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On the weak dependence of water diffusivity on the degree of hydrophobicity of acetylated hydroxypropyl xylan

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ABSTRACT

We used molecular dynamics (MD) simulation to study the diffusion of water at low concentrations in a series of chemically modified xylans, a major hemicellulose, including hydroxypropyl xylan (HPX) and acetoxypropyl xylan (APX) which is essentially acetylated HPX, with different degrees of acetylation (i.e., different degrees of hydrophobicity) at 400 K, a temperature well above the glass transition temperatures of the materials. We used one HPX and three APX models. The three APX models were constructed using the HPX model by substituting 1, 2 or 3 hydroxyl moieties on its repeating units, respectively.

The simulation results showed that the diffusivity of water at low concentrations in the chemically modified xylans decreased slightly (~20%) from HPX to APX with 3 acetylated hydroxyl moieties, a trend that has been experimentally observed for xylans and other cellulosic type materials. Further data analysis shows that acetylation decreases the ability of the xylan to form hydrogen bonds with water and its degree of swelling. And these two factors exert opposite effects on the diffusivity of water. In particular, the first factor increases the mobility (lower activation energy) of the water molecules, while the second factor reduces the free volumes available for diffusion, thereby decreasing the water mobility. This finding implies that it is not likely to obtain orders of magnitude change to the water diffusivity simply by the acetylation of all hydroxyl moieties on xylan. The high degree of swelling observed for HPX compared to those of APXs is attributed to the fact that many hydrogen bonds in HPX are broken by water. It is interesting to note that water in most of the hydrogen bonds formed between water and xylans acted as hydrogen bond acceptors rather than donors.

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1. Introduction

The sustainability issue of using synthetic polymers is of a major concern in today's society as they are derived from non-renewable resources and are being non-biodegradable. As a result, there has been an increasing interest in developing biopolymers from renewable resources to replace synthetic polymers (Gonzalez, Santos, & Parajo, 2011). In particular, there is an extensive effort on modifying natural polymers from various types of plants for such a purpose.

Hemicelluloses are the second abundant component in wood and plants after cellulose. Unlike cellulose, hemicelluloses are hetero-polysaccharides that contain different types of sugar units with different substituents arranged at different proportions. They are short-branch, amorphous polymers with degrees of polymerization around 50–300. Hemicelluloses are hydrophilic and soluble in water (Cordeiro, Gouveia, Moraes, & Amico, 2011; Sun, Sun, & Tomkinson, 2004).

Native or modified forms of hemicelluloses are an important renewable source of biopolymers which can be used in different areas like food and non-food packaging materials, coatings and matrix for bio-based composites (Hansen & Plackett, 2008; Mikkonen & Tenkanen, 2012). They show good properties for making adhesives, thickeners, stabilizers, decorative paints, film formers, hydrogels, and emulsifiers (Cordeiro et al., 2011; Peura, Karppinen, Soovre, Salmi, & Tenkanen, 2008; Phan et al., 2002; Pohjanlehto, Setala, Kammiovirta, & Harlin, 2011; Saxena, Elder, & Ragauskas, 2008; Stepan, Hoije, Schols, de Waard, & Arabinose, 2012).

Being the principal component of hemicelluloses in many plants, xylan constitutes 20–35% of the total dry weight of plants. Xylan, with xylose, a key sugar unit in xylan, content of 60–70%, is one of the highly branched, low molecular weight, non-cellulosic, non-crystalline hetero-polysaccharides. Xylan is now mostly used for conversion process to xylose, xylitol and furfural. Production of xylan derivatives is advantageous as they are easy to process but also biodegradable and environmentally degradable (Ebringerova

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& Heinze, 2000; Glasser, Jain, & Sjostedt, 1995; Jain, Sjostedt, & Glasser, 2000).

Derivatizing hydroxyl groups of xylan to new chemical groups would yield a film forming material that can be used in applications such as edible and non-edible films and coatings (Fundador, Enomoto-Roger, TakemurA, & Iwata, 2012; Goksu, Karamanlioglu, Bakir, Yilmaz, & Yilmazer, 2007; Hartman, Albertsson, Lindblad, & Sjoberg, 2006; Peroval, Debeaufort, Despre, & Voillley, 2002), hydrogels (Gabrielii & Gatenholm, 1998; Pohjanlehto et al., 2011; Tanodekaew, Channasanon, & Uppanan, 2006; Voepel, Edlund, & Albertsson, 2009), biodegradable plastics and plasticizers (Rauschenberg, Dhara, Palmer, & Glasser, 1990; Shaikh, Pandare, Nair, & Varma, 2009). Chemical modification of xylan by substituting xylan's hydroxyl group by alkoxy or acetoxy substitutes helps induce its solubility in water or organic solvents, respectively. Hydroxypropyl cellulose and starch have been found in many applications in industry due to their water solubility. However, hydroxypropyl xylan (HPX) with similar properties has remained obscure. Among the xylan derivatives, only xylan acetate has been studied (Jain et al., 2000).

HPX with degrees of substitution of 0.2–0.5 are water-soluble and can form transparent and tough films that have the potential to be used in food packaging (Jain et al., 2000). In order to be used in such application (i.e., to protect food from contamination and deterioration), it is important for the film to act as oxygen and moisture barrier. Due to hygroscopic nature of hemicelluloses, they are poor moisture barriers. Increasing hydrophobicity by coating the surface of film with a water barrier material, addition of hydrophobic compounds or chemical modification (e.g., acetylation, grafting, etc.) may solve this problem (Escalante et al., 2012). Although there have been many studies for improving barrier properties of HPX, as quantified by water vapor transmission rate (WVTR) and water vapor permeability (WVP), not all of them have comparable results with current commercial products such as low-density polyethylene (Hansen & Plackett, 2008). There are still concerns whether improving hydrophobicity of HPX would decreases WVTR or not (Pan, Xiao, & Song, 2013). According to Pan et al. (2013), WVTR is insensitive to the degree of hydrophobicity of HPX. Gennadios, Weller, and Testin (1993) were able to improve hydrophobicity of gluten-based films using hydrolyzed keratin and mineral oil but the WVTR reduction was only 23–25%.

The counter intuitive experimental results led to the speculation that during the hydrophobization of HPX, the solvent used causes the HPX film to swell. If all of the swelling is not reversible, the extra free volume introduced in the polymer would increase the mobility of water. In addition, the residue solvent may act as a plasticizer, enhancing the mobility of the HPX molecules (Ahlen, 1969). All of such reasons make hydrophobization an inefficiency approach to improve the barrier properties of HPX films. In this regard, we carried out molecular dynamics simulation on a series of chemically modified xylans (one HPX and three acetoxypropyl xylan (APX) with different degrees of acetylation of HPX) to discern the molecular mechanisms that lead to the observed insensitivity of water diffusivity to the degree of hydrophobicity of the materials.

2. Models and simulation method

In this work, the structure of the model HPX resembles to that of a film forming HPX that possesses a linear structure and is a hydrophilic, water-swollen polymer (see Fig. 1). The molecular weight of model HPX is 4404 (10 repeating units).

To increase the hydrophobicity of the polymer, we substituted 1, 2 or 3 hydroxyl moieties on the side chains attached to the repeating unit of HPX with acetic acid to construct three different model APXs (see Fig. 2) with different degrees of acetylation (hydrophobicity).
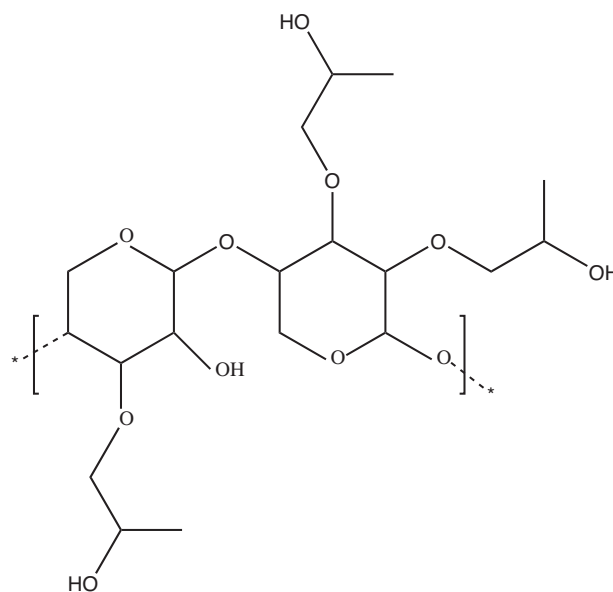

Fig. 1. Structure of the repeating unit of HPX.

The molecular weights of APX1, APX2 and APX3 are 4824, 5244 and 5664, respectively (all APX chains contained 10 repeating units).

Only the amorphous phase of the HPX and APXs was interested in the present work. The amorphous phase was generated by a commercial software Materials Studio version 5.0 based upon the procedure described by Theodorou and Suter (1985), a procedure that has been extensively used to generate amorphous phase of polymers. Nonetheless, when we constructed the initial amorphous configurations, we used a hard core radius to each atom equal to 0.3 times of their van der Waals radius to avoid hard overlaps. This would, in turn, avoid the high-energy structures towards the end of the amorphous model construction process. To mimic the bulk amorphous state of these polymers, one or two chains were used in a cubic box with an initial density as 1×10^3 kg/m^3 and subjected to three-dimensional periodic boundary condition. Once the pure polymer systems were set up, energy minimization was carried out with the steepest descent method. The systems were subjected to isothernal–isobaric (i.e., NPT) molecular dynamics (MD) simulation to equilibrate their density to 1.16×10^3 kg/m^3 (HPX), 1.14×10^3 kg/m^3 (APX1), 1.14×10^3 kg/m^3 (APX2) and 1.12×10^3 kg/m^3 (APX3), respectively. Here, the NPT equilibration temperature was set at 400 K, a temperature significantly higher than the glass transition temperatures of the xylans and the pressure was set at 1 atm. We used Nose–Hoover coupling (Hoover, 1985; Nose, 1984) to control the temperature and Parrinello–Rahman approach (Nose & Klein, 1983; Parrinello & Rahman, 1981) to control the pressure. After that, we inserted water molecules into each system and the energy minimization was carried out again.

For each chemically modified xylan model, a total of 5 systems, corresponding of five water concentrations, were generated (see Table 1). And for each system, 10 NPT MD simulations with different initial positions of water molecules were carried out at the same temperature (400 K) and pressure (1 atm) to improve the statistics. Each simulation was carried out for 12 ns and the time step Δt was 1 fs. We used the leap-frog algorithm (Hockney, Goel, & Eastwood, 1974) to integrate the Newtonian equations of motion.

To calculate the diffusion coefficients of water in the polymers, we used the Einstein's equation:

$$D = \frac{1}{6} \frac{d(\langle (1/N) \sum (\vec{r_i}(t) - \vec{r_i}(0))^2 \rangle)}{dt} \qquad (1)$$