

A review of wood thermal pretreatments to improve wood composite properties

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Received: 3 December 2012 / Published online: 27 July 2013
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Abstract The objective of this paper is to review the published literature on improving properties of wood composites through thermal pretreatment of wood. Thermal pretreatment has been conducted in moist environments using hot water or steam at temperatures up to 180 and 230 °C, respectively, or in dry environments using inert gases at temperatures up to 240 °C. In these conditions, hemicelluloses are removed, crystallinity index of cellulose is increased, and cellulose degree of polymerization is reduced, while lignin is not considerably affected. Thermally modified wood has been used to manufacture wood–plastic composites, particle-board, oriented strand board, binderless panels, fiberboard, waferboard, and flake-board. Thermal pretreatment considerably reduced water absorption and thickness swelling of wood composites, which has been attributed mainly to the removal of

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hemicelluloses. Mechanical properties have been increased or sometimes reduced, depending on the product and the conditions of the pretreatment. Thermal pretreatment has also shown to improve the resistance of composites to decay.

Introduction

Woody biomass is the major source of lignocellulosic fibers (Kim and Pal 2010). Wood is employed for timber, for the production of pulp and paper, wood pellets, and charcoal (used as fuel for home heating via combustion or for co-firing after wood torrefaction in thermoelectric utilities). Woody biomass is also a promising raw material for the production of chemicals and fuels via chemical and thermochemical processes. Additionally, one of the leading uses of wood and wood residues is in the wood composites industry; for instance, approximately 95 % of the lignocellulosic material used for particleboard production is wood (Irle and Barbu 2010).

Wood cannot be used directly as obtained from nature; thus, pretreatment operations are required. Pretreatment intends to make wood suitable for further uses. Accordingly, different operations can be undertaken: mechanical (e.g., sawing, chipping, shredding, grinding, and milling), chemical (e.g., acid, neutral, or alkaline hydrolysis), biological, physicochemical (e.g., ammonia fiber/freeze explosion), thermochemical (i.e., torrefaction, steam explosion, and hot-water extraction), and/or drying. These processes can be used alone or combined (Agbor et al. 2011). The selection of a pretreatment method depends on several factors such as characteristics of the raw material, subsequent conversion operations, final product, and cost.

The final product is a key factor in selecting the pretreatment processes. Production of cellulosic ethanol requires pretreatment operations to disrupt the natural biomass recalcitrance to make cellulose and hemicelluloses susceptible to enzymatic hydrolysis for the production of fermentable sugars (Sun and Cheng 2002; Yang and Wyman 2008; Hendriks and Zeeman 2009; Wang et al. 2009; Zhu and Pan 2010; Agbor et al. 2011); the production of wood composites requires processes such as chipping, reduction of particle size, and drying (Sharp 1969; Kollmann et al. 1975; Maloney 1993; Bowyer et al. 2007; Klyosov 2007; Clemons 2010). Gasification, combustion, and pyrolysis of wood, as well as the production of pellets, have shown that torrefaction after reducing particle size and drying is a promising pretreatment operation (e.g., less oxygen/carbon on biomass after torrefaction improves the quality of gasification products and increases the high heating value) (Bain et al. 1998; Bergman and Kiel 2005; Prins et al. 2006; Zwart et al. 2006; Svoboda et al. 2009; Shen et al. 2009; Couhert et al. 2009). In addition, the paper and pulping industries require removing lignin and hemicelluloses (Sanyer and Chidester 1963; Farmer 1967; Bowyer et al. 2007; Vila et al. 2011).

Recent studies have reviewed processes for biomass pretreatment prior to the production of cellulosic ethanol (Mosier et al. 2005a; Öhgren et al. 2007; Carvalheiro et al. 2008; Taherzadeh and Karimi 2008; Hendriks and Zeeman 2009; Alvira et al. 2010; Girio et al. 2010), pretreatment via torrefaction for the production of synthetic fuels by means of gasification and for co-firing (Svoboda et al. 2009; van der Stelt et al. 2011), and thermal pretreatment of wood to improve durability

(Esteves and Pereira 2009; Ibach 2010). The mechanisms involved in the thermal pretreatment of wood have been reviewed by Garrote et al. (1999), Boonstra (2008), and Liu (2010). Other works have reviewed chemical treatments of wood (Rowell 1983; Kollmann and Côté 2003; Rowell 2005a, 2007; Hill 2006; Li et al. 2007; Kalia et al. 2009; Xie et al. 2010) and chemical modification and characterization of natural fiber-reinforced composites (John and Anandjiwala 2008). Fatehi and Ni (2011) and Smith (2011) assessed literature regarding pretreatment of wood prior pulping and paper manufacture. Mukhopadhyay and Fangueiro (2009) have reviewed physical processes devoted to separating and modifying the surface of natural fibers either for increasing surface roughness or for changing polarity to increase fiber–matrix interaction of composites. Moreover, Youngquist et al. (1994) have carried out an exhaustive review on uses of non-wood lignocellulosic materials for manufacturing building materials and composites. However, to the best of the authors' knowledge, a review of the effect of thermal pretreatment of wood on the properties of wood composites is lacking. The objective of this study is to review works that have been carried out to modify the properties of wood composites by means of thermal pretreatment of wood.

Wood composition and its effect on wood-water affinity

Woody biomass is a heterogeneous material constituted of structural components (cellulose, hemicelluloses, and lignin) and non-structural components (polysaccharides of starch, extractives, proteins, some water-soluble organic compounds, and inorganic compounds) in less percentage (Thomas 1977; Sjöström 1981; Alén 2000). *Cellulose*, the main component (around 40–45 % of dry wood), is a linear polysaccharide with a highly regular structure and high degree of crystallinity, giving wood its characteristic strength. Cellulose consists of chains of 500–10,000 $\beta(1 \rightarrow 4)$ -linked D-glucose units. Highly ordered (or crystalline) regions are alternated by less ordered regions, known as amorphous regions (Sjöström 1981). Six polymorphs of cellulose (I, II, III1, III11, IV1, and IV11) exist, and two polymorphs of cellulose I are reported: I α and I β) (O'Sullivan 1997). Thermogravimetric analysis (TGA) showed that cellulose is more thermally stable than lignin, hemicelluloses, and extractives. Rates of cellulose decomposition become measurable at approximately 225 °C, in both air and nitrogen environments (Órfão et al. 1999). Crystalline cellulose starts degrading at approximately 300 °C (Kim et al. 2001).

Extractives (e.g., terpenes, pinenes, tannins, and carbonyl compounds) give wood its characteristic odor and provide decay resistance (Rowell 1991). Extractives are responsible for low wettability of wood (Nzokou and Kamdem 2004) and bark (White et al. 1974). Extractives can be removed with neutral solvents, although dilute alkali is sometimes necessary (Hillis 1972; Sjöström 1981). Removing these wood constituents increases wood shrinkage (Choong 1969) and improves thermal stability (Shebani et al. 2008). Removal of extractives is expensive and time-consuming (Shebani et al. 2008). The heterogeneous chemical composition of extractives impedes obtaining a common pattern during their thermal degradation.

The thermal degradation and evaporation of extractives are overlapped with that of hemicelluloses, cellulose, and lignin (Órfão et al. 1999).

Lignin (18–30 % of wood weight) is a phenol propane-based amorphous resin that fills the spaces between the polysaccharide fibers (occupying mainly the middle lamella of the wood cells), providing shape, structure, and support to tree trunks. The main precursor of lignin in softwoods is *trans*-coniferyl alcohol, and lignin precursors in hardwoods are *trans*-sinapyl alcohol and *trans-p*-coumaryl alcohol (Sjöström 1981; Alén 2000). Lignin contributes to wood durability and antimicrobial resistance (Rowell 1991) and imparts wood mechanical properties in the presence of moisture (Kluppel and Mai 2012). The thermal degradation of lignin starts at low temperatures (Brebú and Vasile 2010) (approximately 110 °C) and occurs in a narrow range of temperatures. However, degradation of lignin is low in the range of temperatures of torrefaction (Rutherford et al. 2005; Ciolkosz and Wallace 2011). Differential thermogravimetry (DTG) curves of lignin in air and nitrogen are almost similar at temperatures up to approximately 300 °C, showing that lignin heated up to these temperatures does not undergo significant oxidation, but shows reactions typical of pyrolysis, leading to the release of volatiles (Órfão et al. 1999). Good reviews related to a diversity of uses of lignin and lignin catalytic valorization can be found elsewhere (Glasser et al. 1983; Suhas and Ribeiro 2007; Brebú and Vasile 2010; Zakzeski et al. 2010; Doherty et al. 2011).

Hemicelluloses [20–32 % of wood weight (Pettersen 1984)] consist of heteropolysaccharides made up of pentoses (xylose, arabinose), hexoses (mannose, glucose, and galactose), and sugar acids with random and amorphous structure. The degree of polymerization of hemicelluloses is lower than that of cellulose (typically around 200) (Kollmann and Côté 2003; Rowell 2005b). There are two major classes of hemicelluloses: glucomannans and xylans. The main hemicelluloses in softwood are acetylgalactoglucomannan and arabinoglucuronoxylan. Hardwood hemicelluloses consist mainly of glucuronoxylan (*O*-acetyl-4-Omethyl-glucuronoxylan) with a small amount of glucomannan (Sjöström 1981; Laine 2005; Scheller and Ulvskov 2010). Wood hemicelluloses are highly branched and easily soluble in water (Sjöström 1981). Removal of hemicelluloses in a pure form from wood involves hydrolysis of covalent bonds (ester and ether) that link the hemicelluloses to lignin.

Hemicelluloses are less thermally stable than cellulose and lignin (Shafizadeh 1984; Rowell 1991). TGA of xylans showed that this compound starts degrading at 160 °C (Órfão et al. 1999). Hemicelluloses' low degradation temperatures and their tendency to be easily hydrolysable by dilute acid or base convert these wood constituents into raw material for the production of biofuels (Saha 2003; Amidon et al. 2008). Hemicelluloses are more hydrophilic than cellulose and lignin (Skaar 1972; Rowell 1991), holocellulose (the sum of cellulose and hemicelluloses), or the gross wood (see Fig. 1). Therefore, hemicelluloses promote affinity of wood with water (Hillis 1984) and affect the surface energy of wood (Zhang et al. 2011). The low thermal stability of hemicelluloses can be disadvantageous for the production of wood–plastic composites (WPCs), because hemicelluloses degrade during press molding or extrusion, releasing volatile organic compounds (VOC), affecting the density (a critical property) of WPCs, and attacking parts of the equipment used for compounding WPCs (Klyosov 2007).

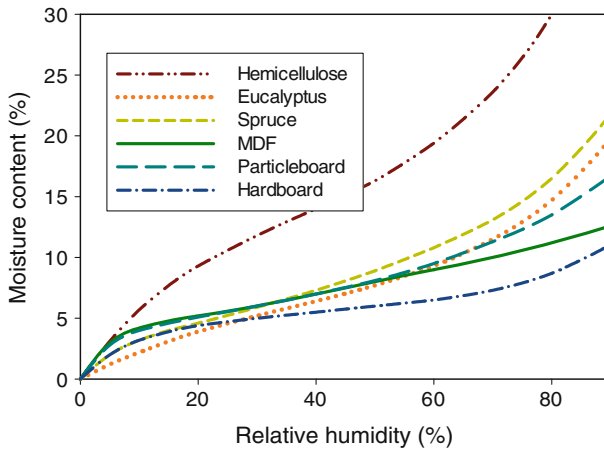


Fig. 1 Sorption isotherms of hemicelluloses (obtained from eucalyptus), eucalyptus, spruce, and selected wood composites (at 22–25 °C). Adapted from Christensen and Kelsey (1959), Skaar (1972), Eckelman (1998), Suchsland (2004), and Niemz (2010)

Wood–water interaction

Hygroscopicity is an inherent property of wood that affects dimensional stability, mechanical properties, thermal properties, density (Skaar 1984), affinity with other materials, and durability. Wood can hold water in the cell walls as bound water or in the cell cavities as free water. When subjected to moist or dry environments, wood's natural tendency is to reach equilibrium with the environment (the equilibrium moisture content—EMC) by absorbing or desorbing moisture. During wood drying, the free water leaves the cell cavities first; the bound water is then removed from the cell wall. Retention of bound water results from the presence of hydroxyl groups of wood constituents. The hydroxyl groups attract and hold water molecules through hydrogen bonding (Skaar 1972). The hemicelluloses and the non-crystalline region of the cellulose chains are more prone to attract water due to the availability of hydroxyl groups. Christensen and Kelsey (1959) estimated that cellulose, hemicelluloses, and lignin in *Eucalyptus regnans* are responsible for approximately 47, 37, and 16 % of the total water sorption of this wood species. In theory, most, if not all, of the hydroxyl groups in hemicelluloses are accessible to moisture (Rowell 2005b).

The sorption behavior of wood resulting from changes in the relative humidity of the environment is described by an S-shaped isotherm. Three parts can be identified: (a) chemisorption, which predominates at low relative humidity and is characterized by the buildup of a monomolecular layer of water held by the free hydroxyls of the non-crystalline regions, (b) physisorption, which is characterized by the formation of a polymolecular layer of water, and (c) capillary condensation, which occurs when water vapor condenses in the void space of the cell wall at relatively high humidity (Hansen 1986; Fengel and Wegener 1989; Tsoumis 1991; Niemz 2010) [i.e., higher than 90 % (Boonstra 2008)]. Sorption isotherms can be obtained experimentally using saturated salt solutions (Acharjee et al. 2011) and environmental chambers, or can be predicted using sorption models such as the Hailwood–

Horrobin model (Papadopoulos and Hill 2003) or the parallel exponential kinetics (PEK) model (Hill et al. 2012).

The sorption characteristic of wood is quite similar irrespective of the wood species, except in woods with high extractives content (Skaar 1972). However, temperature can affect the sorption behavior of wood (Stamm 1952; Skaar 1972, 1984; Hansen 1986; Kollmann and Côté 2003; Hill and Xie 2010). The sorption behavior of wood composites is different from that of gross wood (Suchsland 2004). Figure 1 shows a comparison of sorption curves of hemicelluloses, two types of wood (eucalyptus and spruce), and three types of wood composites (particleboard, medium density fiber board, and hardboard). It can be observed that the sorption of wood composites is lower than that of wood, especially at relative humidity greater than 30 %.

The production and behavior of engineered wood products are directly affected by wood hygroscopicity. Moisture is the most important issue for improving the durability of WPCs (Morrell et al. 2010). Therefore, pretreatment processes to remove high hygroscopic wood components are a strategy to reduce water absorption. Removal of wood fractions solubilizable in water helps decrease water absorption of wood composites (Boehm 1936). Water absorption of heat-treated solid *Pinus radiata* in the range of temperatures from 180 to 240 °C is reduced by 50 % (Popper et al. 2002). Thermal treatment is, in fact, responsible for reduction of equilibrium moisture content of wood (Hill et al. 2012). This change of properties in wood is mainly attributed to the removal of hemicelluloses because at temperatures of 170 °C or higher, essentially all the arabinan-arabino-galactan fraction is dissolved and the arabinose substituents, under the acidic conditions, are hydrolyzed to free sugars (Casebier et al. 1969; Amidon et al. 2008). Thermal treatment has been sought as an alternative to meet phytosanitary requirement of wood (Wang et al. 2011).

Thermal pretreatment of wood to remove hemicelluloses

Modification of wood characteristics involves operations that promote irreversible changes in the structure and/or in the chemical composition of wood. These changes can result for example from the removal of hemicelluloses, delignification, the alteration of the crystallinity index of cellulose, or the reduction of the degree of polymerization of cellulose and lignin. The modification of wood properties can be conducted through chemical, thermal, and biological processes (active treatments) or by impregnation (passive treatment) (Hill 2006).

The main objective of thermal treatment prior to the production of wood composites is to reduce wood hydrophilicity, which is accomplished primarily by partial removal of hemicelluloses. Even though different alternatives exist for isolating hemicelluloses from wood (e.g., extraction with alkali or neutral solutions) (Sjöström 1981; Kollmann and Côté 2003), thermal pretreatment avoids using chemicals since water or gases (e.g., nitrogen) and heat are employed. Thermal pretreatment has been used for a long time. Processes such as Iotech, Siropulper, Rapid Steam Hydrolysis/Continuous Extraction–RASH, Stake II (Henuningson and

Newman 1985; Garrote et al. 1999), the American process, the Ant-Wuorinen, and the Scholler process (Harris 1952) have been reported. Currently, thermal treatment is the process most advanced commercially among the wood modification processes (Hill 2006). Several companies use heat (or heating in combination with other processes) to alter the properties of wood (e.g., BioGasol (www.biogasol.com), Thermowood[®] (www.superiorthermowood.com), Plato[®] (www.platowood.nl), Retified wood (www.retiwood.com), Perdure Technology (www.perdure.com), Masonite[®] (www.masonite.com), Bingaman (www.bingamanlumber.com), Thermotreated Wood/Westwood (www.westwoodcorporation.com), Thermory[®] (www.thermoryusa.com), Opel Therm (www.opel3.com), and THOR Torrefied Wood[®] (www.silvatimber.co.uk)).

Thermal pretreatment consists normally of heating the wood at predetermined temperatures and durations in moist environments (environment that wood is exposed to) using hot water or steam, or in dry environments (dry refers to an environment without any liquid such as water; however, there could be some moisture in the wood) using nitrogen or air. Thus, two types of pretreatment can be distinguished: *moist* or *wet processes* (e.g., hot water extraction and steam explosion) and *dry processes* (e.g., torrefaction). This is not a formal classification of thermal pretreatment processes, but used in this paper for distinguishing the two processes. In fact, combination of “moist” processes with “dry” processes is possible, as in the Plato[®] technology (Militz and Tjeerdsma 2001; Boonstra 2008). However, the environment in which the treatment is conducted can define preprocessing (for example pre-drying before torrefaction) and postprocessing operations (for example drying of wood after steam explosion), and use or disposal of by-products (e.g., the hemicelluloses-rich fractions or the torrefaction gases). Since the environment has a significant influence upon the reaction chemistry occurring in the pretreatment operation (Hill 2006), a separation of processes into moist and dry is advantageous. Although the material used for torrefaction can contain some moisture, this intrinsic moisture in biomass is not high enough to change the conditions of the environment from “dry” to “wet.” Vegetable oils can be used for thermal treatment of wood as well (Tjeerdsma et al. 2005; Jones et al. 2005; Hill 2006; Fang et al. 2011, 2012), but this topic is out of the scope of this paper because apparently no works have been conducted using oil for modifying wood prior to the manufacture of wood composites.

Hemicelluloses removal in moist environments (“wet” thermal methods)

The importance of combining heat with water to shape wood more easily (e.g., for manufacturing canoes and ships) has been recognized since ancient times (Navi and Sandberg 2012). Rue (1925) (referred by Harris 1952) mentioned that Behrend in 1869 found that when wood is exposed to hot water at temperatures from 160 to 180 °C, it becomes sufficiently softened and the separation of the fibers is easier. Boiling or steaming of wood prior to grinding for mechanical pulping or production of coarse fibers has become common practice since then (Harris 1952). Although wet thermal methods have been carried out to remove hemicelluloses from lignocellulosic materials other than wood and, in some cases, some composites have

been manufactured with those materials after thermal pretreatment (see for example Vignon et al. 1996; Focher et al. 1998; Suzuki et al. 1998; Laemsak and Okuma 2000; Keller 2003; Velasquez et al. 2003; Mosier et al. 2005b; Widyorini et al. 2005; Mohebbi et al. 2008; Shao et al. 2009; Quintana et al. 2009; Mancera et al. 2011; Luo and Yang 2011; and other fifteen works referred by Youngquist et al. 1994), this review is focused on studies that have involved wood.

Tiemann (1915) (referred by Hill 2006) reported that pre-dried wood subjected to steam at 150 °C and 4 h reduced moisture sorption by up to 25 %, with low negative effects on mechanical properties. The Asplund process (Asplund 1935) is an example of processes in which wood chips were mechanically defiberized in the presence of steam at temperatures from 160 to 182 °C. Boehm (1930, 1936) disclosed a patent for producing wood composites with steam-treated wood and recovering soluble fractions from lignocellulosic materials. This process was based on the Masonite technology developed in 1924 (www.masonite.com) and patented by Mason (1926, 1931). The work conducted at the Masonite Corporation was a pioneering process that combined thermal pretreatment of wood with (a) the production of wood composites (hardboard) and (b) the recovery of the hemicelluloses-rich fraction for the production of value-added by-products such as furfural and acetic acid. Further works using hot water were carried out by Bobleter in Austria (Bobleter et al. 1976; Bobleter and Bonn 1983). Bobleter and Bonn (1983) stated that until the 1980s “the treatment of carbohydrates with pure water at elevated temperatures has attracted only sporadic interest.” More recently, for fuels production, there has been interest in using steam explosion as a pretreatment to enhance the accessibility of biomass for enzymatic hydrolysis (Schultz et al. 1983; Tanahashi 1990; Schütt et al. 2012) or for the production of wood composites (Takatani et al. 2000b; Angles et al. 2001).

The process in which hot water is used has been referred to as *hot water extraction*–HWE, also called *autohydrolysis* (Hsu et al. 1988; Schwald et al. 1988; Amidon et al. 2008), *hydrothermolysis* (Bobleter and Bonn 1983; Bobleter et al. 1991; Hörmeyer et al. 1988; Hill 2006; Boonstra and Tjeerdsma 2006; Boonstra 2008; Agbor et al. 2011), *hot compressed water treatment* (Kobayashi et al. 2009; Xiao et al. 2011), *water hydrolysis* (Harris 1952), *wet torrefaction* (Yan et al. 2010), *hydrothermal carbonization* (Funke and Ziegler 2010; Falco et al. 2011; Hoekman et al. 2011; Libra et al. 2011), *aqueous fractionation*, *solvolysis* or *aquasolv* (Agbor et al. 2011), *aqueous liquefaction* (Heitz et al. 1986), or *cooking* (Suchsland et al. 1987; Weil et al. 1998). This diversity of terms used to describe the same process could hinder comparison of properties of pretreated biomass under the effect of hot water. HWE has been used to convert lignocellulosic biomass into sugars using water at temperatures from 140 to 190 °C, without added chemicals (Nabarlatz 2006; Tunc and van Heiningen 2008; Amidon et al. 2008; Liu 2010), or to modify wood properties (Boonstra and Tjeerdsma 2006; Boonstra 2008).

During HWE, hemicelluloses from wood are depolymerized by hydrolysis reactions into monomers and oligomers (Garrote et al. 1999; Boonstra 2008; Ibbett et al. 2011). The process involves cleavage of the side chain constituents (arabinose and galactose), followed by degradation of the main chain constituents (mannose, glucose, and xylose). The resulting pentoses and hexoses are dehydrated to furfural

and hydromethylfurfural, respectively (Garrote et al. 1999; Mochidzuki et al. 2003; Boonstra 2008; Liu 2010). Hydronium ions generated from water act as catalysts at the beginning of the process. However, hydronium ions generated from acetic acid become more important than those from water under operational conditions (Garrote et al. 1999).

Scanning electron microscopy (SEM) analysis showed that small spherical-like droplets are present on the surface of biomass after thermal treatment with hot water or steam. This phenomenon has been attributed to the coalescence and migration of lignin to the surface of the wood cells (Marchessault 1991; Selig et al. 2007; Donohoe et al. 2008; Sannigrahi et al. 2011). Selig et al. (2007) hypothesized that once the temperature of the treatment surpasses the phase-transition temperature of lignin (i.e., in the range $\sim 120\text{--}200\text{ }^{\circ}\text{C}$), lignin is fluidized and coalesces within the cell walls. Lignin in a fluid state acquires mobility due to capillary and hydrophobic forces and migrates to the bulk liquid phase of the pretreatment mixture. Coalesced lignin could harden upon cooling after the treatment and either become trapped within the cell wall layers or deposited back on the surface of the treated material. Figure 2 shows examples of deposited material (likely lignin and lignin-based compounds) on the surfaces of fibers of (a) sugar maple after HWE at $160\text{ }^{\circ}\text{C}$ and 120 min and (b) ponderosa pine after HWE at $160\text{ }^{\circ}\text{C}$ and 90 min, as has been observed using SEM.

Thermal pretreatment in wet environments is responsible for increased dimensional stability of wood (Hillis 1984). The degree of crystallinity of cellulose is increased (Bhuiyan et al. 2000), and partial depolymerization of cellulose and lignin, especially at high temperatures, occurs (Tjeerdsma et al. 1998; Sweet and Winandy 1999; Garrote et al. 1999). Lignin can also be subjected to partial solubilization (Tunc and van Heiningen 2008; Carvalho et al. 2008), plasticization (Bouajila et al. 2005; Angles et al. 2001), and condensation and/or repolymerization reactions (Boonstra 2008). During the thermal modification, the color of the resulting solid fraction changes to dark brown (Harris 1952; Angles et al. 2001; Boonstra 2008). Change in color has been attributed to the oxidation of

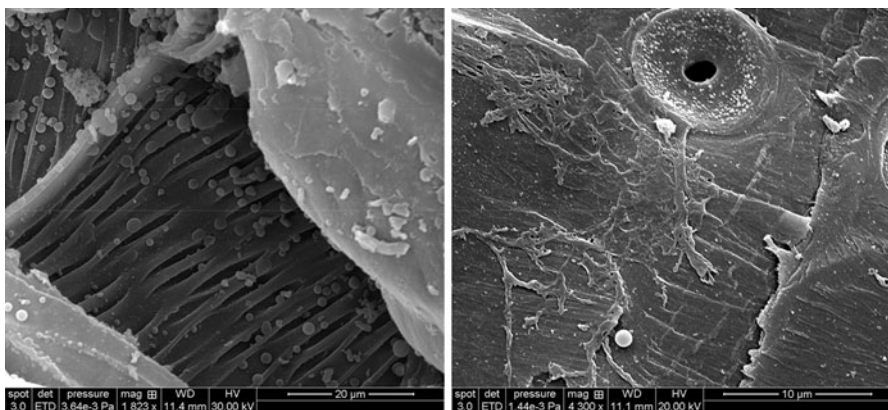


Fig. 2 SEM of hot water extracted sugar maple (*left*) and ponderosa pine (*right*)

phenolic compounds (Sundqvist 2002, 2004), the presence of reduced sugars and amino acids, the emanation of formaldehydes (Sandoval-Torres et al. 2010), the formation of quinines, or the caramelization of holocellulose components (Boonstra 2008). The color of thermal-treated wood affects the color of wood composites such as WPCs (Pelaez-Samaniego et al. 2012) and particleboard (Hsu et al. 1988).

Softwood and hardwood behave differently during wet thermal treatment (Harris 1952; Niemz et al. 2010; Hill 2006; Shi et al. 2007). HWE of ponderosa pine at 160 °C and 90 min and sugar maple at 160 °C and 120 min showed that up to 20 and 23 % of the initial dry mass, respectively, is removed (Chaffee 2011; Amidon et al. 2008) (Figs. 3, 4). Cellulose is more stable than the other wood constituents and starts degrading at temperatures above 200 °C (Mok and Antal 1992; Amidon et al. 2008; Boonstra 2008). Increasing time and/or temperature, the autohydrolysis of pine increases the yields of xylose and mannose; HWE at 100 °C yields very low amounts of extracted fractions. Heating pine wood at 130 °C for 7 h reduces the pentoses content from 11 to 9 % (Hillis 1984). In processes up to 170 °C, essentially the entire arabinan-arabino-galactan fraction is dissolved, and the arabinose substituents, under the acidic conditions, are hydrolyzed to free sugar. Extraction at temperatures over 170–180 °C and 45 min has been considered severe (Casebier et al. 1969).

Few works have been devoted to analyzing the properties of the extracted wood relevant to the production of wood composites. Wood subjected to HWE showed that important changes occur on the solid residue: particle shape and diameter, as well as pore size changed depending on the reaction temperature (Hietala et al. 2002; Kobayashi et al. 2009; Paredes et al. 2009; Duarte et al. 2011). The degree of crystallinity as well as liquid wetting and penetration is also increased proportionally to the increase of the severity factor (Paredes et al. 2009). Cracks in the cell walls (Boonstra 2008) and increased surface roughness (Angles et al. 1999; Duarte et al. 2011; Pelaez-Samaniego et al. 2012) have also been observed. The physical and chemical changes of the solid residue have normally been attributed to the removal of wood chemical constituents (Kobayashi et al. 2009).

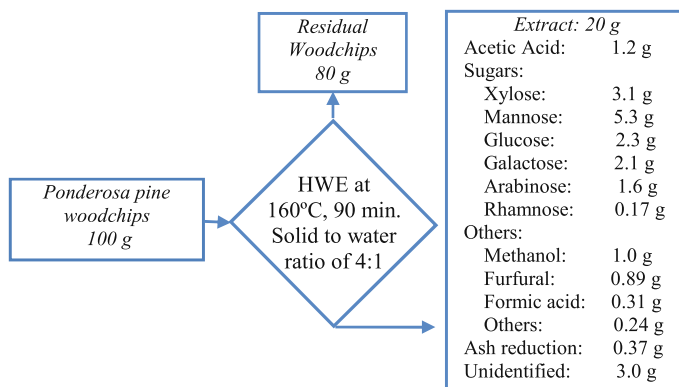


Fig. 3 Typical hot water extraction (HWE) yields of ponderosa pine (Chaffee 2011)

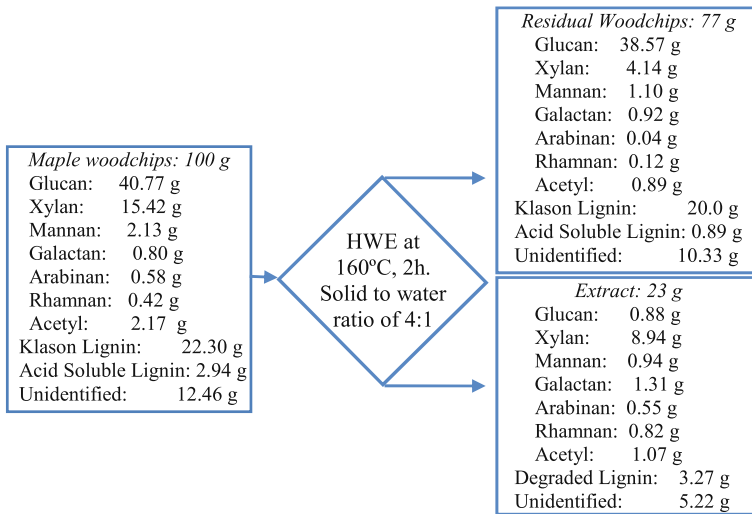


Fig. 4 Typical hot water extraction (HWE) yields of sugar maple (Amidon et al. 2008)

Hot water extraction is of interest in the paper and pulp industry (Li et al. 2010; Duarte et al. 2011; Lu et al. 2011) as a pretreatment operation for the production of lignocellulosic ethanol (Kim 2004; Kobayashi et al. 2009), as part of biorefinery concepts involving biomass pyrolysis (Brown and Holmgren 2006), or as a pretreatment operation prior to the production of wood composites (Paredes et al. 2009; Pelaez-Samaniego et al. 2012). The goal of most works related to HWE is to maximize the yield of sugars, acids, or other chemicals from lignocellulosic materials, without paying attention to the structural changes in extracted wood (Sattler et al. 2008). However, studies integrating the effect of HWE on the yield of by-products (e.g., hemicelluloses-derived sugars) with the manufacture of wood composites could promote HWE as a pretreatment option to be considered within the engineered wood industry. An advantage of using HWE wood prior to the production of wood composites is that readily available lignin (due to plasticization and possible redistribution during HWE) can play an important role during the manufacturing of the composite (Mason 1928).

Hemicelluloses removal in dry environments (“dry” thermal methods)

Heat has been used to improve the physical properties of wood for a long time (Rowell et al. 2002). The Vikings would burn the wood surface to make it more durable (Mayes and Oksanen 2002). Stamm and Hansen (1937) mentioned different works conducted from 1915 to 1936 aiming to reduce hygroscopicity of wood through thermal treatment in dry environments (i.e., in nitrogen or other types of inert environment). Further works were observed during the 1930s. For example, Bouteille (1939) patented a continuous system to “torrefy” small wood logs in a counter-flow vertical reactor. In fact, the term “torrefaction” is commonly used to best describe the thermal treatment of wood in “dry” environments.

Torrefaction, also known as *mild pyrolysis* (Inari et al. 2007), *low temperature pyrolysis* (Yan et al. 2009), or *thermal rectification* (Gohar and Guyonnet 1998; Weiland and Guyonnet 2003), occurs when wood is heated in the presence of inert gases at temperatures between 200 and 300 °C, without using external chemicals. These conditions avoid combustion and oxidation of wood. Heating rates during torrefaction are close to 50 °C/min (Svoboda et al. 2009). The mechanism of biomass torrefaction has been widely studied and reported elsewhere (Fonseca et al. 2005; Bellais et al. 2003; Turner et al. 2010; Repellin et al. 2010a; Ciolkosz and Wallace 2011).

In the range of temperatures of torrefaction, degradation of hemicelluloses occurs (Hillis 1984; Jämsä and Viitaniemi 2001; Repellin and Guyonnet 2005; Inari et al. 2007). Cellulose is subjected to dehydration (Mamleev et al. 2009), lignin and cellulose are subjected to partial depolymerization, and the crystallinity index (CrI) of cellulose is increased (Broido et al. 1973; Nimlos et al. 2003; Pétrissans et al. 2003; Windeisen et al. 2009; Tumuluru et al. 2011). However, it is not clear if the increase of the CrI is due to degradation of amorphous cellulose, recrystallization of amorphous cellulose, or to a combination of both (Boonstra 2008). Reduction of the degree of polymerization of cellulose results from the regeneration of free radicals, elimination of moisture, formation of carbonyl and carboxyl groups, and formation of carbon dioxide (Bhuiyan et al. 2000, 2001). Similar to wood pretreatment in the presence of moist environments, the color of wood changes to dark brown during torrefaction (Jämsä and Viitaniemi 2001). The porosity of the remaining solid does not change during torrefaction at short residence times (i.e., less than 1 h) (Rutherford et al. 2005).

The yields and energy contents of the products depend on the temperature, reaction time, and type of biomass (Svoboda et al. 2009). Chen and Kuo (2010) mentioned that in torrefaction at 240 °C and 1 h, the maximum hemicelluloses extraction occurred in four types of biomass: bamboo, willow, coconut shell, and wood (*Ficus benjamina* L.); at temperatures up to 240 °C, cellulose and lignin were

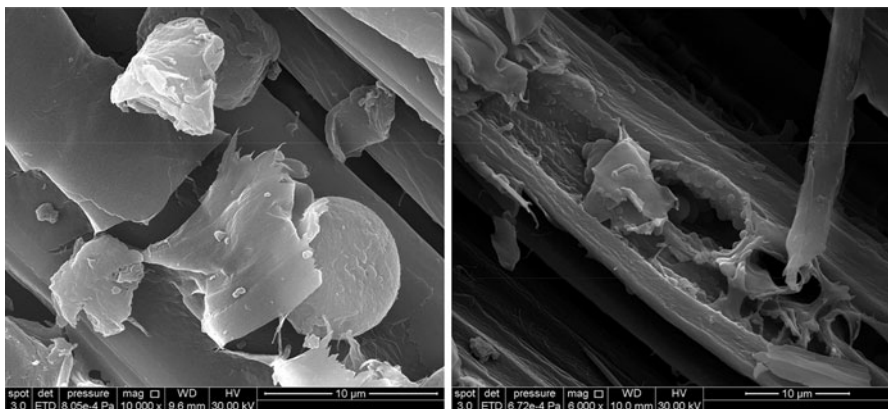


Fig. 5 SEM micrographs of torrefied sugar maple at 290 °C (a) and 310 °C (b) and ~10 min of residence time in an auger reactor

not affected in the types of biomass the authors studied. Nevertheless, torrefaction at temperatures as low as 180 °C can degrade hemicelluloses (Kamdem et al. 2002).

Dimensional stability, resistance against fungal degradation, water vapor sorption, and durability are improved in torrefied wood (Jämsä and Viitaniemi 2001; Kamdem et al. 2002; Tjeerdsma and Militz 2005; Hakkou et al. 2006; Borrega and Kärenlampi 2008; Ates et al. 2009; Ibach 2010; Pfriem et al. 2010; Dubey et al. 2012). The moisture content of torrefied wood, on the other hand, is reduced to 2 % or less, and the heating value is increased up to 23–24 MJ/kg (Fonseca et al. 2005). The degree of grindability is improved as consequence of the brittleness that torrefied wood acquires (Svoboda et al. 2009), reducing energy consumption during grinding (Bridgeman et al. 2010; Repellin et al. 2010b; Phanphanich and Mani 2011). However, irreversible negative impacts such as loss of strength, toughness, and abrasion resistance have been reported (Harris 1952; Stamm 1956; Mayes and Oksanen 2002; Kamdem et al. 2002; Tjeerdsma and Militz 2005; Shi et al. 2007; Stanzl-Tschegg et al. 2009; Ibach 2010). The reduction of the tenacious nature of wood during torrefaction results mainly from the breakdown of the hemicelluloses matrix and cellulose depolymerization (Bergman et al. 2005; Bergman and Kiel 2005).

Torrefaction of sugar maple tests showed that superficial morphological changes occur. As in HWE, spherical-like particles are deposited on the cell walls or seem to emerge from the cell walls. The mechanism and kinetics of the formation of this deposited material, its composition, and its impact on wood properties and wood composites deserve more study. Figure 5 shows SEM micrographs of sugar maple chips torrefied at 290 and 310 °C (measured on the outer reactor's surface) and approximately 10 min of residence time (time inside the hot section of the reactor's chamber) conducted using an auger pyrolysis reactor under nitrogen environment.

The by-products released from torrefaction are water vapor, acetic acid, CO₂, methanol, CO, and other minor compounds (i.e., phenol fractions and chemical compounds of low energy content) (Degroot et al. 1988; Mani 2009; Chiaramonti et al. 2011). A typical experimental result of torrefaction of willow has been reported by Kiel (2007) (Fig. 6). By-products of torrefaction are frequently burnt (Bergman and Kiel 2005; Chiaramonti et al. 2011), but most works do not report uses or disposal of gases.

Use of thermally treated wood for the manufacture of wood composites

A number of studies have been performed on the effects of thermal pretreatment of wood for the production of wood composites (summarized in Table 1). Some studies have also analyzed the effects of *postmanufacture* thermal treatment of wood composites (e.g., Hann 1965; Suchsland and Enlow 1968; Hsu et al. 1989; Zhang et al. 1997; Okino et al. 2007; Ayrilmis and Winandy 2009; Ayrilmis et al. 2009; Mendes et al. 2013) but, since this review is focused on thermal *pretreatment*, this topic is not covered. Main findings on the influence of thermal pretreatment of wood on end composite products are compiled in Table 2.

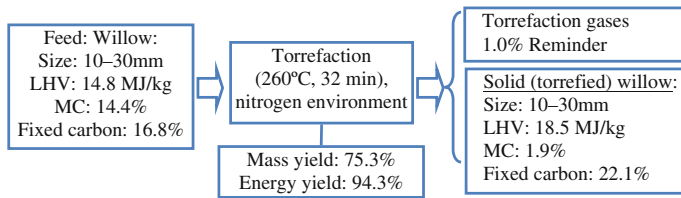


Fig. 6 Typical torrefaction yields of willow (Kiel 2007). *MC* moisture content, *LHV* low heating value

Effect of wood thermal pretreatment on wood–plastic composites

The effect of thermal pretreatment (both wet and dry) on properties of wood–plastic composites (WPCs) has been investigated by Angles et al. (1999), Andrusyk et al. (2008), Westin et al. (2008), Follrich et al. (2010), Ayrilmis et al. (2011a), Hosseinaei et al. (2012a, b), and Pelaez-Samaniego et al. (2012). The main findings of the impact of thermal pretreatment on wood composites are summarized in Table 2.

Andrusyk et al. (2008) produced extruded wood–plastic composites (WPCs) using hot-water-extracted hardwood and polypropylene (PP); mechanical properties (tensile, flexural, and Izod impact) were compared with WPCs produced with unextracted wood. In addition, the authors compared specific gravities and linear burn rate. Evaluation of mechanical properties showed that tensile modulus, tensile strength, flexural modulus, and flexural strength are significantly increased (14.38, 19.25, 8.16, and 13.39 %, respectively). The specific gravity of the products showed similar results (1.01 and 1.02 g/cm³ for WPCs from unextracted and extracted wood, respectively). Linear burn rate was increased by approximately 21 %.

Hosseinaei et al. (2012a, b) reported that hot-pressed WPCs manufactured with hot-water-extracted southern yellow pine and isotactic polypropylene homopolymer or maleic anhydride grafted polypropylene (MAPP) showed less water absorption and higher tensile properties, a probable consequence of better interfacial bonding and lower hydrophylicity of extracted wood. The presence of coupling agents was responsible for better wood–polymer interaction. Similar results have been observed by Takatani et al. (2000a), who produced WPCs using steam-exploded beechwood flour of different particle sizes with poly(vinyl chloride) (PVC) and polystyrene (PSt). WPCs boards manufactured from steam-exploded beech had better mechanical properties and reduced water absorption (WA) than boards with unextracted material. An interesting result showed a relationship between performance of the products and particle size: the smaller the particle size, the higher the performance of the product. Furthermore, only a slight effect of the wood species was observed (Takatani et al. 2000b).

HWE conducted on ponderosa pine changed dramatically its chemical composition and increased the amount of fines in flour pine used for the manufacture of WPCs (Pelaez-Samaniego et al. 2012). Two types of thermoplastics were used in the referred work: PP and high density polyethylene (HDPE). Formulations based on HDPE + extracted pine and PP+ extracted pine absorbed 46.5 and 45 % less

Table 1 Some works conducted to modify wood properties through thermal pretreatment and wood composites manufactured with pretreated wood

Product	Type of pretreatment	Materials employed	Wood pretreatment conditions	Reference(s)
Pressed WPC panels	Steam (saturated) pretreatment	<i>Eucalyptus camaldulensis</i> + PP	Steam at 120, 150 or 180 °C for 20 or 40 min	Ayrlimis et al. (2011a)
Pressed WPCs	Steam explosion	Newspaper flour, beech wood flour + PVC and PST	Steam explosion after cooking at 210 °C, 10 min	Takatani et al. (2000a)
Pressed WPCs	Steam explosion	Beech (<i>Fagus crenata</i>), Japanese cedar (<i>Cryptomeria japonica</i>), and red meranti (<i>Shorea negrosensis</i>) + PST, PMMA, and PVC	Steam explosion after cooking at 215 °C, 8 min	Takatani et al. (2000b)
Extruded WPCs	HWE in two stages	Southern hardwood chips + PP	Cooking at 95 °C (1st stage) and cooking until 160 °C (2nd stage)	Andrusyk et al. (2008)
Extruded WPCs	HWE	Pine (<i>Pinus ponderosa</i>) + PP or HDPE	90 min at 160 °C	Pelaez-Samaniego et al. (2012)
Extruded WPCs	Dry	Spruce wood + PP	Thermal modification in kiln at 210 °C for 15 and 30 min	Follrich et al. (2010)
Injected and extruded WPCs	Dry (Thermowood® process)	Scots pine + CAP or PLA; Norway spruce (<i>Picea abies</i>)	Thermal treatment: 212 °C in N ₂ atmosphere	Westin et al. (2008)
Injected and extruded WPCs	HWE	Southern yellow pine (<i>Pinus spp.</i>) + isotactic PP homopolymer and (MAPP)	140, 155, and 170 °C, for 60 min	Hosseinaei et al. (2012a, b)
Extruded WPCs	Steam explosion	Spruce (<i>Abies alba</i>) and pine (<i>Pinus insignis</i>)	Temperature: 176, 215, and 220 °C. Time: 2.5, 3.0, 2.1 min, respectively	Angles et al. (1999)
Binderless panels	Steam explosion	Spruce (<i>Abies alba</i>) and pine (<i>Pinus insignis</i>)	176–231 °C (0.9 and 2.8 MPa, respectively), for 1.2–5.5 min	Angles et al. (2001)
Binderless hardboard	Steam “cooking”	Mixed southern hardwood chips	Steam: 1.4–3.5 MPa, for 2.5 min	Suchsland et al. (1987)

Table 1 continued

Product	Type of pretreatment	Materials employed	Wood pretreatment conditions	Reference(s)
Composite boards (thermobalite)	Steam explosion	Birch chips	170–230 °C for 1–15 min	Startsev et al. (1999)
Particleboard	Steam (saturated) pretreatment + Curing	Norway spruce (<i>Picea abies</i> KARST) and Scots pine (<i>Pinus sylvestris</i> L.), plus MUF	Steam for 1st stage (8–10 bar, 165–185 °C); Nitrogen for curing (1 bar, 180 °C); 30 min each stage	Boonstra et al. (2006)
Particleboard	Steam explosion	Sugi (<i>Cryptomeria japonica</i>) sapwood sawn veneers	160–220 °C for 10 min	Sekino et al. (1999)
Particleboard	Steam (overheated)	Pine (<i>Pinus silvestris</i> L.) and birch (<i>Betula verrucosa</i> Ehrh.)	Two-step heating: 104 °C for 24 min, then 200 °C for 7 min	Borysiuk et al. (2007)
Particleboard	Steam (saturated) treatment	A mix of Norway spruce (<i>Picea abies</i> Karst) and Scots pine (<i>Pinus sylvestris</i> L.) + MUF or MDI	Saturated steam at 165–185 °C, for 30 min with or without a curing step in dry conditions	Boonstra et al. (2006), Boonstra (2008)
Particleboard	Dry	Pine + MUPF	240 °C, nitrogen atmosphere	Ohlmeyer and Lukowsky (2004)
Particleboard, fiberboard and waferboard	Steam (saturated) pretreatment	Aspen (<i>Populus tremuloides</i> Michx.) + PF for waferboard. Pine <i>Pinus contorta</i> Dougl.) with spruce + UF for particleboard	Steam (saturated at 1.55 MPa), for 1–4 min	Hsu (1986), Hsu et al. (1988)
Particleboard (using bark)	HWE	Black spruce (<i>Picea mariana</i>) and trembling aspen (<i>Populus tremuloides</i>) bark	Hot water at 100 °C for 3 h	Ngueho Yemele et al. (2008)
Particleboard	HWE	Athel tree, <i>Tamarix aphylla</i> (L.) + UF, and PMDI	Hot water at 100 °C for 1 h	Zheng et al. (2006)
Wood-gypsum-cement particleboard	HWE	Four eastern Canadian wood species	Hot water at 105 °C for 3 h	Espinoza-Herrera and Cloutier (2008)

Table 1 continued

Product	Type of pretreatment	Materials employed	Wood pretreatment conditions	Reference(s)
OSB	HWE	Red maple (<i>Acer rubrum</i>), aspen (<i>Populus tremuloides</i>); mixture of southern yellow pine and hemlock (<i>Tsuga canadensis</i>) + pPMDI resin	Hot water extraction at 160 °C, at 45 and 90 min	Paredes et al. (2008, 2010), Paredes (2009)
OSB	HWE	Red maple (<i>Acer rubrum</i>), + pMDI resin	Hot water extraction at 160 °C, at 45 and 90 min	Howell et al. (2009)
OSB	HWE	Red maple (<i>Acer rubrum</i>), + pMDI resin	Hot water extraction (no additional data)	Taylor et al. (2008)
OSB	Dry	Scots pine (<i>Pinus sylvestris</i> L.) + MUPF or pMDI	Inert environment, 220 and 240 °C, 30 min.	Paul et al. (2006, 2007)
OSB	Dry	Wood species <i>P. taeda</i> L. + PF	30 min at 200 and 240 °C	Mendes et al. (2013)
Flakeboard	HWE	Southern yellow pine (<i>Pinus spp.</i>)	30 and 60 min at 140, 155, and 160 °C	Hosseinaei et al. (2011)
MDF	Steam (saturated) pretreatment	Rubberwood fibers and UF	Steam at 120, 150 or 180 °C for 15 or 30 min	Ayrilmis et al. (2011b)
MDF	HWE	Industrial fibers (not defined)	30 and 60 min at 120, 150 and 180 °C	Mohebbi et al. (2008)
MDF	Dry	Mixture of softwoods + UF	150–180 °C during 15–60 min, in vacuum conditions	Garcia et al. (2006)
Insulation board (or LDF)	Steam pretreatment	Aspen fiber + isocyanate resin	200 °C during 4 min	Rowell et al. (1995)

CAP cellulose acetate propionate, HDPE high density polyethylene, HWE hot water extraction, LDF low density fiberboard, MDF medium density fiberboard, MAPP maleic anhydride grafted polypropylene, MUF modified urea formaldehyde, MUPF melamine-urea-phenol-formaldehyde, PF phenol formaldehyde, PLA poly-lactic acid, pMDI polymeric diphenyl methane diisocyanate, PMMA polymethylmethacrylate, PO polyolefin, PSY polystyrene, PVC poly(vinyl chloride), PP polypropylene, UF urea formaldehyde, OSB oriented strand board, MDF medium density fiberboard

Table 2 Main findings on wood composite properties manufactured with thermally pretreated wood

Product	Authors	Main findings
WPCs	Ayrilmis et al. (2011a), Takatani et al. (2000a, b), Andrusyk et al. (2008), Pelaez-Samaniego et al. (2012), Follrich et al. (2010), Westin et al. (2008), Hosseinaei et al. (2012a), Angles et al. (1999), Hosseinaei et al. (2012b)	Improved mechanical properties Reduced water affinity and swelling Reduced water diffusion constant Particle size of wood affected WPC's performance Improved resistance to decay Better affinity of pretreated wood with compatibilizers
Binderless panels	Angles et al. (2001), Suchsland et al. (1987), Startsev et al. (1999)	Reduced water absorption and thickness swelling Improved MOR
Particleboard	Boonstra et al. (2006), Sekino et al. (1999), Borysiuk et al. (2007), Boonstra (2008), Ohlmeyer and Lukowsky (2004), Hsu (1986), Hsu et al. (1988), Zheng et al. (2006)	Improved MOE; similar MOR (although some authors showed reduction of MOR) Reduced internal bonding Reduced water absorption Better dimensional stability
OSB	Paredes et al. (2008, 2010), Paredes (2009), Howell et al. (2009), Taylor et al. (2008), Paul et al. (2006, 2007), Mendes et al. (2013)	Better dimensional stability Wood species and pretreatment conditions affect mechanical properties. Reduced or improved mechanical properties are reported Better resistance to decay
Flakeboard	Hosseinaei et al. (2011)	Increased MOR and MOE IB was unaffected
Waferboard	Hsu et al. (1988)	Better dimensional stability Mechanical properties of the composite were not significantly affected when pretreatment was conducted at relatively low temperatures
Fiberboard (MDF and LDF)	Ayrilmis et al. (2011b), Mohebby et al. (2008), Garcia et al. (2006), Rowell et al. (1995)	Better dimensional stability Reduced water absorption Slight reduction or improvement of mechanical properties (it appears that the conditions of the pretreatment affect these results)

water than formulations based on HDPE + unextracted pine and PP+ unextracted pine, respectively. Thickness swelling (TS) was reduced by 45 and 59 %, respectively, after 2,520 h of immersion (Fig. 7). Modulus of rupture (MOR) in bending was increased by approximately 15 and 13 % in treated pine + HDPE and treated pine + PP, respectively. The water diffusion constant was decreased by approximately 36 %. This improvement in water resistance and mechanical properties was attributed mainly to the removal of hemicelluloses.

Westin et al. (2008) analyzed the effect of thermal pretreatment of wood on decay resistance of WPCs produced with bio-derived raw materials (cellulose

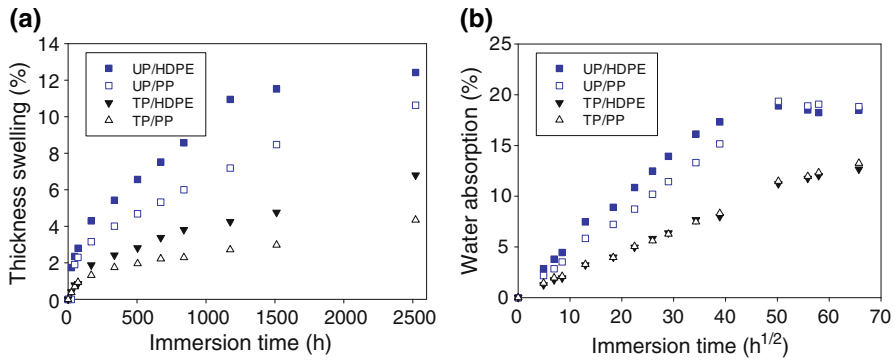


Fig. 7 Comparison of water absorption (a) and thickness swelling (b) of WPCs produced with pretreated and untreated pine (TP and UP, respectively) (Pelaez-Samaniego et al. 2012)

acetate propionate–CAP or poly-lactic acid–PLA). Thermal modification was conducted in accordance with the Thermowood[®] process (Mayes and Oksanen 2002) at a temperature of 212 °C. The authors combined 50 % of treated wood with 50 % of CAP or PLA for manufacturing injection-molded WPCs that were tested in laboratory conditions. Another set of WPCs specimens were manufactured via extrusion combining 60 % of wood with 40 % of CAP and tested in field conditions. Laboratory tests consisted of exposing WPCs specimens to attack by three types of fungi (*Postia placenta*, *Coniophora puteana*, and *Gloeophyllum trabeum*) over 10 weeks. Field tests consisted of a two-year in-ground test and a test of specimens subjected to marine exposure. Results showed better resistance to decay of all specimens produced with thermally modified wood. In-ground tests, on the other hand, showed that buried WPCs specimens produced with treated wood resisted the attack of terrestrial microcosms after 32–47 weeks. Specimens tested on the marine field also resisted the attack of shipworm. WPCs produced with thermally treated wood and CAP showed equal or better mechanical properties than boards produced with untreated wood. Improved resistance to decay of WPCs produced with thermally treated wood has also been observed by Hosseinaei et al. (2012b).

It has been reported that long-term storage of WPCs produced with heat-treated wood affects mechanical properties of extruded WPCs. Follrich et al. (2010) investigated the effect of thermal pretreatment of wood in dry conditions, using a kiln (presumably in inert environment) and the effect of storing samples under constant conditions after 5 years. The authors showed that WPCs specimens stored for a long time had an increased Young's modulus and decreased strain, and that tensile strength was higher than that recorded on composites tested immediately after production. Flexural tests showed that modulus of elasticity (MOE) increased, but MOR decreased. The increase in mechanical properties of WPCs was attributed to possibly improved interactions between OH groups of thermally treated wood and the degradation of polymer chains emerging during the long-term storage.

WPCs produced with thermally treated eucalyptus (using steam at 180 °C for 40 min) reduced TS by more than 80 % and WA by more than 70 % after 28-day submersion compared with untreated wood (Ayrlimis et al. 2011a). Thermal

pretreatment was responsible for decrease of screw withdrawal resistance. Additionally, MOR and MOE were reduced up to 19 and 22 %, depending on the conditions of the treatment. Temperature during treatment impacted on results more than time. They attributed the reduction of mechanical properties to the reduction of the degree of wettability of wood after the thermal treatment.

Startsev et al. (1999) used steam explosion to modify wood prior to manufacturing wood–plastic pressed panels (referred to as “thermobalite”). Mechanical and durability tests showed that MOR was doubled in comparison with particleboard produced with untreated wood. WA was reduced to half in comparison with common particleboard. The authors also found that the glass transition temperature of the products was reduced, and the degree of crystallinity of cellulose was not affected considerably during the pretreatment.

Angles et al. (1999) conducted steam explosion pretreatment to modify softwood sawdust prior to the production of extruded WPCs. The authors produced WPCs using treated wood and PP with and without maleic anhydride-polypropylene copolymer (MAPP) as compatibilizer. WPCs produced with treated wood without compatibilizer presented, in general, similar physical and mechanical properties to WPCs produced with untreated wood. WPCs that included the compatibilizer presented a better adhesion due to the positive effect of MAPP. This observation suggested that thermal pretreatment improved compatibility between MAPP and wood, resulting from the increase in roughness on the surface of the fibers and changes on chemical composition of wood. Tensile strength and modulus were increased in the presence of MAPP, which was attributed to better adhesion between treated wood and PP. Good bonding between these materials in the presence of the compatibilizer was, therefore, the main factor that affected mechanical properties.

Effect of wood thermal pretreatment on binderless panels

Angles et al. (2001) produced binderless panels with steam-exploded wood. In some experiments, the authors added sulfuric acid during the steam treatment to increase the severity factor. Severity factor was evaluated using the R parameter (Eq. 1):

$$R[\text{min}] = \int_0^{t[\text{min}]} \exp\left(\frac{T[^\circ\text{C}]}{14.75}\right) dt \quad (1)$$

where T refers to temperature and t to time (Angles et al. 2001). Increase of pretreatment severity factor increased surface energy and reactive area (Table 2). The entirety of the fibers was reduced when severity factor was increased. Presence of coalesced lignin (in the form of small droplets) on the surface of the fibers was observed. The panels were produced, in some experiments, adding lignin to the pretreated wood in percentages of 5, 10, and 20 %. Mechanical and physical properties of the panels improved as the severity factor increased to a maximum, which corresponded to R approximately equal to 4 (better internal bonding was attributed to depend on the higher amounts of lignin). Panels produced with wood treated at severity $R = 4$ showed that WA and TS were reduced more than three

times, while MOR and MOE increased more than twice, compared with controls. After $R = 4$, mechanical and physical properties dropped drastically. The addition of lignin did not affect the density, internal bonding, and thickness swelling of the boards. However, MOR was notably increased by the addition of 20 % of lignin.

Another study related to binderless hardboard was carried out by Suchsland et al. (1987), who found that both mechanical properties and resistance to water are improved up to a maximum pressure of 2.8 MPa during thermal pretreatment. Further increases of pressure impacted negatively mechanical properties, and water resistance was not increased.

Effect of wood thermal pretreatment on particleboard

Hsu (1986) and Hsu et al. (1988) reported steam pretreatment as a method for improving dimensional stability of wood-based composites such as waferboard and particleboard. The authors removed part of the hemicelluloses from wood by steam pretreatment under different conditions. Results of chemical analysis of the residual solid fraction showed that hemicelluloses are reduced during the thermochemical process and that cellulose and lignin remain mostly intact. The authors hypothesized that “the partial hydrolysis of hemicelluloses increases the compressibility of wood, reduces the tendency for stresses to be built-up in pressed composites, and lowers the springback of the compressed wood” (Hsu et al. 1988). MOR was not affected, and MOE was improved. Internal bonding (IB) was reduced slightly. For particleboard, linear expansion and thickness swelling were reduced significantly. They observed that longer treatments tended to improve physical properties. MOR of particleboard was not significantly changed, and MOE was improved after steam pretreatment. IB slightly decreased with longer treatments (Table 2).

Sekino et al. (1999) produced particleboard with steam-treated wood and studied the effect of pretreatment at different temperatures on bond quality, recovery stress of compressed wood, and thickness swelling. Dimensional stability of particleboard was increased. This resulted from reduction of internal stresses imposed on adhesive bonds and a subsequent improvement of adhesive bonds. As in other studies, thickness change was considerably reduced in particleboard after using steam-treated wood. Reduction of swelling was correlated with reduction of both hygroscopicity and elasticity of wood particles. An additional study with steam-treated wood for manufacturing particleboard (Borysiuk et al. 2007) showed mechanical properties slightly decreased when treated wood is used. Thickness swelling was reduced for birch panels, but increased for pine.

Boonstra et al. (2006) reported the effect of a two-stage (hydrotreatment plus curing) thermal treatment of wood chips on swelling, IB, and durability of particleboard. The pretreatment was conducted with steam at temperatures below 200 °C. They found that the reduction in swelling of particleboard manufactured with particles that were only hydrotreated (without the curing stage) was greater than when the curing process was added. Moreover, the IB and the EMC of particleboard produced with one-stage heat-treated wood was higher than that of particleboard produced with the two-stage treated wood (Table 2). The effect of temperature was more important than the effect of treatment duration on the

properties of particleboard. Particleboard was also produced with thermally modified pine (species unknown) in dry conditions (nitrogen atmosphere) by Ohlmeyer and Lukowsky (2004). The authors pressed panels under different conditions to study the effect of thermal pretreatment. Their results show that EMC of panels pressed with treated pine is reduced by up to 10 % (environment was 65 % RH and 20 °C), TS is reduced up to 13 %, and WA is reduced by more than 20 %, in comparison with controls. Tests of mechanical properties showed that while MOE is approximately the same, MOR and IB are considerably reduced (up to 25 and 30 %, respectively) in particleboard panels manufactured with treated pine.

Effect of wood thermal pretreatment on oriented strand board

Paredes (2009) studied the effect of HWE in oriented strand board (OSB) manufacture. According to the author, HWE improves dimensional stability of OSB. Mechanical properties of OSB manufactured with softwood are enhanced, but they are reduced when hardwood is employed. IB was slightly reduced as consequence of HWE (Table 2). The extraction time had a significant effect on properties of strands. Strand thickness and tree source did not influence WA (Paredes et al. 2008, 2009). The work reported by Howell et al. (2009) adds information to the works of Paredes and coworkers on the effects of HWE on OSB produced with HWE red maple. They tested the effect of brown rots (*M. incrassata* and *G. trabeum*) and white rots (*P. sanguineus* and *I. lacteus*) on OSB and found limited effect of HWE on the susceptibility of OSB to decay. Similar results were also reported by Taylor et al. (2008), who found a slight increase in resistance of OSB to mold attack, although not statistically significant.

Another work related to the production of OSB (Paul et al. 2006) found that the thermal pretreatment leads to a reduced EMC of the OSB panels. TS was significantly lower when treated wood was used, independently of the resin used. IB was better for treated wood. However, WA was not reduced when melamine-urea-phenol-formaldehyde (MUPF) and PF resins were used and only polymeric diphenyl methane diisocyanate (pMDI)-bonded panels absorbed less water, showing an additional effect of the type of resin. They also reported that mechanical properties (MOE and MOR) of OSB panels were reduced up to 30 and 50 %, respectively, after the pretreatment of the wood. Durability tests of thermally modified strands used for OSB showed improved fungal resistance in comparison with untreated material (Paul et al. 2007). Some results of Paul et al. (2006) are corroborated by the work of Mendes et al. (2013). The work of Mendes et al. (2013) also compared the effects of thermal pretreatment of strands with the effect of thermal posttreatment of the OSB panels and concluded that pretreatment has a more visible impact in terms of reduction of mechanical properties and improved resistance to the effect of moisture. The authors observed that the thermal pretreatment of strands improved the positive effect of added wax, which suggested better compatibility between wax and pretreated wood.

Effect of wood thermal pretreatment on waferboard

Only work on the use of thermally modified wood for production of waferboard was reported by Hsu et al. (1988). The authors found that the impact of steam explosion on waferboard is similar to the impact on particleboard. Dimensional stability of the composite was increased. Mechanical properties were susceptible to the temperature at which the pretreatment was carried out because high temperatures appear to impact the mechanical properties negatively.

Effect of wood thermal pretreatment on flakeboard

Production of flakeboard using hemicelluloses extracted pine has been reported by Hosseinaei et al. (2011). The extraction process was responsible for mass loss up to 24.6 ± 3.1 % and increase in the degree of crystallinity of wood. The flakeboards produced with treated wood showed increased MOE and MOR. IB results met standard requirements, but were reduced after hemicelluloses removal. TS and WA were significantly reduced after HWE, and thus, dimensional stability was improved. The removal of hemicelluloses was attributed to be the main reason for the reduction of hydroxyl groups and hygroscopicity.

Effect of wood thermal pretreatment on fiberboard

Medium density fiberboard (MDF) panels produced using rubberwood (*Hevea brasiliensis*) fibers and UF showed that wet thermal treatment was responsible for a reduction of TS. But thermal pretreatment negatively affected WA for treatment conditions at temperatures above 120 °C, independent of the treatment time (Ayrlimis et al. 2011b). This result, according to the authors, can be explained by the fact that no wax or other substances that limit or reduce hydrophilicity were used. Mechanical properties (MOR and MOE) were reduced as a consequence of the wood thermal pretreatment. Nevertheless, values of MOR and MOE met the minimum requirements of EN 622–5 standard for MDF. IB was also negatively affected by the thermal treatment, which was attributed to the reduction of polarity of the wood surface, resulting in less wettability and, therefore, less adhesion between wood and UF (Ayrlimis et al. 2011b). Another work (Mohebbi et al. 2008) found similar results: water absorption of MDF manufactured with wet thermal pretreated wood was not affected, thickness stability was improved, and mechanical properties were reduced. Garcia et al. (2006) showed also reduction of thickness swelling and water absorption of MDF after water soaking. The authors showed that the springback of panels after repeated cycles of adsorption and desorption do not change after thermal pretreatment of wood. According to this work, MOR, MOE, and IB did not show statistically significant differences between panels manufactured with treated and untreated panels. Very low density fiberboard produced with steam-treated wood showed reduction of thickness swelling higher than 60 %. MOE did not show changes, while MOR and IB showed a slight reduction as consequence of using thermal pretreatment (Rowell et al. 1995).

Results of the different works presented confirm that the main factor contributing to improvement of dimensional stability and reduction of water absorption of wood composites is the removal of hemicelluloses, which occurred normally at temperatures above 150 °C in the presence of either water or nitrogen. Thermal pretreatment of wood and bark at temperatures at which hemicelluloses are not removed (100 °C or less) showed negative effects on particleboard (Zheng et al. 2006; Ngueho Yemele et al. 2008). Water absorption and thickness swelling of particleboard manufactured with pretreated wood at or below 100 °C were increased by approximately 31 and 21 %, respectively (Zheng et al. 2006). The authors hypothesized that the removal of some extractives (salts and phenolic substances) and the increase of pH of wood during the thermal pretreatment could have reduced wood-adhesive compatibility and affected negatively particleboard properties. Similarly, particleboard produced from extracted bark at 100 °C showed reduction of mechanical and physical properties compared with controls (Nguého Yemele et al. 2008). Removal of hot-water-soluble extractives (as per ASTM D1110-84) has, on the other hand, reduced the time required to reach maximum heat flux during the manufacture of wood-gypsum-cement particleboards (Espinoza-Herrera and Cloutier 2008).

Disposal or use of hemicelluloses-rich fractions

Thermal treatment of 1 m³ of spruce can liberate up to 40 kg of different compounds that require some type of treatment to avoid environmental loading (Militz 2002). Burning of gases has been the common operation to reduce that load. However, the recovery of the extracted hemicelluloses-rich fractions could positively impact the simultaneous production of wood composites and other high-value products. Hemicelluloses-rich fractions have been studied for the production of ethanol and lactic acid via fermentation using *Escherichia coli* K011 and *Bacillus coagulans* MXL-9 (Walton 2009). This author showed that, since the hemicelluloses extracts do not contain sufficient sugars, sugar concentration steps are necessary to make production of ethanol attractive. Evaporation and ultrafiltration were tested as concentration steps, but resulted in poor yields of ethanol (1 %) and lactic acid (3 %). Baddam (2006) showed that hot water extracts can be used for the production of carboxylic acids. During the process, steps to inhibit the production of methane were necessary. Mixed microbial cultures were capable of converting glucose and xylose sugars and hydrolyzing oligomeric hemicelluloses without addition of supplemental enzymes. Other works mention a diversity of options for using the extracted liquor in biorefinery concepts (Amidon et al. 2008; Amidon and Liu 2009). Since most of these alternatives have been tested at laboratory scale, economic aspects are not reported in the works analyzed in this paper.

Literature regarding emissions when HWE wood is used for the manufacture of engineered wood products is poor. A recent work conducted by Paredes et al. (2010) compared the emissions resulting from the hot pressing of OSB produced with extracted and unextracted wood. They analyzed VOCs, phenol content, and the

content of other compounds such as methanol, formaldehyde, and acetaldehyde. Phenol emissions were not detected on treated or on untreated wood processing. Methanol emissions were not significantly affected by hemicelluloses extraction. However, acetaldehyde and formaldehyde emissions were reduced after HWE.

Further work

Removal of hemicelluloses from wood by means of thermal treatment, keeping most of the cellulose and lignin, is responsible for reduced water-composites affinity and, in most cases, increased mechanical properties of wood composites. The importance of lignin in wood composites has been recognized since the 1920s (Mason 1928). Lignin could act as a binder (especially in wet environments) (Mason 1928; Byrd 1979; Suchsland and Woodson 1986; Back 1987; Angles et al. 2001), as a bio-protection agent (Agbor et al. 2011; Chirkova et al. 2011), and as a water repellent (Horn 1979; Winandy and Rowell 1984; Hosseinaei et al. 2011; Klüppel and Mai 2012). However, it is apparent that more work is required to understand how the lignin and/or lignin-derived compounds (deposited on the surface of wood fibers) and the structural changes of wood resulting from thermal treatment (e.g., change of porosity) impact the manufacturing process and the properties of wood composites. Understanding these phenomena could contribute to a better control of the pretreatment operations. Likewise, additional study on the impact of thermal pretreatment on the durability of wood composites under outdoor conditions is necessary.

Conclusion

Thermal pretreatment either in “wet” or “dry” environments is used to modify the composition and the structure of wood. The main effects of thermal treatment are the removal of hemicelluloses, the increase of the degree of crystallinity of amorphous cellulose, or the depolymerization of long-chain hydrocarbons and lignin. Although a reduction of mechanical properties of thermally modified wood has been observed, thermal treatment of wood is the most commercially developed strategy to modify wood characteristics. There exists a renewed interest in using heat-treated wood for the production of wood composites due to the advantages of employing less hydrophilic wood. Improved resistance to water absorption and dimensional stability was observed in particleboard, OSB, MDF, and WPCs produced with low hemicelluloses-content wood. In general, mechanical properties are increased, although a slight reduction has been reported in some cases. The engineered wood industry offers the advantage of using thermally modified wood without the necessity of isolating lignin and the possibility of recovering hemicelluloses-rich fractions to produce by-products. Research at larger scale is necessary to determine the advantages of integrating the manufacture of wood composites with thermal pretreatment of wood.

Acknowledgments This project was funded through the USDA Forest Service Research and Development Woody Biomass, Bioenergy, and Bioproducts 2009 Grant Program. M.R. Pelaez-Samaniego acknowledges the Fulbright Faculty Development Program Scholarship.

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