

THE “LOVE-HATE” RELATIONSHIP PRESENT IN LIGNOCELLULOSIC MATERIALS

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The three main types of chemical components in wood are cellulose, hemicellulose, and lignin. These three components have rather different physical and chemical characteristics. In some respects, the three types of materials can be described as “incompatible.” However, most of the biomass existing on the planet depends on their successful interactions. It can be useful to think of wood as being a natural composite structure. Concepts related to composites also are useful as we envision possible new and improved uses of wood-derived materials.

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A RELATIONSHIP MEANT TO LAST?

Most of the world’s biomass consists primarily of three somewhat incompatible types of biopolymers – cellulose, hemicellulose, and lignin. Together, these are the most abundant natural organic polymers. Our very existence depends on the successful interactions and structures involving an intimate relationship among these three.

Let us examine each of these biopolymers piecemeal. Cellulose is a regular, linear polymer, having a high tendency to form crystalline regions. Though it has a very strong hydrogen bonding tendency, many of the hydrogen bonding sites of cellulose become tied up in the intra-chain and inter-chain associations inherent in the crystalline nature of this macromolecule. From a materials standpoint, cellulose is quite rigid, having a high dimensional stability in the direction of the macromolecular chains. It also has a tendency to swell – especially in the amorphous regions – in dimensions perpendicular to the primary orientation of the macromolecules and fibrils.

Despite their similar name, hemicelluloses are quite different from cellulose. The macromolecules are irregular, having side groups or substituent groups, as well as different sugar units along the chains. Hemicellulose materials, by themselves, do not have sufficient moduli of elasticity to hold promise as a structural material. Rather, hemicellulose acts like a semi-soluble polyelectrolyte and bonding agent.

Finally, lignin’s characteristics from a constructionist’s point of view can cause even greater doubts regarding whether the relationship among these three types of chemicals is destined to last. Lignin is a highly randomized condensed polymer, full of aromatic groups, as well as chemically resistant cross-links of various types. Lignin is much more hydrophobic than cellulose, let alone hemicellulose. Based on solubility principles alone, the three components would be classed as “incompatible”

A NATURAL COMPOSITE

As in any composite, the physical properties of wood seldom equal what would be predicted from a linear sum of properties of its main constituents. Manufacturers of counter-top laminates take advantage of this principle when they impregnate highly porous “saturating kraft” paper with phenolic or melamine resins. The combination of the cellulosic fiber matrix, together with solidified resin filling the void spaces, achieves a dimensional stability far in excess of what can be achieved by either component.

The success of a final paper product often depends on the relative abundance of hemicelluloses. Paper’s tear strength is directly related to the levels of hemicelluloses, but pulping operations tend to remove it easily by virtue of its relatively labile nature. Clever scientists are pursuing the concept of VPP (Value Prior to Pulping) to take advantage of this materials loss. The idea is to collect the hemicelluloses and then use them in standard fermentation reactions to make bioethanol.

To further extend the idea of a “natural composite” (perhaps dangerously so), one can regard hemicellulose as an adhesive between the rigid semi-crystalline cellulose and the tough “inclusions” of lignin within the wood structure. A need to explain the coupling between the cellulosic and lignin-rich phases lends credibility to some recent results supporting the existence of covalent bonds between hemicelluloses and lignin.

Hemicellulose and lignin also help wood resist microbial attack. Whereas it can take as few as three enzymes to efficiently degrade cellulose, it takes a wide assortment of enzymes, working together, to degrade all of the different types of chemical structures present in hemicellulose and lignin. These same factors help to explain why it has been such a challenge to bring lignocellulosic ethanol into widespread commercial success.

NEW USES AND NEW OPPORTUNITIES

Manufacturers of kraft pulp for papermaking work hard to remove lignin, retaining just the polysaccharide materials to make paper structures having high strength or high brightness. The lignin portion is mainly incinerated to recover its heat value, providing power and steam for the pulping and papermaking processes, as well as recovering the pulping chemicals. Opportunities to make fuller use of byproducts from pulping will be featured in future review articles and editorials in this journal.

Considering how long cellulose, hemicellulose, and lignin have coexisted in woody systems, it may be surprising to see how easily the material can be manipulated. For example, by genetic engineering it is possible to vary the ratio of lignin to cellulose, and also to control whether the lignin is rich in syringyl vs. guaiacyl groups. Though *a priori* it is doubtful whether seriously lignin-deficient trees would thrive in the wild, some of them appear to grow satisfactorily under controlled conditions.

Another way that lignocellulosic materials can be transformed is by dissolving the wood material and then reconstituting it. Such transformations have become possible to contemplate recently due to advances in ionic liquids. The reconstituted wood material can take on a wide range of properties and be chemically manipulated according to the type of solvent in which it is dissolved.