(3), 1690–1699.
- El Oudiani, A., Chaabouni, Y., Msahli, S., & Sakli, F. (2011). Crystal transition from cellulose I to cellulose II in NaOH treated Agave Americana L. Fibre. Carbohydrate Polymers, 86, 1221–1229.
- Etün, N. S., & Zmen, N. (2003). Studies on lignin-based adhesives for particleboard panels. Turkish Journal of Agriculture and Forestry, 27, 83–189.
- FAO. (2010). Forest Products annual market review 2009–2010. New York/Geneva: United Nations.
- Felby, C., Hassingboe, J., & Lund, M. (2002). Pilot-scale production of fibreboards made by laccase oxidized wood fibers: Board properties and evidence for crosslinking of lignin. Enzyme and Microbial Technology, 31(6), 736–741.
- Fraeye, I., Duvetter, T., Doungla, E., Van Loey, A., & Hendreickx, M. (2010). Fine-tuning the properties of pectin-calcium gels by control of pectin fine structure, gel composition and environmental conditions. *Trends in Food Science & Technology*, 21, 219–228.
- Gassan, J., & Bledzki, A. K. (1999). Alkali treatment of jute fibres: Relationship between structure and mechanical properties. *Journal of Applied Polymer Science*, 71(4), 623–629.
- Glasser, W. G., Saraf, V. P., & Newman, W. H. (1982). Hydroxy propylated lignin-isocyanate combinations as bonding agents for wood and cellulosic fibres. *Journal of Adhesion*, 14(3–4), 233–255.
- Gopalakrisnan, P., Saiah, R., Gattin, R., & Saiter, J. M. (2008). Effects of mercerisation of flax fibres on wheat flour/flax fibres biocomposite with respect to thermal and tensile properties. *Composite Interfaces*, 15(7–9), 759–770.

- Helm, R. F. (2000). Lignin-polysaccharide interactions in woody plants. In W. G. Glasser, R. A. Northey, & T. P. Schultz (Eds.), Lignin: Historical, biological and materials perspectives. ACS symposium series. Washington, DC, USA.
- Hoareau, W., Oliveira, F. B., Grelier, S., Siegmund, B., Frollini, E., & Castellan, A. (2006). Fiberboards based on sugarcane bagasse lignin and fibers. *Macromolecular Materials and Engineering*, 291(7), 829–839.
- Holser, R. A., & Akin, D. A. (2008). Extraction of lipids from flax processing waste using hot ethanol. *Industrial Crops and Products*, 27, 236–240.
- Hu, T. Q. (2002). Chemical modification, properties, and usage of lignin. New York, USA: Kluwer Academic/Plenum Publishers.
- Kazayawoko, Riedl, B., Poliquin, J., Barry, A. O., & Matuana, L. M. (1992). A lignin-phenol-formaldehyde binder for particleboard. Part 1, Thermal characteristics. Holzforschung, 46(3), 257–262.
- Koshijima, T., & Watanabe, T. (2003). Association between lignin and carbohydrates in wood and other plant tissues. Springer series in wood science.
- Kunst, L., & Samuels, A. L. (2003). Biosynthesis and secretion of plant cuticular wax. Progress in Lipid Research, 42(1), 51–80.
- Lairez, D., Cathala, B., Monties, B., Bedos-Belval, F., Duran, H., & Gorrichon, L. (2005). Aggregation during coniferyl alcohol polymerization in pectin solution: A biomimetic approach of the first steps of lignification. *Biomacromolecules*, 6(2), 763–774.
- Lora, J. H., & Glasser, W. G. (2002). Recent industrial applications of lignin: A sustainable alternative to non renewable materials. *Journal of Polymers and the Environment*, 10(1–2), 39–48.
- Mathiasson, A., & Kubát, D. G. (1994). Lignin as binder in particle boards using high frequency heating, Properties and modulus calculations. Holz als Roh- und Werkstoff, 52, 9–18.
- Megiatto, J. D., Silva, C. G., Rosa, D. S., & Frollini, E. (2008). Sisal chemically modified with lignins: Correlation between fibres and phenolic composites properties. *Polymer Degradation and Stability*, 93, 1109–1121.
- Olivares, M., Guzmán, J. A., Natho, A., & Saavedra, A. (1988). Kraft lignin utilization in adhesives. *Wood Science and Technology*, 22(2), 157–165.
- Paiva, J. M. F., & Frollini, E. (2002). Sugarcane bagasse reinforced phenolic and lignophenolic composites. *Journal of Applied Polymer Science*, 83(4), 880–888.
- Parka, Y., Doherty, W. O. S., & Halley, P. J. (2008). Developing lignin-based resin coatings and composites. *Industrial Crops and Products*, 27, 163–167.
- Peng, F., Ren, J.-L., Xu, F., Bian, J., Peng, P., & Sun, R.-C. (2010). Fractional study of alkali-soluble hemicelluloses obtained by graded ethanol precipitation from sugar cane bagasse. *Journal of Agricultural and Food Chemistry*, 58(3), 1768–1776.
- Pizzi, A. (2006). Developments in biobased adhesives for wood bonding: Opportunities and issues. Journal of Adhesion Science and Technology, 20(8), 829–846.
- Pizzi, A., Kueny, R., Lecoanet, F., Massetau, B., Carpentier, D., Krebs, A., et al. (2009). High resin content natural matrix-natural fibre biocomposites. *Industrial Crops and Products*, 30, 235–240.
- Reich, S., El Sabbagh, A., & Steuernagel, L. (2008). Improvement of fibre-matrix adhesion of natural fibres by chemical treatment. *Macromolecular Symposium*, 262, 170–181.
- Roy, A. K., Sardar, D., & Sen, S. K. (1989). Jute stick lignin-based adhesives for particle boards. *Biological Wastes*, 27(1), 63–66.
- Sala, J. M. (2000). Content, chemical composition and morphology of epicuticular wax of Fortune mandarin fruits in relation to peel pitting. *Journal of the Science* of Food and Agriculture, 80, 1887–1894.
- Salmen, L., & Patterson, B. (1995). The primary wall: Importance for fibre separation in mechanical pulping. Cellulose Chemistry and Technology, 29, 331–337.
- Sarkanen, K. V., & Ludwig, C. H. (Eds.). (1971). Lignins: Occurrence, formation, structure, and reactions. New York: Wiley Interscience.
- Smock, G. A. (2002). Handbook for pulp and paper technologies (3rd ed). Vancouver BC, USA: Angus Wilde Publications INC.
- Srndovic, J.S. (2008). Ultrastructure of the primary cell wall of softwood fibres studied using dynamic FT-IR spectroscopy, Licentiate Thesis, Royal Institute of Technology, Stockholm, Sweden.
- Stewart, D. (2008). Lignin as a base material for materials applications: Chemistry, application and economics. *Industrial Crops and Products*, 27, 202–207.
- Tejado, A., Kortaberria, G., Peña, C., & Labidi, J. (2007). Lignins for phenol replacement in novolac-type phenolic formulations, part I: Lignophenolic resins synthesis and characterization. *Journal of Applied Polymer Science*, 106(4), 2313–2319.
- Thielemans, W., & Wool, R. P. (2005). Kraft lignin as fibre treatment for natural fibre-reinforced composites. *Polymer Composites*, 26(5), 695–705.
- Touzel, J. P., Chabbert, B., Monties, B., Debeire, P., & Cathala, B. (2003). Synthesis and characterisation of dehydrogenation polymers in *Gluconacetabacter xyli*nus cellulose and cellulose/pectin composites. *Journal of Agricultural and Food Chemistry*, 51, 981–986.
- Van Dam, J., van den Oever, M. J. A., Teunissen, W., Keijsers, E. K. P., & Peralta, A. G. (2004). Process for production of high density/high performance binderless boards from whole coconut husk. Part 1: Lignin as intrinsic thermosetting binder resin. Industrial Crops and Products, 19, 207–216.
- Van Dam, J., van den Oever, M. J. A., Teunissen, W., Keijsers, E. K. P., & Peralta, A. G. (2006). Process for production of high density/high performance binderless boards from whole coconut husk. Part 2: Coconut husk morphology, composition and properties. *Industrial Crops and Products*, 24, 96–104.

Velásquez, J. A., Ferrando, F., & Salvadó, J. (2003). Effects of kraft lignin addition in the production of binderless fibreboard from steam exploded *Miscanthus sinensis*. *Industrial Crops and Products*, 18, 17–23.

Westermark, U., Samuelson, B., Simonson, R., & Pihl, R. (1887). Investigation of selective sulfonation of wood chips. Part 5. Thermomechanical pulping

with low addition of sulfite. Nordic Pulp and Paper Research, 2(4), 146–151.

Zugenmaier, P. (2001). Conformation and packing of various crystalline cellulose fibers. Progress in Polymer Science, 26, 1341–1417.