REVIEW ARTICLE bioresources.com

Critical Links Governing Performance of Self-binding and Natural Binders for Hot-pressed Reconstituted Lignocellulosic Board without Added Formaldehyde: A Review

Martin A. Hubbe,[a],* Antonio Pizzi,[b] Haiyang Zhang,[c] and Rasmina Halis [d]

The production of fiberboard, particleboard, and related hot-pressed biomass products can convert small, relatively low-valued pieces of wood into valuable products. There is strong interest in being able to manufacture such products without the addition of formaldehyde, which is a health hazard during both production and use. This article reviews literature describing various challenges that need to be faced in order to achieve satisfactory bonding properties in hot-pressed bio-based board products without the addition of formaldehyde. Bonding mechanisms are examined in the form of a hypothesis, in which the strength development is represented by a chain with four links. Failure of a board is expected to occur at the weakest of these mechanistic links, which include mechanical contact, molecular-scale wetting and contact, various chemical-based linkages, and structural integrity. The most promising technologies for environmentally friendly production of hot-pressed board with use of lignocellulosic materials tend to be those that favor success in the development of at least three of the mechanistic links in the hypothetical chain.

Keywords: Formaldehyde-free; Particleboard; Pressed wood; Furfural; Lignin; Tannins

*Contact information: a: North Carolina State University, Department of Forest Biomaterials, Campus Box 8005, Raleigh, NC 27695-8005 USA; b: University of Lorraine, LERMAB, 27 Rue Philippe Seguin, F-88000 Epinal, France; c: Nanjing Forestry University, College of Materials Science and Engineering, Longpan RD, Nanjing, China; d: University of Putra Malaysia, Faculty of Forestry, UPM Serdang 43400, Selangor Darul, Malaysia; *Corresponding author: hubbe@ncsu.edu*

Contents

INTRODUCTION

Technology for using natural binders and for the production of self-binding fiberboards and other products from reconstituted lignocellulose-based materials has grown rapidly, at least partly due to concerns about formaldehyde emissions. This development has taken place in the shadow of over 300 million m^3 of formaldehyde-containing fiberboards, particleboards, plywood, oriented strand boards, and related products, which are consumed annually in the world for such applications as housing and furniture (FAO 2014). Formaldehyde emissions have been credited with acute (Zhang *et al.* 2009) and chronic (Krzyzanowski *et al.* 1990; Hun *et al.* 2010; Wolkoff and Nielsen 2010) effects on human health, especially when the gas is allowed to accumulate in indoor spaces. Thus, there is strong motivation to be able to manufacture reconstituted lignocellulosic products without the use of formaldehyde (Nikvash *et al.* 2012; Almusawi *et al.* 2016). Ideally, the goal would be to manufacture high-performing wood-based products, starting with low-value lignocellulosic scrap material, with low application of energy, and without using or generating any toxic substances (Pizzi 2006). And to make things yet more challenging, in order to be competitive, these eco-advantageous reconstituted wood products ought to achieve strength and water-resistance properties comparable to those presently achieved using state-of-the-art formaldehyde-based adhesives technology, all without adding too much to the cost.

Historical Notes

Starting in the 1920s, the patents of Mason and coworkers showed the world that, with application of heat, pressure, and time, the fragments of wood can be put back together, achieving a useful panel material, *i.e.* hardboard (Mason 1926a,b; 1928; Mason *et al.* 1937). In retrospect, Mason was way ahead of his time in being able to attribute the bonding within the Masonite® panel products to such processes as the flow of steam-moistened lignin and the hydrolysis of hemicellulose. Runkel and Jost (1956) later showed that binderless boards could be prepared without the use of steam, taking advantage of the moisture content of the material, plus the addition of heat.

Reviews of More Recent Work

More recent progress in the technology of binderless boards has been reviewed by Pintiaux *et al.* (2015), who placed emphasis on particleboard and fiberboard. Other review articles, focusing on various aspects of the topic, have included the following (Pizzi 2006; Müller *et al.* 2007; Pizzi 2013; Zhang *et al.* 2015; Hashim *et al.* 2016; Tajuddin *et al.* 2016). Review articles related to conventional particleboard and fiberboard, made with formaldehyde-based resins, are also relevant, since many of the materials and processes are the same as those to be considered in the present review article (Kelly 1977; Pelaez-Samaniego *et al.* 2013).

The related topic of cellulose-based reinforcements in composites with synthetic plastic matrices also has been reviewed (Stokke *et al.* 2013; Gandini and Lacerda 2015; Gandini *et al.* 2016; Jawaid *et al.* 2017). Review articles on the surface modification of wood and wood fibers also provide relevant background for the present topic (Hill 2006; Hubbe *et al.* 2015b).

In view of continued developments in lignocellulose-based board products that are prepared without adding formaldehyde and that are reassembled using heat and pressure, the present review shares a similar scope as that of Pintiaux *et al.* (2015), but a new perspective is introduced. As described below, the review article is structured based on a hypothesis. In addition, the present review article includes discussion of some more recently reported findings.

Factors Contributing to Development of Board Strength

As will be considered more deeply in subsequent parts of this article, the reviewed literature points to some key factors that tend to play important roles with respect to the development of strength in hot-pressed board products. These include temperature, applied mechanical pressure, moisture content, chemical composition, and the morphological aspects of pieces of lignocellulosic material that are being pressed together.

The multiplicity of published research related to this topic now makes it possible to look behind these factors affecting strength development in an attempt to understand the mechanisms. For instance, heat, pressure, and time may be important to allow adjacent surfaces to undergo viscoelastic deformation such that they can come into mechanical contact. The chemical nature of materials may be critical in governing whether contact is achieved efficiently at a molecular level. Other aspects of chemistry may be critical in establishing chemical bonding within a hot-pressed board. And finally, a variety of processing factors might lead to defects or to a lack of continuity within a pressed board's structure.

Practical Considerations

Though the published literature includes a very wide range of compositions and conditions for production of hot-pressed boards that do not involve use of formaldehyde, one should not lose sight of issues related to costs. Low-cost options tend to favor relatively low or zero addition of any high-cost components. Thus, high ratios of fibers to added glue generally would seem attractive, as long as the target end-use performance levels can be achieved, meeting the relevant standards. Mechanical strength and resistance to moisture are often key priorities. Such considerations help define the challenges that face researchers and entrepreneurs in this field.

HYPOTHESIS

A hypothesis is proposed here in which the development of strength in reconstituted lignocellulosic products is regarded in terms of links in a chain. In principle, failure is likely to occur at the weakest link. The proposed links are set forth in Table 1. A related concept by Marra (1992) used the analogy of a chain to explain the adhesive bonding of wood surfaces.

Table 1. Proposed Critical Links in the Development of Bonding within Reconstituted Wood Products by Self-Bonding or Natural Adhesives

Link	Description	Selected references
Mechanical contact	Materials and conditions must be suitable to achieve proximity (say within a few μm) of surfaces that will need to adhere, with a sufficient area of contact.	Mason *et al.* 1937; Wellons and Krahmer 1973; Back 1987; Pintiaux *et al.* 2015
Molecular contact	Flowable matrix components (*e.g.* plasticized lignin or hemicellulose) must be able to wet the reinforcing component (cellulose, including cellulose that is coated with other substances) so that bonds can form between the surfaces.	Fowkes *et al.* 1990; Back 1991; Gardner *et al.* 2008; Hubbe *et al*. 2015a; Tajuddin *et al.* 2016
Chemical bonding	To achieve levels of bonding that can compete with conventional board products, there needs to be some form of chemical bonding, for example covalent bonds. Alternatively, a multitude of secondary forces between the adhesive and the substrate, or even between adjacent lignocellulosic components may be sufficient.	Allan and Neogi 1971 ; Pizzi *et al.* 1994; Pizzi and Owens 1995; Widyorini *et al.* 2005c; Okuda & Sato 2006; Pizzi 2006; Lamaming *et al.* 2013; Zhang *et al.* 2015
Structural integrity	The arrangement of particles or fibers needs to have suitable uniformity, connectivity, and absence of large defects.	Plath & Schnitzier 1974; Kelly 1977; Inoue *et al.* 1993; Ando & Sato 2009; Pintiaux *et al.* 2013

Products such as fiberboard and particleboard can have approximately the same composition as wood, so it is perhaps not unreasonable to expect that the separated fragments of wood can be reassembled in such a way as to achieve almost the original strength without the assistance of synthetic adhesives. Such an expectation is consistent with the perspective of wood (and other lignocellulosic material) as being a natural composite (Pintiaux *et al.* 2015). As an alternative hypothesis, it is also reasonable to propose that the reassembled material would be weaker than the original wood due to such factors as loss of degree of polymerization and the breakdown of higher architecture levels of the material.

The cellulose component of wood is fibrous and relatively rigid in comparison with the hemicellulose and lignin, especially when heated under moist conditions. But to accomplish the targeted strength properties, based on the hypothesis just described, at least one of the natural components of lignocellulosic material (or some natural adhesive) needs to be able to deform and increase the area of contact, to wet and achieve molecular-scale contact with the solid surface, to undergo either covalent bonding or multiple secondary forces interactions with the substrate (within the bond-line) leading to adequate cross-linking, and to be arranged in such a manner as to distribute the load effectively during usage of the product. The sections that follow will consider the main factors affecting each of the links in this conceptual chain.

As stated in the abstract, at least three of the four conceptual links ultimately will be judged to have been well supported by research findings. What about the fourth link? The reason for stating "at least three" is that some researchers will be concerned about whether or not covalent bonding must take place at the interface between biomass particles and an adjacent phase, such as bondable material or another lignocellulosic particle. Other researchers may be more concerned about broader questions, such as whether chemical effects of various types and locations are critically important for strength development. So different readers, depending on their interests, may wish to judge the link related to chemical bonding by different criteria. Hydrogen bonds, and a multitude of other secondary bonds such as van der Waals forces, *etc*., as well as long chain physical entanglements exist between the domains, but covalent bonds are present too. The so-called lignin-polysaccharide complex is nothing other than the presence of covalent bonds between lignin and wood hemicelluloses. Thus, (i) benzyl ester linkages exist between the alpha site of lignin units and the carboxylic acid function of hardwoods and softwoods glucuronoxylans, (ii) benzyl ether links exist between the alpha site of lignin units and the arabinose side chain of softwoods arabinoglucuronoxylans, and finally (iii) phenyl glycosidic links between the O4 lignin site and the C1 site of glucose of softwoods and hardwoods glucomannans (Fengel and Wegener 1989). All of these are examples of covalent bonds between the domains.

EXAMINING THE LINKS

Evidence to support or dispute different critical factors in the preparation of an eco-friendly reconstituted wood product can be found in a wide variety of published studies. Such findings will be considered here, in the following subsections, according to the conceptual links listed in Table 1.

Mechanical Contact

The first critical link – "mechanical contact" – can be justified by the fact that bonding cannot reasonably be achieved in regions where the solid particles or fibers in a board product have air spaces between them. Contributing evidence to support this assertion includes the very strong correlations that have been observed between board properties and density (Xu *et al.* 2001; Gravitis *et al.* 2010).

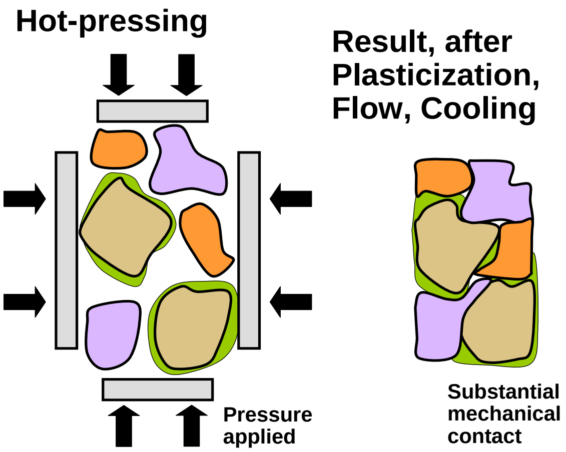

Fig. 1. Conceptual illustration of how plastic flow of hot, moist lignin or hemicellulose phases in biomass can be expected to flow during hot-pressing, thus achieving a degree of mechanical contact between particle or fiber surfaces

In principle, achievement of mechanical contact must involve either deformation of solid components or temporary conversion of at least some of the components into a liquid or viscoelastic state, capable of flow. The concept is illustrated pictorially in Fig. 1. Thus, as proposed by Wellons and Krahmer (1973), thermoplastic flow ought to be regarded as an important mechanistic step in preparation of binderless board.

Types of biomass

Binderless board and related products have been prepared from a very wide range of biomass materials. Presumably this list includes materials that differ greatly with respect to such attributes as deformability of particles and viscoelastic properties of the matrix components, with emphasis on the lignin. Because of the wide diversity of underutilized lignocellulosic materials that are locally available around the world, it is reasonable to expect that a very broad range of materials will be used in the future, both at the commercial level and in future research. For example, Hashim *et al.* (2012) prepared binderless board from different types of oil palm biomass; panels prepared from the bark and leaves were unsatisfactory, whereas particles obtained from the core of the trunk yielded the most favorable properties.

Noting the very broad range of properties of biomass materials, not all of them are suitable for producing various forms for reconstituted board. In particular, in some cases biomass with low density can be inappropriate for making medium- to high-density particleboard products. This is because the target mechanical properties are higher than those of the lower-density biomass, and excessively low-density raw materials are difficult to process and compress. Problems also can arise when the biomass has an initial density that is much higher than appropriate for the desired product. In such cases, the compression ratio of the higher density biomass will be small and there will be a lot of air in the reconstituted board, which will influence the final properties. Vital *et al.* (1974) used four hardwood species with density from 0.28 to 0.65 g/cm^2 to make three-layer particleboard, and the compression ratio of the particleboard was studied. Although urea formaldehyde was used in the experiment, the study can also be used as a reference for binderless board for purposes of selecting the target density of a board product. When preparing particleboard with similar actual density, the board with the lower original material density always achieved better mechanical properties, which might be attributable to a higher compression ratio.

Particle size

Many publications have reported important effects on board strength as a consequence of differences in particle size (Gupta *et al.* 2011). Higher strength generally has been reported when the particles were smaller, either due to milling or due to classification by screens (Shen 1986; Okuda and Sato 2004; Gravitis *et al.* 2010; Marashdeh *et al.* 2011; Xu *et al.* 2012; Fahmy and Mobarak 2013; Kurokochi and Sato 2015a; Almusawi *et al.* 2016; Huang *et al.* 2016; Juliana *et al.* 2017). It has been proposed that smaller particles might be easier to pack into a dense structure, such that the surfaces come into mechanical contact over a larger proportion of the surface area (Pintiaux *et al.* 2015).

Particleboards commonly are prepared with smaller particles in the surface layers and larger particles in the core. The distribution either can be varied gradually, or it can be arranged in abrupt layers. Either approach, when compared to a uniform distribution of particles in the board, can provide a denser, smoother surface, as well as providing better flexural properties (Geimer *et al.* 1975; Kuklewski *et al.* 2007; Jin *et al.* 2009; Wilczyński and Kociszewski 2012).

However, it is also possible that the smaller particles, in a given case, may have exhibited consistent differences in either chemical composition (Kurokochi and Sato 2015a) or in factors leading to easier deformation. Miki *et al.* (2007a), who applied very high pressure molding conditions, observed an optimum particle size (about 100 μm) for strength maximization; presumably the pressure was enough to fully press together particles of the optimum size.

Particle deformability and conformability

Only in a few cases have authors made reference to the conformability of different solid particles in their studies of binderless board production. Fahmy and Mobarak (2013) noted that pith parenchyma cells (fines) of bark-containing corn stalks have a high ratio of lumen dimension to cell wall dimension, and such a shape renders them more susceptible to deformation when pressed or sheared. By contrast, Hashim *et al.* (2011a) reported that some of the bark cells from oil palm, having thick and rigid cell walls, were not deformable enough to be effectively molded in the course of their study. Widyorini *et al.* (2005a,c) noticed that steam was needed in order to achieve good bonding with coarser (non-parenchyma) kenaf material, whereas strong cohesion could be achieved among the parenchyma cells by application of just heat and pressure. Although Mason *et al.* (1937) understood particle deformation to be important, that variable did not explain all of their observations; therefore they proposed that other factors, such as chemistry, must be important as well. The influence of particle deformability or lack of it in panel pressing was outlined in applying particleboard technology when using hard eucalyptus wood particles. These hard particles negatively affected the performance of the particleboard. Eucalyptus wood cell walls failed to crack under standard particleboard manufacturing pressures, leading to regeneration of full cell sizes and hence excessive board swelling and springback (Van Niekerk and Pizzi 1994). Evidence related to conformability also has been revealed in dynamic mechanical analysis (DMA) testing (Saadaoui *et al.* 2013). It was shown in the cited work that fractions of date palm exhibiting relaxation phenomena in the DMA tests gave better strength results.

Pretreatments affecting conformability

Many authors have found evidence that pretreatment of cellulosic biomass, in various ways, can contribute to the strength of binderless board. Though it generally has not been demonstrated whether the strength improvement was related to increased particle conformability, that is a possible explanation. Beneficial effects of thermal pretreatment on strength were reviewed by Pelaez-Samaniego *et al.* (2013) and Tajuddin *et al.* (2016). Moist conditioning at temperatures between 180 and 230 °C has been shown to improve the properties of wood composites. In particular, water absorption and thickness swelling were reduced in various cases, which is consistent with possible hydrolysis and loss of hemicellulose from the biomass. Combinations of high temperatures (at least 100 °C) and added moisture, *i.e.* hydrothermal treatments, have been shown to be beneficial to binderless board strength in reported cases (Bouajila *et al.* 2005; Imanishi *et al.* 2005; Luo and Yang 2012).

Thermal-hydromechanical (THM) processes for panels and other timber products were reviewed in depth by Navi and Pizzi (2015). During THM wood undergoes chemical and structural transformations depending on the processing parameters and material properties. Consequently, this transformation brings about changes to the mechanical, physical, and biological durability of wood with positive as well as negative effects. One of the challenges in THM treatment is to reduce or eliminate the negative aspects of THM-treated wood. The review presented the relationship between processing parameters and product properties. Important aspects were associated with eliminating the set-recovery of densified wood, in panels or otherwise, by THM post-treatments and the chemical origin of the relaxation of internal stresses induced by densification.

Steam explosion is among the most widely studied and generally effective pretreatments that has been used to enhance the strength of binderless board. In such pretreatments the biomass is heated under pressure with steam, and then the pressure is suddenly released through a valve, causing particles to rupture with the sudden expansion of the steam within them. The following researchers reported substantially stronger binderless board following such treatments (Suzuki *et al.* 1998; Anglès *et al.* 1999, 2001; Laemsak and Okuma 2000; Salvadó *et al.* 2003; Velasquez *et al.* 2003a,b,c; Mancera *et al.* 2008; Quintana *et al.* 2009; Luo and Yang 2011; Mancera *et al.* 2011a; Shang *et al.* 2012; Luo *et al.* 2014; Mejía *et al.* 2014; Kurokochi and Sato 2015a).

A yet more aggressive approach can involve mechanically grinding the biomass. For instance, the following authors reported improved bonding properties of board products after thermo-mechanical pulping (Imanishi *et al.* 2005; Geng *et al.* 2006; Gao *et al.* 2011). Velasquez *et al.* (2002) and Kurokochi and Sato (2015a) showed benefits of grinding biomass after it had been steam-exploded. The beneficial effect of such grinding on self-bonding was attributed to the increased surface area (Kurokochi and Sato 2015a). In follow-up work, some of the beneficial effects of the grinding were also ascribed to breakdown of protuberances on straw particle surfaces (Kurokochi and Sato 2015b).

Though all of the described pretreatments, including moist heating, steam explosion, thermomechanical pulping, and grinding, have been reported to improve properties of binderless board, the effects cannot be uniquely attributed to changes in conformability of the particles. In fact, there is a need for studies that specifically quantify conformability as a function of various pretreatments.

Glass transition temperatures

It is well known that many pure polymeric materials become soft when the temperature reaches a critical point, known as the glass transition temperature. The glass transition temperatures of dry cellulose, hemicellulose, and lignin have been reported to be approximately 220, 170, and 200 to 220 °C, respectively (Back 1987; Hashim *et al.* 2011b). However, it is also known that much lower values of T_g are found in the presence of increasing amounts of moisture (Back 1987; Pintiaux *et al.* 2015). Figure 2 is a replotting of selected data from Pintiaux *et al.* (2015) originally derived from the work of Kelley *et al*. (1987).

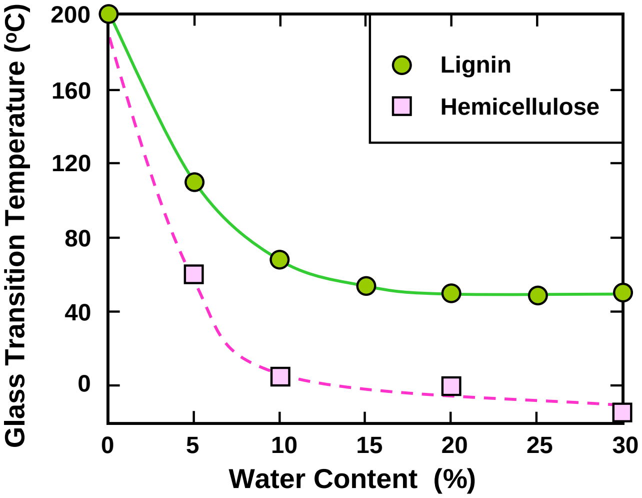

Fig. 2. Effect of moisture content on the glass transition temperatures of hemicellulose, and lignin. Data selected and replotted from Pintiaux *et al.* (2015)

Several studies have shown increased bonding or compression of binderless board in the presence of increasing levels of moisture, with specified conditions of temperature and pressure (Heebink *et al.* 1972; Xu *et al.* 2006; Miki *et al.* 2008; Zhou *et al.* 2011; Pintiaux *et al.* 2013). Notably, Takahashi *et al.* (2009) observed that the thermal flow temperature of wood flour was progressively decreased with increasing temperature and time of a previous steam treatment. According to Tajuddin *et al.* (2016), steam treatment is known to decrease the glass transition temperature of lignin. Thus, the matrix material of the wood can become plasticized during compressive molding (Takahashi *et al.* 2010).

Pressure and temperature

In light of the effect of moisture on glass transition temperatures of the lignin and hemicellulose, it is reasonable to anticipate there to be a joint dependency on these variables with respect to the development of binderless board properties. This expectation has been confirmed in several studies (Xu *et al.* 2006; Pintiaux *et al.* 2013; Almusawi *et al.* 2016). According to Pintiaux *et al.* (2015), binderless board products are more highly dependent on whether or not there is sufficiently high pressure, temperature, and time during pressing, in comparison with comparable products formed in the presence of a formaldehyde-containing adhesive.

Time has been found to be an important parameter in several studies. It is generally found that board density and strength properties at least initially increase progressively with increasing duration of pressing (Velasquez *et al.* 2003b; Okuda and Sato 2004; Winyorini *et al.* 2005b; Ando and Sato 2009; Gao *et al.* 2011; Luo and Yang 2012; Boon *et al.* 2013; Nadhari *et al.* 2013; Huang *et al.* 2016). However, in a few cases there was evidence of negative effects if the duration of treatment was excessive, depending on the temperature (Anglès *et al.* 1999; Salvadó *et al.* 2003; Velasquez *et al.* 2003b; Winyorini *et al.* 2005c; Ando and Sato 2009; Mancera *et al.* 2011a; Shang *et al.* 2012; Xu *et al.* 2012; Saari *et al.* 2014). The effects of excessive hot-pressing duration generally have been attributed to chemical breakdown, especially the hydrolysis of the hemicellulose components of biomass (Hsu *et al.* 1988).

The analysis of Bouajila *et al.* (2005) suggests that certain time effects may be attributed to the speed at which heat can be conducted through layers of lignocellulosic material; their results showed that major increases in strength were not achieved in the center of binderless fiberboard until the local temperature exceeded the glass transition point of lignin. Although the initial beneficial effects of hot-pressing time on board properties are consistent with viscoelastic flow of the matrix components of the biomass, other mechanistic contributions are also possible, as will be described in later sections.

Molecular Contact

Relative to the other mechanistic steps to be considered in this article, the step involving the molecular-level spreading (*i.e.* wetting) of lignocellulosic surfaces by binding materials (including plasticized lignin and hemicellulose), has received less attention from researchers. However, it is well known that wettability phenomena can play a decisive role relative to adhesion (Mittal 2013). So it will be proposed here that, at least in some cases, the critical step in achieving good bonding within a reassembled lignocellulosic structure will depend on whether or not certain components that are at least temporarily behaving as liquids (or as mobilized chemical groups bound to solids) are able to advance, at a molecular level, across the surfaces of adjacent solid-like particles, fibers, or flakes during hot-pressing.

Though in many cases the term “molecular contact,” as considered here, might have much similarity to the mechanical contact considered in the previous section, the focus is on different mechanisms that might impede the effective development of adhesion. Based on literature cited in the previous section, issues related to rheology and ability to flow (as a function of temperature, pressure, and time) can determine the degree to which mechanical contact is established. But this section is concerned with cases in which issues related to wettability are favorable or not favorable for contact at the molecular level.

Wettability principles

Theoretical and practical issues related to the wetting and wettability of cellulose-based surfaces have been reviewed in this journal (Hubbe *et al.* 2015a). To summarize, experiments in which selected probe liquids are placed onto solid surfaces can yield two kinds of information that are useful for understanding and for predicting the efficacy of adhesive systems: The first question involves whether or not close contact is likely to be accomplished at a molecular scale, *i.e.* whether wetting takes place effectively. The second question involves the types of physical forces operating across the interfaces, even before or in the absence of any covalent bonding. Such information can be obtained by comparing the contact angle results obtained with probe liquids that are either (a) nonpolar, (b) polar, or (c) capable of forming hydrogen bonds (Hubbe *et al.* 2015a). Readers are referred to the following sources for additional background (Owens and Wendt 1969; Fowkes *et al.* 1990; Back 1991; Hansen 2007; Gardner *et al.* 2008; Yuan and Randall 2013).

Removal of substances blocking contact

A key finding, which is described in more detail in the sources just cited, has been that liquid phases having a higher free energy of their surface generally will tend not to spontaneously wet surfaces having lower surface energy. To give a practical illustration, if the solid surface is coated with a wax, then a droplet of water will tend to bead up rather than to wet the surface. Terms such as "tend to" are intentionally used in this description due to the fact that wetting also depends on morphological aspects, including pores and nano-scale structures, as well as chemical heterogeneity, *etc.* In agreement with such concepts, the following studies have reported generally poor bonding within binderless board materials when waxy materials were present (Back 1987; Gollob and Wellons 1990; Widyorini and Satiti 2011; Alvarez *et al.* 2015; Kurokochi and Sato 2015b). Increased bonding of wood surfaces, in the case of a lignin-based bonding system, was observed following extraction of the wood surfaces or bark surfaces with NaOH (Young *et al.* 1985; Geng *et al.* 2006). Presumably such a treatment tends to saponify and remove fatty acids and resin acids from the wood or bark. Removal of such relatively hydrophobic compounds tends to make the cellulosic surfaces more water-wettable. Alvarez *et al.* (2015) showed that particleboard strength was increased in cases where the particles had been extracted with a 2:1 toluene:ethanol mixture before hot-pressing.

Figure 3 presents a conceptual illustration of how a low-energy, waxy layer covering part of a cellulosic surface can be expected to impede the wetting and spreading of a matrix material such as lignin or hemicellulose that has been temporarily rendered fluid-like by the conditions of heat and moisture. As shown at the left side of the figure, the contact angle of the matrix material relative to the uncovered cellulose is expected to be below 90 degrees, such that the surface is classified as being "wettable". The fluidized matrix material would be expected to continue to advance over the cellulose in such areas, achieving efficient molecular-level contact. By contrast, a waxy layer could decrease the forces of interaction to such an extent that hemicellulose, and possibly also some lignin materials would not be able to efficiently wet such surfaces. One likely possibility, as implied by the drawing, is that the contact line facing the waxy layer might remain stationary, perhaps blocked by minor features of roughness (Hubbe *et al.* 2015a). It is worth noting that lignin, which typically has a relative low surface energy, would be expected to have a greater ability to spread across low-energy waxy layers.

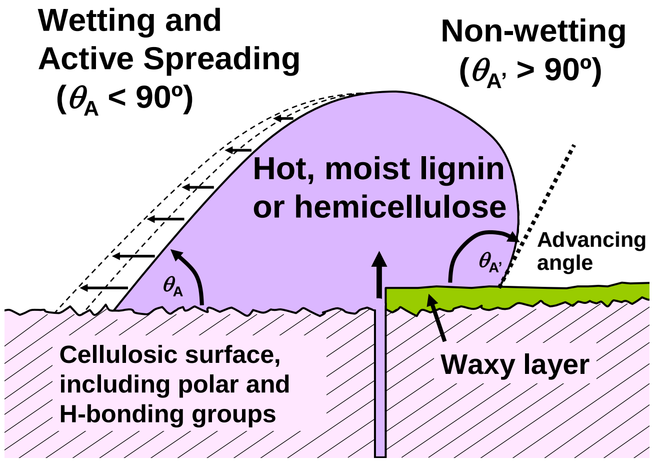

Fig. 3. Conceptual illustration of how a low-energy waxy surface on a cellulosic material would be expected to resist the molecular-level wetting and spreading of a matrix material such as lignin or hemicellulose that has been made fluid-like by the combination of heat and moisture

Though the inability of matrix materials such as hot, moist hemicellulose or lignin to be able to spread over the surface of a wax-coated cellulosic particle is one way to explain reduced bond strength in the presence of wax, this is clearly only part of the story. Suppose that, due to the application of high pressure, the surfaces are able to be forced into true molecular contact, despite the less-than-favorable interactions at the surface. In that case, one can still envision a waxy layer as "blocking" the development of key aspects of bonding, such as hydrogen bonds connecting the adjacent solid particles or fibers (Back 1987). This is because waxy materials lack the functional groups (especially –OH) that are needed to participate in a hydrogen bonding mechanism.

The next issue to consider is almost the opposite of the previous one. Several researchers have reported improved adhesion and other properties of binderless board products when the fibers have been treated to remove some or all of the hemicellulose, which can be regarded as a relatively high-energy component. For instance, the following authors noted higher bonding strength after steam explosion treatment, which resulted in less hemicellulose remaining in the solid material (Pelaez-Samaniego *et al.* 2013). The physical strength of the resulting wood composite material may either increase or decrease, depending on the details, according to the cited work. Another reported benefit of hemicellulose removal has been reduced water absorption and thickness-swelling of particleboard (Pelaez-Samaniego *et al.* 2014a). In apparent disagreement with other studies mentioned earlier in this paragraph, the cited authors reported no significant change in other strength-related properties following the extraction of hemicellulose by hot water. In another study, hot water extraction of bamboo, with the removal of water-soluble components, was found to decrease the internal bonding of binderless boards (Saito *et al.* 2013). Alvarez *et al.* (2015) observed lower strength of particleboard in cases where the particles had been extracted with hot water; it was proposed that the effects were due to decreases in the amount of polar compounds, including lower-mass phenolic species.

Another item that has the potential to get in the way of bonding within a reconstituted lignocellulosic product is silica, which is present in important amounts in grasses and various other plants. Silica particles appear to serve as a defense mechanism, tending to discourage consumption by animals (Massey *et al.* 2006). Kurokochi and Sato (2015b) reported improved strength of binderless board products following removal of silica. The effect, however, was not regarded as large. Though the cited authors found that the amount of silica present could be decreased by fractionating the material and discarding the silica-rich fine dust fraction, they did not believe that such a procedure would be justifiable in practical situations. There does not appear to be consistent evidence in the literature to support the idea that solid materials such as silica play a major role in blocking molecular-scale contact between solid surfaces hot-pressing.

Another possibility is that in some situations inorganic particles might play the role of reinforcements within a bonding layer. Examples of such a concept find support in articles having to do with synthetic binder systems. For example, Hsieh *et al*. (2017) showed that high carbon/silica dual component particles served not only as reinforcing agent but also as thermal transport medium used in an epoxy composite. The system resulted in a reduction of the coefficient of thermal expansion (CTE) and cure temperature as well as enhancement of storage modulus and thermal conductivity. An improvement in composite properties resulting from mild acid-hydrothermal treatment of rice husk (RH) was attributed to high compatibility and good interaction between filler and epoxy matrix from superior surface properties (surface area, porosity, and silica segment) and high content of carbon component in the RH-carbon/silica. Furthermore, the characteristics of the epoxy biocomposite significantly improved with the increase of the RH-carbon/silica filler content (Hsieh *et al*. 2017).

NaOH is often used as a simple and effective pretreatment. Alkaline pretreatment promotes saponification of intermolecular ester bonds. Higher NaOH concentrations will lead more degradation of hemicellulose. NaOH at sufficiently high levels can play the critical role of removing lignin due to alkaline cleavage of ether linkages in the lignin (dissolve and fragment), which may be accompanied by condensation reactions (Wang *et al*. 2003). Crosslinking of xylan, other hemicelluloses, and lignin has been shown to occur during treatment (Low *et al*. 2015). Dissolution of hemicelluloses results from a combination of peeling and alkaline hydrolysis reactions. Geng *et al.* (2006) reported higher strength of binderless fiberboard after alkaline pretreatment of spruce fibers.

Re-positioning of components

One of the reported effects of the steam explosion treatment of lignocellulosic biomass has been coating of the resulting solids with a sparsely distributed superficial layer of microscopic sphere-like lignin particles (Anglès *et al.* 1999; Gao *et al.* 2011; Luo *et al.* 2014; Pelaez-Samaniego *et al.* 2014b). Tajuddin *et al.* (2016), based on their review of the literature, stated that steam treatments tend to expose more lignin at the surface, presumably as a result of dissolution of hemicellulose. Likewise, Felby *et al.* (2004) attributed the beneficial effects of laccase enzymatic treatments on bonding strength to the exposure of more lignin at the fiber surface. The difficulty to apply paint to wood that has been thermally treated has been attributed to migration of lignin to the surface (Boonstra 2008).

Chemical Bonding

The third conceptual link in the bonding mechanism being discussed here is chemical bonding. Aspects to be considered for this topic are (a) covalent reactions that can take place involving different components of the biomass, (b) other types of chemical bonding, (c) the addition of other natural organic compounds that have some possibility of covalent reactions, and (d) chemical treatments of biomass to render the surfaces more suitable for bonding. Earlier reviews that have focused on chemical changes during hot-pressing of board products, leading to bond formation, include the following (Pizzi 2014; Pintiaux *et al.* 2015; Tajuddin *et al.* 2016).

To start the discussion, Fig. 4 presents the concept of development of covalent bonds connecting solid particles. Two covalent bond examples are represented in the figure, an ester bond at left and an amide bond at right. By contrast, the hydrogen bond (indicated in the middle of the figure) is generally temporary in character, with at last one important exception, involving the formation of relatively permanent and regularly organized hydrogen bonding within crystalline phases (Pönni *et al.* 2012). Although Fig. 4 pictures two particles in contact, the same concept can be applied in the case of a selected "adhesive" phase developing covalent bonding with a wood fiber or particle surface.

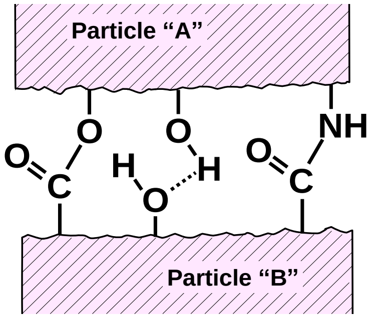

Fig. 4. Representation of covalent bonding at an interface

Certain publications have claimed that successful formation of hot-pressed board in the absence of synthetic binders requires covalent bonds to form at the interface between natural adhesives and wood surfaces and/or directly linking the two wood surfaces together (Felby *et al.* 2002, 2004; Álvarez *et al.* 2011). According to this concept, covalent bonding would help to ensure a continuous connection within the final product. A fully covalently bonded structure would be expected to resist the debonding effects of moisture. However, in other publications the necessity or the existence of covalent bonds at the interfaces has been questioned (Pizzi *et al.* 1994; Pizzi and Owens 1995). The issue is difficult to settle, in general, since there is such a wide variety of thermally bonded, formaldehyde-free wood structures. Also, it can be inherently difficult to detect low numbers of covalent bonds forming at the interface between two macroscopic phases.

While there is no doubt that adhesive-to-wood covalent bonds can form under specific experimental conditions, and there is abundant literature on the subject, the conditions employed in studies reporting such bond formation generally have not corresponded to the conditions commonly used in the pressing of wood panels. For instance, covalent bonds between wood and a synthetic adhesive can form at temperature higher than 120°C maintained for two hours (Pizzi *et al.* 1994). But extensive covalent bonding appears unlikely in the core of a particleboard, which is able to reach only 115 °C to 120 °C for no more than 1 to 1.5 minutes when pressed at 200 °C for 3 minutes. Allan and Neogi (1971) found in the case of phenol-formaldehyde bonding of wood at 120 °C for 2 h that only one adhesive-to-substrate covalent bond was formed for approximately every 1200 cross-links within the resin itself (see also Pizzi *et al.* 1994). This was also the case with isocyanate binders, for which the original misconception of a predominance of covalent bonding between adhesive and substrate, which has been used to explain the high strength of the panels obtained in that manner, was disproved (Pizzi and Owens 1995; Wandler and Frazier 1996).

While panel core adhesion appears to be mainly due to the multitude of secondary forces involved, mainly van der Waals forces and H-bonds, the situation is different for panel surfaces in direct contact with the hot platens of the press. Here, the panel temperature reaches temperatures between 190 °C and 220 °C, albeit for a short time, but at a much lowered percentage moisture content as water is driven as steam towards the board core. Under these conditions it is rather likely that covalent bonds do form in much higher proportion (Pizzi and Owens 1995).

Molecular entanglement

Molecular entanglement can be considered as a bonding mechanism. Entanglement of long-chain molecules has been proposed to play an important role in adhesion and cohesion of various polymers (Willett and Wool 1993; da Silva *et al.* 1996; Lin *et al.* 2004) and even in the bonding of paper products (McKenzie 1984). In the case of binderless boards, Felby *et al.* (2004) attributed as least part of the strength to such a mechanism. Gfeller *et al.* (2003, 2004) proposed likewise that a melting of matrix materials in the wood can take place during a friction-based treatment called "wood welding". It was proposed that the momentarily fluidized polymeric chains become entangled and that they then lock themselves together when the friction is removed, allowing the system to cool. Though such ideas seem logical, there has been a lack of persuasive demonstration of whether or not such a mechanism is important in the context of wood-based composites.

Ionic contributions

Ionic bonding is another type of interaction that does not involve the formation of covalent bonds. Ionic bonds clearly play a dominant role in the formation of salt crystals. Halvarsson *et al.* (2009) proposed a bonding mechanism related to ionic interactions in the case of reconstituted wood products. They found that the addition of calcium chloride to wheat straw that had been oxidized (or "activated") by treatment with Fenton's reagent led to an increase in physical properties, as well as water repellency. Such effects would reasonably involve an association between the divalent calcium cations and the negatively charged carboxylate groups at the lignocellulosic surfaces. However, in common with the mechanisms of bonding within a sheet of paper (Hubbe 2006), there generally does not seem to be much evidence in favor of the importance of ionic bonding contributions to the strength of hot-pressed board.

Lignin

Given the long-held belief that lignin plays a central role in bond development in binderless board products (Mason *et al.* 1937; Pizzi 2006; Zhang *et al.* 2015), chemical effects related to lignin and bonding will be considered first. To lay the groundwork, a very brief overview of lignin composition will be presented. The following articles have discussed how the presence of lignin may affect bond development, in terms of chemical changes and reactions (Felby *et al.* 2002; Müller *et al.* 2007; Gravitis *et al.* 2010; Navarrete *et al.* 2010; González-García *et al.* 2011; Bertaud *et al.* 2012; Pizzi 2013, 2014; Li *et al.* 2015; Zhang *et al.* 2015; Le *et al.* 2016).

Lignin can be briefly described as being a random polymer that is biologically synthesized from three main building blocks, the proportions of which differ greatly between different classes of lignocellulosic plants (Vanholme *et al.* 2010). The lignin of softwoods is rich in guaiacyl groups, that of hardwoods is rich in syringyl groups, and various grasses also have significant amounts of *p*-hydroxyphenyl groups. In addition, the listed "phenol-propane" units within lignin's irregular, three-dimension structure are bound together by a variety of ether (β-O-4 and α-O-4), and carbon-carbon linkages, among others. Within wood, lignin appears to play the role of bonding agent between the fibers, greatly contributing to compression strength and rigidity.

From various perspectives, lignin has been regarded as a resilient substance. Although lignin has a reputation for being slow to biodegrade, it can be eventually reduced to monomeric form by the action of various fungi, *e.g.* the white-rot fungus, which secrete lignin-degrading enzymes (Martinez *et al.* 2005; Halis 2011; Mohamed *et al*. 2013). Various pre-treatments using white-rot fungi have been examined (Leatham and Kirk 1982; Bhardwaj *et al.* 1996; Ahmed *et al.* 1998; Pandey and Pitman 2003; Taniguchi *et al.* 2005; Litthauer *et al.* 2007; Ferraz *et al.* 2008). Fungal species, wood types, chip sizes, and movements during treatment can markedly affect the amount of energy saved. There are three types of extra-cellular lignolytic enzymes, which are also known as oxidative enzymes and often referred to as lignin modifying enzymes (LMEs). These are lignin peroxidase (LiP), manganese-dependent peroxidase (MnP), and laccase (Lac), each of which is able to break down lignin effectively.

Papermakers, when they wish to remove lignin from wood during pulping, are required to use harsh alkaline conditions and/or solvents (Biermann 1996; Norhaslida *et al*. 2014). Kraft lignin is a material that has undergone vigorous changes in its native chemical structure during the pulping process. In the course of kraft pulping, the lignin is eliminated from the fiber wall by solubilized it in the pulping liquor. The lignin can remain in solution as long as the alkalinity is kept high, favoring the dissociation of the weakly acidic phenolic groups. There have been many research models published explaining the dissolution of lignin in alkaline media (Ralph *et al.* 2004; Gellerstedt 2015). Dimmel and Gellerstedt (2010) reported that alkylaryl ether (β-O-4) linkages are largely broken, resulting in lignin fragments with a high percentage of free phenolic structures but no lignin fragmentation for other types of lignin structures on side-chain and also aromatic units. The presence of sulfur in the kraft pulping liquor has been shown to induce radical reactions between dissolved phenols (from lignin) and lignin moieties, thereby giving rise to new biphenyl and biphenyl ether structures both in the dissolved and in the residual fiber lignin (Majtnerova and Gellerstedt 2006).

The selectivity of the initial delignification is very poor, since up to 40% of hemicelluloses are concomitantly degraded and dissolved during this phase. In contrast, the intermediate phase of the process (sometimes called the bulk phase) is characterized by a selective delignification, where up to about 75 to 93% of the original lignin present in wood is removed while only minor amounts of polysaccharides are degraded (Alekhina *et al*. 2015). It was reported that there are three main approaches to fractionation of lignin. Fractionation can be based on solubility in organic solvents, selective acid precipitation at reduced pH values, and membrane ultrafiltration.

When chemists think of lignin as a possible component in a bonding system, it is most common for them to consider the reaction of lignin's free phenol functional groups as potential reaction sites for formaldehyde (Effendi *et al.* 2008). In other words, the most common approach has been to attempt to use lignin, or some modified form of lignin, as a cheaper substitute for at least some of the phenolic components in a phenol-formaldehyde resin (Abdelwahab and Nasser 2011). Such efforts, when attempted with ordinary types of available lignin, tend to have only limited success due to the relatively low proportion of free phenolic –OH groups in ordinary lignins (Hu *et al.* 2016). This results in a low reactivity of the lignin aromatic nuclei. In an effort to compensate, there can be a considerable lengthening of the required panel press time when lignin is added to a traditional formaldehyde-based adhesive, thus discouraging its use in this manner. This can be solved by pre-methylolating lignin in a reactor before adding such pre-methylolated lignin to a traditional PF adhesive for panels. In this manner lignin has been used with as much as 20% to 30% substitution of phenol in PF resins for plywood (Calvé 1990; Tahir and Sellers 1990). The concept of pre-methylolation of lignin has been taken up by a number of authors for a variety of different applications in wood panels. One major North American Company (Georgia Pacific) used this system for many years. Because most technology related to formaldehyde-free fiberboard and particleboard involves unmodified (or mostly unmodified lignin), some of the same limitations in potential reactivity can be expected to apply.

Some researchers have introduced additional lignin as an adhesive for the preparation of all-natural biomass board (Mancera *et al.* 2011b; Nasir 2013; Sun *et al.* 2014). For instance, lignin in the absence of other additives can be used as a panel binder in different systems, such as acid and/or peroxide-induced phenoxy-coupling. Such a treatment can yield very interesting particleboard without any adhesive other than lignin itself (Nimz and Hitze 1980; Nimz 1983). In such applications it is important to expect there to be differences in results depending not only on the species of wood material from which the lignin is derived, but also on the pulping method. For example, Sun *et al.* (2014) prepared binderless boards either with milled wood lignin or lignin obtained by mild enzyme acidolysis. The so-called “enzyme hydrolysis lignin” is generally regarded as being of higher purity than other commercially available lignin types, and accordingly there have been several studies in which it was used with some success to improve the bonding within fiberboard or particleboard (Zhou *et al.* 2011, 2013; Nasir 2013; Sun *et al.* 2014). Organosolv lignin, which likewise is regarded as likely to be purer than ordinary commercial lignin, has been shown to be effective as a binder for wood panels made in combination with glyoxal (Navarrete *et al.* 2010). Other researchers have employed kraft lignin, which is widely available and inexpensive, for board production (Velasquez *et al.* 2003a; Mancera *et al.* 2011b; 2012). Maisarah *et al.* (2015) even demonstrated promising effects of the addition of black liquor, which is a very impure, highly alkaline mixture that contains kraft lignin. In summary, in cases where a manufacturer suspects that a biomaterial does not have enough lignin of its own, or maybe not of the best variety, there are many options of adding more, and there are several main types to choose among.

Lignin modifications

As a strategy to overcome limitations of the native forms of lignin, as well as industrial lignins, various authors have evaluated the effects of chemical modifications. These range from general treatments such as oxidation (Widsten and Laine 2004; Gosselink *et al.* 2011) and alkaline hydrolysis (Young *et al.* 1985; Mancera *et al.* 2012) to highly specific derivatization reactions. Rammon *et al.* (1982) showed that treatment of wood with nitric acid was able to convert lignin to a nitrated form, while hydrolyzing and removing most of the xylan (hemicellulose). This reaction is known to activate the wood surface, enabling more effective bonding in the course of hot-pressing. Other researchers have used formaldehyde to generate methylolated forms of lignin for use in hot-pressed board products (Young *et al.* 1985; Calvé 1990; Tahir and Sellers 1990; Zhao 1994); though such treatments can achieve improvements in binding and in water resistance, they do not meet the present aims of avoiding the use of formaldehyde. Bertaud *et al.* (2012) got around this concern by use of glyoxal in place of formaldehyde to modify lignin and improve its performance as an adhesive for fiberboard. Extensive studies on the glyoxalation reaction of lignin to obtain panel binders and on the products formed were conducted by Navarrete *et al.* (2012, 2013). These concerned mainly the stability of the resin binder so prepared. Furthermore, very recently, totally new lignin cross-linking reactions leading to resins and binders have also been described. Among these, particularly noteworthy is the reaction of lignin with triethyl phosphate, leading to high temperature resistant resins (Basso *et al.* 2017) and with diamines and polyamines (Santiago-Medina *et al.* 2017b), which open new possibilities for this raw material.

Lignin-based reactions

During the process of hot-pressing, the lignin components can undergo a variety of reactions. Many of these can be summarized using the simple terms of "coming apart" and "linking back together". Reactions involving bond cleavage within lignin will be considered first.

Several researchers have documented the breakdown of lignin in the course of preparing binderless boards (Widyorini *et al.* 2005c; Okuda and Sato 2006; Pintiaux *et al.* 2015). Chemical species resulting from such molecular breakdown can be expected to mostly remain within the board material, possibly taking part in subsequent reactions. The added lignin will tend to undergo even easier rearrangements, as it is not fixed in the wood network, yielding grafting of added lignin fragments of different sizes onto the fixed lignin of the wood solid network. Kim *et al.* (2014) showed a loss of lignin mass on heating, with some of the change taking place within the ranges often used in binderless board preparation. Various forms of phenols were released. Cleavage of lignin in the beta-O ether position was detected by ^{13}C NMR measurements. The contents of methyoxyl groups and phenolic groups were decreased as well. Belleville *et al.* (2013) reported related effects, including lignin depolymerization, during frictional welding of hardwood. Cristescu and Karlsson (2013) and Le *et al.* (2016) found evidence of the cleavage of β-O-4 bonds within lignin during hot-pressing of lignocellulosic material. Kim *et al.* (2014) found basically the same results when lignin was heat-treated by itself. Li *et al.* (2015) reported the cleavage of both β-O-4 and β-β linkages in the course of hot-pressing of bamboo biomass. Li *et al.* (2007a) described a competition between depolymerization and repolymerization of lignin during steam explosion treatment of aspen; they showed that the repolymerization could be suppressed by the addition of 2-napthol. Shang *et al.* (2012) detected the cleavage of both ester and ether bonds during hot-pressing of steam-exploded bamboo residue. Bonds between lignin and *p*-coumaric acid were cleaved. Sun *et al.* (2014) reported NMR evidence of cleavage of lignin-carbohydrate linkages during hot-pressing of thermomechanical pulp.

Terms such as condensation, coupling, and cross-linking refer in general to reactions in which covalent bonds are formed (Tjeerdsma *et al.* 1998; Boonstra and Tjeerdsma 2006). Though there is some overlap in the common usage of these terms, the word "condensation" will be used here to refer to the creation for bonds between lignin-derived chemical moieties (Chakar and Ragauskas 2004). The term "coupling" will be applied to the formation of bonds that can include linkages to other wood components, such as hemicelluloses or cellulose. The term "cross-linking" will refer to the usage of an added bio-functional agent capable of forming two or more bonds, thus having the potential to connect woody particles or fibers together in the course of hot-pressing.

Evidence of coupling reactions has been reported in several studies of the hot-pressing of binderless boards (Nimz and Hitze 1980; Nimz 1983; Suzuki *et al.* 1998;

Laemsak and Okuma 2000; Hüttermann *et al.* 2001; Widsten and Laine 2004; Pizzi 2006; Lamaming *et al.* 2013; Zhang *et al.* 2015; Le *et al.* 2016). Phenoxy radicals, formed in the course of hot-pressing or steam explosion, have been proposed as having a central role in enabling covalent linkages to be established between particles or fibers in the material (Widsten and Laine 2004).

The self-bonding of lignin moieties, *i.e.* condensation, has been found to be important during hot-pressing of binderless board products (Hüttermann *et al.* 1989, 2000, 2001; Okuda *et al.* 2006a,b; Li *et al.* 2007a; Cristescu and Karlsson 2013; Kim *et al.* 2014; Sun *et al.* 2014; Kurokochi and Sato 2015a,b; Zhang *et al.* 2015) and even for the preparation of binderless plywood panels (Mansouri *et al.* 2010). In principle, the resulting increases in molecular mass of the lignin component of hot-pressed lignocellulosic board can be expected to result in stiffer, more water-resistant structures. One can envision a dynamic situation in which there may be simultaneous breakdown of chemical structures (as discussed earlier in this subsection) together with the creation of some new covalent linkages. An inherent challenge in ongoing research and product development lies in controlling the extent and completion of lignin condensation in the hot-pressed board.

Hemicellulose

In light of the generally lower thermal stability of hemicellulose, in comparison to cellulose and most of the lignin structures, there has been much attention paid to the role of hemicellulose and the products of its decomposition as likely contributors to the development of strength in biomass board products (Tjeerdsma *et al.* 1998; Boonstra and Tjeerdsma 2006; Pizzi 2006; Li *et al.* 2007b; Miki *et al.* 2008; Rowell and McSweeny 2008; Quintana *et al.* 2009; Weigl *et al.* 2012a,b; Lamaming *et al.* 2013; Luo *et al.* 2014; Kurokochi and Sato 2015a; Pintiaux *et al.* 2015; Zhang *et al.* 2015; Le *et al.* 2016). As mentioned in the discussion of lignin, heat-induced chemical effects may proceed in the manner of something coming apart, and then fragments joining back together. With respect to the decomposition of the hemicellulose macromolecule, many studies related to binderless board products have shown the susceptibility of certain hemicelluloses to hydrolysis of acetyl groups, with the release of acetic acid (Mobarak *et al.* 1982; Tjeerdsma *et al.* 1998; Boonstra and Tjeerdsma 2006; Li *et al.* 2007b; Delmotte *et al.* 2008; Pintiaux *et al.* 2015). Other studies have indicated decreases in hemicellulose molecular mass due to thermal depolymerization (Widyorini *et al.* 2005c; Okuda *et al.* 2006a; Belleville *et al.* 2013; Tajuddin *et al.* 2016).

Decomposition of polysaccharides having five-membered rings, *e.g.* xylans, is known to result in furfural, especially when catalyzed by acidic conditions (Mamman *et al.* 2008; Sheldon 2014; Zhang *et al.* 2015). A likely reaction scheme is shown in Fig. 5 (note the reaction path involving acetyl groups). Several studies have shown that furfural is produced during steam explosion and/or hot-pressing operations in the production of binderless boards (Suzuki *et al.* 1998; Laemsak and Okuma 2000; Rowell and McSweeny 2008; Müller *et al.* 2009b; Tshabalala *et al.* 2012; Cristescu and Karlsson 2013; Lamaming *et al.* 2013; Brazdausks *et al.* 2015). Brazdausks *et al.* (2015) detected between 64 and 68% of the theoretically possible yield of furfural, based on the composition of the hemp biomass that was being used to make binderless panels.

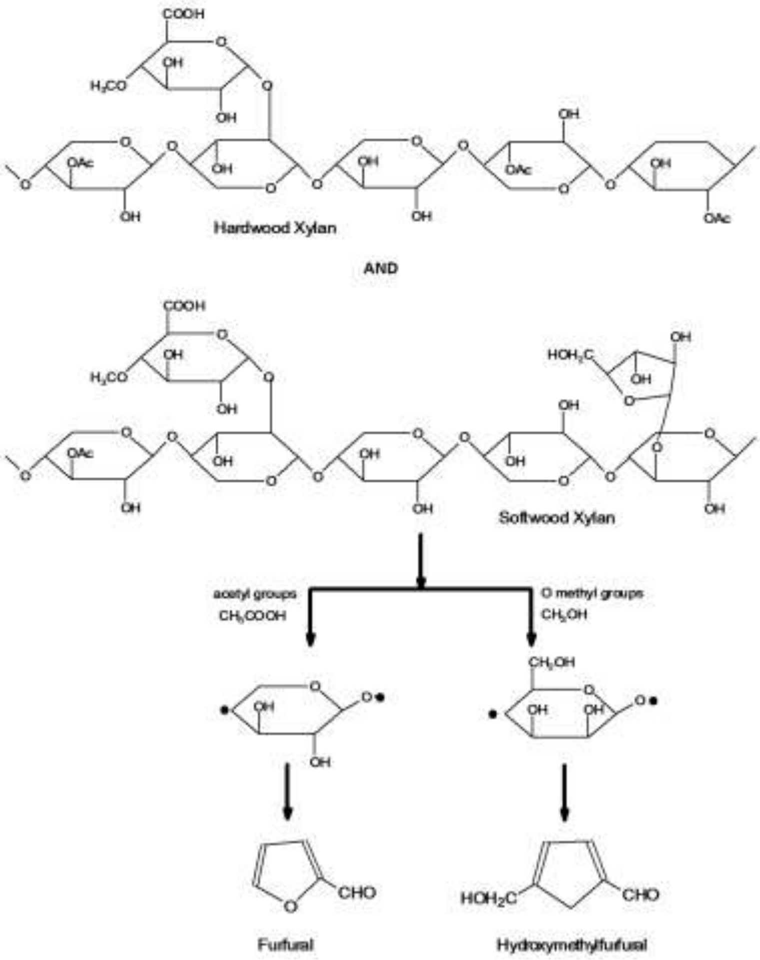

Fig. 5. Reaction scheme for the generation of furfural and 5-hydroxymethylfurfural from the decomposition of hemicelluloses based on five-membered and six-membered anhydro sugar units

The decomposition of six-membered saccharide rings, such as those in cellulose and in the galactan and mannan components of hemicellulose, can give rise to 5-hydroxymethylfurfural (Sandermann and Augustin 1963a,b; Popoff and Theander 1972; Fengel and Wegener 1989; Suzuki *et al.* 1998; Boonstra and Tjeerdsma 2006; Cristescu and Karlsson 2013; Pintiaux *et al.* 2015; Zhang *et al.* 2015). Such a reaction is depicted at the lower right in Fig. 5.

Regarding the re-connecting, as facilitated by the presence of furfural, Laemsak and Okuma (2000) proposed that the main bonding strength of boards made from oil palm fronds was attributable to covalent bonding between furfural and lignin moieties. Work by Lamaming *et al.* (2013) supports a crosslinking role of furfural during hot-pressing of binderless particleboard from oil palm trunk. Figure 6 suggests some reactions by which furfural can achieve a higher molecular mass and a more rigid structure in lignin-derived materials. Furfural self-polymerization also has been suggested (Zhang *et al.* 2015), but there does not seem to yet be a consensus that such a reaction plays an important role in the hot-pressing of biomass-based board.

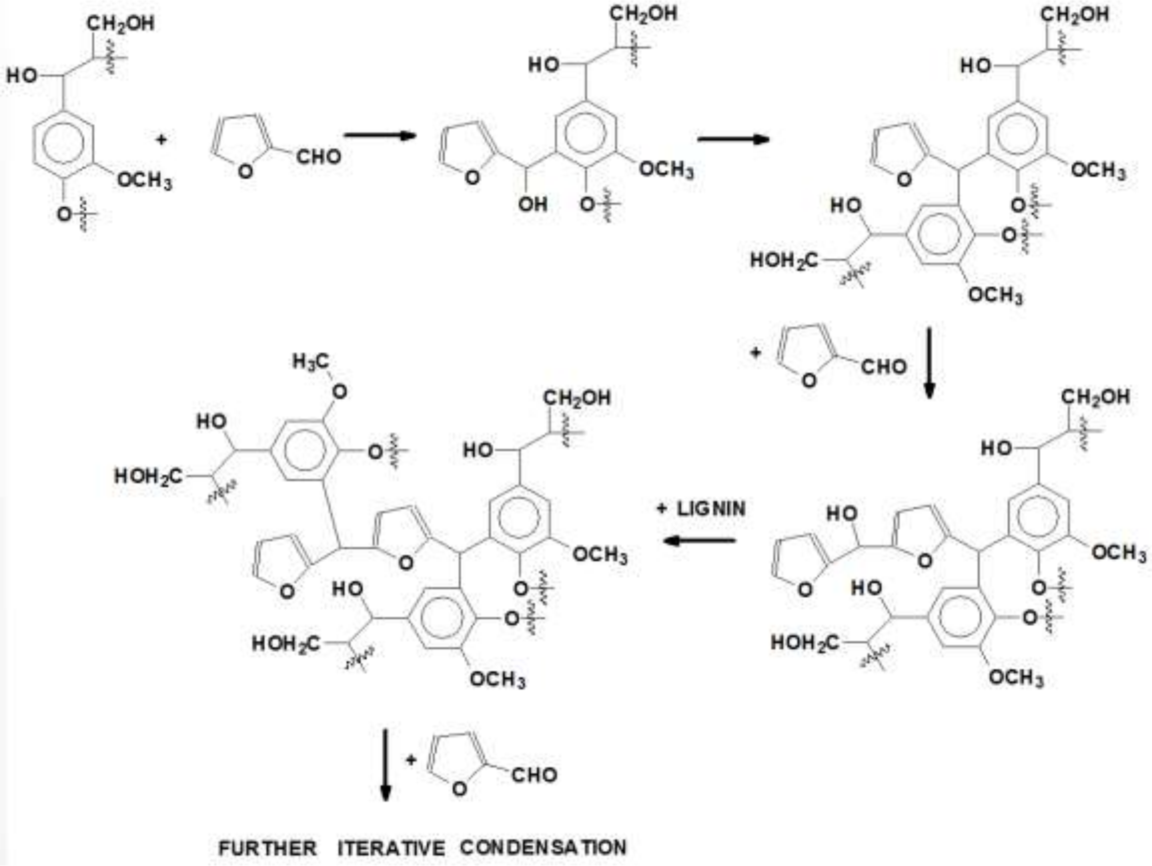

Fig. 6. Reaction scheme of likely linking reactions involving furfural and lignin

There are a number of mixed reactions that 5-hydroxymethyl furfural (HMF) can undergo with lignin. Of the possible reactions involving structural rearrangements of lignin, only those that involve HMF will be considered here. The reactions to consider are:

Reaction 1: Attack of the hydroxymethyl group of HMF on a lignin unit (Fig. 7). This can only occur at very acid or very alkaline pH, as has been shown already for the reaction of furfuryl alcohol with other polyphenols (Guigo *et al.* 2010; Abdullah and Pizzi 2013). This leaves the aldehyde group of HMF free to continue reacting as shown for the reaction scheme of furfural.

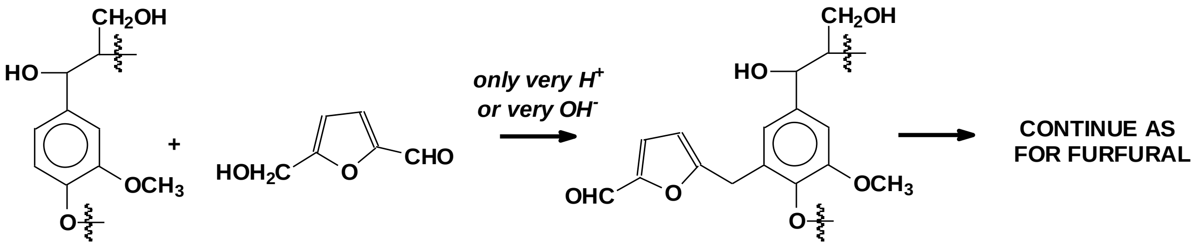

Fig. 7. Scheme for reaction involving 5-hydroxymethylfurfural and guaiacyl lignin structures, as a beginning step in crosslinking

Reaction 2: The first attack on a lignin unit is carried out by the aldehyde group of the HMF. In this case two possibilities exist:

(1) On the one hand, the reaction can continue by water elimination with the formation of a methylene ether bridge between furanic moieties. This leaves free the aldehyde group, which can then continue reacting. The reaction can involve either two lignin units, or a lignin unit and another HMF again through the formation of a methylene ether bridge (-CH_2OCH_2-), and the reaction can go on in this way.

(2) Alternatively, the reaction can continue as in the scheme shown in Fig. 8.

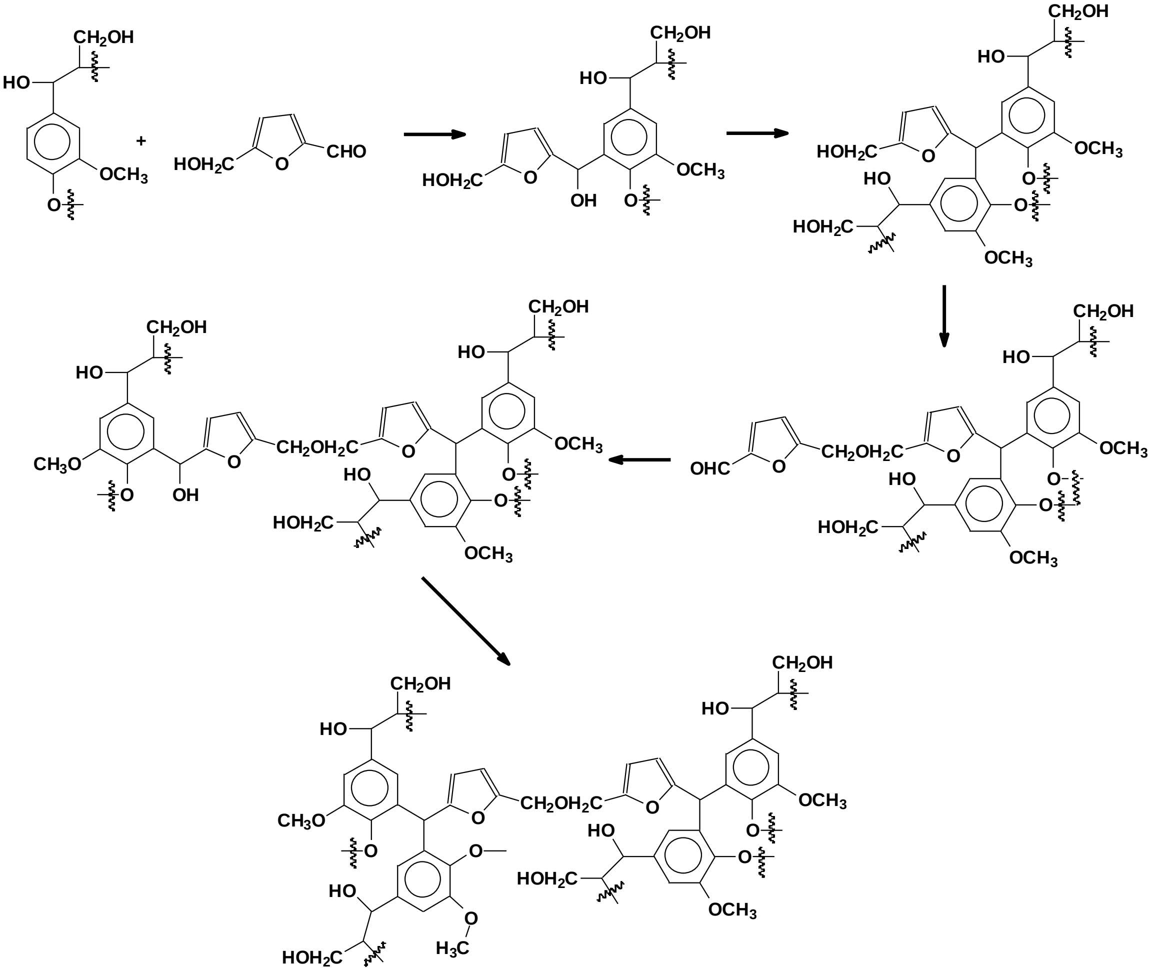

Fig. 8. Scheme for reaction involving 5-hydroxymethylfurfural and guaiacyl lignin structures, with continuing crosslinking and condensation

It must be pointed out that the schemes in Figs. 6 to 8 have been shown with a single lignin phenylpropane unit for simplicity of understanding. Within biomass the reaction can be expected to take place mainly with lignin oligomers and polymers, very likely leading to early immobilisation of the three-dimensional network formed. This is due to rapidly reaching the point where diffusional problems severely limit the reactions and further cross-linking.

Furthermore, under very acidic or very alkaline conditions the hydroxymethyl group of HMF will react to form either linear or branched furanic polymers with the aldehyde group of HMF. Reactions of this type occur also under milder conditions just through the aldehyde group of HMF. It has been shown very recently with other natural polyphenols that under neutral and mildly alkaline conditions the HMF reacts mainly through its aldehyde group and much less or not at all through the hydroxymethyl group (Santiago-Medina *et al.* 2017a).

Cellulose

Relative to hemicellulose and lignin, the cellulose macromolecule has been far less often considered by researchers as being an important source of reactivity in the development of bonds during hot-pressing operations. Cellulose in woody tissues often has a crystallinity in the range of about 40 to 86% (Park *et al.* 2010; Ahvenainen *et al.* 2016), which limits its exposure to potential reagents. Also, it does not substantially break down thermally until about 300 °C, at which point the hemicelluloses have undergone major breakdown, and parts of the lignin have suffered chemical changes (Cozzani *et al.* 1997; Serapiglia *et al.* 2008; Chen *et al.* 2015). Apparently this is why, when looking to account for the mechanisms of self-bonding within hot-pressed lignocellulosic boards, most investigators have focused on the breakdown products of hemicellulose, and occasionally lignin. The present search of the literature did not reveal any report of a case in which bonding had been instigated by breakdown products of cellulose itself. Instead, the cellulose surfaces appear to be involved in the bonding mechanisms mainly initiated by decomposition products of hemicellulose, as already covered in the earlier subsection devoted to hemicellulose.

On the other hand, it is known that strong, moisture-resistant structures can be formed by the hot-pressing of pure cellulose fibers (Nilsson *et al.* 2010). So another mechanism, other than covalent bonding, needs to be considered. One possible mechanism involves the physical entanglement of long polymers (Pizzi *et al.* 1998; Garcia and Pizzi 1998a-c). In principle, physical entanglement can lead to considerably high strengths, as indicated for example by the strength of a joint bonded by polyvinyl alcohol (Basta *et al.* 2013). But no evidence was found in the search of the literature to support a hypothesis that such entanglement takes place among cellulose chains exposed to hot-pressing conditions.

Hydrogen bonds are generally regarded as a highly transient phenomenon, with individual bond lifetimes lasting very small fractions of a second (Luzar and Chandler 1996). However, several researchers have attributed the development of bonding in biomass-based composites to a process of cellulose crystal growth or healing, occurring at the border between adjacent solid phases of cellulose pressed together (Tanahashi 1990; Ito *et al.* 1998a; Nilsson *et al.* 2010; Pintiaux *et al.* 2013, 2015; Le *et al.* 2016). For example, Pintiaux *et al.* (2013) observed development of bonding in hot-pressed structures composed of pure cellulose, a situation that makes it possible to rule out some other mechanisms, such as flow of lignin or hemicellulose, or some of the hemicellulose-related chemical changes. Nilsson *et al.* (2010) likewise showed that strong structures could be formed from pure cellulose I fibers, with only water, heat, and pressure as the enabling agents. These authors reported a growth in cellulose crystallite size from 20 to 45 nm, which they interpreted as being due to cellulose fibril aggregation. Similar findings were reported by Le *et al.* (2016). The topic of the coalescence of cellulose molecules at a molecular scale to form highly ordered and hard-to-reverse crystalline structures has been reviewed by Pönni *et al.* (2012).

Extractives

As mentioned earlier in this article, when considering wettability and molecular contact, compounds belonging to the extractives component of biomass have been usually found to decrease the bonding that can be achieved by hot pressing of biomass fibers or particles (Alvarez *et al.* 2015). There appear to be exceptions, however. Alvarez *et al.* (2015) observed that compounds extractable by hot water contributed positively to the self-bonding in leaf plantain fiberboards. The effect was attributed to the thermal instability of those extractives, along with their ability to retain stable free radicals, leading to further reactions during hot-pressing. Presumably some of the subsequent reactions can include covalent linkages, contributing to bonding. Contradictory findings had been reported earlier by Widyorini and Satiti (2011). These authors observed that the boiling of three types of tropical wood particles, with the removal of those water-soluble extractives, led to an increase in the strength of the resulting binderless particleboard. In summary, there is only scant evidence that typical extractive materials, in their native form, can play a favorable role with respect to development of chemical-based self-bonding in fiberboard or particleboard.

Natural compounds that might be classed as extractives also can be modified to make them suitable for use as bonding agents. Pizzi (2006, 2014) describes the development of adhesives by epoxidation of unsaturated vegetable oils, mainly consisting of triglycerides. Following the epoxidation step, the mixture is treated with a cyclic anhydride, *e.g.* maleic anhydride, plus a small amount of polycarboxylic acid to form crosslinks and increase the molecular mass. Another approach involved the condensation of modified cashew nut oil to prepare an adhesive, possibly useful for wood. Results superior to phenol-formaldehyde resin were reported by an industrial source (Miller and Shonfled, as cited by Pizzi 2006). A similar approach employed ozonization of cashew nut oil to open and cut the double bond of cardanol and thus create two aldehyde groups on the two fragments so obtained (Tomkinson 2002; Fitchett *et al.* 2003). As shown in Fig. 9, the aldehyde groups so formed, which were non-volatile, were then reacted with the resorcinol moiety of cardanol to give cross-linked resins (Thomkinson 2002; Fitchett *et al.* 2003). This was not enough to yield good panels bonding, and thus resorcinol was added to obtain enough cross-linking by Cambridge Polymers (Guezguez 2011). The results obtained were marginal, but the main problem was the too high cost of resorcinol (Guezguez 2011). The much cheaper tannins were then used as substitution of resorcinol, but as the commercial tannins available were not sufficiently reactive, the results were far lower than standard panel bonding requirements.

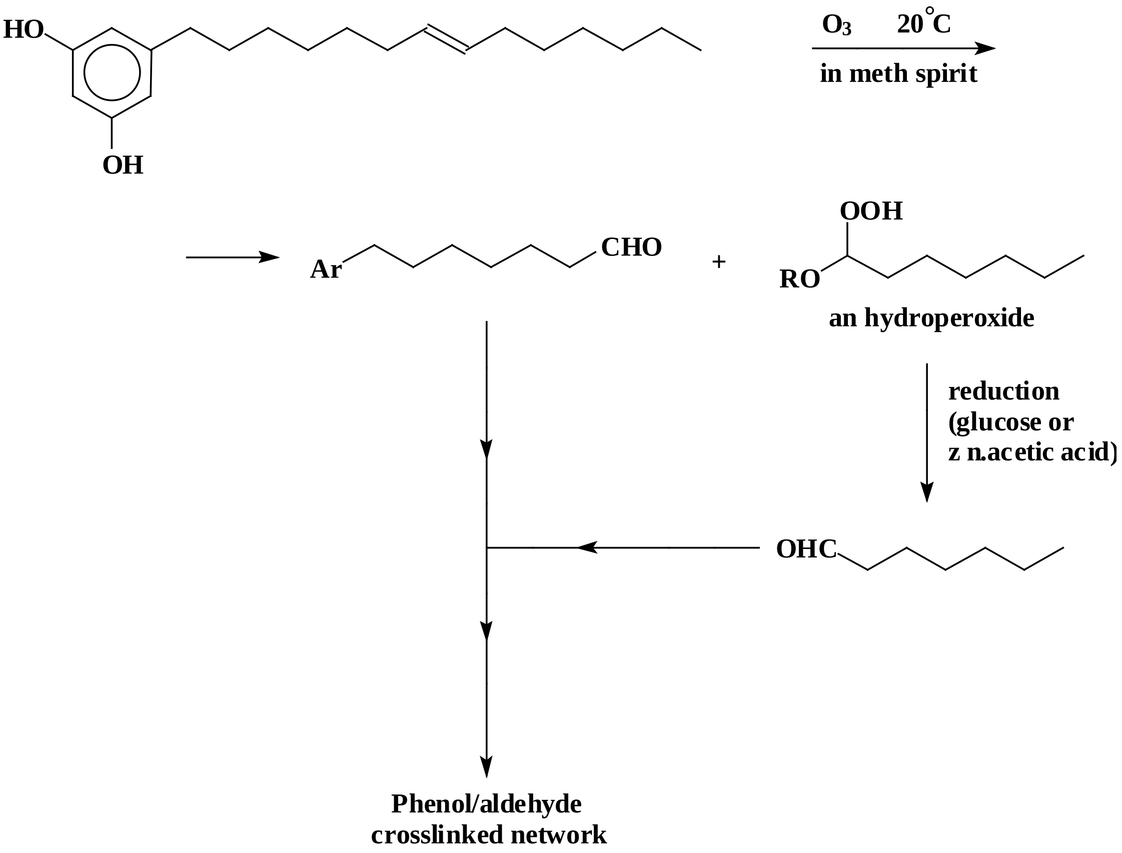

Fig. 9. Reaction scheme for ozonation and crosslinking of cashew nut oil to provide adhesive resin

The same approach was used by another research group by preparing the non-volatile aldehydes from inexpensive and easily available oils such as sunflower oil without using any cardanol, but using a much more reactive procyanidin tannin, namely pine tannin, to obtain panel binders (Thebault *et al.* 2013). Again, the results, although improved, needed supplementation with a small addition of a suitable aldehyde to yield acceptable properties.

Structural Integrity

The fourth link in the hypothetical mechanistic chain, accounting for strength development in hot-pressed boards, involves structural integrity. The issue here is whether the board structure has sufficient connectivity and continuity, and whether there are major gaps or defects. In other words even if (a) the conditions of temperature, moisture, pressure, and time have been sufficient to establish mechanical contact between lignocellulosic solids over increased areas, (b) the surface chemistry has been favorable for the establishment of molecular-level contact between the surfaces, and (c) covalent bond links or a sufficient level of secondary chemical interactions also have been created across interfaces, all of this might still add up to failure if there are sufficient cracks, delamination, or other kinds of significant air spaces in the material.

Particle shape

In principle, isolated areas lacking in bonding are especially of concern in typical particleboard structures, due to the low aspect ratio of the pieces from which the structure is composed. Fiberboard, because of the multiple contacts established by each fiber at crossing points with other fibers, is inherently less reliant on the dependability of each individual bonding interface. In agreement with this concept, Hashim *et al.* (2010) and Saari *et al.* (2014) reported much higher modulus of rupture and internal bond strength of board specimens prepared from "strands" in comparison with specimens prepared from "fine particles". The materials all were obtained from the same starting mixture of oil palm trunk material. Kelly (1977), in a review of earlier literature related to conventional particleboard, found that the usage of bigger flakes resulted in higher strength properties.

Apparent density

Density is a tricky variable. On the one hand, studies have shown that the modulus of elasticity of many biomass-based products increases markedly with increasing density (Gravitis *et al.* 2010; Pintiaux *et al.* 2015). But on the other hand, dense structures are sometime too brittle to meet various needs. For example, van Dam *et al.* (2004a,b) reported that hardboard prepared from coconut husk was very strong but unsuitable for nailing. As noted by Okuda and Sato (2007), the particles that comprise a board product may need to be forced together tightly, with no space remaining between them, in order for chemical bonding to be able to develop. But such a structure might be too brittle or simply weigh too much to be ideal for many applications. Also, the material might lead to excessive wear of cutting tools.

Steam-induced delamination

Plath and Schnitzier (1974) carried out a careful analysis of particleboard density relative to the thickness direction, showing that the highest density in each case was about 2 mm below the surface. While the board density was highest within the near-surface layers, the surface density was lower in the first 0.5 to 1 mm surface thickness. Figure 10 illustrates this point (Pichelin 1999; Pichelin *et al.* 2001, 2002; Pizzi 2016).

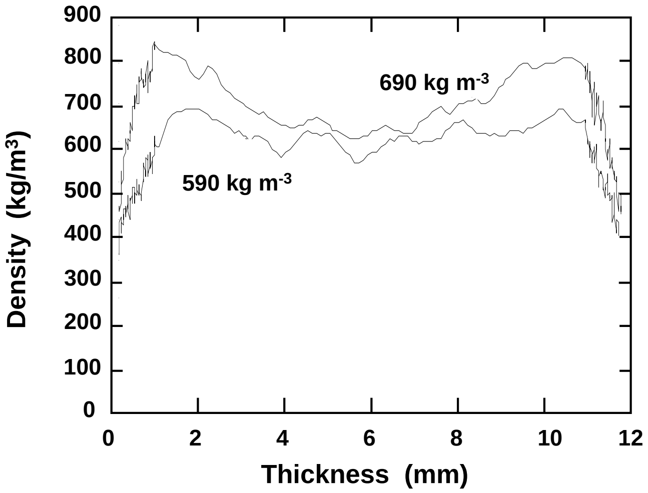

Fig. 10. Example of density distributions relative to the thickness of particleboard for two overall board densities (figure redrawn from Pizzi 2016)

The lower density right at the outer surface was attributed to various factors, such as surface damage by the high temperature of the press in direct contact with the surface furnish. The extent of this lower density layer is influenced by different parameters, such as board density, surface/core compression ratio, surface/core differential moisture content (Sedano-Mendoza *et al*. 2010), rate of closing of the press, and others (Pichelin 1999; Pichelin *et al.* 2001, 2002; Pizzi 2016).

In the example shown in Fig. 10, the average density in the center of the board's core thickness was about 2/3 of the maximum value. The ideal ratio between core/surfaces relative densities may be between 83% and 86% for standard boards of average density of 680 kg/m^3. This can vary according to the use of the final board that is required; boards of both higher and lower density ratios are produced for specific purposes. Kelly (1977) proposed that the effect may be related to the gradients of temperature and moisture, especially during the early parts of hot-pressing. The heated surfaces come into contact with the outer surfaces of the material, which initially tend to contain a higher moisture content than they will later in the pressing operation. Also, high temperatures reach the outer parts of the board early in the pressing process. The combination of high temperature and sufficient moisture, along with compression, causes densification of the material mainly to take place in the regions that become plasticized first.

The distribution of fine particles in the surface and coarse particleboards in the core also tends to increase the density variation with respect to the particleboard thickness (Wong *et al.* 1999). Fine particles, which typically have a larger specific surface area, can be compressed more tightly with less interspaces between them in comparison to coarse particles under the same pressure. Accordingly, the apparent density of fine particles located in the particleboard surface tends to be much higher than in the core (Kutnar *et al.* 2009).

Once the interior regions of the board reach the temperature of plasticization, the press might already have reached its "stop" positions, defining the selected thickness of the product. The fact that moisture plays a role in this mechanism is supported by the work of Heebink *et al.* (1972). These researchers observed that the skin effect became increasingly prominent with increasing moisture of particleboard material before pressing. As was shown earlier in Fig. 2, moisture is needed in order to bring the glass transition temperatures of lignin and hemicellulose to suitable levels, enabling flow to take place under pressure. Another factor, as illustrated in Fig. 11, is the fact that the densified outer surfaces of a pressed board might tend to impede the passage of steam, thus causing the board to delaminate instead of letting the steam leak out.

The relative percentage of moisture content of the surface and the core layers of particleboard, during its preparation, markedly influences the internal bond (IB) strength of the board (Sedano-Mendoza *et al.* 2010). This is well known in industrial practice due to the differential compression imparted to different layers, depending on their moisture content. The surfaces typically have higher percentage moisture content than the core. The lower the difference between the two, the higher tends to be the IB strength of the panel, and the softer the surfaces. The higher the difference, the tougher and stiffer are the surfaces but the lower the IB strength. In the case of biosourced adhesives, for which these differences can be more pronounced than for synthetic adhesives, the effect is even more easily observable (Sedano-Mendoza *et al.* 2010).

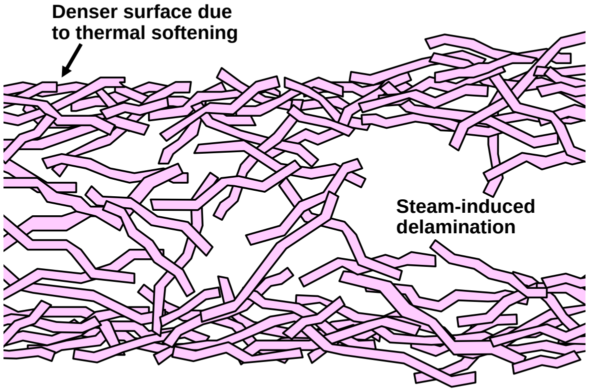

Fig. 11. Illustration of two effects known to sometimes affect structural properties of hot-pressed binderless board – surface densification ("skin effect") and steam-induced delamination

As mentioned earlier, various researchers have reported decreases in the strength of hot-pressed board products when the steam pressure or temperature were above an optimum level (Anglès *et al.* 1999; Salvadó *et al.* 2003; Velasquez *et al.* 2003b; Winyorini *et al.* 2005b; Ando and Sato 2009; Mancera *et al.* 2011a; Shang *et al.* 2012; Xu *et al.* 2012; Saari *et al.* 2014). There are at least four likely contributing explanations for the decline of strength under the most severe conditions: (a) dissolution and unfavorable repositioning of water-soluble bond-promoting chemicals, such as hemicellulose byproducts, and non-water-resistant adhesives in particleboard, (b) chemical breakdown of the matrix materials that might have served as bonding agents, (c) chemical breakdown of the solid materials (primarily the cellulose) that would make up the structure, and (d) delamination of the structure upon opening of the press, with the release of entrapped steam.

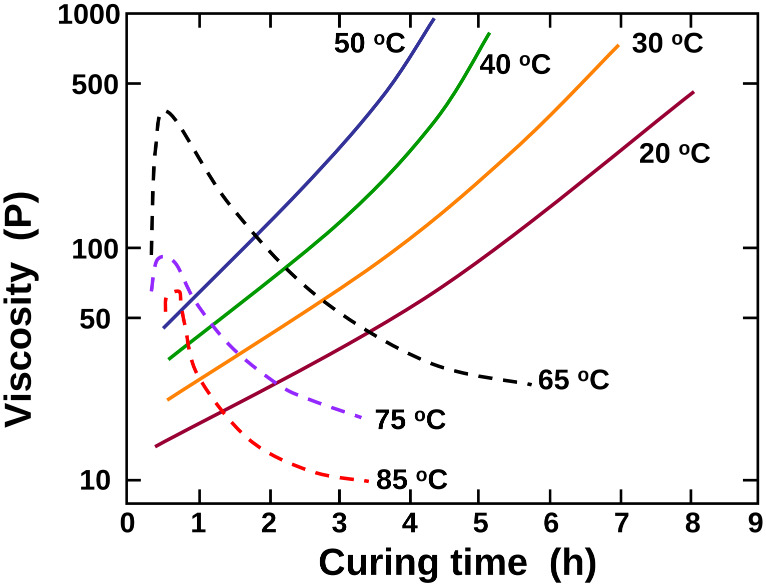

Fig. 12. Viscosity of urea-formaldehyde resin as a function of time at different temperatures, all at pH=2 (figure redrawn from Pizzi 1983)

In the case of urea-formaldehyde bonded particleboard, evidence of competition between curing and decomposition has been observed (Pizzi 1983). As shown in Fig. 12, at relatively low hot-press temperatures the viscosity of the adhesive was found to increase steadily with time, consistent with increasing levels of crosslinking and higher molecular mass. The polycondensation reactions led to curing and hardening. But at temperatures above 50 ^{o}C the viscosity was observed to pass through a maximum as a function of time. The subsequent decrease in viscosity was attributed to hydrolytic decomposition and loss of molecular mass of the polymeric material. Though the example considered here involved urea-formaldehyde resin, the same general effects probably can be expected for other systems, including natural adhesives and binderless hot-pressed board.

The pattern of rising and falling viscosity was reproduced at much shorter times when the temperature was higher, including temperatures corresponding to hot-pressing of panels. This can be attributed to the fact that hardening involves an equilibrium reaction, as indicated in Eq. 1. Presumably the reaction can go back towards the left when high temperatures make the polymeric material unstable.

$$2\ NH_2\text{-}CO\text{-}NH_2 + HCHO \quad \leftrightarrows \quad NH_2\text{-}CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}CO\text{-}NH_2 \qquad (1)$$

Delamination under conditions of high steam pressure and its sudden release has been reported by various researchers investigating hot-pressing variables (Ando and Sato 2009; Pintiaux *et al.* 2013). As noted by Pintiaux *et al.* (2015), the danger of delamination increases with temperature, due to the fact that the pressure of condensing steam increases with its temperature. During pressing of a panel the internal steam pressure increases gradually, sometimes to high values depending on both initial moisture content of the furnish and length of press time. If at press opening such a pressure is higher than the initial, “green” IB strength, the board will fly apart, sometimes silently delaminating, and sometimes violently “exploding” at press opening (Pichelin 1999; Pichelin *et al.* 2002). An example of this is shown in Fig. 13.

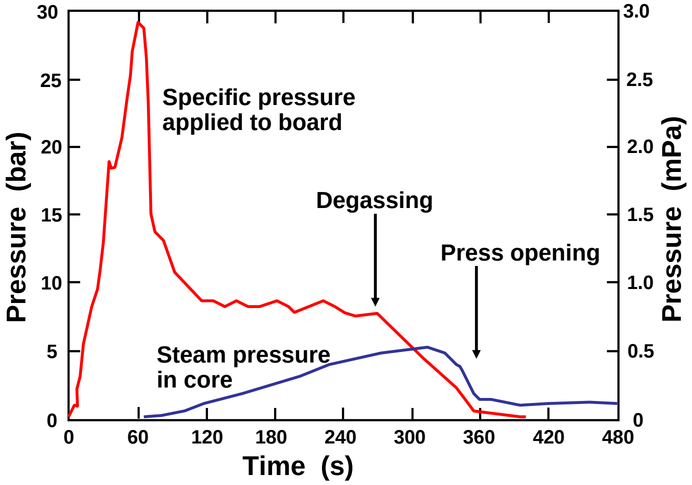

Fig. 13. Steam pressure as a function of time during and immediately following hot-pressing of oriented strand board. Figure redrawn from Pichelin (1999) and Pichelin *et al.* (2002).

In the specific case represented in Fig. 13, if the press had been opened at 300 to 330 seconds the board would have delaminated more or less violently, while at press opening at 350 to 360 seconds no damage would have occurred.

During routine production, industrial panels are typically prepared on caul sheets or grids and never in closed molds. The increase in steam pressure shown on Fig. 13 is of an open platen system, and the increase in steam pressure observed is exclusively due to the densifying of the particleboard edges due to the pressure exercised on the mat during pressing. As the edge increases in density and the adhesives cures, the flow of steam through the edges towards the outside becomes progressively slower, and thus degassing time becomes progressively longer. Delamination may occur in principle when the steam pressure increases to an excessive level due to extreme slow-down of steam flow, which can result in steam blisters upon opening of the press. Such events, which can be silent or explosive, are brought about by the high steam pressure retained within the panel. In the rare occasion where molds are used, effective degassing paths must be provided to avoid such happenings.

Layering

One of the favorable attributes of densified surface layers, as illustrated in Figs. 10 and 11, is a relatively high stiffness of the board product. The higher density near the surfaces will tend to develop a higher modulus of elasticity and modulus of rupture in those locations. Since the high-modulus layers are held apart by lighter material, one ends up with a kind of "I-beam effect" (Ridgway and Gane 2012). Gao *et al.* (2011) reported a related structure in which a weak, low-density bark layer was placed between an upper and lower layers made with wood fibers.

Post-steaming

Dimensional stability is an important attribute in many likely applications of hot-pressed board products. There is potential for problems to occur if the humidity changes, and especially if the materials gets wet during its later usage. One of the concerns, when using hot-press procedures, is that the product might contain dried-in stresses, leading to dimensional changes when the board is later placed in environments having different relative humidity. In particular, the product can suffer spring-back when placed into a high-humidity or moist environment. Boon *et al.* (2013) observed that spring-back effects are often more prominent in binderless boards, compared to those bonded using formaldehyde-based resins. Presumably such susceptibility to water molecules is a consequence of the generally hydrophilic nature of many natural compounds that may participate in bonding.

To minimize such problems, Inoue *et al.* (1993) and Rowell and McSweeny (2008) recommend heating of board products in a closed press for several minutes. Such treatment was found to increase dimensional stability. The same authors also recommended steam treatment, and in that case some of the improvement in dimensional stability could be attributed to the loss of various hemicellulose components, which tend to be hydrophilic and swellable in water. In addition, the steam treatment resulted in the presence of furan intermediates in the treated board, which provides evidence that some covalent bonding also contributed to dimensional stability after such treatment. Inoue *et al.* (1993) concluded that the steam-assisted compression-set procedure was more effective, resulting in almost complete fixation of shape. Post-steaming to prevent “set-back” or “spring-back”, *i.e.* dimensional changes that tend to reverse the effects of pressing, have been widely recommended (Kelly 1977; Inoue *et al.* 1993). Miki *et al.* (2007b) showed a contrasting procedure in which the initial compression was carried out in a wet condition, and then a press-drying process was carried out to fix the shape and achieve a stable bonded condition. The conditions of curing were sufficient to cause cross-linking among the biomaterials, as described earlier in this article.

An especially dramatic demonstration of the use of steam to be able to change and then “set” the shape of a lignocellulosic structure was reported by Ito *et al.* (1998b). These authors softened whole logs by steaming, followed by compressing the logs into a square cross-sectional shape, holding the shape for a few minutes, and then gradually releasing the pressure. Pictures of the resulting logs show a perfectly square shape. Though such results go way beyond what is expected to be needed for hot-pressed board production, they can provide support for the compression-set concept.

ADDITIVES

Supplemental Binding Components

Thermal treatment of biomass often does not yield sufficient deformable materials or reactive species to achieve the needed levels of bonding for a given application. In such cases, many researchers have explored options that involve the addition of other natural materials, either in native form or after chemical modification (Pizzi 2006; Pintiaux 2015).

Tannins

Tannins, which can be obtained especially from the barks of *Acacia*, *Tsuga*, *Rhus*, and *Pinus* (Pizzi 1983, 1994, 2006; Bertaud *et al.* 2012), hold particular promise as bond-promoting additives for the hot-pressing of particles or fibers (Pizzi 1978; Pizzi and Scharfetter 1978; Kelly *et al.* 1983; Pizzi 2006; Müller *et al.* 2007; Widsten *et al.* 2009; Navarrete *et al.* 2010; Bertaud *et al.* 2012; Pizzi 2013, 2014; Nenonene *et al.* 2014; Faris *et al.* 2016). Bertaud *et al.* 2012) reported their best success when using tannins from Aleppo pine bark. According to Pizzi (2006) it is the condensed form of tannins, rather than the low-molecular-mass fraction, that is promising for use as an adhesive component. In the 1970s there were several reports of successful preparation of binderless boards from bark (Chow 1972, 1975, 1977), and such results are consistent with a binding role of tannins.

Figure 14 shows an example of a tannin molecule, which can be classified as polyhydroxyphenols (polyflavinoids) (Pizzi 2014). As shown, tannins are rich in phenolic –OH groups. Early evidence that such a chemical composition can be effective for particleboard production was shown by Pizzi (1978) and Valenzuela *et al.* (2012), who prepared wood particleboard industrially from mimosa tannin extract used for leather, along with pine tannin, and by Yalinkilic *et al.* (1998), who manufactured particleboard from waste tea leaves. Kelly *et al.* (1983) used nitric acid to promote the strength of solid wood panels that were heat-treated after addition of tannins. Pizzi (1983, 1994, 2014) attributed the reactivity of tannins, under conditions of hot-pressing, to their resorcinol structures, having two phenolic –OH groups on aromatic rings.

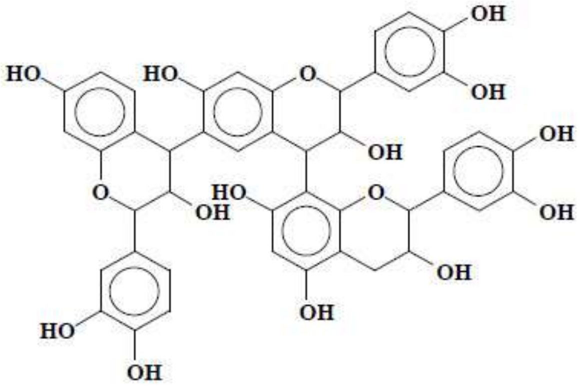

Fig. 14. Example of a tannin molecule, which has been shown to promote development of bonding in hot-pressed biomass-based board (Pizzi 2014)

Hardeners for the tannins can include methylolated species (Pizzi 2014). Böhm *et al.* (2016) considered different crosslinking systems for tannins and the reaction kinetics. Tannins also can undergo autocondensation, which is a reaction not requiring formaldehyde or any other aldehydes. Tannins autocondensation yields interior grade boards, especially when faster-condensing procyanidin-type tannins such pine bark or pecan nut tannins (and others) are used, and thus yielding boards that are totally environment friendly (Pizzi *et al.* 1995; Garcia and Pizzi 1998a-c). Figure 15 shows the development of IB strength of panels made by tannin autocondensation. As can be seen in Fig. 15, the source of tannins is important, and alkaline conditions are favorable for bond development.

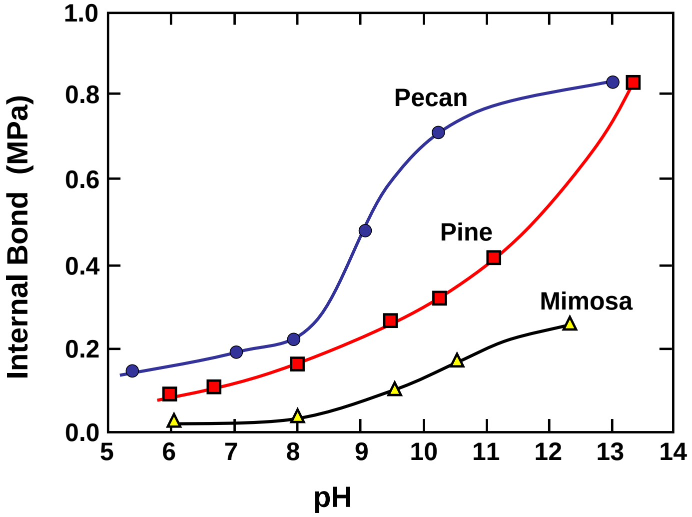

Fig. 15. Dry internal bond strength as a function of tannin solution pH of laboratory particleboard prepared with four different tannin extracts by tannins autocondensation without any aldehyde hardener, using the lignocellulosic substrate-induced tannin autocondensation (figure redrawn from Pizzi *et al.* 1995)

Widsten *et al.* (2009) demonstrated a laccase enzymatic treatment to activate tannins for the production of fiberboard. Tannic acid and chestnut tannins were found to be more reactive to laccase in comparison to condensed tannins. This approach made it possible to prepare wet-process hardboard having superior strength. Combinations of lignin and tannin additives have shown promise as wood panel adhesives (Navarrete *et al.* 2010; Pizzi 2014).

Other saccharides

Another class of natural polymers that has been often reported as having promise as an additive for production of hot-pressed biomass board products is the non-lignocellulosic saccharides and polysaccharides. This makes sense in light of the substantial role already described in this article for the hemicellulose polysaccharide component of biomass. Research has been carried out related to starch and simple sugars and their effects on bonding of hot-pressed board (Pizzi 2014). Similarly to the hemicelluloses, such compounds are for the most part non-crystalline and more susceptible to thermal decomposition than cellulose.

Starch has been considered in several studies as a binder for hot-pressed board (Imam *et al.* 2001; Lamaming *et al.* 2013). Müller *et al.* (2007) regarded starch as a promising, but possibly overlooked potential component of binders for hot-pressed boards. Lamaming *et al.* (2013) reported that added starch increased the strength of particleboard, but that the effects were not as great as the addition of sugars. Inspection of the reported error-bar intervals, however, suggests that the starch did not significantly affect either the modulus of rupture or the internal bond strength. Imam *et al.* (2001) employed a formaldehyde-derived compound, hexamethoxymethylmelamine, as a crosslinker, and the starch was used in combination with polyvinylalcohol. Thus, there is not much evidence of positive effects when using starch to produce eco-friendly hot-pressed board.

Already in 1986 Shen patented the use of sugars as a binding system for woody materials. The fact that Lamaming *et al.* (2013) observed strong increases in strength when adding glucose and sucrose before the hot-pressing of particleboard helps to dispel any expectation that an initial polymeric structure is required for effective bonding. Rather, such results are consistent with the mechanisms described earlier with respect to hemicellulose, where reactions among active forms of lower-mass compounds appear to play a role (Golon and Kuhnert 2012; Pintiaux *et al.* 2015). Temperatures above 180 °C appear to be able to cure the sugar-based bonding system, leading to significantly higher strength properties, in addition to reductions in water absorption and thickness swelling (Lamaming *et al.* 2013).

Abuarra *et al.* (2014) evaluated gum arabic, which is highly hydrophilic, as a binder for particleboard. The particleboard specimens were hot-pressed at 210 °C. Though the strength properties of dry specimens were improved, the water absorption and thickness swelling both increased as well. In other words, the board showed promise only for exclusively dry applications, *e.g.* indoor furniture.

Polyhydroxyalkanoates, which are bacterially-produced natural polyesters, have been considered as an adhesive for particleboard from oil palm trunk (Baskaran *et al.* 2012). Addition of the polyhydroxyalkanoates was found to increase the overall properties.

Protein

Proteins have been widely considered as binders for hot-pressed boards (Pizzi 2006; Müller *et al.* 2007; Nikvash *et al.* 2012; Pizzi 2014; Zhang *et al.* 2015). Migneault *et al.* (2011) attributed the binding ability of hot-pressed primary and secondary sludge from pulp and paper manufacture to the presence of proteins and lignin. Nasir (2013) achieved promising results with combinations of alkali-treated soy protein and lignin. Mechanical properties were comparable to commercial medium-density fiberboards, and the water-resistant properties were improved. The water-resistant properties could be further improved by the addition of hydrophobic additives. Evon *et al.* (2012, 2014a,b) prepared fiberboard from sunflower and jatropha residuals associated with biorefining; they attributed favorable development of strength partly to the presence of protein. Though Nikvash *et al.* (2012) employed protein as a binder for particleboard, they used a formaldehyde-based curing system.

Cross-linkers

Formaldehyde replacements

Given the fact that formaldehyde was involved with several of the reported promising applications already discussed involving tannins (Pizzi 2014), starch (Imam *et al.* 2001), and proteins (Nikvash *et al.* 2012), it is important to consider alternative crosslinking agents that might be used instead.

Before considering added crosslinking agents, it is worth noting that researchers for a long time have proposed crosslinking reactions involving compounds inherent in the biomass itself, as well as those generated during steam explosion or hot-pressing. Thus, Back *et al.* (1987) proposed the involvement of hemi-acetal bonds as an explanation for the self-bonding during production of hardboard. Hemi-acetal bonds are usually associated with the usage of a cross-linking agent such as glyoxal (Navarrete *et al.* 2010; Pizzi 2014). Tjeerdsma *et al.* (1998), as already discussed, attributed self-bonding of thermally modified wood to reactions including hydrolysis of acetate groups in hemicellulose, releasing acetic acid, followed by acid-catalyzed reactions leading to furfural, which served as a crosslinker. Condensation reactions of lignin were also credited with part of the observed bonding effects.

Turning attention now to added compounds, Kelley *et al.* (1983) found that diacids and diamines, which under suitable conditions might be expected to form amide-type crosslinking (Jursic and Zdravkovski 1993; Arnold *et al.* 2006), were both effective of increasing the strength of solid wood panels.

Pizzi and associates have evaluated several aldehydes as possible alternatives to formaldehyde as wood adhesives (Pizzi 1983; Despres *et al.* 2008; Navarrete *et al.* 2010; Pizzi 2014; Böhm *et al.* 2016). Despres *et al.* (2008) showed that dimethoxyethanal was able to work together with melamine as an effective bonding agent. The system performed its intended function as a curable resin, but the properties were lower than conventional melamine-formaldehyde adhesive, presumably due to lower reactivity of the aldehyde. Only by further addition of a difunctional isocyanate was the adhesive capable of meeting the commercial standards.

Recently, a totally non-toxic aldehyde, vanillin, easily produced as a recovery side stream from the pulp and paper industry, and dialdehydes prepared from it, have been shown to yield totally natural adhesives when coupled with a fast-reacting procyanidin tannin, such as pine bark tannin. This totally biosourced adhesive system yielded particleboard that satisfied the strength targets and the requirements of the relevant standards, and it accomplished this without objectionable levels of emissions (Santiago-Medina *et al.* 2016).

Furan derivatives, such as furfural and 5-hyroxymethlfurfural already have been noted as likely contributors to self-binding of hot-pressed board, so it is reasonable to consider either adding such chemicals directly or adding compounds likely to yield furans upon heating (Okuda and Sato 2004; Ghafari *et al.* 2016). Okuda and Sato (2004) observed only a slight increase in internal bonding upon addition of increasing amounts of furfural. Ghafari *et al.* (2016) found positive effects on strength due to furfural addition. Though the substitution of furfural in place of formaldehyde led to less effective bonding under matched conditions, it was possible to achieve promising strength characteristics at 180 °C, which is in the usual range for hot-pressing of binderless board. Various kinds of reactions involving furan-type compounds have been reviewed (Gandini 2008; Gandini *et al.* 2016). Recently furfuryl alcohol has been used in conjunction with tannins to yield panels (Abdullah and Pizzi 2013) and for other applications.

Widyorini *et al.* (2016) recently reported promising results upon the addition of citric acid as a natural crosslinker for bamboo particleboard. The mechanical properties and dimensional stability achieved by hot-pressing were improved, presumably through formation of ester-type crosslinks. Studies on the suitability of citric acid as a binding promoter of boards without adhesives showed that its major action is in the waterproofing of lignin-bonded joints. This is also the case in wood welding, for which the mobilized lignin of the substrate itself serves as the binder (Amirou *et al.* 2017). Extensive investigation by CP-MAS ^{13}C NMR and MALDI-ToF mass spectroscopy indicated that citric acid has a catalytic effect on bonding without adhesives (Amirou *et al.* 2017). Its main effect appears to involve the catalytic rearrangement and further polycondensation of the lignin structure, rendering it even less susceptible to water (Amirou *et al.* 2017).

Only citric acid and sucrose were used as adhesive by Umemura *et al.* (2013) to produce particleboard. The results indicated that the adhesive had excellent bond strength and the particleboard did not decompose even under more severe accelerated treatments. A mixture of citric acid and sucrose can be used as a natural adhesive for particleboard owing to the formation of ester linkages to bond wood together under certain hot press conditions.

Kusumah *et al.* (2016) used only citric acid for the production of sweet sorghum bagasse particleboard. The results showed that the physical properties of the boards were improved with increasing citric acid content up to 20% and the properties of these boards were comparable to those boards bonded using PF resin and pMDI owing to the presence of ester linkages between the carboxyl groups of citric acid and hydroxyl groups of the sorghum bagasse.

Amirou *et al.* (2017) used citric acid to improve water resistance of welded wood joints. The results showed that 10 to 20% citric acid pretreatment can markedly improve both the mechanical performance and the water resistance of the welded spruce. But the improvement can be attributed to a stronger welded interface modified by citric acid, rather than the ester linkage formation in the welded interface.

ACTIVATION

Heat activation

As noted earlier, one of the key functions of elevated temperature during hot-pressing is to enable plasticization and pressure-induced flow of matrix materials such as moistened lignin and hemicellulose in the biomass. But clearly that is not the only result of high temperature. The fact that other mechanisms must be involved is shown by the fact that the trend of improving strength properties often shows a maximum at a certain temperature, beyond which the properties fall (Anglès *et al.* 1999; Salvadó *et al.* 2003; Velasquez *et al.* 2003b; Winyorini *et al.* 2005b; Ando and Sato 2009; Mancera *et al.* 2011a; Shang *et al.* 2012; Xu *et al.* 2012; Saari *et al.* 2014). The eventual drop in properties at excessive temperature of hot-pressing is consistent with an expectation of chemical decomposition. It follows that, at somewhat lower temperatures, the initial decomposition may yield "activated" chemical species, such as free radicals or otherwise reactive compounds capable of initiating reactions leading to covalent bonding. The word "activation" was used by Tajuddin *et al.* (2016) to describe such effects due to the heating. Kim *et al.* (2014) regarded color changes of the heated lignin as another clue of activation, leading to such reactions as condensation of lignin fragments.

Steam-induced Activation

There is considerable evidence that application of steam during such processes as steam explosion or hot-pressing can favor the activation of chemical species that participate in bonding reactions during hot-pressing. Self-bonding properties of biomass board often increase with increasing steam pressure and temperature, within suitable ranges (Kwon and Geimer 1998; Widyorini *et al.* 2005c; Miki *et al.* 2008). For example, Kwon and Geimer (1998) considered the temperature (pressure) range of condensing steam between 170 °C (690 kPa) and 198 °C (1380 kPa). Xu *et al.* (2001, 2004) reported corresponding improvements with increasing pressure and duration of steam-injection pressing. Pre-steaming before hot-pressing also has been shown to improve bonding properties in such cases (Sekino *et al.* 1999; Xu *et al.* 2006; Miki *et al.* 2008; Salim *et al.* 2013; Saari *et al.* 2014; Pintiaux *et al.* 2015). Though such findings were earlier cited as possible support for the concept of plastic flow and a lowering of glass-transition temperatures, the development of active chemical species also has been used as an explanation to account for such effects (Pintiaux *et al.* 2015). In support of this concept, Widyorini *et al.* (2005b) detected the generation of cinnamic acid, which was thought to be involved in steam-induced development of self-bonding of binderless kenaf core composites. The generation of active species is also consistent with an observed degradation and weight loss of the solids under such conditions (Widyorini *et al.* 2005c).

Hydrothermal treatment is one of the effective thermal treatment methods that have been implemented by several researchers (Tjeerdsma and Millitz 2005; Endo *et al.* 2016; Saliman *et al.* 2017). The effectiveness of hydrothermal treatment has been found to be highly dependent on treatment temperature and time. The dimensional stability of oil palm wood was enhanced by the hydrothermal treatment. Treatment time is a less crucial factor in the dimensional improvement of oil palm wood (OPW) compared to treatment temperature. Better dimensional stability could be observed in the samples treated at higher temperature even when exposed for a shorter time (Saliman *et al.* 2017). Being the less thermally stable constituent, hemicellulose degrades first during hydrothermal treatment, followed by cellulose and lignin (Kamdem *et al.* 2002).

Acid Activation

Given the fact that acid-catalysis appears to be a factor in the generation of the reactive furfural and 5-hydroxymethylfurfural (Mobarak *et al.* 1982; Li *et al.* 2007b; Mamman *et al.* 2008), it is logical to consider the addition of acidic species before hot-pressing as a possible means to promotion of self-bonding within biomass board. Accordingly, Okuda *et al.* (2006b) showed that addition of acetic acid before hot-pressing of kenaf core material was effective for improved bonding and generation of active chemical species. More research, to follow up on this progress, appears to be warranted.

Lewis acids also have been shown to promote the generation of furfural and 5-hydroxymethylfurfural (Tschabalala *et al.* 2012). The cited work noted that such an approach needs to be implemented with caution; excessive severity of treatment has the potential to degrade the wood material.

Oxidative Activation

Activation, meaning the generation of species likely to participate in enhanced bond development, also can be achieved by oxidation (Tischer 1939; Rammon *et al.* 1982; Young *et al.* 1982; Kelley *et al.* 1983; Widsten 2002; Widsten and Kandelbauer 2008a,b). Gosselink *et al.* (2011) used periodate to promote the activation of lignin, increasing its acidity and the proportion of quinone-type groups. These moieties appear to have a higher reactivity toward furfuryl alcohol, leading to better curing. Treatment of cashew nut oil with ozone was shown to provide a self-condensed material with bonding ability for board (Pizzi 2006; Thebault *et al.* 2013). All these reactions are radical phenoxycoupling reactions yielding linking of phenolic rings in two different manners but more generally aromatic ring to aromatic ring, as shown as shown in Fig. 16:

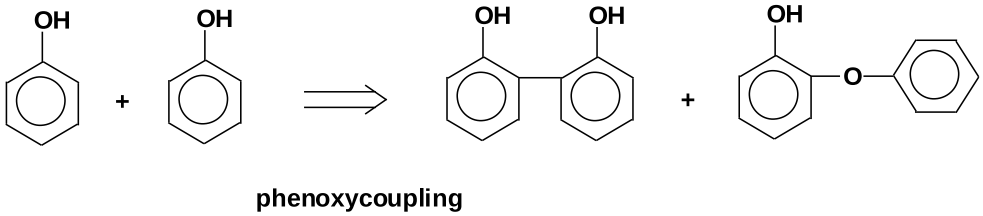

Fig. 16. Reaction for free-radical-initiated phenoxycoupling of phenol

The Fenton reagent, which involves a combination of hydrogen peroxide and iron compounds, was shown to be effective for promoting bonding in fiberboards (Widsten *et al.* 2003; Widsten and Laine 2004; Halvarsson *et al.* 2009; Mejía *et al.* 2014). According to Widsten *et al.* (2003), such treatment yielded a large increase in free radical concentration, which helped to account for the improved bonding. Effective particleboard bonding with lignin and hydrogen peroxide under acid reaction conditions was successfully demonstrated (Nimz and Hitze 1980; Nimz 1983).

Enzymatic Activation

Enzymes can offer an alternative approach for activation of biomass components, usually either by oxidation or by generating free radical species (Eriksson *et al*. 1990; Kharazipour and Euring 2010, 2013; Zhang *et al*. 2007, 2015). Improvements in self-bonded board properties after such treatments have been documented (Kharazipour *et al.* 1997; Halis 2011).

Laccase has been widely studied as a means of activating lignin surfaces (Hüttermann *et al.* 1989, 2001; Felby *et al.* 1997a,b; 2002, 2004; Müller *et al.* 2007, 2009a; Widsten and Kandelbauer 2008a,b; Widsten *et al.* 2009; Nyanhongo *et al.* 2010; Álvarez *et al.* 2011; González-García *et al.* 2011; Kudanga *et al.* 2011; Nasir *et al.* 2013; Widsten and Kandelbauer 2014; Norhaslida *et al*. 2014). Potential uses of laccase in industry are very large, including mediated systems in textile industry, pulp and paper industry, wood industry, bioremediation, biosensors, food industry, and organic synthesis (Javed *et al.* 2017). Laccase has oxidative ability (degradation, delignification, polymerization, demethylation or dechlorination, oligomerization), as well as ability to promote coupling, grafting, co-polymerization, and crosslinking reactions (Javed *et al.* 2017). Laccase is believed to catalyze the one-electron oxidation of phenolic groups (Felby *et al.* 1997b). Such interactions can lead to covalent bonding between fibers (Felby *et al.* 2004). Álvarez *et al.* (2011) confirmed the enzymatic treatment's ability to generate free radicals by use of an enzyme scavenging assay. Though enzymatic treatments are almost universally regarded as being an environmentally friendly approach, González-García *et al.* (2011) expressed concern about the amount of energy that may be expended in the preparation of laccase for treatment of biomass before hot-pressing.

An enzyme system can be called "mediated" if its oxidation state is repeatedly refreshed by the presence of a supplementally added oxidizing agent. Several research teams have reported laccase-mediated oxidation systems for activation of the lignin component before hot-pressing of board (Felby *et al.* 1997a; Euring *et al.* 2011a,b; 2013). Related work was reported by Kharazipour *et al.* (1998) in which a peroxidase was applied as a mediated system with hydrogen peroxide.

The system described by Euring *et al.* (2011a) is unusual in that the mediative compounds did not consist of conventional oxidizing agents. Rather, 4-hydroxybenzoic acid (HBA), 1-hydroxybenzotriazole (HBT), and acetosyringone (AS) were used. Of these, the most promising results were with HBA. Follow-up work (Euring *et al.* 2011b) used a lignin model compound to demonstrate a likely mechanistic path. Further demonstration was provided by electron spin resonance, to characterize the role of odd electrons. Interestingly, Felby *et al.* (1997a,b) and Hassingboe *et al.* (1998) suggested that phenoxy radicals, due to their small size, can serve a role as mediators by transporting free electrons to sites not accessible to the laccase itself. Hüttermann *et al.* (2000) and Müller *et al.* (2009a) likewise suggested a prominent role of species within the biomass mixture that were capable of sustaining relatively stable free radicals. Alvarez *et al.* (2015) showed that there was substantially lower development of strength when compounds soluble in hot water had been removed from leaf plantain biomass after steam explosion; it was proposed that those compounds had been the carriers of free radicals, having potential to generate crosslinking during hot-pressing. All of these systems, however, generally needed the addition of 1% isocyanate for the panels to satisfy standard internal bond strength requirements.

Plasma for Free Radical Activation

Though the laccase and related enzymatic treatments have been the most widely studied approaches to creating free-radical species to help develop covalent bonding in binderless board products, some researchers have employed quite different strategies to achieve that result. Zhou *et al.* (2013) treated enzyme hydrolysis lignin with an oxygen plasma. The strength properties of board made from poplar fibers increased with increasing plasma treatment intensity.

Curing Conditions

When attempting to meet the performance levels expected for industrial products by hot-pressing in the absence of formaldehyde, the conditions of temperature and time tend to be more severe than would be applied in equivalent cases when dealing either with solid wood or with board bonding with conventional formaldehyde-based resins (Pintiaux *et al.* 2015). As stated by Okuda and Sato (2007), such severe conditions are needed to "melt the solid-solid interfaces between the particles and to supply the activation energy for chemical reactions". Here the word "melt" can be interpreted in terms of the glass transition temperatures of the main components of wood, as affected by the prevailing moisture conditions. Pintiaux *et al.* (2015) observed that the press platen temperature of hot-pressing with steam usually has been reported in the range 180 to 200 °C. Today's industrial particleboard and MDF panels are pressed at 220 °C (Pizzi 2016).

Unique conditions are created during friction welding, a process that combines shearing and the development of very high local temperatures at the rubbed surfaces of woody material. Such systems are well known to produce promising bonding effects (Gfeller *et al.* 2003, 2004; Pizzi 2006, 2014). Belleville *et al.* (2013) showed that such bonding could be attributed to processes outlined earlier in this article, including degradation of hemicelluloses and lignin, followed by reactions of some of the breakdown products. Presumably the polysaccharide degradation yields furfural and 5HMF, which can react according to the schemes shown earlier in Figs. 6 through 8. Meanwhile, the lignin-derived compounds can undergo condensation reactions, leading to higher molecular mass and a curing effect. Gfeller *et al.* (2003, 2004) showed the central role of localized melting and flow of matrix polymers – mainly lignin but also including hemicellulose, especially the xylans (Gfeller *et al.* 2003; Stamm *et al.* 2005; Delmotte 2008, 2009) – in the development of welded wood bonding.

COMBINING THE LINKS OF THE CHAIN

Each of the four hypothetical main links, which have been considered here to account for instances of effective bond development within hot-pressed products, was shown to be supported by evidence from the literature. However, there were some exceptions. Though covalent bonds, of various types, clearly are important with respect to bond development, the literature generally does not provide clear evidence that covalent bonds need to form at the interfaces of wood materials in order to achieve well-bonded structures in typical cases. Each of the links was shown to be important, at least in specific instances, relative to product attributes when forming binderless fiberboard and other such hot-pressed products. The question to be considered next, consistent with the links-of-a-chain model, is how to carry out any treatments and hot-pressing in such a way that all of the links become strong together, minimizing the chance that any one of them is a point of particular vulnerability in an eco-friendly hot-pressed biomass board product.

Focus on Processes

An emphasis on key processes can be a good strategy when attempting to optimize the overall bonding performance of hot-pressed board formed without the addition of formaldehyde. Pintiaux *et al.* (2015) in their major review report, gave an example of how this can be done: Different reported treatment conditions were designated according to the categories of "steam pretreated", "steam injected", and "no steam". Such categories can help practical people to envision what kinds of equipment can be installed to carry out efficient, cost-effective operations at an industrial scale, while maintaining conditions likely to support the strengthening of each of the links in the chain: mechanical contact, molecular-scale contact, covalent or other chemical linkages, and structural integrity. Keeping in mind that the findings of different studies, using different materials and conditions, give widely diverse results, Table 2 is intended to serve as a starting point for discussion regarding how widely different kinds of processes might be anticipated to include the viability of different links in a mechanistic chain for strength development.

Table 2. Example of How Contrasting Processing Conditions Might Affect Mechanistic Links in Different Ways

Mechanistic link	Pre-steaming	Steam injection	No steam
Mechanical contact	+	++	0
Molecular contact	+	+	-
Covalent bonding	++	+	0
Structural integrity	0	-	+

Key: ++ = very positive effect; + = positive effect; 0 = neutral effect; and - = negative effect

Though the entries in Table 2 are more intended as an example of an approach, rather than as a serious demonstration, some explanations can be offered, based generally on the literature cited in this article:

- **Presteaming** is expected to have a positive effect on mechanical contact due to evidence that it can lower the glass transition temperatures of some matrix materials (Takahashi *et al.* 2009). It is expected to have a beneficial effect on molecular contact under the assumption that there is a decrease in waxy materials on the solid surface (Widyorini and Satiti 2011). It is expected to have a very positive effect on covalent bonding due to the opportunity for development of furan species (Mamman *et al.* 2008; Sheldon 2014; Zhang *et al.* 2015). It is given a neutral rating regarding structural integrity, since there is a possibility of steam-induced delamination (Ando and Sato 2009; Pintiaux *et al.* 2013).
- **Steam injection** is given top rating with respect to mechanical contact based on the idea that such a process gives the best opportunity for plastic flow during the hot-pressing operation, a merely positive rating for molecular contact, since there is less opportunity for waxy substances to get flushed away from the solid surfaces, a

merely positive rating for covalent bonding, since there is less opportunity for development and reaction of furan-related species, and a negative rating for structural integrity, based on the idea that this option results in the highest steam pressure during hot-pressing, giving rise to greater danger of delamination upon opening of the press. Steam injection can be regarded as a better way to heat the center of particleboard, in light of the relatively low thermal conductivity of lignocellulose. However, industrial steam-injection presses for wood panels are rather rare. For this reason, an inexpensive way to achieve a similar effect involves the steam wave concept. In the first step of steam wave treatment, water sprays are applied on the furnish surfaces just before going into the hot press. The violent vaporization of this water in contact with the hot press platens causes a rapidly moving steam wave to travel through the panels from the surfaces to the board core and coming out though the board edges. When steam injection is used, it can strengthen the "steam wave" and make the heat transference quicker. The temperature difference will decrease and the density profile of the particleboard will become more flat.

- **No steam** is assigned a neutral rating for mechanical contact on the theory that sufficient water is likely to be present in the biomass to achieve at least some plasticization of matrix materials when hot-pressing is started, a negative rating for molecular contact, since nothing has been done to deal with the presence of waxy layers, if present, which will impede wetting, a neutral rating on covalent bonding, since nothing has been done to promote furan chemistry, and a positive rating for structural integrity, since the product is not likely to suffer from delamination due to steam.

The forgoing analysis, based on Table 2, runs the risk of amplifying inconsequential factors. In particular, although steam-delamination of hot-pressed board products is a real concern, commercial hot-press operators can be expected to continually optimize their operating conditions to avoid the onset of delamination. The entries in Table 2 also tend to hide potential effects of countless details inherent in different hot-pressing operations. So while Table 2 may have some explanatory value, it is not intended as a basis for making predictions in specific cases.

Pretreatments

Another take-away message, in general, from the literature that was reviewed in preparing this article, is that pretreatments of the lignocellulosic material, in advance of the hot-pressing, can be advantageous (Zhang *et al.* 2015). In fact, pretreatments can be related to each of the chain links that have been considered in this article:

Flow-related

Although the word "pretreatment" can include everything from heat, to chemicals, to mechanical refining, *etc.*, the most widely studied option involves steam explosion, so that is a good place to focus the discussion. It is interesting that several authors have attributed greater plasticization of lignin or hemicellulose to the fact that the material had been steam-treated (Takahashi *et al.* 2009; Tajuddin *et al.* 2016). However, it is usually hard in such cases to make a separation between effects attributable to the pretreatment and those more correctly associated with the temperature and moisture conditions present during hot pressing (which can unintentionally be affected by the pretreatment). To get around this problem, one approach may be to carry out some studies dealing with various semi-isolated cases, such as the effects on glass transition temperatures when lignin or hemicellulose isolates are exposed separately to different conditions of steam, hydrothermal processing, and various other factors.

Microwave heating as a pretreatment

Okuda *et al.* (2006b) showed that microwave heating could be used as a pretreatment before hot-pressing. In principle, microwave heating applies energy preferentially to the parts of a material where water is present. This may be beneficial in cases where excessive heating of the surfaces has led to sub-standard results. In general, however, microwave heating can be expected to be expensive in comparison to, say, heating with steam or radiant heat (Acevedo *et al.* 2015).

Wetting-related

With the possible exception of high levels of silica in certain herbaceous plants and grasses (Massey *et al.* 2006), it seems that waxes, fatty acids, and other low-surface-energy compounds are likely to be the greatest barriers to molecular contact and spreading of plasticized phases during hot-pressing of board products. As has already been noted, measures to remove non-polar materials by extraction have been shown to significantly increase the strength after hot-pressing of the material, in several cases (Widyorini and Satiti 2011; Alvarez *et al.* 2015; Kurokochi and Sato 2015b). But it is less certain whether such processes make sense on an industrial scale. Extraction may be too expensive an option to be considered for typical board products, and in such cases the extractable materials would just be left within the board product, subject to possible redistribution. To minimize costs and toxic effects during extraction, relatively benign solvents such as ethanol/water mixtures, or possibly surfactant solutions could be studied as means of "washing" bond-inhibiting compounds. Another, completely different approach is also possible, as a means to overcome problems of waxy substances that tend to inhibit bonding in hot-pressed board. By judicious selection of materials, one approach is just to avoid the usage of leaves, small stalks, aquatic plants, and related materials likely to be coated with solvent-extractable substances. Instead, if the end product can benefit from being hydrophobic, it makes sense to apply a hydrophobic treatment agent (*e.g.* wax, stearic anhydride, alkylketene dimer, rosin and alum combinations, *etc.*) only after the bonding of the hot-press board has been established (Roffael *et al.* 2005). If a slow-reacting hydrophobic agent such as alkylketene dimer were added to the formulation or biomass particles or fibers before hot-pressing, it is likely that it would not completely melt and spread until most of the water had been driven off, allowing the temperature to rise; by such a mechanism, the development of bonding would be less affected by the hydrophobic treatment (Hubbe 2014).

Activation-related

Based on studies dealing with formation of active chemical species, including furfural, 5-hydroxymethylfurfural, or free radical species, one can speculate regarding potential fruitful areas of future research. Findings considered in this review suggest that a general emphasis should be placed on optimization. Conditions need to be sufficiently severe is to create reactive chemical species, but not so severe as to cause their premature decomposition. With factors to consider including acid catalysts, additives such as tannins, enzymes including peroxidases, and different temperatures, times, and moisture levels, there is much research work to be done. At the leading edge of such work there seems to be a need for a focus on non-formaldehyde crosslinking agents, including glyoxal and other aldehydes such as vanillin and its derivatives, citric acid, redox conditions, plasma treatments, and isocyanates. With so many factors that may lead to promising combinations, it may be an appropriate time to consider the use of fractional factorial experimental designs (Lundstedt *et al.* 1998), making it possible to test combinations of multiple ingredients, possibly at different levels and treatment conditions, with a manageable number of replications.

Uniformity-related strategies: Layers

As was discussed earlier, important changes in the structure of a hot-pressed board product have been observed to take place during pressing, and these can include the development of densified "skin effect" regions near the surfaces (Heebink *et al.* 1972; Plath and Schnitzier 1974). Also, there is the possibility of delamination if the steam pressure within the press is too high, relative to the structure and its cohesion, when the press is opened (Ando and Sato 2009; Pintiaux *et al.* 2013). Although the occurrence of skin formation and delamination both can be reduced by adjusting conditions such as the incoming moisture to the press (Heebink *et al.* 1972) or the pressure of injected steam (Pintiaux *et al.* 2013), various alternative approaches may be more advantageous in specific cases. First of all, it is important to question, in a given case, whether a U-shaped density profile – which may result from greater plastic flow and densification of surfaces adjacent to the hot-press platen surfaces – may actually be an advantage. Such a structure can be favorable for a given application, for instance if the board needs to maintain a specified stiffness. It was noted by Pintiaux *et al.* (2015) that only the study by Gao *et al.* (2011) had evaluated the use of different compositions for the center and the exteriors of a hot-pressed product. These authors designed a product with higher levels of Young's modulus in the outer layers; however, that kind of result is actually similar to what was reported by Plath and Schnitzier (1974), who studied the structure of conventionally-hot-pressed particleboard. In other words, a favorable distribution of density can result from the dynamics of heating and plasticization during conventional hot-pressing (Kelly 1977). It follows that there are a huge range of possible layered structures that future researchers can investigate as possible means of achieving either greater steam-permeability of outer layers or changes in the density or cohesiveness of inner layers in a particleboard or fiberboard product. The possibility of placing different materials at the outsides relative to the center needs to be included among the promising options for future research.

It must be stressed that in industrial practice the rate of press closing and the highest pressure reached during the panels press cycle are two parameters almost on the level of the differential surface/core percentage moisture content to obtain boards of rather different performance suitable for different final uses. A fast press closing speed can lead to a "U" sharp density profile. In other words, the density profile can become very steep. A longer closing time typically results in an M-shaped density profile. The surface density is lower than a little deeper inside the panel, and the density of the core become more flat (Pichelin *et al.* 2001).

Consolidation and Binding

Within the hot-press itself, the key tools and parameters to consider are the temperature and pressure, as well as the means of their adjustment. Pintiaux *et al.* (2015) observed that different optimum conditions can be anticipated depending on whether the binding system, including natural compounds that may be already present in the cellulosic material, functions mainly as a thermoplastic or as a thermo-set adhesive. In the case of a thermoplastic material, such as polyethylene, there may be no point in using temperature conditions that greatly exceed the softening point. By contrast, when high temperature is needed in order to drive hardening reactions to completion, mere melting of the matrix materials in a composition may not correspond to a sufficiently high temperature.

Another promising approach, as taught by many articles that have been cited in this review, involves usage of supplemental additives to the process, aimed at achieving better results when the board is within the hot-press. Many natural materials, including tannins and furan-related compounds, have inherently higher reactivity and tendency to form covalent bonds, compared to the levels of potential reactive species that would have been present in typical lignocellulosic material when it is subjected to heat and pressure. Therefore, in addition to optimizing the temperature and pressure, it is likely that many performance-related issues can be resolved by imaginative optimization of additives to the board composition.

Post-treatments

Post-treatments, *i.e.* processes that are applied to hot-pressed board after the densification process has been completed, can offer ways to improve upon many performance issues that were not otherwise achieved in manufacturing a hot-pressed board product (Lu and Pizzi 1998). Attributes of interest may especially involve the surface of the board, including its water-resistance, appearance, and smoothness.

Hydrophobic post-treatments of board can make sense in cases where direct incorporation of hydrophobic materials into the mixture entering the hot press would have interfered with bonding (Back 1987; Gollob and Wellons 1990; Widyorini and Satiti 2011; Alvarez *et al.* 2015; Kurokochi and Sato 2015b). If the hydrophobic agents are instead applied at the surface, as a post-treatment, then they presumably will not be able to spread within interfaces where effective bonding at the molecular level already has been established. Such hydrophobic treatments, which are less likely to adversely the development of bonding strength, may offer protection of the product in cases where low tolerance of moisture has been reported (Halvarsson *et al.* 2009; Pelaez-Samaniego *et al.* 2013; Abuarra *et al.* 2014; Almusawi *et al.* 2016).

CLOSING COMMENTS

One of the potential advantages of reconstituted lignocellulosic products such as particleboard and fiberboard is that the adverse effects of defects such as knots and cracks present in natural wood can be avoided. In addition, effective usage can be made from pieces of woody material that may be too small or otherwise unsuitable for manufacture of conventional solid wood lumber or panel pieces. But any structure, even a structure that has been carefully reassembled using self-bonding or an adhesive system, can fail at its weakest link. If the cause of such failure cannot be traced to an obvious defect, such as a crack or nonuniformity of the product, then it is possible that the defect is of a more subtle kind. These may include the failure of the lignin or hemicellulose matrix materials of the biomass to effectively spread over the adjacent cellulosic particles or fibers to develop bonding. Underlying causes of failure can include a lack of plasticization, wetting, or development of covalent or other chemical linkages. Such chemical linkages do not necessarily have to involve covalent bonding at the interfaces of wood particles; instead they may involve crosslinking or condensation of natural matrix materials and/or development of a sufficient level of secondary chemical interactions at interfaces. The authors hope that this way of considering such issues, in terms of critical links, will be helpful in terms of future research to further improve the efficient usage of environmentally friendly hot-pressed biomass board technology to meet the needs of future generations.

ACKNOWLEDGEMENTS

The authors wish to thank the following volunteers, who made many suggestions to improve the correctness, clarity, and completeness of the text: Charles Frihart, Forest Products Laboratory, Performance Enhanced Biopolymers, Madison, WI, USA; Francesc Fernando, University of Rovira & Virgili, Dept. of Mechanical Engineering, Avinguda Paisos Catalans; Grzegorz Kowaluk, Warsaw University of Life Science, Faculty of Wood Technology, Warsaw, Poland; M. Raul Pelaez Samaniego, Washington State University, Pullman, WA and Universidad de Cuenca, Cuenca-Ecuador; Antoine Rouilly, University of Toulouse, INRA, INPT, Lab. Chim. Agroind., Toulouse, France; and Yong-Chang Sun, Beijing Forestry University, Beijing Key Laboratory of Lignocellulosic Chemistry.

REFERENCES CITED

Abdelwahab, N. A., and Nassar, M. A. (2011). "Preparation, optimization, and characterization of lignin phenol formaldehyde resin as wood adhesive," *Pigm. Resin Technol.* 40(3), 169-174. DOI: 10.1108/03699421111130432

Abdullah, U. H. B., and Pizzi, A. (2013). "Tannin-furfuryl alcohol wood panel adhesives without formaldehyde," *Eur. J. Wood Prod.* 71(1), 131-132. DOI: 10.1007/s00107-012-0629-4

Abuarra, A., Hashim, R., Bauk, S., Kandaiya, S., and Tousi, E. T. (2014). "Fabrication and characterization of gum Arabic bonded *Rhizophora* spp. particleboards," *Materials & Design* 60, 108-115. DOI: 10.1016/j.matdes.2014.03.032

Acevedo, L., Uson, S., and Uche, J. (2015). "Local exergy cost analysis of microwave heating systems," *Energy* 80, 437-451. DOI: 10.1016/j.energy.2014.11.085

Ahmed, A., Scott, G. M., Akhtar, M., and Myers, G. C. (1998). "Biokraft pulping of kenaf and its bleachability," TAPPI Proceedings. TAPPI Press, Atlanta.

Ahvenainen, P., Kontro, I., and Svedstrom, K. (2016). "Comparison of sample crystallinity determination methods by X-ray diffraction for challenging cellulose I materials," *Cellulose* 23(2), 1073-1086. DOI: 10.1007/s10570-016-0881-6

Alekhina, M., Ershova, O., Ebert, A., Heikkinen, S., and Sixta. H. (2015). "Softwood kraft lignin for value-added applications: Fractionation and structural characterization," *Industrial Crops and Products* 66, 220-228. DOI: 10.1016/j.indcrop.2014.12.021

Allan, G. C, and Neogi, A. N. (1971). "Fiber surface modification, Part VIII: The mechanism of adhesion of phenol-formaldehyde resins to cellulosic and lignocellulosic substrates," *J. Adhesion* 3(1), 13-18. DOI: 10.1080/00218467108075002

Almusawi, A., Lachat, R., Atcholi, K. E., and Gomes, S. (2016). "Proposal of manufacturing and characterization test of binderless hemp shive composite," *Intl. Biodeter. Biodegrad.* 115, 302-307. DOI: 10.1016/j.ibiod.2016.09.011

Álvarez, C., Rojano, B., Almaza, O., Rojas, O. J., and Gañán, P. (2011). "Self-bonding boards from plantain fiber bundles after enzymatic treatment: Adhesion improvement of lignocellulosic products by enzymatic pre-treatment," *J. Polym. Environ.* 19(1), 182-188. DOI: 10.1007/s10924-010-0260-6

Alvarez, C., Rojas, O. J., Rojano, B., and Ganán, P. (2015). "Development of self-bonded fiberboards from fiber of leaf plantain: Effect of water and organic extractives removal," *BioResources* 10(1), 672-683. DOI: 10.15376/biores.10.1.672-683

Amirou, S., Pizzi, A., and Delmotte, L. (2017). "Citric acid as waterproofing additive in butt joints linear wood welding," *European Journal of Wood and Wood Products* 75(4), 651-654. DOI 10.1007/s00107-017-1167-x

Ando, M., and Sato, M. (2009). "Manufacture of plywood bonded with kenaf core powder," *J. Wood Sci.* 55(4), 283-288. DOI: 10.1007/s10086-009-1022-8

Anglès, M. N., Ferrando, F., Farriol, X., and 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 Bioenergy* 21(3), 211-224. DOI: 10.1016/S0961-9534(01)00031-9

Anglès, M. N., Reguant, J., Montané, D., Ferrando, F., Farriol, X., and Salvadó, J. (1999). "Binderless composites from pretreated residual softwood," *J. Appl. Polymer Sci.* 73(12), 2485-2491. DOI: 10.1002/(SICI)1097-4628(19990919)73:12<2485::AID-APP17>3.0.CO;2-G

Arnold, K., Davies, B., Giles, R. L., Grosjean, C., Smith, G. E., and Whiting, A. (2006). "To catalyze or not to catalyze? Insight into direct amide bond formation from amines and carboxylic acids under thermal and catalyzed conditions," *Advan. Synth. Catal.* 348(7-8), 813-820. DOI: 10.1002/adsc.200606018

Back, E. L. (1987). "The bonding mechanism in hardboard manufacture," *Holzforschung* 41(4), 247-258. DOI: 10.1515/hfsg.1987.41.4.247

Back, E. L. (1991). "Oxidative activation of wood surfaces for glue bonding," *For. Prod. J.* 41(2), 30-36.

Baskaran, M., Hashim, R., Said, N., Raffi, S. M., Balakrishnan, K., Sudesh, K., Sulaiman, O., Arai, T., Kosugi, A., Mori, Y., Sugimoto, T., and Sato, M. (2012). "Properties of binderless particleboard from oil palm trunk with addition of polyhydroxyalkanoates," *Composites: Part B* 43, 1109-1116. DOI: 10.1016/j.compositesb.2011.10.008

Basso, M. C., Pizzi, A., Delmotte, L., and Abdalla, S. (2017). "MALDI-TOF and ^{13}C NMR analysis of the cross-linking reaction of lignin by triethyl phosphate," *Polymers* 9, 206 (pp. 1-15).

Basta, A. H., El-Saied, H., and Lotfy, V. F. (2013). "Performance of rice straw-based composites using environmentally friendly polyalcoholic polymers-based adhesive system," *Pigment & Resin Technol.* 42(1), 24-33. DOI: 10.1108/03699421311288733

Belleville, B., Stevanovic, T., Cloutier, A., Pizzi, A., Prado, M., Erakovic, S., Diouf, P. N., and Royer, M. (2013). "An investigation of thermochemical changes in Canadian hardwood species during wood welding," *Eur. J. Wood Wood Prods.* 71(2), 245-257. DOI: 10.1007/s00107-013-0671-x

Bertaud, F., Tapin-Lingua, S., Pizzi, A., Navarrete, P., and Petit-Conil, M. (2012). "Development of green adhesives for fiberboard manufacturing, using tannins and lignin from pulp mill residues," *Cellulose Chem. Technol.* 46(7-8), 449-455.

Bhardwaj, N. K., Bajpai, P., and Bajpai, P. K. (1996). "Use of enzymes in modification of fibres for improved beatability," *J. Biotechnol.* 51(1), 21-26. DOI: 10.1016/0168-1656(96)01556-8

Biermann, C. J. (1996). *Handbook of Pulping and Papermaking*, Academic Press, San Diego.

Böhm, R., Hauptmann, M., Pizzi, A., Friederich, C., and Laborie, M.-P. (2016). "The chemical, kinetic and mechanical characterization of tannin-based adhesives with different crosslinking systems," *Int. J. Adhesion Adhesives* 68, 1-8. DOI: 10.1016/j.ijadhadh.2016.01.006.

Boon, J. G., Hashim, R., Sulaiman, O., Hiziroglu, S., Sugimoto, T., and Sato, M. (2013). "Influence of processing parameters on some properties of oil palm trunk binderless particleboard," *Eur. J. Wood Prod.* (Holz Roh Werkst.) 71(5), 583-589. DOI: 10.1007/s00107-013-0712-5

Boonstra, M. J. (2008). "Une modification thermique du bois en deux étappes," ("A thermal modification of wood in two steps"), Joint PhD, University of Gent, Belgium, and University of Nancy 1, France.

Boonstra, M. J., and Tjeerdsma, B. (2006). "Chemical analysis of heat treated softwoods," *Holz Roh- Werkstoff* 64(3), 204-211. DOI: 10.1007/s00107-005-0078-4

Bouajila, J., Limare, A., Joly, C., and Dole, P. (2005). "Lignin plasticization to improve binderless fiberboard mechanical properties," *Polymer Eng. Sci.* 45(6), 809-816. DOI: 10.1002/pen.20342

Brazdausks, P., Tupciauskas, R., Andzs, M., Rizhikovs, J., Puke, M., Paze, A., Meile, K., and Vedernikovs, N. (2015). "Preliminary study of the biorefinery concept to obtain furfural and binder-less panels from hemp (*Cannabis sativa* L.) shives," *Energy Procedia* 72, 34-41. DOI: 10.1016/j.egypro.2015.06.006

Calvé, L. R. (1990). 19th IUFRO World Congress, Montreal, Canada, August 1990.

Chakar, F. S., and Ragauskas, A. J. (2004). "Review of current and future softwood kraft lignin process chemistry," *Indust. Crops Prod.* 20(2), 131-141. DOI: 10.1016/j.indcrop.2004.04.016

Chen, Z. H., Hu, M., Zhu, X. L., Guo, D. B., Liu, S. M., Hu, Z. Q., Xiao, B., Wang, J. B., and Laghari, M. (2015). "Characteristics and kinetic study on pyrolysis of five lignocellulosic biomass via thermogravimetric analysis," *Bioresour. Technol.* 192, 441-450. DOI: 10.1016/j.biortech.2015.05.062

Chow, S. (1972). "Thermal reactions and industrial uses of bark," *Wood Fiber Sci*. 4(3), 130-138.

Chow, S. (1975). "Bark boards without synthetic resins," *For. Prod. J*. 25(11), 32-37.

Chow, S. (1977). "Properties of bark boards made with ozone treatment," *Wood Sci.* 9(3), 124-129.

Cozzani, V., Lucchesi, A., Stoppato, G., and Maschio, G. (1997). "A new method to determine the composition of biomass by thermogravimetric analysis," *Canadian J. Chem. Eng.* 75(1), 127-133. DOI: 10.1002/cjce.5450750120

Cristescu, C., and Karlsson, O. (2013). "Changes in content of furfurals and phenols in self-bonded laminated boards," *BioResources* 8(3), 4056-4071. DOI: 10.15376/biores.8.3.4056-4071

da Silva, A. M. G., Filipe, E. J. M., d'Oliveira, J. M. R., and Martinho, J. M. G. (1996). "Interfacial behavior of poly(styrene)-poly(ethylene oxide) diblock copolymer monolayers at the air-water interface. Hydrophilic block chain length and temperature influence," *Langmuir* 12(26), 6547-6553. DOI: 10.1021/la960604+

Delmotte, L., Ganne-Chedeville, C., Leban, J. M., Pizzi, A., and Pichelin, F. (2008). "CP-MAS, ^{13}C NMR and FTIR investigation of the degradation reactions of polymer constituents in wood welding," *Polymer Degrad. & Stabil*. 93, 406-412. DOI: 10.1016/j.polymdegradstab.2007.11.020

Delmotte, L., Mansouri, H. R., Omrani, P., and Pizzi, A. (2009). "Influence of wood welding frequency on wood constituents chemical modifications," *J. Adhesion Sci. Technol.* 23, 1271-1279 (2009). DOI: 10.1163/156856109X433991

Despres, A., Pizzi, A., Vu, C., and Pasch, H. (2008). "Formaldehyde-free aminoresin wood adhesives based on dimethoxyethanal," *J. Appl. Polym. Sci.* 110(6), 3908-3916. DOI: 10.1002/app.28936

Dimmel, D., and Gellerstedt, G. (2010). "Chemistry of pulp bleaching," in: *Advances in Chemistry*, C. Heitner, D. Dimmel, and J. A. Schmidt (eds.), Taylor and Francis, Boca Raton, Ch. 10.

Effendi, A., Gerhauser, H., and Bridgwater, A. V. (2008). "Production of renewable phenolic resins by thermochemical conversion of biomass: A review," *Renew. Sustain. Energy Rev.* 12(8), 2092-2116. DOI: 10.1016/j.rser.2007.04.008

Endo, K., Obataya, E., Zeniya, N., and Matsuo, M. (2016). "Effects of heating humidity on the physical properties of hydrothermally treated spruce wood," *Wood Sci. Technol.* 50(6), 1161-1179. DOI: 10.1007/s00226-016-0822-4

Eriksson, K. E. L., Blanchette, R. A., and Ander, P. (1990). *Microbial and Enzymatic Degradation of Wood and Wood Components*, Springer Series in Wood Science, Springer Verlag, Berlin. DOI: 10.1007/978-3-642-46687-8

Euring, M., Rühl, M., Ritter, N., Kües, U., and Kharazipour, A. (2011a). "Laccase mediator systems for eco-friendly production of medium-density fiberboard (MDF) on a pilot scale: Physicochemical analysis of the reaction mechanism," *Biotechnol. J.* 6(10), 1253-1261. DOI: 10.1002/biot.201100119

Euring, M., Trojanowski, J., Horstmann, M., and Kharazipour, A. (2011b). "Studies of enzymatic oxidation of TMP fibers and lignin model compounds by a laccase-mediator-system using different 14C and 13C techniques," *Wood Sci. Technol.* 46(4), 699-708. DOI: 10.1007/s00226-011-0439-6

Euring, M., Trojanowski, J., and Kharazipour, A. (2013). "Laccase-mediator catalyzed modification of wood fibers: Studies on the reaction mechanism and making of medium-density fiberboard," *For. Prod. J.* 63(1–2), 54-60. DOI: 10.13073/FPJ-D-12-00075

Evon, P., Kartika, I. A., and Rigal, L. (2014a). "New renewable and biodegradable particleboards from jatropha press cakes," *Journal of Renewable Materials* 2, 52-65. DOI: 10.7569/JRM.2013.634131

Evon, P., Vandenbossche, V., Pontalier, P.-Y., and Rigal, L. (2014b). "New thermal insulation fiberboards from cake generated during biorefinery of sunflower whole plant in a twin-screw extruder," *Industrial Crops and Products* 52, 354-362. DOI: 10.1016/j.indcrop.2013.10.049

Evon, P., Vandenbossche, V., and Rigal, L. (2012). "Manufacturing of renewable and biodegradable fiberboards from cake generated during biorefinery of sunflower whole plant in twin-screw extruder: Influence of thermo-pressing conditions," *Polym. Degrad. Stabil.* 97, 1940-1947. DOI: 10.1016/j.polymdegradstab.2012.01.025

Fahmy, T. Y. A., and Mobarak, F. (2013). "Advanced binderless board-like green nanocomposites from undebarked cotton stalks and mechanism of self-bonding," *Cellulose* 20(3), 1453-1457. DOI: 10.1007/s10570-013-9911-9

FAO (2014). "Forest products statistics: 2014 global forest products facts and figures," Food and Agriculture Organization of the United Nations, http://www.fao.org/forestry/statistics

Faris, A. H., Rahim, A. A., Ibrahim, M. N. M., Alkurdi, A. M., and Shah, I. (2016). "Combination of lignin polyol tannin adhesives and polyethylenimine for the preparation of green water-resistant adhesives," *J. Appl. Polym. Sci.* 133(20), 43437. DOI: 10.1002/APP.43437.

Felby, C., Hassingboe, J., and Lund, M. (2002). "Pilot-scale production of fiberboards made by laccase oxidized wood fibers: Board properties and evidence for cross-linking of lignin," *Enzyme Microb. Tech.* 31(6), 736-741. DOI: 10.1016/S0141-0229(02)00111-4

Felby, C., Nielsen, B. R., Olesen, P. O., and Skibsted, L. H. (1997a). "Identification and quantification of radical reaction intermediates by electron spin resonance spectrometry of laccase-catalyzed oxidation of wood fibers from beech (*Fagus sylvatica*)," *Appl. Microbiol. Biot.* 48(4), 459-464. DOI: 10.1007/s002530051080

Felby, C., Pedersen, L. S., and Nielsen, B. R. (1997b). "Enhanced auto adhesion of wood fibers using phenol oxidases," *Holzforschung* 51(3), 281-286. DOI: 10.1515/hfsg.1997.51.3.281

Felby, C., Thygesen, L. G., Sanadi, A., and Barsberg, S. (2004). "Native lignin for bonding of fiber boards—Evaluation of bonding mechanisms in boards made from laccase-treated fibers of beech (*Fagus sylvatica*)," *Ind. Crops Prod.* 20(2), 181-189. DOI: 10.1016/j.indcrop.2004.04.020

Fengel, C., and Wegener, G. (1989). *Wood, Chemistry, Ultrastructure, Reactions,* 2nd Ed., De Gruyter, Berlin, 1989

Ferraz, A., Guerra, A., Mendonca, R., Masarin, F., Vicetim, M., Aguira, A., and Pavan, P. C. (2008). "Technological advances and mechanistic basis for fungal biopulping," *Enzyme and Microbial Technology* 43, 178-185. DOI: 10.1016/j.enzmictec.2007.10.002

Fitchett, C. S., Laughton, N. G., Chappell, C. G., Lokman Khan, M., Tverezovskiy, V., Tomkinson, J., and Fowler, P. (2003). "Oil ozonolysis," US Patent 2005/0010069 A1 assigned to Cambridge Biopolymers Limited.

Fowkes, F. M., Riddle, F. L., Pastore, W. E., and Weber, A. L. (1990). "Interfacial interactions between self-associated polar liquids and squaline used to test equations for solid liquid interfacial interactions," *Colloids Surf.* 43, 367-387. DOI: 10.1016/0166-6622(90)80298-I

Gandini, A. (2008). "Polymers from renewable resources: A challenge for the future of macromolecular materials," *Macromol.* 41(24), 9491-9504. DOI: 10.1021/ma801735u

Gandini, A., and Lacerda, T. M. (2015). "From monomers to polymers from renewable resources: Recent advances," *Prog. Polymer Sci.* 48, 1-39. DOI: 10.1016/j.progpolymsci.2014.11.002

Gandini, A., Lacerda, T. M., Carvalho, A. J. F., and Trovatti, E. (2016). "Progress of polymers from renewable resources: Furans, vegetable oils, and polysaccharides," *Chem. Rev.* 116(3), 1637-1669. DOI: 10.1021/acs.chemrev.5b00264

Gao, Z. H., Wang, X.-M., Wan, H., and Brunette, G. (2011). "Binderless panels made with black spruce bark," *BioResources* 6(4), 3960-3972. DOI: 10.15376/biores.6.4.3960-3972

Garcia, R., and Pizzi, A. (1998a). "Polycondensation and autocondensation networks in polyflavonoid tannins, Part 1: Final networks," *J. Appl. Polym. Sci*. 70(6), 1083-1091. DOI: 10.1002/(SICI)1097-4628(19981107)70:6<1083::AID-APP5>3.0.CO;2-K

Garcia, R., and Pizzi, A. (1998b). "Polycondensation and autocondensation networks in polyflavonoid tannins. II. Polycondensation versus autocondensation," *Journal of Applied Polymer Science* 70(6), 1093-1110. DOI: 10.1002/(SICI)1097-4628(19981107)70:6<1093::AID-APP6>3.0.CO;2-J

Garcia, R. and Pizzi, A. (1998c). "Cross-linked and entanglement networks in thermomechanical analysis of polycondensation resins," *J. Appl. Polymer Sci*. 70(6), 1111-1116. DOI: 10.1002/(SICI)1097-4628(19981107)70:6<1111::AID-APP7>3.0.CO;2-R

Gardner, D. J., Oporto, G. S., Mills, R., and Samir, M. A. S. A. (2008). "Adhesion and surface issues in cellulose and nanocellulose," *J. Adhes. Sci. Technol*. 22(5-6), 545-567. DOI: 10.1163/156856108X295509

Geimer, R. L., Montrey, H. M., and Lehmann, W. F. (1975). "Effects of layer characteristics on the properties of three-layer particleboards," *Forest Prod. J*. 25(3), 19-29.

Gellerstedt, G. (2015). "Softwood kraft lignin: Raw material for the future," *Industrial Crops and Products* 77, 845-854. DOI: 10.1016/j.indcrop.2015.09.040

Geng, X. L., Zhang, S. Y., and Deng, J. (2006). "Alkaline treatment of black spruce bark for the manufacture of binderless fiberboard," *J. Wood Chem. Technol.* 26(4), 313-324. DOI: 10.1080/02773810601076857

Gfeller, B., Properzi, M., Zanetti, M., Pizzi, A., Pichelin, F., Lehmann, M., and Delmotte, L. (2004). "Wood bonding by mechanically-induced *in situ* welding of polymeric structural wood constituents," *J. Appl. Polym. Sci.* 92(1), 243-251. DOI: 10.1002/app.13648

Gfeller, B., Zanetti, M., Properzi, M., Pizzi, A., Pichelin, F., Lehmann, M., and Delmotte, L. (2003). "Wood bonding by vibrational welding," *J. Adhes. Sci. Technol*. 17(11), 1573-1589. DOI: 10.1163/156856103769207419

Ghafari, R., DoostHossieni, K., Abdulkhani, A., and Mirshkokraie, S. A. (2016). "Replacing formaldehyde by furfural in urea formaldehyde resin: Effect on formaldehyde emission and physical-mechanical properties of particleboards," *Eur. J. Wood Wood Prod.* 74(4), 609-616. DOI: 10.1007/s00107-016-1005-6

Gollob, L., and Wellons, J. D. (1990). "Wood adhesion," in: *Handbook of Adhesives*, van Nostrand Reinhold, New York, Ch. 36, pp. 598-610. DOI: 10.1007/978-1-4613-0671-9_36

Golon, A., and Kuhnert, N. (2012). "Unraveling the chemical composition of caramel," *J. Agric. Food Chem.* 60(12), 3266-3274. DOI: 10.1021/jf204807z

González-García, S., Feijoo, G., Heathcote, C., Kandelbauer, A., and Moreirra, M. T. (2011). "Environmental assessment of green hardboard production coupled with a laccase activated system," *J. Cleaner Prod.* 19(5), 445-453. DOI: 10.1016/j.jclepro.2010.10.016

Gosselink, R. J. A., van Dam, J. E. G., de Jong, E., Gellerstedt, G., Scott, E. L., and Sanders, J. P. M. (2011). "Effect of periodate on lignin for wood adhesive application," *Holzforschung* 65(2), 155-162. DOI: 10.1515/hf.2011.025

Gravitis, J., Abolins, J., Tupciauskas, R., and Veveris, A. (2010). "Lignin from steam-exploded wood as binder in wood composites," *J. Environ. Eng. Landscape Manag.* 18(2), 75-84. DOI: 10.3846/jeelm.2010.09

Guezguez, B. (2011). *Compréhension des Phénomènes de Diffusion du Formaldéhyde dans les Panneaux à Base de Bois: Utilisation dans la Réduction des Émissions Industrielles et Domestiques de Composés Organiques Volatils*, These de doctorat en Sciences des Materiaux, Ecole Superieure du Bois, Nantes, France, pp. 113-121.

Guigo, N., Mija, A., Vincent, L., and Sbirrazzuoli, N. (2010). "Eco-friendly composite resins based on renewable biomass resources: Polyfurfuryl alcohol/lignin thermosets," *Eur. Polym. J*. 46(5), 1016-1023. DOI: 10.1016/j.eurpolymj.2010.02.010

Gupta, G., Ning, Y., and Feng, M. W. (2011). "Effects of pressing temperature and particle size on bark board properties made from beetle-infested lodgepole pine (*Pinus contorta*) barks," *Forest Prod. J*. 61(6), 478-488. DOI: 10.13073/0015-7473-61.6.478

Halis, R. (2011). "Optimization of kraft and biokraft pulping for kenaf ," V36. Ph.D. Thesis, Universiti Putra Malaysia, Serdang, Selangor, Malaysia (Unpublished).

Halvarsson, S., Edlund, H., and Norgren, M. (2009). "Manufacture of non-resin wheat straw fibreboards," *Ind. Crops Prod*. 29(2), 437-445. DOI: 10.1016/j.indcrop.2008.08.007

Hansen, C. M. (2007). *Hansen Solubility Parameters: A User's Handbook*, 2nd Ed., CRC Press, Boca Raton, FL, USA. DOI: 10.1201/9781420006834

Hashim, R., Nadhari, W. N. A. W., and Sulaiman, O. (2016). "Green binderless board from oil palm biomass," in: *Renewable Energy and Sustainable Technologies for Building and Environmental Applications*, M. I. Ahmad, M. Ismail, and S. Riffat (eds.), pp. 175-186. DOI: 10.1007/978-3-319-31840-0_11

Hashim, R., Nadhari, W. N. A. W., Sulaiman, O., Kawamura, F., Hiziroglu, S., Sato, M., Sugimoto, T., Seng, T. G., and Tanaka, R. (2011a). “Characterization of raw materials and manufactured binderless particleboard from oil palm biomass,” *Mater. Design* 32(1), 246-254. DOI: 10.1016/j.matdes.2010.05.059

Hashim, R., Nadhari, W. N. A. W., Sulaiman, O., Sato, M., Hiziroglu, S., Kawamura, F., Sugimoto, T., Seng, T. G., and Tanaka, R. (2012). “Properties of binderless particleboard panels manufactured from oil palm biomass,” *BioResources* 7(1), 1352-1365. DOI: 10.15376/biores.7.1.1352-1365

Hashim, R., Saari, N., Sulaiman, O., Sugimoto, T., Hiziroglu, S., Sato, M., and Tanaka, R. (2010). “Effect of particle geometry on the properties of binderless particleboard manufactured from oil palm trunk,” *Mater. Design* 31(9), 4251-4257. DOI: 10.1016/j.matdes.2010.04.012

Hashim, R., Said, N., Lamaming, J., Baskaran, M., Sulaiman, O., Sato, M., Hiziroglu, S., and Sugimoto, T. (2011b). “Influence of press temperature on the properties of binderless particleboard made from oil palm trunk,” *Mater. Design* 32(5), 2520-2525. DOI: 10.1016/j.matdes.2011.01.053

Hassingboe, J., Lawther, J. M., and Felby, C. (1998). “Influence of extractives on enzymatic catalyzed bonding of Norway spruce TMP fibers,” Book Group Author(s): Canadian Pulp & Paper Assoc, 7th International Conference on Biotechnology in the Pulp and Paper Industry, Vol. A: Oral Presentations, pp. A125-A128.

Heebink, B. G., Lehmann, W. F., and Hefty, F. V. (1972). “Reducing particleboard pressing time: Exploratory study,” USDA Forest Service Res. Paper, FPL 180, Madison, WI.

Hill, C. A. S. (2006). *Wood Modification: Chemical, Thermal and Other Processes*, Wiley, Chichester. DOI: 10.1002/0470021748

Hsieh, Y.-Y., Chen, T.-Y., Kuo, W. C., Lai, Y. S., Yang, P.-F., and Lin, H.-P. (2017). “Rice husk-derived porous carbon/silica particles as green filler for electronic package application,” *Journal of Applied Polymer Sci.* 134(15), article 44699, DOI: 10.1002/app.44699

Hsu, W. E., Schwald, W., Schwald, J., and Shields, J. A. (1988). “Chemical and physical changes required for producing dimensionally stable wood-based composites; Part 1: Steam pretreatment,” *Wood Sci.Technol.* 22(3), 281-289. DOI: 10.1007/BF00386023

Hu, Z. J., Du, X. Y., Liu, J., Chang, H. M., and Jameel, H. (2016). “Structural characterization of pine kraft lignin: BioChoice lignin *vs* Indulin AT,” *J. Wood Chem. Technol.* 36(6), 432-446. DOI: 10.1080/02773813.2016.1214732

Huang, L. L., Xia, P., Liu, Y. M., Fu, Y., Jiang, Y. Y., Liu, S. Q., and Wang, X. L. (2016). “Production of biodegradable board using rape straw and analysis of mechanical properties,” *BioResources* 11(1), 772-785. DOI: 10.15376/biores.11.1.772-785

Hubbe, M. A. (2006). “Bonding between cellulosic fibers in the absence and presence of dry-strength agents – A review,” *BioResources* 1(2), 281-318. DOI: 10.15376/biores.1.2.281-318

Hubbe, M. A. (2014). "Puzzling aspects of the hydrophobic sizing of paper and its inter-fiber bonding ability," *BioResources* 9(4), 5782-5783. DOI: 10.15376/biores.9.4.5782-5783

Hubbe, M. A., Gardner, D. J., and Shen, W. (2015a). "Contact angles and wettability of cellulosic surfaces: A review of proposed mechanisms and test strategies," *BioResources* 10(4), 8657-8749. DOI: 10.15376/biores.10.4.Hubbe_Gardner_Shen

Hubbe, M. A., Rojas, O. J., and Lucia, L. A. (2015b). "Green modification of surface characteristics of cellulosic materials at the molecular or nano scale: A review," *BioResources* 10(3), 6095-6229. DOI: 10.15376/biores.10.3.Hubbe

Hun, D. E., Corsi, R. L., Morandi, M. T., and Siegel, J. A. (2010). "Formaldehyde in residences: Long-term indoor concentrations and influencing factors," *Indoor Air* 20(3), 196-203. DOI: 10.1111/j.1600-0668.2010.00644.x

Hüttermann, A., Mai, C., and Kharazipour, A. (2001). "Modification of lignin for the production of new compounded materials," *Appl. Microbiol. Biot.* 55(4), 387-394. DOI: 10.1007/s002530000590

Hüttermann, A., Majcherczyk, A., Braun-Lüllemann, A., Mai, C., Fastenrath, M., Kharazipour, A., Hüttermann, J., and Hüttermann, A. H. (2000). "Enzymatic activation of lignin leads to an unexpected copolymerization with carbohydrates," *Naturwiss.* 87(12), 539-541. DOI: 10.1007/s001140050774

Hüttermann, A., Milstein, O., Nicklas, B., Trojanowski, J., Haars, A., and Kharazipour, A. (1989). "Enzymatic modification of lignin for technical use – Strategies and results," *ACS Symp. Ser.* 397, 361-370. DOI: 10.1021/bk-1989-0397.ch027

Imam, S. H., Gordon, S. H., Mao, L., and Chen, L. (2001). "Environmentally friendly wood adhesive from a renewable plant polymer: Characteristics and optimization," *Polym. Degrad. Stabil.* 73(3), 529-533. DOI: 10.1016/S0141-3910(01)00114-8

Imanishi, H., Soma, N., Yamashita, O., Miki, T., and Kanamaya, K. (2005). "Effect of production conditions of wood powder on bending properties of wood powder molding material without adhesive," *JSME Int. J., Ser. A* 48(4), 432-436. DOI: 10.1299/jsmea.48.432

Inoue, M., Norimoto, M., Tanahashi, M., and Rowell, R. M. (1993). "Steam or heat fixation of compressed wood," *Wood Fiber Sci.* 25(3), 224-235.

Ito, Y., Tanahashi, M., Shigematsu, M., and Shinoda, Y. (1998a). "Compressive-molding of wood by high-pressure steam-treatment: Part 2. Mechanism of permanent fixation," *Holzforschung* 52(2), 217-221. DOI: 10.1515/hfsg.1998.52.2.217

Ito, Y., Tanahashi, M., Shigematsu, M., Shinoda, T., and Ohta, C. (1998b). "Compressive-molding of wood by high-pressure steam-treatment: Part 1. Development of compressively molded squares from thinnings," *Holzforschung* 52(2), 211-216. DOI: 10.1515/hfsg.1998.52.2.211

Javed, A., Ali, S., Abid W., and Ali, N. (2017). "A review on the potential industrial applications of microbial laccases," *European Journal of Pharmaceutical and Medical Research* 4(4) 238-247.

Jawaid, M., Mohd Sapuan, S., and Alothman, O. Y. (eds.). (2017). *Green Biocomposites – Manufacturing and Properties*, Springer.

Jin, J., Dai, C., Hsu, W. E., and Yu, C. M. (2009). "Properties of strand boards with uniform and conventional vertical density profiles," *Wood Science and Technology* 43(7-8), 559-574. DOI: 10.1007/s00226-009-0248-3

Juliana, A. H., Lee, S. H., Paridah, M. T., Ashaari, Z., and Lum, W. C. (2017). "Development and characterization of wood and non-wood particle based green composites," in: *Green Biocomposites – Manufacturing and Properties*, M. Jawaid,

S. Mohd Sapuan, and O. Y. Alothman (eds.), Springer. DOI: 10.1007/978-3-319-46610-1_8

Jursic, B. S., and Zdravkovski, Z. (1993). "A simple preparation of amides from acids and amines by heating of their mixture," *Synth. Commun.* 23(19), 2761-2770. DOI: 10.1080/00397919308013807

Kamdem, D. P., Pizzi, A., and Jermannaud, A. (2002). "Durability of heat-treated wood," *Holz Roh- Werkstoff* 60(1), 1-6. DOI: 10.1007/s00107-001-0261-1

Kelly, M. W. (1977). "Critical literature review of relationships between processing parameters and physical properties of particleboard," USDA Forest Service General Technical Report FPL (USA).

Kelley, S. S., Rials, T. G., and Glasser, W. G. (1987). "Relaxation behaviour of the amorphous components of wood," *J. Material Sci*. 22(2), 617-624. DOI: 10.1007/BF01160778

Kelley, S. S., Young, R. A., Rammon, R. M., and Gillespie, R. H. (1983). "Bond formation by wood surface reactions: Part III. Parameters affecting the bond strength of solid wood panels," *Forest Prod. J.* 33(2), 21-28.

Kharazipour, A., Bergmann, K., Nonninger, K., and Hüttermann, A. (1998). "Properties of fibre boards obtained by activation of the middle lamella lignin of wood fibres with peroxidase and H_2O_2 before conventional pressing," *J. Adhes. Sci. Technol*. 12(10), 1045-1053. DOI: 10.1163/156856198X00713

Kharazipour, A., and Euring, M. (2010). "Use of mediators in the production of fibreboards," *World Patent* WO 2010020409 A3

Kharazipour, A., and Euring, M. (2013). "Method for producing wood materials and/or composite materials," *World Patent* WO 2013127947 A1

Kharazipour, A., Hüttermann, A., and Lüdemann, H. (1997). "Enzymatic activation of wood fibres as a means for the production of wood composites," *J. Adhes. Sci. Technol*. 11(3), 419-427. DOI: 10.1163/156856197X00796

Kim, J.-Y., Hwang, H., Oh, S., Kim, Y.-S., Kim, U.-J., and Choi, J. W. (2014). "Investigation of structural modification and thermal characteristics of lignin after heat treatment," *Int. J. Biol. Macromol.* 66, 57-65. DOI: 10.1016/j.ijbiomac.2014.02.013

Krzyzanowski, M., Quackenboss, J. J., and Lebowitz, M. D. (1990). "Chronic respiratory effects of indoor formaldehyde exposure," *Environ. Res.* 52(2), 117-125. DOI: 10.1016/S0013-9351(05)80247-6

Kudanga, T., Nyanhongo, G. S., Guebitz, G. M., and Burton, S. (2011). "Potential applications of laccase-mediated coupling and grafting reactions: A review," *Enzyme Microb. Technol.* 48, 195-208. DOI: 10.1016/j.enzmictec.2010.11.007

Kuklewski, K. M., Blankenhorn, P. R., and Rishel, L. E. (2007). "Comparison of selected physical and mechanical properties of red maple (*Acer rubrum* L.) and aspen (*Populus grandidentata* Michx.) flakeboard," *Wood and Fiber Science* 17(1), 11-21.

Kurokochi, Y., and Sato, M. (2015a). "Effect of steam explosion and grinding on binderless board made from rice straw," *Wood Res.* 60(5), 791-799.

Kurokochi, Y., and Sato, M. (2015b). "Effect of surface structure, wax and silica on the properties of binderless board made from rice straw," *Indust. Crops Prod.* 77, 949-953. DOI: 10.1016/j.indcrop.2015.10.007

Kusumah, S. S., Umemura, K., Yoshioka, K., Miyafuji, H., and Kanayama, K. (2016). “Utilization of sweet sorghum bagasse and citric acid for manufacturing of particleboard. I: Effects of pre-drying treatment and citric acid content on the board properties,” *Industrial Crops and Products* 84, 34-42. DOI: 10.1016/j.indcrop.2016.01.042

Kutnar, A., Kamke, F. A., and Sernek, M. (2009). “Density profile and morphology of viscoelastic thermal compressed wood,” *Wood Science and Technology* 43(1-2), 57-68. DOI: 10.1007/s00226-008-0198-1

Kwon, J. H., and Geimer, R. L. (1998). “Impact of steam pressing variables on the dimensional stabilization of flakeboard,” *For. Prod. J.* 48(4), 55-61.

Laemsak, N., and Okuma, M. (2000). “Development of boards made from oil palm frond. II: Properties of binderless boards from steam-exploded fibers of oil palm frond,” *J. Wood Sci.* 46(4), 322-326. DOI: 10.1007/BF00766224

Lamaming, J., Sulaiman, O., Sugimoto, T., Hashim, R., Said, N., and Sato, M. (2013). “Influence of chemical components of oil palm on properties of binderless particleboard,” *BioResources* 8(3), 3358-3371. DOI: 10.15376/biores.8.3.3358-3371

Le, X., An, J. J., Zhang, G. Y., Wang, L., Fan, J. Y., Wang, P., and Xie, Y. M. (2016). “Investigation of the structural characteristics of corn stalk during hot-pressing,” *BioResources* 11(4), 10213-10225. DOI: 10.15376/biores.11.4.10213-10225

Leatham, G. F., and Kirk, T. K. (1982). “Regulation of ligninolytic activity by nutrient nitrogen in white-rot basidiomycetes,” *FEMS Microbiology Letters* 16, 65-67. DOI: 10.1111/j.1574-6968.1983.tb00260.x

Li, D.-L., Wu, J.-Q., Peng, W.-X., Xiao, W.-F., Wu, J.-G., Zhuo, J.-Y., Yuan, T.-Q., and Sun, R.-C. (2015). “Effect of lignin on bamboo biomass self-bonding during hot-pressing: Lignin structure and characterization,” *BioResources* 10(4), 6769-6782. DOI: 10.15376/biores.10.4.6769-6782

Li, J. B., Henriksson, G., and Gellerstedt, G. (2007a). “Lignin depolymerization/ repolymerization and its critical role for delignification of aspen wood by steam explosion,” *Bioresource Technol.* 98(16), 3061-3068. DOI: 10.1016/j.biortech.2006.10.018

Li, X., Tabil, L. G., and Panigrahi, S. (2007b). “Chemical treatments of natural fibre for use in natural fibre-reinforced composites: A review,” *Journal of Polymers and the Environment* 15(1), 25-33. DOI: 10.1007/s10924-006-0042-3

Lin, J. J., Silas, J. A., Bermudez, H., Milam, V. T., Bates, F. S., and Hammer, D. A. (2004). “The effect of polymer chain length and surface density on the adhesiveness of functionalized polymersomes,” *Langmuir* 20(13), 5493-5500. DOI: 10.1021/la036417a

Litthauer, D., van Vuuren, M. J., van Tonder, A., and Wolfaardt, F. W. (2007). “Purification and kinetics of a thermostable laccase from *Pycnoporous sanguineus* (SCC108),” *Enzyme and Microbial Technology* 40, 563-568. DOI: 10.1016/j.enzmictec.2006.05.011

Low, J. C., Halis, R., Shah, U. K. M., Tahir, P., Abood, F., Tukimin, T., Idris, M. D., Lanika, L., and Razali, N. (2015). “Enhancing enzymatic digestibility of alkaline pretreated banana pseudostem for sugar production,” *BioResources* 10(1), 1213-1223. DOI: 10.15376/biores.10.1.1213-1223

Lu, X., and Pizzi, A. (1998). "Curing conditions effects on the characteristics of thermosetting adhesives-bonded wood joints - Part 2: Hot postcuring improvement of UF particleboards and its temperature forecasting model," *Holz Roh Werkst*. 56(5), 393-401. DOI: 10.1007/s001070050339

Lundstedt, T., Seifert, E., Abramo, L., Thelin, B., Nystrom, A., Pettersen, J., and Bergman, R. (1998). "Experimental design and optimization," *Chemometrics Intel. Lab. Sys*. 42, 3-40. DOI: 10.1016/S0169-7439(98)00065-3

Luo, H., Yue, L., Wang, N. W., Zhang, H. Y., and Lu, X. N. (2014). "Manufacture of binderless fiberboard made from bamboo processing residues by steam explosion pretreatment," *Wood Res.* 59(5), 861-869.

Luo, P., and Yang, C. M. (2011). "Binderless particleboard from steam exploded wheat straw," *Applied Materials Research* 179-180, 807-811. DOI: 10.4028/www.scientific.net/amr.179-180.807

Luo, P., and Yang, C. (2012). "Production of binderless particleboard using rice straw pre-treated with liquid hot water," *Applied Mechanics and Materials* 200, 331-334. DOI: 10.4028/www.scientific.net/AMM.200.331

Luzar, A., and Chandler, D. (1996). "Hydrogen-bond kinetics in liquid water," *Nature* 379(6560), 55-57. DOI: 10.1038/379055a0

Maisarah, T., Zuraida, A., Marjan, A. (2015). "The effect of black liquor on rattan waste binderless board (BPB) produced via digestion-hot pressing (DHP) process," *ARPN J. Eng. Appl. Sci.* 10(21), 9753-9758.

Majtnerova, A., and Gellerstedt, G. (2006). "Radical coupling—A major obstacle to delignification in kraft pulping," *Nordic Pulp Paper Res. J.* 21, 129-134. DOI: 10.3183/NPPRJ-2006-21-01-p129-134

Mamman, A. S., Lee, J.-M., Kim, Y.-C., Hwang, I. T., Park, N.-J., Hwang, Y. K., Chang, J.-S., and Hwang, J.-S. (2008). "Furfural: Hemicellulose/xylose-derived biochemical," *Biofuels Bioprod. Bioref – BioFPR* 2(5), 438-454. DOI: 10.1002/bbb.95

Mancera, C., El Mansouri, N.-E., Ferrando, F., and Salvado, J. (2011a). "The suitability of steam exploded *Vitis vinifera* and alkaline lignin for the manufacture of fiberboard," *BioResources* 6(4), 4439-4453. DOI: 10.15376/biores.6.4.4439-4453

Mancera, C., El Mansouri, N.-E., Pelach, M. A., Francesc, F., and Salvadó, J. (2012). "Feasibility of incorporating treated lignins in fiberboards made from agricultural waste," *Waste Management* 32(10), 1962-1967. DOI: 10.1016/j.wasman.2012.05.019

Mancera, C., El Mansouri, N.-E., Vilaseca, F., Ferrando, F., and Salvado, J. (2011b). "The effect of lignin as a natural adhesive on the physico-mechanical properties of vitis vinifera fiberboards," *BioResources* 6(3), 2851-2860. DOI: 10.15376/biores.6.3.2851-2860

Mancera, C., Ferrando, F., and Salvadó, J. (2008). "*Cynara cardunculus* as raw material for the production of binderless fiberboards: Optimization of pretreatment and pressing conditions," *J. Wood Chem. Technol.* 28(3), 207-226. DOI: 10.1080/02773810802347024

Mansouri, M., Leban, J.-M., and Pizzi, A. (2010). "High density panels by wood veneers welding without any adhesives," *J. Adhesion Sci. Technol.* 24(8), 1529-1534. DOI: 10.1163/016942410X501061

Marashdeh, M. W., Hashim, R., Tajuddin, A. A., Bauk, S., and Sulaiman, O. (2011). "Effect of particle size on the characterization of binderless particleboard made from *Rhizophora* spp. mangrove wood for use as phantom material," *BioResources* 6(4), 4028-4044. DOI: 10.15376/biores.6.4.4028-4044

Marra, A. A. (1992). *Technology of Wood Bonding. Principles in Practice*, Van Nostrand Reinhold, New York.

Martinez, A. T., Speranza, M., Ruiz-Duenas, F. J., Ferreira, P., Camarero, S., Guillen, F., Martinez, M. J., Gutierrez, A., and del Rio, J. C. (2005). "Biodegradation of lignocellulosics: Microbial chemical, and enzymatic aspects of the fungal attack of lignin," *Intl. Microbiol.* 8(3), 195-204.

Massey, F. P., Ennos, A. R., and Hartley, S. E. (2006). "Silica in grasses as a defence against insect herbivores: Contrasting effects on folivores and a phloem feeder," *J. Animal Ecol.* 75(2), 595-603. DOI: 10.1111/j.1365-2656.2006.01082.x

Mason, W. H. (1926a). US 1578609. "Process and apparatus for disintegration of wood and the like."

Mason, W. H. (1926b). US 1586159. "Low-temperature explosion process of disintegrating wood and the like."

Mason, W. H. (1928). US 1663504. "Press-dried structural insulating board and process of making same."

Mason, W. H., Boehm, R. M., and Euclid, K. W. (1937). US 2080078. "Molding composition and process of making same."

McKenzie, A. W. (1984). "The structure and properties of paper. Part XXI: The diffusion theory of adhesion applied to interfiber bonding," *Appita* 37(7), 580-583.

Mejía, E. H., Quintana, G. C., and Ogunsile, B. O. (2014). "Development of binderless fiberboards from steam exploded and oxidized oil palm wastes," *BioResources* 9(2), 2922-2936. DOI: 10.15376/biores.9.2.2922-2936

Migneault, S., Koubaa, A., Riedl, B., Nadji, H., Deng, J., and Zhang, S. Y. (2011). "Binderless fiberboard made from primary and secondary pulp and paper sludge," *Wood Fiber Sci.* 43(2), 180-193.

Miki, T., Takeuchi, K., Sugimoto, H., and Kanayama, K. (2007a). "Performance study of compact wood powder material processing for improved impact characteristics aiming at substitute for plastics," *J. Mater. Proc. Technol.* 192-193, 422-427. DOI: 10.1016/j.jmatprotec.2007.04.078

Miki, T., Sugimoto, H., and Kanayama, K. (2007b). "Thermoplastic behavior of wood powder compacted materials," *J. Mater. Sci*. 42(18), 7913-7919. DOI: 10.1007/s10853-007-1723-6

Miki, T., Takeuchi, K., Sugimoto, H., and Kanayama, K. (2008). "Material development from wood powder without adhesive by vapor steaming compaction process," *J. Mater. Process. Technol*. 199(1–3), 396-401. DOI: 10.1016/j.jmatprotec.2007.08.010

Mittal, K. L. (2013). *Advances in Contact Angle, Wettability and Adhesion*, Wiley, New York. DOI: 10.1002/9781118795620

Mobarak, F., Fahmy, Y., and Augustin, H. (1982). "Binderless lignocellulose composite from bagasse and mechanism of self-bonding," *Holzforschung* 36, 131-135. DOI: 10.1515/hfsg.1982.36.3.131

Mohamed, R., Lim, M. T., and Halis, R. (2013). "Biodegrading ability and enzymatic activities of some white rot fungi on kenaf (*Hibiscus cannabinus*)," *Sains Malaysiana* 42(10), 1365-1370.

Müller, C., Euring, M., and Kharazipour, A. (2009a). "Enzymatic modification of wood fibres for activating their ability of self bonding," *Int. J. Mater. Prod. Tec*. 36(1), 189-199. DOI: 10.1504/IJMPT.2009.027830

Müller, C., Kües, U., Schöpper, C., and Kharazipour, A. (2007). "Natural binders," in: *Wood Production, Wood Technology, and Biotechnological Impacts*, U. Kües (ed.), Univ. Göttingen, Ch. 16, pp. 347-381.

Müller, G., Schöpper, C., Vos, H., Kharazipour, A., and Polle, A. (2009b). "FTIR-ATR spectroscopic analyses of changes in wood properties during particle- and fiberboard production of hard- and softwood trees," *BioResources* 4(1), 49-71. DOI: 10.15376/biores.4.1.49-71

Nadhari, W. N. A. W., Hashim, R., Sulaiman, O., Sato, M., Sugimoto, T., and Selamat, M. E. (2013). "Utilization of oil palm trunk waste for manufacturing of binderless particleboard: Optimization study," *BioResources* 8(2), 1675-1696. DOI: 10.15376/biores.8.2.1675-1696

Nasir, M. (2013). "Fabrication and characterization of medium density fiber board prepared from enzyme treated fiber and lignin based bio adhesive," PhD. Dissertation, Univ. Malaysia Pahang.

Nasir, M., Gupta, A., Beg, M. D. H., Chua, G. K., Jawaid, M., Kumar, A., and Khan, T. A. (2013). "Fabricating eco-friendly binderless fiberboard from laccase-treated rubber wood fiber," *BioResources* 8(3), 3599-3608. DOI: 10.15376/biores.8.3.3599-3608

Navarrete, P., Mansouri, H. R., Pizzi, A., Tapin-Lingua, S., Benjelloun-Mlayah, B., Pasch, H., and Rigolet, S. (2010). "Wood panel adhesives from low molecular mass lignin and tannin without synthetic resins," *J. Adhes. Sci. Technol.* 24(8), 1597-1610. DOI: 10.1163/016942410X500972

Navarrete, P., Pizzi, A., Pasch, H., and Delmotte, L. (2012). "Study on lignin-glyoxal reaction by MALDI-TOF and CP-MAS ^{13}C NMR," *J. Adh. Sci.Technol.* 26, 1069-1082.

Navarrete, P., Pizzi, A., Rode, K., Vignali, M., and Pasch, H. (2013). "MALDI-TOF study of oligomers distribution for stability-durable spray-dried glyoxalated lignin for wood adhesives," *J. Adh. Sci. Technol*. 27(5-6), 586-597. DOI: 10.1080/01694243.2012.690618

Navi, P., and Pizzi, A. (2015). "Properties changes in Thermo-Hydro-Mechanical processing," *Holzforschung* 69(7), 863-873. DOI: 10.1515/hf-2014-0198

Nenonene, A. Y., Koba, K., Rigal, L., and Sanda, K. (2014). "Development of kenaf particleboards agglomerated with products of some tannin plant's organs from Togo," *Sciences de la Vie, de la Terre et Agronomie* 2(1), [NENONENE].

Nikvash, N., Kharazipour, A., and Euring, M. (2012). "Effects of wheat protein as a biological binder in the manufacture of particleboards using a mixture of canola, hemp, bagasse, and commercial wood," *For. Prod. J.* 62(1), 49-57; 62(6), 418. DOI: 10.13073/FPJ-D-11-00102.1

Nilsson, H., Galland, S., Larsson, P. T., Gamstedt, E. K., Nishino, T., Berglund, L. A., and Iversen, T. (2010). "A non-solvent approach for high-stiffness all-cellulose biocomposites based on pure wood cellulose," *Compos. Sci. Technol.* 70(12), 1704-1712. DOI: 10.1016/j.compscitech.2010.06.016

Nimz, H. H (1983). "Lignin-based wood adhesives," in: *Wood Adhesives Chemistry and Technology*, A. Pizzi (ed.), Marcel Dekker, New York, Vol. 1, Ch. 5.

Nimz, H. H., and Hitze, G. (1980). "The application of spent sulfite liquor as an adhesive for particleboards," *Cell. Chem. Technol*. 14, 371-375.

Norhaslida, R., Halis, R., Lakarim, L., Danial, M. I., Low, J. C., and Naimah, M. S. (2014). "Chemical alteration of banana pseudostems by white rot fungi," *Biomass and Bioenergy* 61, 206-210. DOI: 10.1016/j.biombioe.2013.12.015

Nyanhongo, G. S., Kudanga, T., Prasetyo, E. N., and Guebitz, G. M. (2010). "Mechanistic insights into laccase mediated functionalisation of lignocellulose material," *Biotechnol. Genet. Eng.* 27, 305-329. DOI: 10.1080/02648725.2010.10648155

Okuda, N., Hori, K., and Sato, M. (2006a). "Chemical changes of kenaf core binderless boards during hot pressing (I): Influence of the pressing temperature condition," *J. Wood Sci.* 52(3), 244-248. DOI: 10.1007/s10086-005-0761-4

Okuda, N., Hori, K., and Sato, M. (2006b). "Chemical changes of kenaf core binderless boards during hot pressing (II): Effects on the binderless board properties," *J. Wood Sci*. 52(3), 249-254. DOI: 10.1007/s10086-005-0744-5

Okuda, N., and Sato, M. (2004). "Manufacture and mechanical properties of binderless boards from kenaf core," *J. Wood Sci*. 50(1), 53-61. DOI:10.1007/s10086-003-0528-8

Okuda, N., and Sato, M. (2006). "Water resistance properties of kenaf core binderless boards," *J. Wood Sci*. 52(5), 422-428. DOI: 10.1007/s10086-005-0785-9

Okuda, N., and Sato, M. (2007). "Finely milled kenaf core as a natural plywood binder," *Holzforschung* 61(4), 439-444. DOI: 10.1515/HF.2007.076

Owens, D. K., and Wendt, R. C. (1969). "Estimation of the surface free energy of polymers," *J. Appl. Polym. Sci.* 13, 1741-1747. DOI: 10.1002/app.1969.070130815

Pandey, K. K., and Pitman, A. J. (2003). "FTIR studies of the changes in wood chemistry following decay by brown-rot and white-rot fungi," *International Biodeterioration and Biodegradation* 52(3), 151-160. DOI: 10.1016/S0964-8305(03)00052-0

Park, S., Baker, J. O., Himmel, M. E., Parilla, P. A., and Johnson, D. K. (2010). "Cellulose crystallinity index: Measurement techniques and their impact on interpreting cellulase performance," *Biotech. Biofuels* 3(10), article no. 10. DOI: 10.1186/1754-6834-3-10

Pelaez-Samaniego, M. R., Yadama, V., Garcia-Perez, T., Lowell, E., and Amidon, T. (2014a). "Effect of hot water extracted hardwood and softwood chips on particleboard properties," *Holzforschung* 68(7), 807-815. DOI: 10.1515/hf-2013-0150

Pelaez-Samaniego, M. R., Yadama, V., Garcia-Perez, T., Lowell, E., and McDonald, A. (2014b). "Effect of temperature during wood torrefaction on the formation of lignin liquid intermediates," *J. Anal. Appl. Pyrol.* 109, 222-233. DOI: 10.1016/j.jaap.2014.06.008

Pelaez-Samaniego, M. R., Yadama, V., Lowell, E., and Espinoza-Herrera, R. (2013). "A review of wood thermal pretreatments to improve wood composite properties," *Wood Sci. Technol.* 47(6), 1285-1319. DOI: 10.1007/s00226-013-0574-3

Pichelin, F. (1999). *Manufacture of Oriented Strand Board with High Moisture Tolerant Adhesives*, Ph.D. thesis, University of Hamburg, Hamburg, Germany

Pichelin, F., Pizzi, A., and Frühwald, A. (2001). "Exterior OSB preparation technology at high moisture content. Part 1: Transfer mechanisms and pressing parameters," *European Journal of Wood and Wood Products* 59(4), 256-265. DOI: 10.1007/s001070100219

Pichelin, F., Pizzi, A., and Frühwald, A. (2002). "Exterior OSB preparation technology at high moisture content – Part 2: Stress relaxation, pressing technology, board properties," *Holz Roh Werkstoff* 60(1), 9-17. DOI: 10.1007/s00107-001-0270-0

Pintiaux, T., Viet, D., Vandenbossche, V., Rigal, L., and Rouilly, A. (2013). "High Pressure Compression-molding of alpha-cellulose and effects of operating conditions," *Mater.* 6(6), 2240-2261. DOI: 10.3390/ma6062240

Pintiaux, T., Viet, D., Vandenbossche, V., Rigal, L., and Rouilly, A. (2015). "Binderless materials obtained by thermo-compressive processing of lignocellulosic fibers: A comprehensive review," *BioResources* 10(1), 1915-1963.

Pizzi, A. (1978). "Wattle-based adhesives for exterior grade particleboard," *Forest Prod. J.* 28(12), 42- 45.

Pizzi, A. (1983). *Wood Adhesives Chemistry and Technology*, Vol. 1, Marcel Dekker, New York.

Pizzi, A. (1994). *Advanced Wood Adhesives Technology*, Marcel Dekker, New York.

Pizzi, A. (2006). "Recent developments in eco-efficient bio-based adhesives for wood bonding: Opportunities and issues," *J. Adhes. Sci. Technol.* 20(8), 829-846. DOI: 10.1163/156856106777638635

Pizzi, A. (2013). "Bioadhesives for wood and fibres," *Reviews of Adhesion and Adhesives* 1, 88-113(26).

Pizzi, A. (2014). "Natural adhesives, binders, and matrices for wood and fiber composites: Chemistry and technology," in: *Research Developments in Wood Engineering and Technology*, A. Aguilera and J. P. Davim (eds.), IGI Global, Ch. 4, pp. 131-181. DOI: 10.4018/978-1-4666-4554-7.ch004

Pizzi, A. (2016). *Wood and Fiber Panels Technology*, in: *Lignocellulosic Fibers and Wood Handbook: Renewable Materials for To-day's Environment,* M. N. Belgacem and A. Pizzi (eds.), Scrivener-Wiley, New York, April 2016, Chapter 15, pp. 385-406.

Pizzi, A., Garcia, R., and Deglise, X. (1998). "Thermomechanical analysis of entanglement networks - Correlation of some calculated and experimental parameters," *J. Appl. Polymer Sci.* 67(9), 1673-1678. DOI: 10.1002/(SICI)1097-4628(19980228)67:9<1673::AID-APP19>3.0.CO;2-V

Pizzi, A., Meikleham, N., Dombo, B., and Roll, W. (1995). "Autocondensation-based, zero-emission, tannin adhesives for particleboard," *Holz Roh Werkstoff* 53, 201-204. DOI: 10.1007/BF02716424

Pizzi, A., Mtsweni, B., and Parsons, W. (1994). "Wood-induced catalytic activation of PF adhesives autopolymerization *vs*. PF/wood covalent bonding," *J. Appl. Polymer Sci.* 52, 1847-1856. DOI: 10.1002/app.1994.070521302

Pizzi, A., and Owens, N. A. (1995). "Interface covalent bonding *vs.* wood-induced catalytic autocondensation of diisocyanate wood adhesives," *Holzforschung* 49, 269-272.

Pizzi, A., and Scharfetter, H. (1978). "The chemistry and development of tannin-based wood adhesives for exterior plywood," *J. Appl. Polymer Sci*. 22, 1745-1761. DOI: 10.1002/app.1978.070220623

Plath, L., and Schnitzier, E. (1974). "The density profile, a criterion for evaluating particleboard," *Holz Roh- Werkst.* 32(11), 443-449. DOI: 10.1007/BF02612838

Pönni, R., Vuorinen, T., and Kontturi, E. (2012). "Proposed nano-scale coalescence of cellulose in chemical pulp fibers during technical treatments," *BioResources* 7(4), 6077-6108. DOI: 10.15376/biores.7.4.6077-6108

Popoff, T., and Theander, O. (1972). "Formation of aromatic compounds from carbohydrates: Part 1. Reaction of D-glucuronic acid, D-glacturonic acid, D-xylose, and L-arabinose in slightly acidic, aqueous solutions," *Carbohydr. Res*. 22, 139-146. DOI: 10.1016/S0008-6215(00)85733-X

Quintana, G., Velásquez, J., Betancourt, S., and Gañán, P. (2009). "Binderless fiberboard from steam exploded banana bunch," *Indust. Crops Prod.* 29(1), 60-66. DOI: 10.1016/j.indcrop.2008.04.007

Ralph, J., Lundquist, K., Brunow, G., Lu, F., Kim, H., Schatz, P. F., Marita, J. M., Hatfield, R. D., Ralph, S. A., Christensen, J. H., and Boerjan, W. (2004). "Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl-propanoids," *Phytochem. Rev*. 3, 29-60. DOI: 10.1023/B:PHYT.0000047809.65444.a4

Rammon, R. M., Kelley, S. S., Young, R. A., and Gillespie, R. H. (1982). "Bond formation by wood surface-reactions. 2. Chemical mechanisms of nitric-acid activation," *J. Adhes.* 14(3-4), 257-282. DOI: 10.1080/00218468208073207

Ridgway, C. J., and Gane, P. A. C. (2012). "Constructing NFC-pigment composite surface treatment for enhanced paper stiffness and surface properties," *Cellulose* 19(2), 547-560. DOI: 10.1007/s10570-011-9634-8

Roffael, E., Schneider, T., Dix, B., and Buchholz, T. (2005). "On paraffin sizing of medium density fiberboards (MDF). Part 1: Influence of the chemical composition of paraffin and type of emulsifier on the hydrophobic properties of MDF," *Holz Roh-Werkst.* 63(3), 192-203. DOI: 10.1007/s00107-004-0556-0

Rowell, R. M., and McSweeny, J. D. (2008). "Heat treatments of wood fibers for self-bonding and stabilized fiberboards," *Molec. Cryst. Liq. Cryst.* 483, 307-325. DOI: 10.1080/15421400801918179

Runkel, R., and Jost, J. (1956). GB Patent 743401. "Method for the production of articles by moulding substances of vegetable origin under pressure and at elevated temperatures."

Saadaoui, N., Rouilly, A., Fares, K., and Rigal, L. (2013). "Characterization of date palm lignocellulosic by-products and self-bonded composite materials obtained thereof," *Mater. Des*. 50, 302-308. DOI: 10.1016/j.matdes.2013.03.011

Saari, N., Hashim, R., Sulaiman, O., Hiziroglu, S., Sato, M., and Sugimoto, T. (2014). "Properties of steam treated binderless particleboard made from oil palm trunks," *Composites Part B* 56, 344-349. DOI: 10.1016/j.compositesb.2013.08.062

Saito, Y., Ishii, M., and Sato, M. (2013). "The suitable harvesting season and the part of moso bamboo (*Phyllostachys pubescens*) for producing binderless boards," *Wood Sci. Technol*. 47(5), 1071-1081. DOI: 10.1007/s00226-013-0560-9

Salim, N., Hashim, R., Sulaiman, O., Nordin, N. A., Ibrahim, M., Akil, H. M., Sato, M., Sugimoto, T., and Hiziroglu, S. (2013). "Effect of steaming on some properties of compressed oil palm trunk lumber," *BioResources* 8(2), 2310-2324. DOI: 10.15376/biores.8.2.2310-2324

Saliman, M. A. R., Ashaari, Z., Bakar, E. S., Lee, S. H., Tahir, P. M., Halip. J., and Leemon, N. F. (2017). "Hydrothermal treatment of oil palm wood: Effect of treatment variables on dimensional stability using response surface methodology," *Journal of Oil Palm Research* 29(1), 130-135. DOI: 10.21894/jopr.2017.2901.14

Salvadó, J., Velasquez, J. A., and Ferrando, F. (2003). "Binderless fiberboard from steam exploded *Miscanthus sinensis*: Optimization of pressing and pretreatment conditions," *Wood Sci. Technol.* 37(3-4), 279-286. DOI: 10.1007/s00226-003-0186-4

Sandermann, W., and Augustin, H. (1963a). "Chemische Untersuchungen über die thermische Zersetzung von Holz. Erste Mitteilung: Stand der Forschung," *Holz Roh-Werkst.* 21, 256-265. DOI: 10.1007/BF02616316

Sandermann, W., and Augustin, H. (1963b). "Chemische Untersuchungen über die thermische Zersetzung von Holz. Zweite Mitteilung: Untersuchungen mit Hilfe der Differential-Thermo-Analyse," *Holz Roh-Werkst*. 21, 305-315. DOI: 10.1007/BF02610964

Santiago-Medina, F. J., Foyer, G., Pizzi, A., Caillol, S., and Delmotte, L. (2016). "Lignin-derived non-toxic aldehydes for ecofriendly tannin adhesives for wood panels," *Int. J. Adhesion Adhesives* 70, 239-248. DOI: 10.1016/j.ijadhadh.2016.07.002

Santiago-Medina, F. J., Pizzi, A., and Abdalla, S. (2017a). "Hydroxymethylfurfural hardening of pine tannin wood adhesives," *J. Renew. Mat*., accepted and in press. DOI: 10.7569/JRM.2017.634166

Santiago-Medina, F.-J., Pizzi, A., Basso, M. C., Delmotte, L., and Abdalla, S. (2017b) "Polycondensation resins by reaction of lignin with (poly)amines," *J. Renew. Mat.* DOI: 10.7569/JRM.2017.634142

Sedano-Mendoza, M., Navarrete, P., and Pizzi, A. (2010). "Effect of layers relative moisture content on the IB strength of pine tannin bonded particleboard," *Eur. J. Wood Prod*. 68, 355-357. DOI: 10.1007/s00107-010-0452-8

Sekino, N., Inoue, M., Irle, M., and Adcock, T. (1999). "The mechanisms behind the improved dimensional stability of particleboards made from steam-pretreated particles," *Holzforschung* 53(4), 435-440. DOI: 10.1515/HF.1999.072

Serapiglia, M. J., Cameron, K. D., Stipanovic, A. J., and Smart, L. B. (2008). "High-resolution thermogravimetric analysis for rapid characterization of biomass composition and selection of shrub willow varieties," *Appl. Biochem. Biotech.* 145, 3-11. DOI: 10.1007/s12010-007-8061-7

Shang, N., Ye, X., Huang, L., and Jin, Z. (2012). "Lignin characteristics of steam exploded bamboo residue during hot pressing," *J. Zhejiang A&F Univ.* 2012-3.

Sheldon, R. A. (2014). "Green and sustainable manufacture of chemicals from biomass: State of the art," *Green Chem.* 16(3), 950-963. DOI: 10.1039/c3gc41935e

Shen, K. C. (1986). "Process for manufacturing composite products from lignocellulosic materials," WO Patent 4627951.

Stamm, B., Natterer, J., Windeisen, E., and Wegener, G. (2005). "Thermal behavior of polysaccharides in wood during friction welding," *Holz Roh Werkst.* 63(5), 388-389. DOI: 10.1007/s00107-005-0002-y

Stokke, D. D., Wu, Q. L., and Han, G. P. (2013). *Introduction to Wood and Natural Fiber Composites*, Wiley, New York. DOI: 10.1002/9780470711804

Sun, Y.-C., Lin, Z., Peng, W.-X., Yuan, T.-Q., Xu, F., Wu, Y.-Q., Yang, J., Wang, Y.-S., and Sun, R.-C. (2014). "Chemical changes of raw materials and manufactured binderless boards during hot pressing: Lignin isolation and characterization," *BioResources* 9(1), 1055-1071. DOI: 10.15376/biores.9.1.1055-1071

Suzuki, S., Shintani, H., Park, S. Y., Saito, K., Laemsak, N., Okuma, M., and Iiyama, K. (1998). "Preparation of binderless boards from steam exploded pulps of oil palm (*Elaeis guineensis* Jaxq.) fronds and structural characteristics of lignin and wall polysaccharides in steam exploded pulps to be discussed for self-bindings," *Holzforschung* 52(4), 417-426. DOI: 10.1515/hfsg.1998.52.4.417

Tahir, P. Md., and Sellers, T. Jr. (1990). 19th IUFRO World Congress, Montreal, Canada, August 1990.

Tajuddin, M., Ahmad, Z., and Ismail, H. (2016). "A review of natural fibers and processing operations for the production of binderless boards," *BioResources* 11(2), 5600-5617. DOI: 10.15376/biores.11.2.

Takahashi, I., Sugimoto, T., Takasu, Y., Yamasaki, M., Sasaki, Y., and Kikata, Y. (2010). "Preparation of thermoplastic molding from steamed Japanese beech flour," *Holzforschung* 64(2), 229-234. DOI: 10.1515/hf.2010.035

Takahashi, I., Takasu, Y., Sugimoto, T., Kikata, Y., and Sasaki, Y. (2009). "Thermoplastic flow behavior of steamed wood flour under heat and compression," *Wood Sci. Technol*. 44(4), 607-619. DOI: 10.1007/s00226-009-0297-7

Tanahashi, M. (1990). "Characterization and degradation mechanisms of wood components by steam explosion and utilization of exploded wood," *Wood Res*. 77, 49-117.

Taniguchi, M., Suzuki, H., Watanabe, D., Sakai, K., Hoshino, K., and Tanaka, K. (2005). "Evaluation of pretreatment of *Pluerotus ostreatus* for enzymatic hydrolysis of rice straw," *Journal of Bioscience and Bioengineering* 100(6), 637-643. DOI: 10.1263/jbb.100.637

Thebault, M., Pizzi, A., and Fredon, E. (2013). "Synthesis of resins with ozonized sunflower oil and radiata pine tannins," *J. Renewable. Mat*. 1(4), 242-252. DOI: 10.7569/JRM.2013.634121

Tischer, F. V. (1939). "Method of drying veneers," US Patent 2,177,160.

Tjeerdsma, B. F., Boonstra, M., Pizzi, A., Tekely, P., and Militz, H. (1998). "Characterisation of thermally modified wood: Molecular reasons for wood performance improvement," *Holz Roh Werkst.* 56(3), 149-153. DOI: 10.1007/s001070050287

Tjeerdsma, B. F., and Militz, H. (2005). "Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat treated wood," *Holz als Roh- und Werkstoff* 63(2), 102-111. DOI: 10.1007 -2Fs00107-004-0532-8

Tomkinson, J. (2002). "Adhesives based on natural resources," in: *Wood Adhesion and Wood Products*, M. Dunky, A. Pizzi, and M. Van Leemput (eds.), Cooperation in Scientific and Technical Research, COST Action E13 (Project, and European Commission, Directorate General for Research, State-ot-the-Art Report: COST Action E13 Wood Adhesion and Glued Products. Vol. 1, Working Group 1, Brussels, pp 46-65

Tshabalala, M. A., McSweeny, J. D., and Rowell, R. M. (2012). "Heat treatment of wet wood fiber: A study of the effect of reaction conditions on the formation of furfurals," *Wood Mat. Sci. Eng.* 7(4), 202-208. DOI: 10.1080/17480272.2012.669406

Umemura, K., Sugihara, O., and Kawai, S. (2013). "Investigation of a new natural adhesive composed of citric acid and sucrose for particleboard," *Journal of Wood Science* 59(3), 203-208. DOI: 10.1007/s10086-013-1326-6

Valenzuela, J., Von Leyser, E., Pizzi, A., Westermeyer, C., and Gorrini, B. (2012). "Industrial production of pine tannin-bonded particleboard and MDF," *Eur. J. Wood & Wood Prod.* 70(5), 735-740 (2012). DOI: 10.1007/s00107-012-0610-2

Van Dam, J. E. G., van den Oever, M. J. A., Teunissen, W., Keijsers, E. R. P., and Peralta, A. G. (2004b). "Process for production of high density/high performance binderless boards from whole coconut husk: Part 1: Lignin as intrinsic thermosetting binder resin," *Ind. Crop. Prod.* 19(3), 207-216. DOI: 10.1016/j.indcrop.2003.10.003

van Dam, J. E. G., van der Oever, M. J. A., and Keijsers, E. R. P. (2004a). "Production process from high density high performance binderless boards from whole coconut husk," *Industrial Crops and Products* 20(1), 97-101. DOI: 10.1016/j.indcrop.2003.12.017

Vanholme, R., Demedts, B., Morreel, K., Ralph, J., and Boerjan, W. (2010). "Lignin biosynthesis and structure," *Plant Physiol.* 153(3), 895-905. DOI: 10.1104/pp.110.155119

Van Niekerk, J., and Pizzi, A. (1994). "Characteristic industrial technology for exterior *Eucalyptus* particleboard," *Holz Roh Werkstoff* 52, 109-112. DOI: 10.1007/BF02615475

Velasquez, J. A., Ferrando, F., and Salvadó, J. (2002). "Binderless fiberboard from steam exploded *Miscanthus sinensis*: The effect of a grinding process," *Holz als Roh- und Werkstoff* 60(4), 297-302. DOI: 10.1007/s00107-002-0204-2

Velasquez, J. A., Ferrando, F., and Salvadó, J. (2003a). "Effects of kraft lignin addition in the production of binderless fiberboard from steam exploded *Miscanthus sinensis*," *Indust. Crops Prod.* 18(1), 17-23. DOI: 10.1016/S0926-6690(03)00016-5

Velasquez, J. A., Ferrando, F., Farriol, X., and Salvado, J. (2003b). "Binderless fiberboard from steam exploded *Miscanthus sinensis*," *Wood Sci. Technol.* 37(3-4), 269-278. DOI: 10.1007/s00226-003-0182-8

Velasquez, J. A., Ferrando, F., and Salvado, J. (2003c). "Binderless fibreboard from steam exploded *Miscanthus sinensis*: Optimization of pressing and pre-treatment conditions," *Wood Science Technology* 37(3), 279-286. DOI: 10.1007/s00226-003-0186-4

Vital, B. R., Lehmann, W. F., and Boone, R. S. (1974). "How species and board densities affect properties of exotic hardwood particleboards," *Forest Products Journal* 24(12), 37-45.

Wandler, S. L., and Frazier, C. E. (1996). "The effects of cure temperature and time on the isocyanate-wood adhesive bondline by 15N CP/MAS NMR," *Int. J. Adhesion Adhesives* 16(3), 179-186. DOI: 10.1016/0143-7496(95)00044-5

Wang, H. M., Postle, R., Kessler, R. W., and Kessler, W. (2003). "Removing pectin and lignin during chemical processing of hemp for textile applications," *Textile Research Journal* 73(8) 664-669. DOI: 10.1177/004051750307300802

Weigl, M., Wimmer, R., Ters, T., Mitter, R., and Kuncinger, T. (2012a). "Within-process and seasonal changes during industrial production of high-density fibreboard. Part 1: Influence of wood species composition on polyoses in the products," *Holzforschung* 66(5), 667-672. DOI: 10.1515/hf-2012-0031

Weigl, M., Maschl, G., Wimmer, R., and Mitter, R. (2012b). "Within-process and seasonal changes during industrial production of high-density fibreboard. Part 2: PLS modelling of chemical alterations, refining conditions and panel thickness swell," *Holzforschung* 66(5), 673-678. DOI: 10.1515/hf-2012-0033

Wellons, J. D., and Krahmer, R. L. (1973). "Self bonding in bark composites," *Wood Sci*. 6(2), 112-122.

Widsten, P. (2002). "Oxidative activation of wood fibers for the manufacture of medium-density fiberboard (MDF)," Helsinki University of Technology, Helsinki

Widsten, P., and Kandelbauer, A. (2008a). "Adhesion improvement of lignocellulosic products by enzymatic pretreatment," *Biotechnol. Adv*. 26(4), 379-386. DOI: 10.1016/j.biotechadv.2008.04.003

Widsten, P., and Kandelbauer, A. (2008b). "Laccase applications in the forest products industry: A review," *Enzyme Microb. Technol*. 42, 293-307. DOI: 10.1016/j.enzmictec.2007.12.003

Widsten, P., and Kandelbauer, A. (2014). "Industrial scale evaluation of cationic tannin as a binder for hardboard," *J. Adhes. Sci. Technol*. 28(13), 1256-1263. DOI: 10.1080/01694243.2014.896068

Widsten, P., Hummer, A., Heathcote, C., and Kandelbauer, A. (2009). "A preliminary study of green production of fiberboard bonded with tannin and laccase in a wet process," *Holzforschung* 63(5), 545-550. DOI: 10.1515/HF.2009.090

Widsten, P., and Laine, J. E. (2004). "Manufacture of resin-free fiberboards from wood fibers activated with Fenton's reagent (H_2O_2/Fe^{2+})," in: *Silanes and Other Coupling Agents*, K. L. Mittal (ed.), Vol. 3, pp. 241-256.

Widsten, P., Qvintus-Leino, L. P., Tuominen, S., and Laine, J. E. (2003). "Manufacture of fiberboard from wood fibers activated with Fenton's reagent ($H_2O_2/FeSO_4$)," *Holzforschung* 57(4), 447-452. DOI: 10.1515/HF.2003.066

Widyorini, R., Higashihara, T., Xu, J. Y., Watanabe, T., and Kawai, S. (2005a). "Self-bonding characteristics of binderless kenaf core composites," *Wood Sci. Technol.* 39(8), 651-662. DOI: 10.1007/s00226-005-0030-0

Widyorini, R., and Satiti, D. A. (2011). "Characteristics of binderless particleboards made from heat-treated wood species," The 3rd Intl. Symp. Indonesian Wood Res. Soc., pp. 125-129.

Widyorini, R., Umemura, K., Isnan, R., Putra, D. R., Awaludin, A., and Prayitno, T. A. (2016). "Manufacture and properties of citric acid-bonded particleboard made from bamboo materials," *Eur. J. Wood Wood Prods.* 74(1), 57-65. DOI: 10.1007/s00107-015-0967-0

Widyorini, R., Xu, J. Y., Umemura, K., and Kawai, S. (2005b). "Manufacture and properties of binderless particleboard from bagasse. I: Effects of raw material type, storage methods, and manufacturing process," *J. Wood Sci.* 51(6), 648-654. DOI: 10.1007/s10086-005-0713-z

Widyorini, R., Xu, J. Y., Watanabe, T., and Kawai, S. (2005c). "Chemical changes in steam-pressed kenaf core binderless particleboard," *J. Wood Sci.* 51(1), 26-32. DOI: 10.1007/s10086-003-0608-9

Wilczyński, A., and Kociszewski, M. (2012). "Elastic properties of the layers of three-layer particleboards," *European Journal of Wood and Wood Products* 70(1-3), 357-359. DOI: 10.1007/s00107-010-0497-8

Willett, J. L., and Wool, R. P. (1993). "Strength of incompatible amorphous polymer interfaces," *Macromol.* 26(20), 5336-5349. DOI: 10.1021/ma00072a010

Wolkoff, P., and Nielsen, G. D. (2010). "Non-cancer effects of formaldehyde and relevance for setting an indoor air guideline," *Environ. Intl.* 36(7), 788-799. DOI: 10.1016/j.envint.2010.05.012

Wong, E. D., Zhang, M., Wang, Q., and Kawai, S. (1999). "Formation of the density profile and its effects on the properties of particleboard," *Wood Science and Technology* 33(4), 327-340. DOI: 10.1007/s002260050119

Xu, J. Y., Sugawara, R., Widyorini, R., Han, G., and Kawai, S. (2004). "Manufacture and properties of low-density binderless particleboard from kenaf core," *J. Wood Sci.* 50(1), 62-67. DOI: 10.1007/s10086-003-0522-1

Xu, J., Widyorini, R., Yamauchi, H., and Kawai, S. (2006). "Development of binderless fiberboard from kenaf core," *J. Wood Sci.* 52(3), 236-243. DOI: 10.1007/s10086-005-0770-3

Xu, J. Y., Han, G. P., Wong, E. D., and Kawai, S. (2001). "Development of binderless particleboard from kenaf core using steam-injection pressing," *J. Wood Sci.* 49(4), 327-332. DOI: 10.1007/s10086-002-0485-7

Xu, J.-Y., Qi, N., Liao, R., and Zhong, Z. (2012). "Study on the bonding characteristics and mechanism of plant-based powder," 2012 Intl. Conf. Biobase Material Sci. Eng. (BMSE), pp. 28-31.

Yalinkilic, M. K., Imamura, Y., Takahashi, M., Kalaycioglu, H., Nemli, G., Demirci, Z., and Ozdemir, T. (1998). "Biological, physical and mechanical properties of particleboard manufactured from waste tea leaves," *Int. Biodeter. Biodegrad.* 41(1), 75-84. DOI: 10.1016/S0964-8305(98)80010-3

Young, R., Rammon, R., Kelley, S., and Gillespie, R. (1982). "Bond formation by wood surface reaction: Part I. Surface analysis by ESCA," *Wood Sci.* 14(3), 110-119.

Young, R. A., Fujita, M., and River, B. H. (1985). "New approaches to wood bonding: A base-activated lignin adhesive system," *Wood Sci. Technol.* 19(4), 363-381.

Yuan, Y. H., and Randall, L. T. (2013). "Contact angle and wetting properties," in: *Surface Science Techniques*, G. Braccoa and B. Holst (eds.), Springer Series in Surface Sciences 51, Chapter 1, DOI 10.1007/978-3-642-34243-11

Zhang, D. H., Zhang, A. J., and Xue, L. X. (2015). "A review of preparation of binderless fiberboards and its self-bonding mechanism," *Wood Sci. Technol.* 49(4), 661-679. DOI: 10.1007/s00226-015-0728-6

Zhang, L. P., Steinmaus, C., Eastmond, D. A., Xin, X. J. K., and Smith, M. T. (2009). "Formaldehyde exposure and leukemia: A new meta-analysis and potential mechanisms," *Mutation Res. – Rev. Mutation Res.* 681(2-3), 150-168. DOI: 10.1016/j.mrrev.2008.07.002

Zhang, X., Yu, H., Huang, H., and Liu, Y. (2007). "Evaluation of biological pretreatment with white rot fungi for the enzymatic hydrolysis of bamboo culms," *International Biodeterioration and Biodegradation* 60, 159-164. DOI: 10.1016/j.ibiod.2007.02.003

Zhao, L.-W., Griggs, B. F., Chen, C.-L., Gratzl, J. S., and Hse, C.-Y. (1994). "Utilization of softwood kraft lignin as adhesive for the manufacture of reconstituted wood," *J. Wood Chem. Technol.* 14(1), 127-145. DOI: 10.1080/02773819408003090

Zhou, X. Y., Tan, L. J., Zhang, W. D., Lv, C. L., Zheng, F., Zhang, R., Du, G. B., Tang, B. J., and Liu, X. Y. (2011). "Enzymatic hydrolysis lignin derived from corn stover as an intrinstic binder for bio-composites manufacture: Effect of fiber moisture content and pressing temperature on boards' properties," *BioResources* 6(1), 253-264. DOI: 10.15376/biores.6.1.253-264

Zhou, X. Y., Zheng, F., Lv, C. L., Tang, L. J., Wei, K. C., Liu, X. Y., Du, G. B., Yong, Q., and Xue, G. (2013). "Properties of formaldehyde-free environmentally friendly lignocellulosic composites made from poplar fibres and oxygen-plasma-treated enzymatic hydrolysis lignin," *Composites Part B – Eng.* 53, 369-375. DOI: 10.1016/j.compositesb.2013.05.037

DOI: 10.15376/biores.13.1.Hubbe