



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; Westermarck, Samuelson, Simonson, & Pihl, 1987). 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 Sabagh, & 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 1
Calcium 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 PhytoStore (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.

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