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Limiting Polysaccharide Motion Protects Wood from Decay

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ABSTRACT

It is well known that chemical modifications to improve decay resistance also reduce the equilibrium moisture content (EMC) of wood. The mechanism of this action, however, has been the subject of much debate. Several groups have suggested that decay resistance is a result of lower diffusion rates of fungal degradation agents through the wood cell wall. A recent paper explained the fundamental principles governing diffusion through the wood cell wall. This current paper summarizes the findings in that paper with respect to decay resistance of modified wood. In short, large scale motions of the amorphous polysaccharides of the wood cell wall are necessary for diffusion of degradation agents during incipient decay. Many wood modifications are likely preventing decay by preventing these motions. Water promotes large scale motions of cell wall polysaccharides by increasing free volume, increasing the distance between polymer chains, and reducing the number of hydrogen bonds between polymer chains.

Keywords: decay resistance, diffusion, glass transition, molecular mobility, hemicellulose

1. INTRODUCTION

It has long been recognized that modifying wood in a way that reduces equilibrium moisture content (EMC) is associated with improved decay resistance (Stamm 1964; Rowell 2005; Hill 2006; Thybring 2013). However the mechanistic relationship between reduced EMC and ind increased decay resistance is poorly understood (Ringman et al. 2019). Recent work has suggested that the decay resistance of many modified wood products lies in the inability of fungal degradation agents to diffuse into, and degradation products which feed the fungus to diffuse out of, the wood cell wall (Jakes et al. 2013; Ringman et al. 2014, Zelinka et al. 2016, Hunt et al. 2018, Ringman et al. 2019). Jakes and co-workers (Jakes et al. 2019) recently developed a phenomenological framework based on polymer science approaches for explaining the fundamental relationships between moisture content, cell wall pores, and diffusion. This current paper summarizes the key points with respect to decay resistance in modified wood products.

2. DIFFUSION THROUGH CELL WALL POLYMERS

Diffusion occurs when a sufficiently large free volume element forms next to a diffusant and the diffusant has sufficient thermal energy to "jump" into the adjoining free volume. Figure 1 depicts diffusion through a solid polymer matrix. Here repeating polymer units, such as sugar monomers, are represented by diamonds. Figure 1A shows the initial polymer matrix with a small (upper) and large (lower) diffusant. In Figure 1B, cooperative molecular motions of small and large polymer segments are illustrated in red near the small and large diffusants, respectively. These motions create paths for diffusant motion (Figure 1C), after which the polymer may return to its original configuration with the diffusants in new locations (Figure 1D).

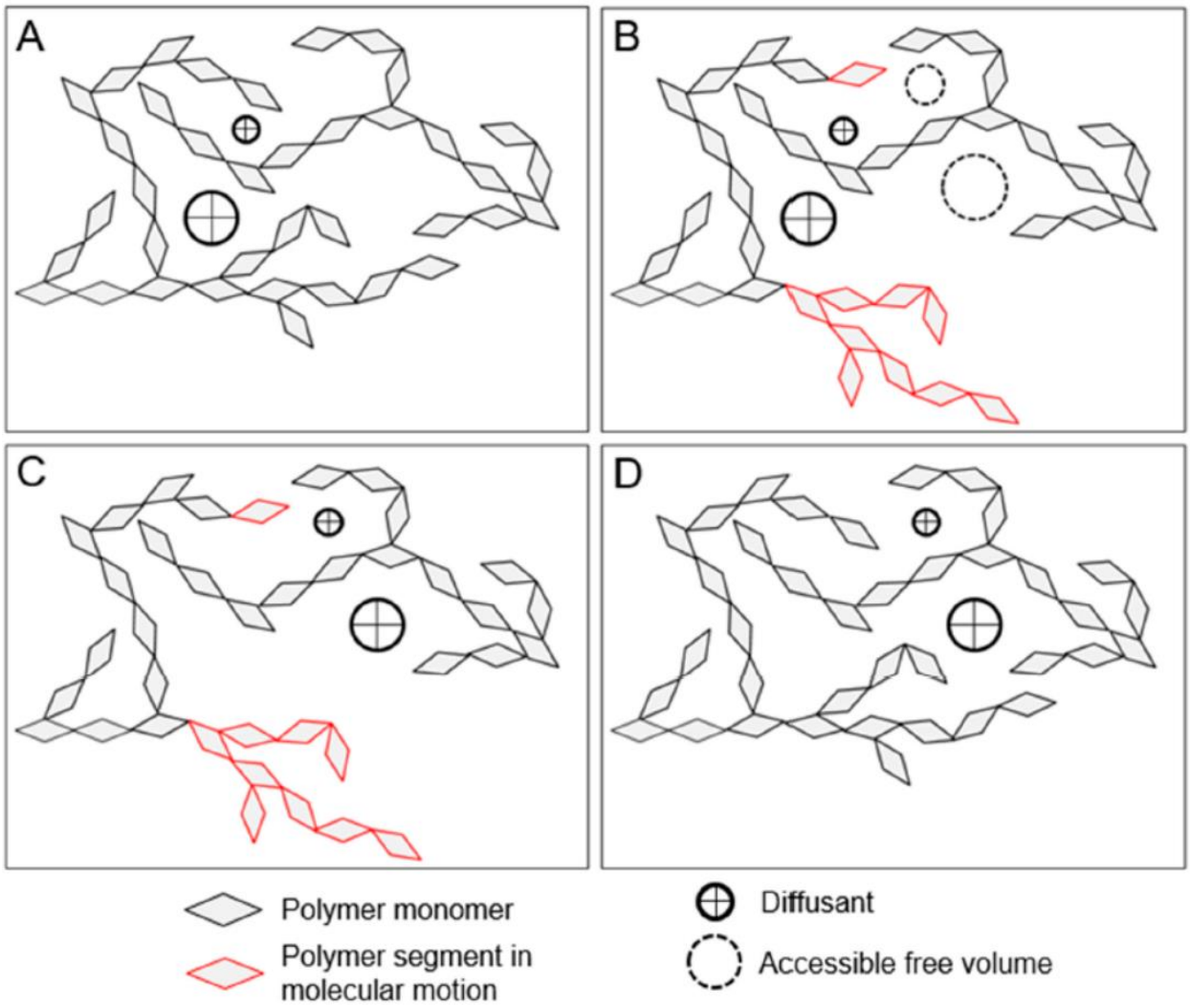

Figure 1: Diffusion through a polymer facilitated by polymer motions. From (Jakes et al. 2019).

As free volume is not normally discussed in the context of wood science or biodeterioration, we will describe this central concept. Thermal expansion is a clear example of an increase in free volume with temperature. The bulk volume increases with no addition of mass: regions of empty space (free volume) are created inside the solid. These free volume elements are the result of molecules flipping back and forth between multiple positions. At any given time, only one position is filled and the others are empty – localized regions of free volume. Swelling and plasticizing polymers with solvent, such as water, not only increases bulk volume by forcing water in between polymer chains, it also increases the free volume (Ferry 1980). A decrease in external pressure also increases free volume, by allowing a slightly larger spacing between polymers. Temperature increases free volume by increasing molecular vibration. If large enough, these free volume elements can be occupied by water or diffusants. More free volume leads to faster diffusion.

It is not only the presence of free volume that is important to diffusion, but also the size of the free volume elements. Water is well known to travel through wood quite quickly. Because of water's small size, it only needs small free volume elements, such as that created by the rotation of an OH group at the C6 position of a hexose. These motions are active even at very low temperatures in dry wood. However wood decay depends on the diffusion of larger molecules (Arantes and Goodell 2014) such as quinones (Suzuki et al. 2006) or manganese chelates (Hatakka and Hammel 2011). The fragments released from the cell wall that the fungus feeds upon are the size of a polysaccharide monomer or larger. The creation of significant quantities of free volume elements

of these sizes requires a significant amount of coordinated motions in the polymer (Frisch 1980), for example entire sugar monomers, or a section of the polymer backbone, as depicted in figure 1. The onset of these larger scale motions in a polymer has a characteristic impact of mechanical properties, called the glass transition (Ferry 1980). These larger scale motions allow stress relaxation within the polymer, evidenced by softening and rubbery behaviour, as opposed to the hard and brittle behaviour of the polymer in the immobile, glassy state. Therefore, the onset of these larger scale polymer motions allows both the creation of free volumes large enough to support diffusion of species relevant to decay, and mechanical relaxation. Mechanical relaxation in wood cell walls with increasing moisture content was recently documented using nanoindentation and linked to diffusion of mineral ions (Jakes 2019).

Water is by far the most important factor supporting cooperative polymer motions in the wood cell wall during decay. By breaking hydrogen bonds between wood polymers, it lowers the energy barrier to polymer motion. Combined with the larger spacing between polymer chains and increased free volume, the result is that water acts as a classical plasticizer of wood polymers. Thybring's observation that many different wood modification methods, performed on different species of wood, achieve decay resistance at approximately 40% reduction in EMC (Thybring 2013) suggests that about a 40% reduction in moisture is enough to prevent the wood polymers from engaging in large scale motions.

3. AMORPHUS POLYSACCHARIDES SUPPORT DIFFUSION

Amorphous polysaccharides such as hemicellulose and amorphous cellulose, are probably the wood polymers responsible for these coordinated molecular motions. Cellulose crystalline domains are clearly not supporting diffusion, as they do not even allow penetration of water molecules (Frilette et al. 1948). Lignin is likely not undergoing a glass transition under wood decay conditions, as lignin transitions are thought to occur at temperatures above 60° C, even at saturation (Cousins 1976, Back 1982). Hemicellulose has been reported to go through glass transitions at room temperature and 60-80% RH (Cousins 1978, Olsson and Salmen 2004). Jakes and co-workers (Jakes et al. 2019) did an exhaustive review of the literature on glass transitions in wood polymers and concluded that the diffusion is very likely in amorphous polysaccharides.

4. APPLICATION TO MODIFIED WOOD

The key to decay resistance in modified wood, then, is to prevent large scale motion of amorphous polysaccharides. Because the total volume available for swelling is limited by the hoop stress of the S1 and S3 layers, space occupied by other molecules is unavailable to water, thereby limiting moisture-induced polymer motion. Bulking is likely provided by acetyl groups (acetylation) or polymerization of 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) (Thygesen and Elder 2008), phenol formaldehyde (Stamm and Baechler 1960), or furfuryl alcohol (Lande et al. 2004, Venås and Wong 2008) in the cell wall. Limiting polymer mobility could also be accomplished by crosslinking, for example with formaldehyde, DMDHEU, or thermal modification (Hill 2006). Thermal modification might also modify amorphous polysaccharides in other ways that prevent large scale motion (Willems 2016). Predicting whether a wood product is decay resistant might be as simple as measuring the diffusion rate through the saturated cell wall, for example with fluorescence recovery after photobleaching (Paës et al. 2017), or by observing the lack of a mechanical relaxation.

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