HYDROGEN BONDING IN WOOD-BASED MATERIALS: AN UPDATE

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Abstract. The contribution of hydrogen bonding to wood science and technology has been well recognized over the past century. The hydrogen bond is an important chemical characteristic contributing to wood-based material behavior and it also provides an important contribution to processing features of wood. However, the current understanding of hydrogen bond strength as a contributor to wood-based material behavior has not been updated in the wood literature. Wood-based material literature typically report hydrogen bond strengths ranging from 12.6 to 25.2 kJ/mol (3-6 kcal/mol) while newer data from the general chemistry field report hydrogen bond strengths up to 189 kJ/mol (45 kcal/mol), which are characteristic of covalent bond strength. In light of these new data regarding hydrogen bond strengths, it provides impetus to discuss the new understanding of hydrogen bond strength relative to wood-based material behavior. Recent developments in nanotechnology of renewable materials leading to the production and applications of cellulose nanomaterials with much higher surface areas and hydrogen bonding capacity also mandate revisiting our knowledge of the hydrogen bonding mechanism and strength.

Keywords: Hydrogen bond, wood, material behavior, bond strength, nanomaterials.

INTRODUCTION

The role of hydrogen bonding in wood-based materials has been long recognized, and as such is a fundamental topic of discussion relative to their material property characteristics including cell wall architecture, interactions among cell wall chemical components, and especially wood-water relations (Stamm 1964; Panshin and DeZeeuw 1980; Skaar 1988). The hydroxyl functional group that is contained in the primary cell wall chemical components (cellulose, hemicellulose, and lignin) as well as a range of secondary components (extractives) plays a major role in the hydrogen bonding behavior of wood-based materials. Hydrogen bonding among wood cell wall components and/or water contributes to wood strength (Winandy and Rowell 1984), viscoelastic behavior (Kelly et al 1987), adhesion (Gardner et al 2008; Gardner et al 2014) as well as processing characteristics of wood (papermaking, preservation, machining, drying, etc.) (FPL 2010). The historical view of hydrogen bond strength in materials like wood and cellulose describes hydrogen bond strength as relatively low energy (Bochek and Petropavlovsky 1993). Recent evidence supports that hydrogen bond strengths can be considerably larger than earlier believed and approach the bond strength of covalent bonds (Gilli and Gilli 2009). With this in mind, it is the purpose of this paper to explore the current understanding of hydrogen bonding from both theoretical and experimental stand points and how these relate to wood-based materials properties and behavior. It should be pointed

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out that the concepts being presented here relative to hydrogen bonding in wood may not be universally accepted and may also be considered somewhat controversial. However, it is hoped that the concepts presented in this paper will spur a healthy dialog among wood scientists in augmenting our basic understanding of wood cell wall behavior.

Hydrogen Bond Definition

"The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. A typical hydrogen bond may be depicted as X–H⋯Y–Z, where the three dots denote the bond. X–H represents the hydrogen bond donor. The acceptor may be an atom or an anion Y, or a fragment or a molecule Y–Z, where Y is bonded to Z. In some cases, X and Y are the same. In more specific cases, X and Y are the same and X–H and Y–H distances are the same as well leading to symmetric hydrogen bonds. In any event, the acceptor is an electron-rich region such as, but not limited to, a lone pair of Y or π-bonded pair of Y–Z. The evidence for hydrogen bond formation may be experimental or theoretical, or ideally, a combination of both" (Arunan et al 2011).

In wood, X–H⋯Y–Z can be represented by O–H⋯O–C for interactions between hydroxyl groups of one chemical component and the hydroxyl of another chemical component or water or between two molecules of the same component.

Current State of the Art regarding Hydrogen Bond Strength

Recent references from the chemical literature define hydrogen bonds in to three types: weak, moderate, and strong (Table 1) (Steiner 2002; Parthasarathi et al 2006; Gilli and Gilli 2009). The weak hydrogen bond exhibits characteristics of electrostatic bond behavior and bond energy of 4.2-16.8 kJ/mol (1-4 kcal/mol), the moderate hydrogen bond exhibits characteristics of both electrostatic and covalent bond behavior with bond energies ranging from 16.8 to 63 kJ/mol (4-15 kcal/mol), and the strong hydrogen bond exhibits mostly covalent bond behavior and bond strengths ranging from 63 to 189 kJ/mol (15-45 kcal/mol).Hydrogen bonds feature binding energies and contact distances that do not simply depend on the donor and acceptor nature. Rather the hydrogen bonding chemical context can lead to large variations even for the same donor-acceptor molecules. Hydrogen bonds vary in bond length and hydrogen bond strength increases with increase in electron density and decreased bond distance (Fig 1). For comparison purposes, the bond strength of various types of chemical bonds and intermolecular forces are listed in Table 2. As such, the strong hydrogen bond strength overlaps with the bond strength of covalent bonds. As will be discussed later, the hydrogen bond strength for cellulose fibril bonding has been experimentally shown to fall in the moderate range.

Hydrogen Bond Strength for Isolated Wood Components

Considerable research effort has focused on the material property behavior of individual wood

Table 1. Some properties of weak, moderate, and strong hydrogen bonds (H-bond).[a]

H-bond	Weak H-bond	Moderate H-bond	Strong H-bond
D-H⋯:A bond	Electrostatic	Electrostatic covalent	Mostly covalent
Bond lengths (nm)	0.22-0.4	0.15-0.32	0.12-0.25
D-H-A angle (°)	90-150	130-180	165-180
Bond energy, E_{HB} (kcal/mol)	1-4	4-15	15-45
Bond energy, E_{HB} (kJ/mol)	4.2-16.8	16.8-63	63-189

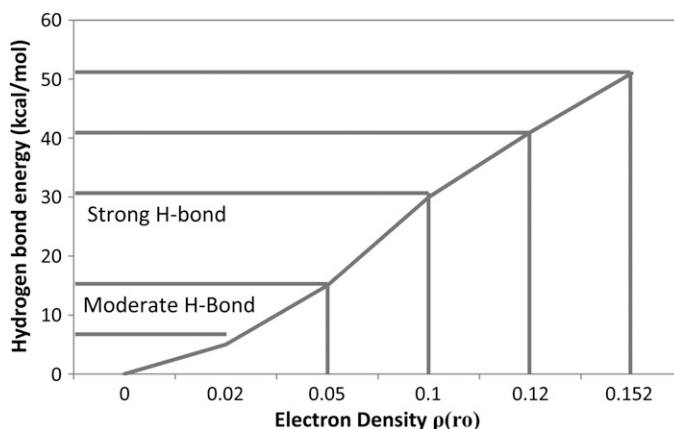[a] Adapted from Table 2.4 (Gilli and Gilli 2009).

Figure 1.   Hydrogen bond energy as a function of functional group electron density. Adapted from Figure 1 (Parthasarathi et al 2006).

chemical components to ascertain the material properties of wood. Analytical techniques to study hydrogen bonding include Fourier transform IR spectroscopy (FTIR), carbon 13 nuclear magnetic resonance spectroscopy (C-13 NMR), as well as molecular modeling. Indirect methods to study the impact of hydrogen bonding include X-ray diffraction (XRD), swelling studies in various solvents with different hydrogen bonding character, thermal analysis methods like dynamic mechanical analysis, and differential scanning calorimetry.

Because of its importance to wood-based material behavior, cellulose has received much attention. The hydrogen bonding that occurs among cellulose molecules is depicted in Fig 2 (O'Sullivan 1997). A common view of hydrogen bond strength behavior in cellulose suggests that the energy of hydrogen bonds in cellulose is up to 25.0 kJ/mol

and because the energy of hydrogen bonds in water ranges from 18.0 to 21.0 kJ/mol, cellulose is insoluble in aqueous media (Bochek and Kalyuzhnaya 2002). In highly crystalline cellulose, it is necessary to break both intermolecular hydrogen bonds and most intramolecular hydrogen bonds to dissolve cellulose and each cellobiose unit will have a pair of hydrogen bonds between them in the repeating cellulose chains or a moderate hydrogen bond strength of 50 kJ/mol (12 kcal/mol) for each cellobiose unit (Bochek and Petropavlovsky 1993). A recent review discussing proposed mechanisms for cellulose microfibril coalescence in chemical pulp fibers during chemical treatments summarizes the debate surrounding this topic relative to hydrogen bonding (Ponni et al 2012). The creation of irreversible hydrogen bonds between hydroxyl groups among cellulose microfibrils has been surmised going back 50 yr

Table 2.   Bond strength of various types of chemical bonds and intermolecular forces.[a]

Chemical bond or intermolecular force	Bond strength (kcal/mol)	Bond strength (kJ/mol)	Bond length
Electrostatic (ionic)	100	418	0.1-1 μm
Lifshitz-van der Waals	2-5	8.4-21	0.5-1.0 nm
Covalent bonding	35-150	147-628	0.1-0.2 nm
Hydrogen bonding (new)[b]	1-45	4.2-188	0.15-0.45 nm
Hydrogen bonding (old)	3-6	12.6-25.1	0.1-0.3 nm

[a] Adapted from Gardner et al 2014.
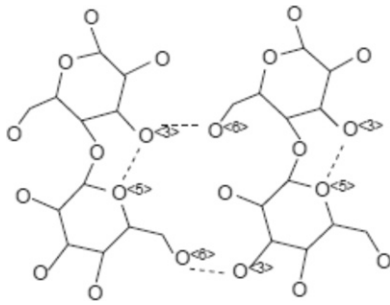[b] Adapted from Gilli and Gilli 2009.

Figure 2. Hydrogen bonding pattern for cellulose I. Adapted from O'Sullivan (1997).

although the scientific basis has never been fully elaborated (Ponni et al 2012).

The organized structure of repeated hydrogen bonding within crystalline regions may be sufficient to account for the irreversible hydrogen bonding in cellulose. Indeed, irreversible hydrogen bonds are evident in crystalline cellulose especially characteristic of cellulose nanocrystals (CNC) isolated from wood pulp during the acid hydrolysis process. Certain drying conditions for cellulose either in the pulp fiber form or the nanoscale fiber form like CNC can lead to the formation of "hornified" pulp fibers or agglomerated CNC particles that exhibit the well-known characteristic of irreversible hydrogen bonding (Higgins and McKenzie 1963; Peng et al 2012). The irreversible hydrogen bonds in cellulose are difficult to disrupt through chemical, mechanical, and thermal means. Bond accessibility is important in breaking chemical bonds but bond strength is as important.

Because of the hydrogen bonding that occurs among cellulose chains and the propensity to form highly crystalline structure, cellulose has a subtle glass transition temperature behavior as determined by differential scanning calorimetry (Szczesniak et al 2008). In essence, cellulose behaves like a thermosetting polymer because of the strong hydrogen bonding cross-links and this supports the long-known thermal degradation and crystallinity characteristics of cellulose (Peng et al 2013). Cellulose does not exhibit substantial softening behavior prior to thermal

degradation and cellulose isolated from wood can exhibit crystallinity up to 80% on the nanoscale. Recent molecular modeling work using ab initio calculations has documented theoretical hydrogen bond strength between paired cellulose chains with a degree of polymerization of 7 at 202 kJ/mol (48 kcal/mol) (Qian 2008). From the molecular modeling simulations, the cumulative cooperative hydrogen bonding energy in a paired cellulose chain is much larger than the corresponding isolated cellulose chain. The cooperative hydrogen bonding energy is significant and offers convincing evidence as to the recalcitrant nature of crystalline cellulose to chemical hydrolysis or solubilization and supports the long-known observations concerning the thermal properties and strength behavior of cellulose.

Theoretical measurements of hydrogen bond strength in lignin and hemicellulose are not currently available but there are studies examining hydrogen bonding behavior of isolated lignin and hemicelluloses as well as model compound and composite studies. Model compound studies on lignin indicate stronger hydrogen bonding in the aliphatic side chain hydroxyl groups as compared with phenolic groups and softwood lignin appears to have greater intensity of hydrogen bonding than hardwood lignin (Kubo and Kadla 2005). During the drying of nanofibrillated pulp composites, the presence of hemicelluloses impedes the formation of irreversible hydrogen bonds between nanofibrils by physically inhibiting their direct contact facilitating mechanical defibrillation (Iwamoto et al 2008). Lignin and hemicellulose exhibit more amorphous character than cellulose and this has been well documented in studies that examined the solubility behavior and swelling behavior as well as viscoelastic behavior of wood (Kelly et al 1987; Mantanis et al 1994a, 1994b; Hansen and Bjorkman 1998). Lignin and hemicellulose display definite glass transition temperatures and they are strongly influenced by solvents that have similar solubility parameters as water. Both hemicellulose and especially lignin influence the hygrothermal softening of wood, which is a characteristic property of wood and is used in wood material processing,
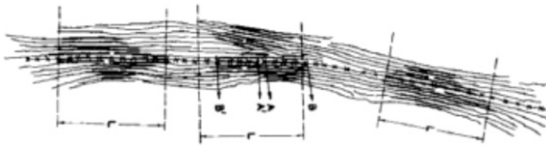
Figure 3.   Main-valence chains going through more than one micella. Adapted from Mark (1940).

eg, thermomechanical pulping and steaming logs prior to veneer cutting.

Cell Wall Models

Models of the cell wall architecture have been around since the middle of the last century with the description of the fibrillary structure of cellulose by Mark (1940) (Fig 3). Model descriptions of the cell wall have been refined with improvements in analytical instrumentation over the years from the electron microscopic studies during the 1950s and 1960s (Cote 1967) up to the present with applications of atomic force microscopy and nanoindentation (Wimmer and Lucas 1997; Zimmermann et al 2006). The nanostructure of cellulose microfibrils in wood is fairly well described (Fernandes et al 2011). Applications of genetics and genomics have been important tools in providing a better understanding of the formation and growth of the plant cell wall (Mellerowicz et al 2001; Cosgrove 2005). Model refinements have allowed the study of topics including: wood cell wall mechanical behavior (Saavedra Flores et al 2011), reaction wood (Barnett and Bonham 2004), swelling behavior during drying (Yamamoto et al 2001), adhesion measurements (Gustafsson et al 2012), and degradation behavior based on lignin chemistry (Grabber 2005).

Do We Need to Augment Our Interpretation of Wood Cell Wall Molecular Structure and Behavior?

If one considers that hydrogen bond strength within and among cell wall chemical components may indeed be much larger than previously thought, do we need to augment our interpretation of wood cell wall molecular struc-

ture and behavior? The organizational hierarchy of polymers within the cell wall is relatively well understood from the nanoscale through the macroscale (Fig 4). Based on the premise of stronger hydrogen bonds, it is proposed that the cellulose molecules contained within the elementary fibrils can now be considered a cross-linked polymer structure within the crystalline regions and an agglomeration of linear molecules within the amorphous regions. Within the fibril-matrix structure length scale of the cell wall layers, the wood cell polymers could be considered as a network of highly cross-linked cellulose fibrils that are interdispersed with a partially cross-linked lignin-hemicellulose complex (Lawoko et al 2005). As such, the fibril-matrix structure of wood on the nanolength scale meets the definition of an interpenetrating polymer network (IPN) (Sperling 2012).

The IUPAC defines an IPN as "A polymer comprising two or more networks which are at least partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken." A more detailed description of IPNs can be found in Sperling 2012. With the above description, the wood cell molecular architecture fits the specific definition of a "**sequential interpenetrating polymer network**: which is an *Interpenetrating polymer network* prepared by a process in which the second component network is formed following the formation of the first component network." Since lignification in the secondary cell wall of wood occurs after the secondary cell wall is formed, the definition of a sequential IPN is very compelling for the interpretation of cell wall molecular structure, and was described as such by Funaoka et al (1995). A recent model depicting the wood polymer assembly during the secondary wall formation also supports this interpretation (Fig 5) (Ruel et al 2006).

Contribution of Hydrogen Bonding to Adhesion in Wood-Based Composites

Studying the theories or mechanisms responsible for wood adhesion is an important aspect of
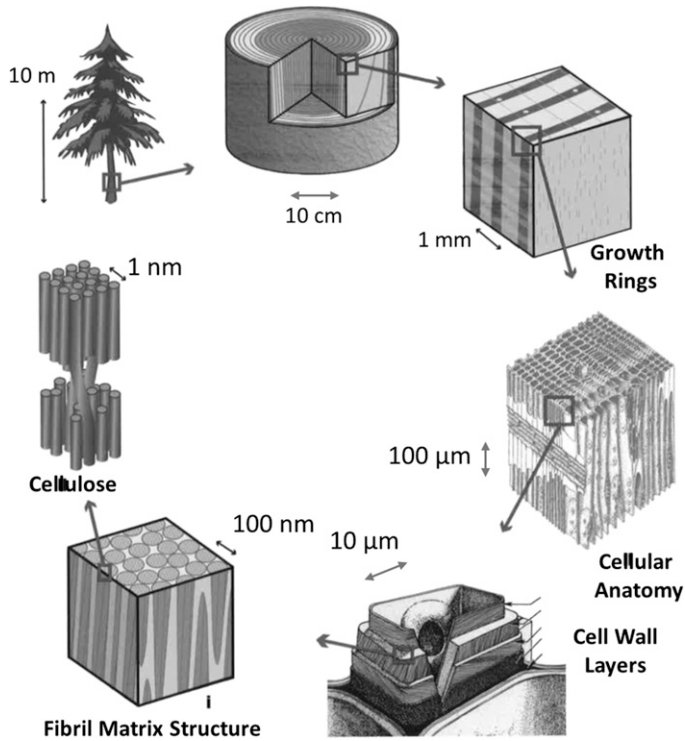
Figure 4.   Schematic of wood hierarchal structure. Adapted from Moon et al (2006).

wood science and technology research. It is anticipated that improvements in the understanding of wood adhesion mechanisms have the potential to result in better adhesive systems and more efficient and effective processing methods for the wide array of wood and wood-based composite materials. For wood adhesive bonding, studying adhesion theories requires an understanding of wood material characteristics, surface science, and the interactions between adhesives and wood surfaces. At present, no practical unifying theory describing all adhesive bonds exists, although a unified adhesion theory has been proposed. Chung (1991) proposed an approach to consolidate adhesion theories related to chemical bonding/intermolecular forces into one coherent concept. The maximum attractive force between two molecules is derived from the Lennard-Jones potential function and calculated with measured bond length and bond energy. Two criteria are required for strong adhesion: intimate molecular contact of closer than 0.9 nm (necessary condition) and maximum attractive force with minimum potential energy (sufficient condition). Hydrogen bonds meet the criteria of intimate molecular contact and maximum attractive force (Table 2) and
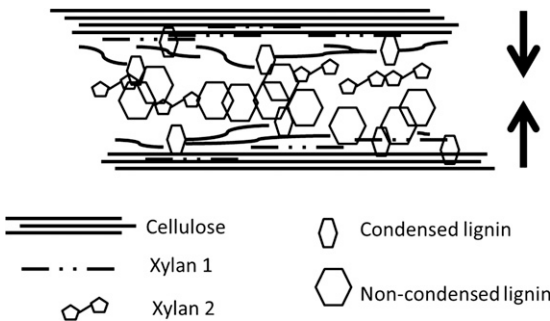

Figure 5.   Proposed schematic representation of polymer assembly during the secondary wall formation. Adapted from Ruel et al (2006).

can be therefore assumed to contribute much to the adhesion strength.

The state-of-the-art categorizes adhesion theories or mechanisms in seven models or areas as follows:

1. Mechanical interlocking theory
2. Electronic or electrostatic theory
3. Adsorption (thermodynamic) or wetting theory
4. Diffusion theory
5. Chemical (covalent) bonding theory
6. Acid-base theory
7. Theory of weak boundary layers

These adhesion theories have been used to describe wood adhesion behavior (Gardner et al 2014), and several of the theories (chemical bonding theory and acid-base theory) can incorporate hydrogen bonding in describing adhesion behavior. A chemical or covalent bond is a bond where two atoms share an electron pair and is believed to improve the bond durability between wood and an adhesive. Recent research in wood-adhesive covalent bonding focused on polymeric isocyanate (PMDI)-based adhesives, since they are most likely to form urethane (or carbamate) bonds with wood polymers and are shown to penetrate the wood cell wall and intimately associate with wood molecules (Wendler and Frazier 1996; Marcinko et al 1998). It is very unlikely that covalent bonds form in any significant amount under conditions characteristic of thermosetting wood adhesive applications, even though the formation of covalent resin-substrate bonds has been demonstrated to exist. Hydrogen bonds that were shown earlier to approach the strength of covalent bonds are very likely to dominate the chemical bonding character of wood adhesive bonds.

According to Fowkes (1983) and van Oss et al (1987), the total work of adhesion in interfacial interaction between solids and liquids can be expressed as the sum of the Lifshitz-van der Waals (LW) and the Lewis acid-base (AB) interactions, viz.

$$W_a = W_a^{LW} + W_a^{AB} \qquad (1)$$

where W_a is the total work of adhesion and W_a^{LW} and W_a^{AB} are work of adhesion Lifshitz-van der Waals and the Lewis acid-base, respectively.

Hydrogen bonding is considered an important subset of the acid-base component contribution. The separation of the work of adhesion into LW and AB components is also applicable to the surface free energies as demonstrated in

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \qquad (2)$$

The acid-base theory plays a critical role in surface chemistry and adhesion and it has been exploited broadly on different materials (Mittal and Anderson 1991; Mittal 2000). Several models of calculating the surface energy of solids have been proposed where acid-base theory is applied, including Fowkes's method, Good's method, van Oss's method, and Chang's method (Etzler 2013). For chemically heterogeneous materials like wood, the acid-base approach is a valuable method because it can provide the most detailed information about the surface chemistry including the values of Lifshitz-van der Waals (dispersion) and Lewis acid-base (polar) components of surface free energy (Gardner 1996). Extractives are the dominant factor influencing the acid-base properties of wood (Wålinder and Gardner 2002). Wood surfaces with extractives exhibit less acidic (electron-accepting) character and greater basic (electron-donating) character and the Lifshitz-van der Waals (dispersion) surface free energy component increases after removal of extractives from wood (Wålinder and Gardner 2000).

Most adhesives used to bond wood have strong hydrogen bonding functionalities (Pizzi 2015). The common exterior adhesives used in wood composite production include phenol-formaldehyde (PF), and polymeric methylene diphenyl diisocyanate (pMDI). Both PF and pMDI have functional groups that will hydrogen bond with the hydroxyl groups present in wood. Interior adhesives including urea-formaldehyde (UF), protein adhesives, and poly vinyl acetate all have functional groups capable of hydrogen bonding formation. It is suggested that the hydrogen bond may significantly contribute to

the chemical bonding adhesion mechanism in wood-based materials.

Contribution of Hydrogen Bonding to the Swelling and Dissolution of Wood

It is well known that chemical bonds indeed need to be broken to separate the wood cell wall polymers. Strong acids or bases used in pulping and ionic liquids can disrupt the bonds among wood polymers. The swelling of wood and cellulose is reported to be well correlated with hydrogen bonding capacity of the swelling liquid (Bochek and Petropavlovsky 1993; Mantanis et al 1994a, 1994b). However, recent studies on the dissolution of cellulose emphasize the role of cellulose charge and concomitant ion entropy effects as well as hydrophobic interactions having the largest effect on cellulose dissolution (Lindman et al 2010; Medronho et al 2012; Medronho and Lindman 2014). The authors of these more recent papers did not consider the newer findings regarding hydrogen bond strength as they reported hydrogen bond strengths of only 21-24 kJ/mol (5.0-5.7 kcal/mol). This suggests that solvent behavior in disrupting hydrogen bonds as an important part of swelling and/or dissolution of wood can be more comprehensively explained with an expanded consideration of hydrogen bond strength.

Importance of Hydrogen Bonding in Nanocellulose Production and Cellulose Nanocomposites

Recent developments in nanotechnology of renewable materials leading to the production and applications of cellulose nanomaterials with much higher surface areas and hydrogen bonding capacity also mandate revisiting our knowledge of hydrogen bonding mechanism and strength. The aqueous counter collision (ACC) technique for the production of cellulose nanofibrils (CNFs) developed by Kondo et al (2008) is in fact based on the fact that high-energy water jets can disrupt hydrogen bonding within cellulose structure to split microfibrils into their nanoscale components. Details on the process are found in Kondo et al (2014) but briefly high-pressure (around 200 MPa) jets of a water suspension containing a cellulose suspension collide at an angle to generate enough energy to break up cellulose fibrils. It is claimed that the ACC process can only disrupt weak hydrogen bonds and van der Waals forces up to about 14 kJ/mol, thereby producing amphiphilic CNFs (Kondo 2016).

Nanocellulose films are of much interest nowadays because they provide an alternative renewable substrate for printed electronics and food packaging. The exceptional strength and barrier properties of microfibrillated cellulose films are attributed to hydrogen bonding (Syverud and Stenius 2009). In all-cellulose magnetic nanocomposites produced through partial dissolution by ionic liquids such as 1-butyl-3-methylimidazolium chloride (BMIMCl), the tensile strength of the nanocomposites was shown to be directly related to the hydrogen bonding index calculated from FTIR spectra (Mashkour et al 2014). Because BMIMCl mainly dissolves cellulose by breaking down the hydrogen bonds, partial dissolution might decrease the diameters of the cellulosic fibrous components more than it does to their lengths leading to anisotropic shrinkage reported by Mashkour et al 2014. Finally, observations made by the authors while developing new applications for CNFs as binder in adhesive-free particleboard panels show that hydrogen bonding between CNF and wood particles plays an important role in the dewatering of the composite mat making it possible to remove a considerable amount of water by a simple dewatering step from an otherwise tenaciously water containing CNF (Tajvidi et al 2016).

CONCLUSIONS

As the fundamental understanding of hydrogen bonding has evolved over the past several decades with hydrogen bond strength comparing favorably with covalent bonds, the diffusion of this knowledge into the material science arena especially lignocellulosic materials is helping

scientists to better describe the material behavior of wood. The contribution of greater bond strength of the hydrogen bond in lignocellulosic materials provides an additional piece of the puzzle to an improved understanding of wood cell wall behavior and can augment the interpretation of wood's chemical, mechanical, and physical properties; viscoelastic behavior; adhesion; and the development of novel materials as well as the processing characteristics.

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