USE OF A NEW METHODOLOGY TO ELUCIDATE ISOCYANATE ADHESION TO WOOD

Charles R. Frihart[1], Daniel J. Yelle, [1,2], Joseph E. Jakes[1,2], John Ralph[2], Donald S. Stone[2], James F. Beecher, [1]
[1] USDA Forest Products Laboratory, Madison, WI, USA
[2] University of Wisconsin-Madison, Madison, WI USA
cfrihart@fs.fed.us

Background

The chemical and structural complexity of wood has made it difficult to understand wood adhesion mechanisms. In addition, variation in anatomy and ultrastructure between tree species, within a species, and even within a single tree make it difficult to do systematic studies to understand these mechanisms. Discussions on the many factors involved in wood adhesion [1] and hypotheses on the crucial aspects for durable bonds [2] help to explain some of the fundamentals of wood adhesion. Nevertheless, it has still been difficult to prove the validity of certain hypotheses. For example, covalent bonds between the adhesive and wood have been proposed, but their formation has not been shown unambiguously. Isocyanates are known to form urethane bonds with cellulosic polymers under dry conditions. However, researchers have yet to directly demonstrate whether the common wood adhesive polymeric diphenylmethane diisocyanate (pMDI) reacts with wood [3].

Adhesive performance is usually concerned mainly with interface properties because many substrates, such as metals and plastics, are not porous, but adhesives can readily penetrate into wood. Because of wood's cellular structure, most adhesives can flow into the cell lumina to give a mechanical interlock. Additionally, low molecular weight adhesives can infiltrate the cell walls. When chemicals enter into the cell wall, they may react with the wood polymers (lignin, cellulose, hemicelluloses) or intersperse between the polymer chains. Norimoto developed models to classify the different processes [4]. In Figure 1, model B1, the ellipse represents the reaction area within the cell wall, while the two lines represent the cell wall polymers, and the small circle is the hydroxyl groups on these polymers. In the subsequent drawings, the large circle is the isocyanate that can react with hydroxyl group to give B2, crosslink the chains as in B3, bulk up the cell wall as in B4, or form its own polymer network as in B5. These models can be used to evaluate interaction of pMDI and model compounds phenyl isocyanate (PI) or benzylphenyl isocyanate (BPI) with wood.

New methods were needed to actually determine the interactions of the pMDI, PI, and BPI with the wood. One method involves being able to dissolve wood and then to run the nuclear magnetic resonance (NMR) spectra to characterize reactivity of hydroxyl groups, shown by a change in chemical shift in the ^{1}H-^{13}C peaks of wood polymers. A second method uses nanoindentation to examine for changes in the cell wall mechanical properties before and after the isocyanate infiltration into cell walls.

Experimental

Well characterized latewood loblolly pine (*Pinus* taeda) was converted to matchstick-sized (1 mm × 1 mm × 30 mm) specimens oriented parallel to the grain. The samples examined were untreated wood, wood heated to 160 °C for 2 hours, wood reacted with PI, BPI, or pMDI at 25 °C with a dibutyltin dilaurate catalyst for 2 hours, and wood reacted with PI or pMDI at 160 °C for 2 hours. To evaluate the effect of water, wood with both ≅ 0% and 14% moisture content was used in these studies. For the NMR studies, the experiments followed similar procedures outlined in previous publications [5, 6], except that a 50 °C and ~10 mbar drying was used to remove unreacted isocyanate. For nanoindentation studies, the techniques are described in detail in references 7 and 8.

Chemical Analysis of Isocyanate Interaction with Wood

The first question to answer in assigning the proper model (B1–B5 in Figure 1) for isocyanate treatment of wood was whether the adhesive formed covalent bonds with the wood, as illustrated in B2 and B3. NMR spectroscopy is a good way to characterize chemical changes in polymer structure and would allow us to determine if the isocyanate reacted with the wood polymers. We needed a method for converting wood into a solution for solution-state NMR to obtain sufficient resolution and peak dispersion. A method had been developed for analysis of

wood acetylated after ball milling [9]. We developed an extension of this method that can be used without acetylation and any separation or purification steps [5, 6]. Many of the NMR signals for the wood polymers (lignin, hemicelluloses, cellulose) were assigned using literature data and model compounds [5]. Making isocyanate-modified lignocellulosic model compounds not only provided information about their chemical shifts but also about suitable reaction conditions and reaction rates. Then, these reaction conditions were applied to wood to examine changes in chemical shifts and to confirm the regiochemistry of the hydroxyl groups that were converted to carbamates [5].

Although many wood adhesive studies show reactions using isocyanates under dry conditions, wood normally has significant moisture levels. This introduces a competing reaction of the isocyanate with water to generate carbon dioxide and an amine that reacts further with another isocyanate group to produce a urea compound. The use of model compounds PI and BPI and wood under dry conditions ≅ 0% and 14% moisture contents led to the observation that although small isocyanate molecules can react with polymers under dry conditions, increasing the molecular weight of the isocyanate and increasing the moisture content significantly lowered the reactivity with the wood hydroxyls [5]. Thus, no covalent bond formation has been observed with the pMDI (even with excess isocyanate) under typical conditions for pMDI adhesives at 160 °C [5]. Thus, models B2 and B3 do not represent how pMDI adhesives interact with wood at normal moisture content.

Mechanical Analysis of Isocyanate Interaction with Wood

With the NMR analysis discussed above, we eliminated two of the four possible interactions within the cell wall as illustrated in Figure 1 and are left with models B4 (bulking of the cell wall) and B5 (formation of an interpenetrating polymer network). B4 would most likely plasticize the cell wall, decreasing the modulus of the wood cell walls, while B5 would decrease creep of the wood cell walls. Thus, the way to examine these processes is to measure wood cell wall mechanical properties. This can be done by using the proper nanoindentation methods, but these methods did not previously exist.

Nanoindentation methods have been used on many materials, including wood. Until recently, these methods did not account for the edge effects that are common in wood given its layered cell walls, the large changes next to the empty lumina, and its middle lamella at joined the cell walls. We also accounted for cell wall flexing, given its cellular structure with empty lumina. Thus, methods were first developed that could correct the elastic modulus and hardness for these structural compliance factors [7]. Then methods were developed to measure time-dependent deformations using nanoindentation [8].

Application of these techniques demonstrated that the phenylisocyanate-treated wood at 160 °C had swollen cell walls and that these cell walls had a decrease in the elastic modulus of the cell wall compared with the unmodified cell wall. This is consistent with the mono-functional isocyanate-forming urea and related structures that bulk the cell wall and with plasticizing the wood polymers. On the other hand, the multi-functional pMDI can actually polymerize, allowing it to form an interpenetrating polymer network [3] that decreased the creep of the cell walls. Thus, the mono-functional isocyanate is consistent with model B4, whereas the multi-functional isocyanate is consistent with model B5 from the nanoindentation data.

Conclusions

Understanding of the crucial durability factors in adhesive bonds to wood is difficult because of the complexity of its wood anatomy on several dimensional scales. Furthermore, the fact that adhesives can flow into the pores and that some adhesives are able to even infiltrate the cell walls increases this complexity. With pMDI adhesive, it has not been clear as to whether or not adhesive performance is dependent upon covalent bond formation between the adhesive and wood. We determined that covalent bonds are not formed under typical bonding conditions using an advanced solution-state NMR method. Using advanced nanoindentation methods, we also determined that the pMDI is not simply bulking the wood cell walls but is probably forming an interpenetrating polymer network within the cell wall. This knowledge should help in the designing of more durable adhesives and better wood modification methods.

References

1. B.H. River, C.B. Vick and R.H. Gillespie, in: Treatise on Adhesion and Adhesives, 1991, J.D. Minford (Ed.), Vol. 7, pp 1–230. Marcel Dekker, New York, NY.
2. C.R. Frihart, *J. Adhes. Sci. Technol.* 2009. 23, pp 601–617.
3. C.E. Frazier and J.W. Ni, *Int. J. Adhes. Adhes*. 1998, 18, pp 81-87.

4. M. Norimoto, in: Wood and Cellulose Chemistry, 2nd Ed., 2001, D.N.-S. Hon and N. Shirashi, Eds., Marcel Dekker, New York. pp 573-598.
5. D.J. Yelle, *A solution-state NMR approach to elucidating pMDI-wood bonding mechanisms in loblolly pine*, in *Forestry/Chemistry*. Ph.D. dissertation, 2009, University of Wisconsin-Madison: Madison, WI.
6. D.J. Yelle, J. Ralph and C.R. Frihart, *Magn. Reson. Chem.* 2008, 46, pp 508–17.
7. J.E. Jakes, C.R. Frihart, J.F. Beecher, R.J. Moon, P.J. Resto, Z.H. Melgarejo, O.M. Suarez, H. Baumagart, A.A. Elmustafa, D.S. Stone, *J. Mater. Res*. 2009, 24(3), pp 1016-1031.
8. J.B. Puthoff, J.E. Jakes, H. Cao, and D.S. Stone, *J. Mater. Res.* 2009, 24(3), pp 1279-1290.
9. F. Lu and J. Ralph, *Plant J*. 2003, 35, pp 535-544.

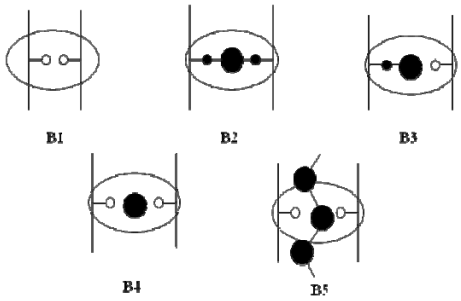

Figure 1. Potenial models for the molecular-scale interactions between wood polymers and pMDI infiltrated into the cell wall. The models are based on those originally proposed by Norimoto [4].

PROCEEDINGS

33rd Annual Meeting

of

The Adhesion Society, Inc.

February 21-24, 2010
Daytona Beach, FL

Raymond Pearson, Program Chair
Gregory Anderson, Editor

ISSN 1086-9506
©2010 The Adhesion Society