

# Monocotyledons in Particleboard Production: Adhesives, Additives, and Surface Modification of Reed Canary Grass

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As a supplier to the furniture industry, the particleboard industry is searching for opportunities to reduce costs, weight, and formaldehyde emissions. One such opportunity is to use monocotyledons such as straw and hemp, as well as grasses like reed canary grass. A major problem when using reed canary grass or other monocotyledons in combination with wood is the difference in their surface properties, leading to poor reactivity and wettability with adhesives such as melamine urea formaldehyde. To this end, either the surface of the particles must be modified in some way, or different adhesives must be used. The purpose of this paper is to present adhesives, surfactants, coupling agents, and pre-treatment methods that can be used in combination with monocotyledons to improve compatibility with wood. Some of the methods have been tested on reed canary grass. The results show a wide range of strength values for the joint between wood and untreated or pre-treated reed canary grass glued with different adhesives, with and without a surfactant and a coupling agent. Isocyanate-based adhesives provided relatively strong bonds, and polyvinyl acetate, acryl, and epoxy adhesives were also effective. The most effective method was pre-treatment followed by adhesives in combination with a coupling agent.

*Keywords:* De-waxing; Surfactant; Coupling agent; Gluing; Lignocellulose plants

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## INTRODUCTION

As a consequence of increased competition from the energy conversion sector based on renewable resources, the particleboard industry is seeking cheap alternatives for wood in their products. The consumption of wood in Europe, and especially of wood used for energy conversion, is expected to increase during the next 10 years (Jonsson *et al.* 2011; Mantau 2010; United Nations 2011). The particleboard industry is also a large consumer of adhesives. For technical and economic reasons, these adhesives are based on the reaction of formaldehyde with a co-monomer; however, formaldehyde emissions during and after production are a problem (Conner 1996; Dunky 1998; Kelly 1977; Nemli and Öztürk 2006). Recently, formaldehyde was classified as carcinogenic (European Parliament 2008; Grosse and Gaudin 2004), which has consequences for products containing free formaldehyde. Another trend in the particleboard industry is towards light-weight panels, *i.e.*, panels with a density of about 400 kg/m<sup>3</sup> or lower (BASF 2013; BSW 2013; ELKA 2013; Pfleiderer 2013; Swedspan 2010). One way to achieve low-density particleboards with less wood is to use monocotyledons such as

straw, grass, and herbs as raw material (Boquillon *et al.* 2004). Most research in this area has been on wheat straw (Azizi *et al.* 2011; Boquillon *et al.* 2004; Frounchi *et al.* 2007; Mo *et al.* 2003; Wang and Sun 2002) and rice straw (Jarusombuti *et al.* 2009; Li *et al.* 2010), but other monocotyledon materials have also been used (Balducci *et al.* 2008; Nikvash *et al.* 2012; Pan *et al.* 2006; Schopper *et al.* 2009). Compared to wood particles, particles of monocotyledons exhibit a high heterogeneity that depends on the part of the plant from which they originate (*e.g.*, the leaf, leaf sheath, or stem) (Finell 2003; Pahkala and Pihala 2000). The chemical composition between external and internal surface areas also differs (Wiśniewska *et al.* 2003) because the plants have a special external surface which consists of cuticles and epicuticular waxes (Barthlott and Neinhuis 1997). The chemical and morphological heterogeneity of the external surface has a strong impact on the water contact angle (Wiśniewska *et al.* 2003). Because the adhesives conventionally used in the particleboard industry are aqueous-based, problems arise regarding the wetting and tacking of the particles. To increase the wettability of the particles, different surface modifications can be used. De-waxing can be achieved by hexane (C<sub>6</sub>H<sub>14</sub>), carbon tetrachloride (CCl<sub>4</sub>), alkali (sodium hydroxide (NaOH), sodium amide (NaNH<sub>2</sub>), calcium hydride (CaH<sub>2</sub>), potassium hydroxide (KOH), oxidative treatments such as with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), or enzymes such as lipases (*Candida cylindracea*) (Bing *et al.* 2011; Fernandes *et al.* 2011; Hua *et al.* 2009; Shen *et al.* 2011; Zhu *et al.* 2012). In addition, the particle size and the choice of adhesives in combination with coupling agents or surfactants have an influence on the bonding strength (Han *et al.* 1998).

### Reed Canary Grass (*Phalaris arundinacea* L.)

Reed canary grass (RCG) is a perennial grass reaching a height of 2 m and a biomass production of 6 to 8 tons per hectare for spring harvest (delayed harvest) and 8 to 10 tons dry mass per hectare for autumn harvest (Finell 2003). This perennial rhizome-building C3-grass can be found in the whole of northern Europe, including Sweden (Xiong *et al.* 2008), Finland (Pahkala *et al.* 2008), and the Baltic countries (Kukk *et al.* 2011). The high biomass production of this species in boreal zones and its adaption to wet soils with a low pH value (Hall 2008) makes it a species of interest for energy production in northern Europe (Xiong *et al.* 2008). For these reasons, areas devoted to RCG for biomass production in Finland increased from 500 to 17,000 hectares between 2001 and 2006 (Casler *et al.* 2009). RCG has been considered not only for energy purposes but also as raw material for pulp and paper production (Finell 2003; Thykesson *et al.* 1998). The chemical composition of RCG differs depending on the harvesting time (Pahkala and Pihala 2000). The main chemical components are given in Table 1.

## Background

### *Particles of monocotyledons-surface characteristics and modification*

The particles of monocotyledons have an external surface that consists of cuticle and epicuticular waxes which give the surface a hydrophobic character (Barthlott and Neinhuis 1997). The structure of the external surface includes a layer of epidermal cells followed by a layer of pectin, on which there is a thick cutinised layer with embedded waxes, and finally an epicuticular wax layer (Wiśniewska *et al.* 2003). The wax layer consists of a thin film, usually only a few nanometres thick, superimposed upon wax structures with a thickness up to 10 micrometres, with various forms that can be grouped into crusts, smooth layers, and fissured layers (Barthlott *et al.* 1998).

**Table 1.** Chemical Composition of Spring and Autumn (Spring/Autumn) Harvested Reed Canary Grass (Pahkala and Pihala 2000)

Plant component	Ash (g/kg)	SiO <sub>2</sub> (g/kg)	K (g/kg)	Cu (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
Stem (internode)	50/47	40/17	3/15	6/6	61/19	48/20
Leaf sheath (node)	90/84	74/43	4/20	7/4	267/67	140/53
Leaf blade	130/115	107/57	4/21	8/6	491/110	214/81

While waxes are long-chain esters, epicuticular waxes are composed of various chemical components, as presented in Table 2.

**Table 2.** Main Chemical Components of Epicuticular Waxes (Barthlott *et al.* 1998)

<b>Aliphatic compounds (most common but rarely dominant in wax composition)</b>		
Name	Formula	Length
Hydrocarbons	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>n</sub> -CH <sub>3</sub>	C <sub>19</sub> to C <sub>37</sub>
Wax esters	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>n</sub> -CO-O-(CH <sub>2</sub> ) <sub>m</sub> -CH <sub>3</sub>	C <sub>30</sub> to C <sub>60</sub>
Primary alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>n</sub> -CH <sub>2</sub> -OH	C <sub>12</sub> to C <sub>36</sub>
Fatty acids	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>n</sub> -COOH	C <sub>12</sub> to C <sub>36</sub>
Aldehydes	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>n</sub> -CHO	C <sub>14</sub> to C <sub>34</sub>
<b>Aliphatic compounds (less common but mostly dominant in wax composition)</b>		
Name	Formula	Length
Ketones	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>n</sub> -CO-(CH <sub>2</sub> ) <sub>m</sub> -CH <sub>3</sub>	C <sub>12</sub> to C <sub>36</sub>
β-diketones	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>n</sub> -CO-CH <sub>2</sub> -CO-(CH <sub>2</sub> ) <sub>m</sub> -CH <sub>3</sub>	C <sub>12</sub> to C <sub>36</sub>
Secondary alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>n</sub> -CHOH-(CH <sub>2</sub> ) <sub>m</sub> -CH <sub>3</sub>	C <sub>12</sub> to C <sub>36</sub>
<b>Cyclic compounds</b>		
e.g., Triterpenoides	β-Anyryn	
e.g., Flavonoides	Quercetin	

The wax layer makes it difficult to use monocotyledons for particleboard in combination with conventional adhesives because of problems with wettability. To increase wettability, treatment of the material to reduce or remove the wax layer is necessary. Fernandes *et al.* (2011) used the alkane hexane (C<sub>6</sub>H<sub>14</sub>) and carbon tetrachloride (CCl<sub>4</sub>) for surface modification of carnauba straw to remove the wax layer, although this lowered the modulus and tensile strength of the straw. Alkalis such as NaOH, NaNH<sub>2</sub>, CaH<sub>2</sub>, KOH, and H<sub>2</sub>O<sub>2</sub> were also tested. Compared to the treatment with CCl<sub>4</sub>, treatment with NaOH was far less effective in removing the wax layer; the alkaline treatment seemed to destroy the crystalline structure of the cellulose, which resulted in a decrease in the mechanical strength of the material (Fernandes *et al.* 2011). In another study, rice straw was treated with four different alkalis (NaOH, NaNH<sub>2</sub>, CaH<sub>2</sub>, KOH) of different concentrations and for different times, and it was found that the NaOH-treatment gave the best de-waxing (Bing *et al.* 2011; Zhu *et al.* 2012). With wheat straw

it has been shown that NaOH is more effective than H<sub>2</sub>O<sub>2</sub> in removing and destroying the wax layer as well as in removing the silica (SiO<sub>2</sub>) (Shen *et al.* 2011).

Enzymes can also be used to reduce the wax layer. On wheat straw, three different types of enzymes (lipase, xylanase, cellulase) were tested (Shen *et al.* 2011). While cellulase and xylanase could not destroy the wax layer because of their specificity (they only destroyed the knot cells), lipase treatment improved the wettability of the external layer by destroying the waxy layer and eliminating the silica (SiO<sub>2</sub>). Treatment with NaOH gave results similar to those with lipase, but the time for enzymatic treatment was about one week. Reaction with NaOH is much faster and probably also cheaper (Shen *et al.* 2011). In another study by Hua *et al.* (2009), wheat straw treated with lipases from *Candida cylindracea* showed that removal of hydrophobic extractives and silica increased the hydroxyl groups on the external surface, while the interior surface was not significantly affected.

In another treatment, triticale straw was treated with steam in one or two stages at temperatures of 160 and 190 °C. For the one-stage treatment, a steam pressure of 0.6 MPa for 5 to 10 min or 1.3 MPa for 2.5 to 5 min was chosen. In the two-stage treatment, the straw was first treated for 30 min at 6 kPa and then for 2.5 min at 1.3 MPa. Steam treatment effectively removed the wax layer and made the exterior surface more similar to the interior (Zhao and Boluk 2010).

In summary, particles of monocotyledons have two surfaces: an inner surface similar to that of wood and an external surface consisting of a wax layer. The hydrophobic character and the structure of the wax layer raises problems regarding wettability when particles of monocotyledons are used in combination with adhesives traditionally used in particleboard manufacture. In the literature, chemical, enzymatic, and physical surface treatments are presented to reduce or remove the wax layer and increase the wettability of the particles. The most effective seems to be surface treatment with NaOH. Alternatively, surfactants to increase wettability, coupling agents to increase tack, or different adhesives can be used.

#### *Surfactants and coupling agents suitable for surfaces of monocotyledons*

Surfactants increase either the wettability of the surface or penetration through the surface. They can generally be divided into spray-modifiers that change the characteristics of the water-based solution, and sorption activators that influence the rate of absorption (Hess and Foy 2000). Coupling agents, particularly silane coupling agents, were developed to improve the strength of the bond across the interface between organic resins and mineral surfaces (Plueddemann 1982).

Surfactants used to increase wettability include alkyl pentosides, which are biomass-derived non-ionic surfactants used in cosmetics, detergents, cold emulsification processes, solvents, and agricultural formulations (Papadopoulou *et al.* 2011). Surfactants related to the surfaces of plants, which are essential in herbicide solutions, can also be effective for the gluing of monocotyledon particles. Different non-ionic and anionic surfactants were tested on corn leaf surfaces. As non-ionic surfactants, polyoxyethylene sorbitan monolaurate (Tween<sup>®</sup> 20; ICI Americas, Inc., Wilmington, DE), polyoxyethylene sorbitan monooleate (Tween<sup>®</sup> 80; ICI Americas, Inc.), 80% alkylaryl polyoxyethylene glycols, free fatty acids, isopropanol (X-77<sup>®</sup>; Colloidal Products Corp., Sausalito, CA; Loveland Products, Inc., Loveland, CO), polyoxyethylene polypropylene polyols (T-1947<sup>®</sup> (American Cyanamid Company, Wayne, NJ), and Dynawet<sup>®</sup> (Dow Corning, Midland, MI) (chemistry undisclosed) were tested. Anionic 75% sodium

dioctylsulfosuccinate (Vatsol OT<sup>®</sup>; BASF) and sodium lauryl sulfate were also used. The results showed that surfactants in general have only a limited effect on the surface tension, with greatest decrease in surface tension being achieved with Vatsol OT<sup>®</sup>. It was also shown that too much surfactant (Tween<sup>®</sup> 80, Tween<sup>®</sup> 20, T-1947<sup>®</sup>) can result in an increase in surface tension (Foy and Smith 1965). With trisiloxan surfactants, it was found that the rate of spreading depends on the surfactant nature, the structure (hydrophobicity), and the concentration as well as on the nature of the subphase. An increase in hydrophobicity, which is dependent on the length of the ethoxy chain, results in a reduction in the superspreading ability of siloxane and hydrocarbon surfactants (Svitova *et al.* 1996).

Surfactants promoting penetration or diffusion across the cuticle include Silwet L-77<sup>®</sup> (Momentive Performance Materials Inc., Columbus, OH), Sylgaard<sup>®</sup> (Dow Corning), X-77<sup>®</sup> (Colloidal Products Corp.; Loveland Products, Inc.), and Agri-Dex<sup>®</sup> (Helena Chemical Co., Collierville, TN) (Dayan *et al.* 1996). Surfactants with a high hydrophile/lipophile balance (HLB) seem to enhance the water-holding capacity of the cuticle and promote the diffusion of hydrophilic substances, while surfactants with a low HLB increase the fluidity of the waxes and promote the diffusion of lipophilic substances (Hess and Foy 2000). The infiltration of both lipophilic (non-polar ions) and hydrophilic (polar ions) substances suggests that there is both an aqueous route and a lipid route (Foy 1964). Some non-ionic surfactants significantly increased the permeability to water, while anionic surfactants had no effect on the permeability. Non-ionic surfactants are soluble in cuticles and can penetrate them quite rapidly, promoting water permeability (Riederer and Schönherr 1990). To achieve the maximum effect, some highly specific requirements regarding surfactant formulation must be fulfilled, such as the molecular interaction between surfactant and herbicide (Freed and Montgomery 1958).

Coupling agents should, in general, improve the compatibility and adhesion between non-polar and polar surfaces and the adhesives. Organic agents show higher adhesion than inorganic and mixed agents. The most popular agents are isocyanates, anhydrides, copolymers modified with anhydrides, and silanes (Lu *et al.* 2000). Organofunctional silicones are hybrids of organic materials and silica (Plueddemann 1982). Experiments on reed and wheat straw have shown that silane coupling agents such as vinyl-, amino-, and epoxide-silane improve the properties of particleboards made from monocotyledons. Nevertheless, boards glued with urea formaldehyde (UF) in combination with these coupling agents did not meet the minimum internal bond requirements for particleboards when the density of the panels was lower than 800 kg/cm<sup>3</sup> (Han *et al.* 1998). Silane coupling agents were also used in particleboards designed for sound absorption consisting of rice straw and wood bonded with UF (Yang *et al.* 2003). In another study, composite particleboards made of fine-milled wheat straw and recycled LDPE (low density polyethylene) were produced in combination with the coupling agents PAL (polyacrylate latex) and PAPI (polymethylene polyphenylene isocyanate) (Kuang *et al.* 2010). Different coupling agents were also tested in composites produced from high density polyethylene (HDPE) in combination with extruded rice husks (Panthapulakkal *et al.* 2005).

As herbicide formulations used in agriculture generally have water as solvent but have to wet and penetrate the waxy layer of the plants, the surfactants used for this purpose might also help to increase the wettability for adhesives in particleboard manufacture. While the surfactants influence the wetting of the waxy layer, coupling agents influence the tack of the adhesive.

*Adhesives suitable for surfaces of monocotyledons*

Wettability tests on wheat straw show that the contact angle depends on the adhesive used. Results for MDI (diphenylmethane diisocyanate) exhibited the lowest contact angles, while MUF (melamine urea formaldehyde) and PF (phenol formaldehyde) had 25% higher values for the contact angle for both untreated and NaOH-pre-treated straw (Liu *et al.* 2004; Russell and Johnston 1996). The differences between MDI and UF or PTP (polymeric material from triglycerides and polycarbonic acid anhydrides) and UF are even higher when the internal bond strength is measured (Boquillon *et al.* 2004; Dziurka *et al.* 2005; Mo *et al.* 2003; Zheng *et al.* 2007). The wax layer of the external surface of monocotyledons requires adhesives with a more lipophilic or non-polar character such as the adhesives used in WPCs (wood plastic composites) (Maheswari *et al.* 2012), where natural fibres, which generally have a hydrophilic (polar) character, are chemically or physically treated or used in combination with coupling agents to increase their compatibility with a hydrophobic matrix (Han and Choi 2010; John and Anandjiwala 2008; Kabir *et al.* 2011; Keener *et al.* 2004; Khalil and Suraya 2011; Li *et al.* 2007; Lu *et al.* 2000; Maheswari *et al.* 2012; Sinha and Rout 2009). Adhesives with a wide range of tack properties such as MDI adhesives (Frazier 2003), or adhesives that allow a high range of modification like polyvinyl alcohol (PVA) (Qiao *et al.* 2002) might also be suitable. For these reasons, one isocyanate-based adhesive (polyurethane), one adhesive with a wide tack range that may be easy to modify (polyvinyl acetate (PVAc)), two matrix-building adhesives (acryl, epoxy), and natural adhesives or additives (kraft-lignin 50%, fish lime 100%) were tested and compared in this study.

The aromatic monomer MDI and the associated methylene-bridged polyphenyl polyisocyanate, polymeric MDI (pMDI), are the base for many polyurethane (PUR) and urethane/urea polymeric products. In the case of wood binders, isocyanates are based on formaldehyde such as MUF or PF, but they do not lead to formaldehyde emission. The advantages of (p)MDI are that they are more thermally stable and are 100% organic, and have a low molecular weight, a low viscosity and a faster curing than standard PF resins, a very good moisture tolerance, and a low surface tension. Disadvantages of pMDI wood binders are that they adhere strongly to almost all surfaces, including steel, and are expensive (Frazier 2003). If monocotyledons are used in particleboard, the non-specific adhesiveness is an advantage to increase bonding (Boquillon *et al.* 2004; Torkaman 2010). Polyisocyanate bonds are more water-resistant than those based on urea formaldehyde (Mason and Kramer 1997; Russell and Johnston 1996), which can be an advantage in straw-particleboard production when compositions of UF and emulsifiable pMDI, reacting with NP40 (EPU) are used (Zhang *et al.* 2011).

Polyvinyl alcohol is a synthetic polymer with a controllable degree of hydrolysis and chain length. PVA-stabilised PVAc emulsions have excellent tack to porous and hydrophilic materials, but a low water resistance. To improve their moisture resistance, PVA can be condensed with formaldehyde and butyraldehyde, treated with ethylene-vinyl alcohol copolymers (EVOH) with sodium hydroxide, modified with hydrophobic end groups or with terminal thiol groups, or acetoacetylated with, for example, a copolymer of vinyl acetate and acetoacetoxy ethyl methacrylate (AAEM) and urea-formaldehyde (Qiao *et al.* 2002). These modifications can improve the properties and performance of PVAc. The variety of modifications may also make it possible to use modified PVA/PVAc as an adhesive for particleboards with a higher content of monocotyledons.

Acrylic adhesives are generally supplied as two-component “Mix in Accelerator” systems containing acrylate and methacrylate monomers generally toughened with elastomeric polymers. They cure by addition polymerisation reactions with free radical initiation, resulting in a very rapid polymer chain growth so that they cure more rapidly than urethane and epoxy resins (Briggs and Jialanella 2010; Damico 2003). The thermoplastic acrylic polymer can be transformed into a thermosetting film adhesive (Gouri *et al.* 2001). Acrylic resin with dibenzoylperoxide as catalyst provides a multifunctional methacrylic monomer (ethoxylated bisphenol A dimethacrylate) which was successfully tested on particleboards (Amazio *et al.* 2011). The addition of an acrylic emulsion generally leads to lower formaldehyde emissions and lower swelling of the boards than a urea formaldehyde adhesive (Amazio *et al.* 2011; Dziurka and Łęcka 2004). Acrylated epoxidised soy oil (AESO) was successfully used as adhesive to produce particleboards of wheat straw (Shakeri *et al.* 2010; Tasooji *et al.* 2010). Acrylate has also been blended with modified soy protein to achieve water resistance and increase the corrosion resistance of the hybrid emulsion (Zhang *et al.* 2010).

An epoxy adhesive may be either a prepolymer containing reactive epoxy groups or a cured polymer in which the reactive groups have reacted already during polymerisation. These adhesives are characterised by the presence of at least two epoxy or oxirane groups which consist of a planar, three-membered ring made up of two carbons and one oxygen atom (Ellis 1993; Hamerton 1996). The viscosity of an epoxy resin is influenced by its structure, its molecular weight distribution, and its temperature. Glycidyl groups in the epoxy resin affect its flexibility and viscosity, but they also lower the heat resistance of the cured resin. The curing temperature of the resin depends on the type of resin and the catalysts and the co-curing agents used (Hamerton 1996). The earliest epoxy resins on the market were reaction products of bisphenol A and epichlorohydrin (Ellis 1993). Epoxy resins are now used mainly for protective surface coatings and in electronics and composites (reinforced resins) (Hamerton 1996). Epoxy resins are used with lignocellulose raw material as matrix-building components consisting sometimes of epoxidised plant oils in fibre-reinforced composites. Examples are composites with hemp, jute, sisal, flax, coir, and ramie fibres (Bledzki and Gassan 1999; Boquillon 2006; Gassan and Bledzki 1999; Rong *et al.* 2001; Sgriccia *et al.* 2008). The idea with these composites is to replace glass fibres with natural fibres (Wambua *et al.* 2003). If epoxidised vegetable oils are used as epoxy resin, triglycerides cross-linked with hydrolysable bonds such as esters remain biodegradable after mineralisation, while those cross-linked with non-degradable bonds are not biodegradable (Shogren *et al.* 2004). Particleboards have been made with groundnut shell particles glued with epoxy resin (Raju and Kumarappa 2011). Tests with wheat straw and 8% or 13% AESO (acrylated epoxidised soy oil) resin provide panels for which the mechanical properties increase with increasing amount of resin and increasing press time (Shakeri *et al.* 2010; Tasooji *et al.* 2010). Tests have also been carried out with alkaline and butyrate kraft-lignin as a substitute or coupling agent between natural fibre and matrix in the epoxy resin additive (El Mansouri *et al.* 2011; Thielemans and Wool 2004).

Lignin constitutes approximately 25% of the mass of the wooden cell wall and is an amorphous aromatic polymer. During the kraft pulping process using sodium sulphide and sodium hydroxide, kraft-lignin accrues as a by-product (Heitner *et al.* 2010), and this is not identical to native lignin as it has undergone significant structural changes (Feldman 2002). Kraft-lignin is generally insoluble in water except in a highly alkaline environment (Lora and Glasser 2002; Widsten and Kandelbauer 2008). Activation or

reactivation of kraft-lignin to use as an adhesive has been reported in several reviews, and modified lignin is often used to partially replace phenol in PF (phenol-formaldehyde) adhesives (Abdelwahab and Nassar 2011; Cetin and Ozmen 2003; Danielson and Simonson 1998; Hu *et al.* 2011; Imam *et al.* 2001; Mankar *et al.* 2012; Olivares *et al.* 1988; Pizzi 2006; Rowell 2012; Sarkar and Adhikari 2000). Total replacement of synthetic adhesives by lignin is also possible (da Silva *et al.* 2013). As the structure of lignin limits its reactivity, modification seems to be essential before it can be mixed with synthetic resins. The most popular modifications are methylolation where hydroxymethyl groups are incorporated into the lignin aromatic rings (Pizzi 2006), phenolation which results in an increase in the number of phenolic hydroxyl groups (Cetin and Ozmen 2003), and demethylating by oxidation to eliminate methyl groups that block potentially reactive aromatic hydroxyl groups (Gonçalves and Benar 2001). The various technical lignins and their modifications have different characteristics, which are also shown by structural and thermal analysis (El Mansouri *et al.* 2011; Jain and Glasser 1993). Technical lignins can also be treated with crosslinking agents such as glyoxal and pMDI or PVAc (Li *et al.* 1997; El Mansouri *et al.* 2007a; 2007b; El Mansouri and Salvadó 2006; Mansouri *et al.* 2011). In the present study kraft-lignin is used to replace epoxy resin by 50% (El Mansouri *et al.* 2011; Thielemans and Wool 2004).

Proteins, both animal- and vegetable-based, can also be used as adhesives. The original wood adhesives were made of collagen extracted from animal bones and hides, casein (milk), blood, fish skins, and soybeans (Rowell 2012). Animal glues include all kinds of gelatine glues derived from by-products of the meat and tanning industries (Anon. 1955). Gelatine is formed by hydrolysis of collagen (Hull and Bangert 1952). The basic constituent of animal and fish skin is collagen, which can be associated with other proteins. Fish glue is collagen or gelatine produced solely from fish skin and bone, but the chemical composition and physical properties of fish glue depend on the species of fish used as raw material (Arnesen and Gildberg 2007; Boonprab *et al.* 2011). Due to their low price and easy handling, proteins from wheat gluten and soy flour are favoured (Wescott *et al.* 2006), and their properties can easily be modified (Liu and Li 2004). Generally, the physical and chemical properties of proteins are influenced by their structure and by the order and presence of amino acids (Rowell 2012). Amino acids are characterised by at least one carboxyl group (-COOH) and one amino group (-NH<sub>2</sub>) each, which makes them ampholytic (Müller *et al.* 2007). To use proteins as adhesives, denaturation is necessary to expose more polar groups for solubilisation and bonding via hydrogen bonds (Rowell 2012). Denaturation is achieved by exposing them to heat, acid/alkali, organic solvents, detergents, or urea (Huang and Sun 2000; Sun and Bian 1999; Wang *et al.* 2005). Proteins such as soy flour can also be treated with sodium dodecyl sulfonate (SDS), sodium dodecyl benzene sulfonate (SDBS), and bio enzymes (Huang and Sun 2000). Enzymes are also used for achieving approved binding and water-resistance properties for wheat gluten (Nordqvist *et al.* 2012) and soy flour (Schmitz 2009). The simplest way to increase the water resistance of a protein adhesive is to cross-link it with a synthetic resin such as PF or MUF (Lin *et al.* 2012; Wescott *et al.* 2006).

Thermosetting and thermoplastic adhesives were considered, even though some of them are not suitable for conventional particleboard production. Since the interest lies not in the adhesive as such but on the reactive groups of the adhesive, they were nevertheless tested to extend the knowledge of adhesives suitable for gluing particles of monocotyledons. The adhesives introduced show a wide range of reactivities or the possibility for considerable modification, are used in WPCs, or are based on a natural



source and might open an opportunity, alone or mixed with surfactants or coupling agents, for using monocotyledon particles in particleboards.

## Objective

The purpose of this study is to demonstrate and compare different adhesives, in pure state or as additives with a surfactant or a coupling agent, and pre-treatment alone or in combination, to glue particles of monocotyledons in panels, particularly when using Reed canary grass (*Phalaris arundinacea* L.) as a core layer.

## EXPERIMENTAL

### Materials

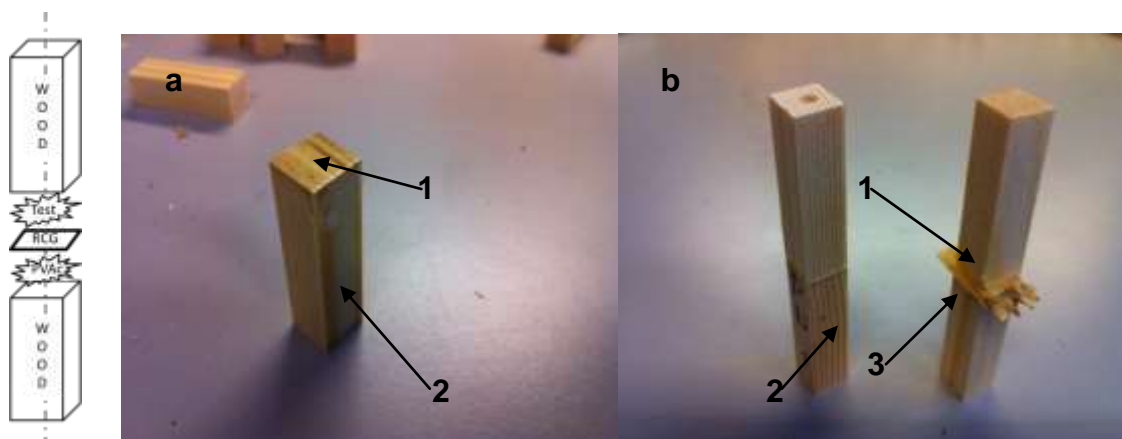
Delayed-harvest reed canary grass (RCG) from northern Sweden was chipped to a length of 1 to 50 mm and stored dry at a moisture content (MC) of 7.4%. The RCG was used either in its natural state or pre-treated with a 25% wt NaOH. Melamine urea formaldehyde (MUF), PVAc, acryl, PUR, epoxy, lignin (kraft-lignin with an amount of 50% epoxy), and fish lime were used as adhesives. The adhesives were either pure or combined with a surfactant, dioctyl sodium sulfosuccinate (DSS), or a coupling agent (CA), silane (Table 3).

### Methods

The bonding between the wood, the adhesives, in pure state or as additives with surfactant or coupling agent, and the external layer of particles from RCG was tested in a tensile test. For the tests, a single straw was “unrolled” and glued with its inner face on a wooden cube with a contact area of 1 cm x 1 cm (Fig. 1). Polyvinyl acetate adhesive was placed between the inner face and the wooden cube. In a second step, the seven different adhesives in the pure state or as additives with surfactant or coupling agent were tested by gluing a second wooden cube with a contact area of 1 cm x 1 cm onto the external layer of the RCG. This external layer was either left in its natural state or treated with a 25% wt NaOH solution for 20 min at room temperature with a solvent ratio of 1:4 (solid/liquid). Thermosetting adhesives were cured in an oven at 100 °C after application, while the others were cured at room temperature. After a curing time of 24 h, the tensile strength of the samples was determined, with the maximum set at 2 N/mm<sup>2</sup>. For each combination, 12 replicates were tested.

For the clamping device, holes were drilled into the end of the wooden cube to fix heels on both sides of the cube. Clamping with the heels made it possible to form joints while avoiding shear stresses, but the combination of materials also resulted in an undefined elongation during the tensile test. The sample was placed vertically in a suspension combined with a tension spring balance (Bosche Wägetechnik, LOOSLI Maschinen GmbH, Schönbühl, CH) to measure the load. The testing speed was 0.2 m/s. This testing method was used for the following reasons: (1) Using a defined area of 1 cm x 1 cm for all samples allowed comparison between the different adhesives, additives, and pre-treatment; (2) MUF was used as reference adhesive since it is conventionally used in particleboard production; (3) It was possible to prepare a large number of samples with a low input of material, energy, and time; (4) It was possible to use the raw material in the way in which it might be delivered to a particleboard factory; (5) Because particleboard might be produced from RCG in combination with wood, the adhesives, in

pure state or as additives with surfactant or coupling agent, had to be tested on both the wood and the RCG; (6) Because the internal surface of RCG is chemically similar to the wooden surface, it was neglected in the tests; (7) The design of the samples made it possible to obtain information from each sample as to whether the weakest point of the bonded joint was between the wooden surface and the adhesive, within the adhesive, or between the adhesive and the (external) wax surface of RCG; and (8) The internal bond strength of particleboards was also tested perpendicular to the surface of the boards according to EN 312 and EN 319 (CEN 1993; 2003).



**Fig. 1.** Design of the samples; (a) reed canary grass (RCG) internal layer glued onto wood with a PVAc adhesive, and in a second step (b) the RCG external layer glued by a “test adhesive” onto the wood. (1) external layer (waxy layer) of RCG; (2) wood as carrier material; (3) internal layer

## RESULTS AND DISCUSSION

Table 3 shows the results of the tensile tests. All values smaller than  $0.01 \text{ N/mm}^2$  are presented as  $0.00 \text{ N/mm}^2$  because of technical restrictions. It was not possible to measure values higher than  $2.00 \text{ N/mm}^2$ . Because of the defined borders, it was decided to present the mean within these borders in combination with the minimum and maximum value instead of the mean and the standard deviation.

The strongest bonds were obtained when the external surface of the RCG was treated with NaOH. MUF was the only adhesive that failed in all combinations to reach a mean strength of  $0.5 \text{ N/mm}^2$ , whereas epoxy reached this value in all cases. Nevertheless, NaOH pre-treatment had a strong influence on the bonding of MUF. In addition to epoxy, in some cases PVAc and even lignin (kraft-lignin with 50% epoxy) reached a strength load of  $0.5 \text{ N/mm}^2$ .

Apart from epoxy, the only adhesives giving a strength exceeding  $0.5 \text{ N/mm}^2$  without additional modification were acryl and PUR. In the case of the natural adhesives based on lignin and fish lime, the surfactant (DSS) seemed to be more suitable than the coupling agent (CA). For PVAc, acryl, and epoxy, CA increased the strength. With PUR, both admixtures with DSS and CA gave lower strength values than the original adhesive, while DSS lowered the strength in the case of acyl and epoxy.

Adhesives such as epoxy, acryl, and PVAc, which are more nonspecific or non-polar, lead to higher bonding strength, as has been reported for MDI and polymeric MDI in the literature. The low values for MUF were also affected by the test design, as this

adhesive had a very low viscosity and oozed out of the glue line. Although the testing method used in this study was not a standardised method, it enabled different adhesives, mixtures, and pre-treatments of reed canary grass to be compared.

**Table 3.** Strength of the Joint between Wood and Untreated (Non) and Pre-treated (NaOH) External Layer of Reed Canary Grass Glued with Seven Different Adhesives with and without Surfactant (DSS) and Coupling Agent (CA)

Adhesive	Pre-treatment/ Modification	Strength (N/mm <sup>2</sup> )
		min – mean – max
MUF	Non	0.00 – 0.07 – 0.17
	DSS	0.00 – 0.01 – 0.08
	NaOH	0.05 – 0.42 – 0.95
	CA	0.00 – 0.03 – 0.16
PVAc	Non	0.16 – 0.45 – 0.91
	DSS	0.18 – 0.54 – 0.97
	NaOH	0.51 – 1.57 – 2.00
	CA	0.50 – 1.09 – 1.72
Acryl	Non	0.53 – 0.71 – 1.02
	DSS	0.23 – 0.34 – 0.45
	NaOH	0.51 – 1.14 – 1.66
	CA	0.95 – 1.25 – 1.88
PUR	Non	0.41 – 0.70 – 1.23
	DSS	0.06 – 0.36 – 0.73
	NaOH	0.70 – 1.48 – 2.00
	CA	0.09 – 0.14 – 0.24
Epoxy	Non	0.00 – 1.46 – 2.00
	DSS	0.50 – 0.83 – 1.44
	NaOH	0.10 – 1.54 – 2.00
	CA	0.00 – 1.52 – 2.00
Lignin	Non	0.14 – 0.34 – 0.60
	DSS	0.23 – 0.51 – 0.81
	NaOH	0.21 – 0.50 – 1.05
	CA	0.22 – 0.47 – 0.80
Fish lime	Non	0.00 – 0.24 – 0.63
	DSS	0.06 – 0.37 – 0.75
	NaHO	0.67 – 1.58 – 2.00
	CA	0.05 – 0.22 – 0.43

12 replicates for each combination

The surfactant affected especially high-end adhesives such as PUR, epoxy, and MUF and lowered the strength. The main reason might be that adding the surfactant destabilized the composition of the adhesive. On the other hand, the addition of the CA silane gave a greater strength than no treatment. Although surfactants seems to introduce curing problems with the high-end adhesives, when blended with the natural adhesives lignin (kraft-lignin with an amount of 50% epoxy) and protein (fish lime) they led to increased bonding strength. Generally, for the natural adhesives, wetting seems to be a greater problem than tack, as compositions with surfactant showed a greater strength than compositions with CA.

The strength values obtained after pre-treatment with NaOH may be critical. First, residual NaOH can affect the adhesive composition and second, parts of the grass were removed which could open passages for the adhesive to penetrate through the grass, which would make the glue line comparable to that between wood only. These might be

intensified by the high concentration of NaOH, which was higher than the one presented in literature to achieve shorter treatment times.

The most interesting adhesive compositions in this study were acryl and lignin (kraft-lignin with an amount of 50% epoxy). Acryl has no formaldehyde emissions, and it opens the opportunity for modification, showing good bonding without any modification. The lignin in combination with epoxy must first be optimised and analysed with regard to health risks because of the epoxide groups. Further, additional research and tests are necessary to find an optimal emulsion. Nevertheless, if it is possible to keep the amount of lignin to at least at 50% as in this study, the high amount of kraft-lignin available opens the opportunity to include a renewable natural resource that is currently available at a low price.

## CONCLUSIONS

1. Tests with different adhesives, in pure state or as additives with a surfactant or a coupling agent, and pre-treatment of external surfaces of reed canary grass (an example of a monocotyledon) showed that the NaOH treatment had a strong impact on the bonding strength for all adhesives. For adhesives like MUF, PVAc, PUR, and fish lime, the bonding strength was at least doubled.
2. MUF was performing worst compared to the other adhesives, which could have been affected by the test design due its very low viscosity. Nevertheless, for MUF the NaOH treatment led to 6-fold increases in bonding strengths, which showed its effectiveness. In case MUF has to be excluded as a potential adhesive for gluing monocotyledons, there are additional adhesives, other than isocyanate-based adhesives, that may be used, including acrylic, epoxy, PVA, or even protein (fish lime) adhesives.
3. A surfactant and coupling agent were each combined with the different adhesives to study the effect of additional wetting or tack compared to the pure adhesive. For all high-end adhesives, coupling agents increased the tack; for the natural adhesives, the surfactants increased the bonding strength.

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Article submitted: March 1, 2014; Peer review completed: April 22, 2014; Revised version received and accepted: May 7, 2014; Published: May 12, 2014.