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Diffusion Behavior of Water at Infinite Dilution in Hydroxypropyl Xylan Films with Sorbitol and Cellulose Nanocrystals

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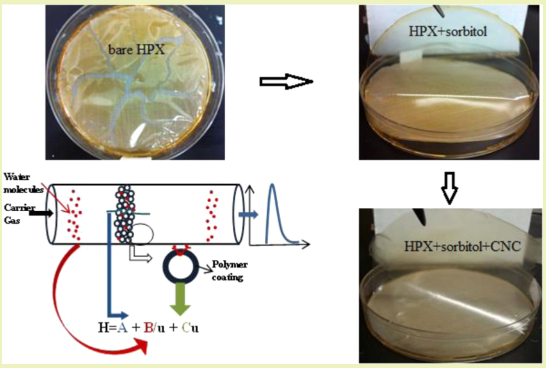
ABSTRACT: Inverse gas chromatography (IGC) was used to measure the infinite dilution diffusion coefficients of water in hydroxypropyl xylan (HPX) films containing sorbitol, a commonly used plasticizer, and cellulose nanocrystals (CNC) at temperatures above their glass transition temperatures (T_g). HPX forms transparent but relatively rigid films and has the potential to be used for certain food-packaging applications. Sorbitol and CNC were added to HPX films to reduce T_g and to reduce the water diffusivity, respectively. It was found that almost 40 wt % of sorbitol was needed to yield a HPX film to have the desired flexibility, as quantified by its T_g, and that addition of a small amount of CNC (1−5 wt %) while maintaining the total concentration of sorbitol and CNC at 40 wt % (39−35 wt % of sorbitol) slightly increased the T_g but significantly decreased the diffusivity of water. In particular, the infinite dilution diffusion coefficient of water for the HPX film with 35 wt % of sorbitol and 5 wt % CNC was comparable to that of the bare HPX film. The diffusion data suggest that effects of sorbitol and CNC on the water diffusivity follow the free volume theory.



KEYWORDS: *Inverse gas chromatography, Hydroxypropyl xylan, Plasticizer, Cellulose nanocrystal, Water diffusivity*

INTRODUCTION

In recent years, increasing awareness of sustainability has driven society to increase its effort to replace petroleum-based polymers by natural polymers.[1] Given that 40% of all plastics consumed are used for packaging purposes, it is not unreasonable to focus such effort on determining whether polymers from bioresources could be used as packaging materials.[2] Among the natural polymers, xylan is a prime candidate, as xylan, one principal component of hemicelluloses, is a film-forming polymer and the second most abundant polysaccharide after cellulose.[3,4] It is worth noting that not all natural polymers are able to form films, an obvious requirement for packaging applications. Cellulose and cellulosic derivatives have found their way in the paper production industry and many other applications, while hemicelluloses, xylan in particular, have not because of their high heterogeneity, low water solubility, and source-dependent composition. However, recently, chemically modified xylan such as xylitol, xylooligosaccharides, and xylose, to name a few, have gradually been used in improving the nutritional properties of food, as prebiotics, or as additives to film-forming biopolymers.[5−7] Also, there has been increasing effort on turning xylan from different sources into biodegradable films by using additives[5,8] (e.g., pretreating xylan before the extraction process[9] or chemically modifying xylan[10,11,3]).

In terms of chemical modification of xylan, Jain et al. found that when the hydroxyl groups of xylan are substituted by alkoxy substituents, water-soluble hydroxypropyl xylan (HPX) (Figure 1) is obtained. HPX forms transparent rigid films upon precipitation from its aqueous solution, a potential material for packaging applications.[3] In this regard, HPX is likely to be used as an internal layer of coating when a layer of good water barrier is available. It means that there would be very low concentration of water present. To use HPX for certain packaging applications, its flexibility has to be increased. Plasticizers are normally used for such purposes. In fact, this is commonly practiced on hemicellulose-based materials.[12] However, this is accomplished at the expense of negatively affecting the barrier properties of the films (e.g., water vapor transmission rate (WVTR) and oxygen permeability),[13,14] obviously not acceptable for the target applications. Naturally, most of the biopolymers do not exhibit desired barrier properties, especially to water vapor, due to the presence of a large number of hydroxyl groups in their structure that makes them hydrophilic.[15] Fillers are expected to improve their barrier properties by reducing the water vapor permeability in the polymer. In this regard, adding nanosized fillers may help, but such fillers will inevitably increase the rigidity of the films. Therefore, it is of great interest to investigate whether there exist optimal concentrations of plasticizer and nanosized filler in HPX films that would exhibit acceptable flexibility and barrier properties. In particular, we will use sorbitol (Figure 1),

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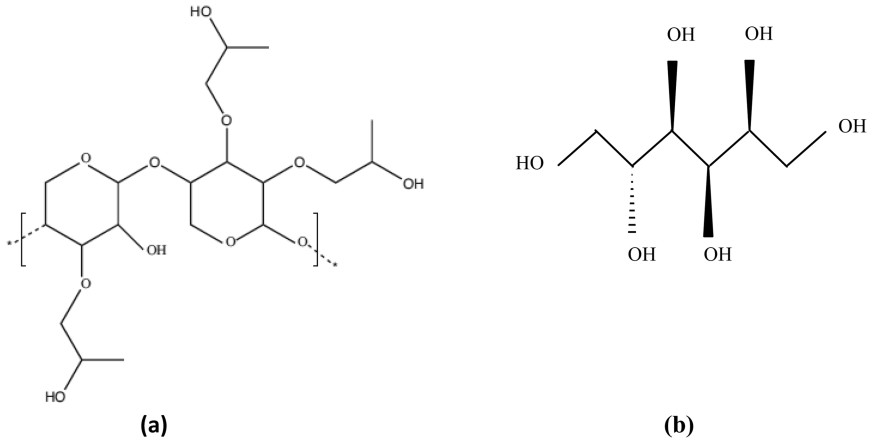

Figure 1. Molecular structures of (a) the repeating unit of HPX[20] and (b) sorbitol ($C_6H_{14}O_6$).

a commonly used plasticizer for hemicellulose, and a cellulosic-based nanosized filler, namely, cellulose nanocrystal (CNC). CNC is produced from the acid hydrolysis of cellulose,[12] and compared to inorganic fillers, it is easily recyclable even at high filling levels.[16] According to Bulota et al., in contrast to other chemically modified nanoparticles, where there are still toxicity issues, no indications of toxicity has been found with regard to CNC.[16] Also, CNC is expected to be compatible with HPX. Typical CNC has a diameter of 5−10 nm and a length of 50−200 nm (i.e., aspect ratios ∼5−40).[15] It is expected that such aspect ratios would significantly improve the barrier properties of the HPX films,[17] as the tortuosity of the penetrating molecules and the mobility of the polymer chains will be increased and decreased, respectively. Several studies have shown enhancement of barrier properties of biopolymers in the presence of CNC. Addition of 1−10% CNC has reduced water vapor permeability in various biopolymers from 20% to even 70% compared to the neat polymer, as the filler is less permeable and disperses well in the matrix.[18,15,12]

Studying moisture permeability or WVTR is an important issue for food packaging applications that includes the study of the thermodynamic process of solubility and diffusivity of the moisture through the polymer film. The penetrant (water) first dissolves on the surface of the polymer and then penetrates through the film by molecular diffusion and then exits the film.[19] Diffusivity of water is of major interest of this work, especially in the case of low water concentrations. In order to study diffusivity of water molecules through HPX films, infinite dilution was chosen as the region of study to minimize the interactions between water molecules. In this work, changes in the glass transition temperatures of the HPX films with the addition of sorbitol and CNC will be measured by differential scanning calorimetry, and the corresponding diffusivity behaviors will be characterized by measuring the diffusion coefficients of water in HPX films with various amounts of sorbitol and CNC using the technique of inverse gas chromatography (IGC). In order to meet the conditions for the applicability of the method, infinite dilution was used as the absorption isotherm is linear. Also, the activation energy of the diffusion of water in the HPX films with or without sorbitol and CNC will be calculated at temperatures above the glass transition. The reasons that IGC is used are fast analysis (minutes), reliability and simplicity, sensitivity to even low concentrations (infinite dilution), and accuracy for low diffusion coefficients.

■ INVERSE GAS CHROMATOGRAPHY

As mentioned, IGC was used to measure the diffusion coefficients of water at infinite dilution in a series of HPX films. At infinite dilution, retention time of the probe is independent of concentration, and the concentration of probe molecules in the stationary phase is in equilibrium with that of the gas phase. In order to measure the diffusion coefficient at infinite dilution, the Van Deemter equation was used.[21,22]

$$H = A + (B/u) + Cu \tag{1}$$

where H is the equivalent theoretical plate height that is determined from the widths of the eluting peaks for different carrier gas flow rates, and u is the average linear carrier gas flow rate. A is attributed to the eddy diffusion that is defined as $2\lambda d_p$. Here, d_p is the diameter of the inert support, and λ is a packing factor. The B term denotes the longitudinal molecular diffusion that is given by $2\gamma D_g$. Here, D_g is the diffusion coefficient of the solute in the carrier gas, and γ is a constant, less than unity, signifying the curvy path experienced by the gas in a packed column. The C term corresponds to the mass transfer in the stationary phase. It is worth noting that C is independent of the flow rate but depends on a number of factors including the diffusion coefficient of the solute molecule in the stationary phase D_p. By plotting eq 1 at higher gas flow rates ($B/u \rightarrow 0$), the slope of the linear portion is equal to C. Then, D_p can be obtained

$$C = \left(\frac{8}{\pi^2}\right)\left(\frac{d_f^2}{D_p}\right)\left(\frac{k}{(1+k)^2}\right) \tag{2}$$

where k is the partition ratio, and d_f is the thickness of the stationary phase that is determined by the following equation

$$d_f = \left(\frac{1}{3}\right)W\left(\frac{\rho_s}{\rho_p}\right)r_s \tag{3}$$

where W is the percentage loading of the polymer; ρ_s and ρ_p are the density of inert support and polymer, respectively; and r_s is the average radius of inert support particles.

The partition ratio, k, is calculated from the following equation

$$k = (t_r - t_f)/t_f \tag{4}$$

where t_r and t_f are the retention times of solvent and noninteracting indicator, such as air, respectively.

H in the Van Deemter equation can be obtained by equation

$$H = \left(\frac{L}{5.54}\right)\left(\frac{W_{1/2}}{t_r}\right)^2 \qquad (5)$$

where L is the column length, and $W_{1/2}$ is the peak width at half of the peak height.

Also, u is the linear velocity of carrier gas that can be obtained by

$$u = \frac{jV_0}{\bar{a}}\frac{T_{col}}{T_{flow}} \qquad (6)$$

where T_{col} is the temperature of the column; T_{flow} is the temperature of the flow meter; $\bar{a}$ is volume of gas phase per unit length determined by dividing the retention volume of air by the column length [retention volume: volume of gas phase that passes through the column from the time of injection to the elution time of the peak maximum]; V_0 is the corrected flow rate; and j is the compressibility (James Martin correction) factor that is defined from

$$j = \frac{3}{2}\frac{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]} \qquad (7)$$

Here, P_i and P_o are the inlet and outlet pressures of the column.

MATERIALS AND METHODS

Materials. Xylan from beechwood, propylene oxide, sodium hydroxide, and sorbitol were purchased from Sigma-Aldrich (Oakville, ON, Canada) and used as received. Cellulose nanocrystals (CNC) with diameters of 5−10 nm and lengths of 150 nm were provided by Alberta Innovates Technology Futures (AITF). Acid-washed glass beads with a diameter range of 150−212 mm, also purchased from Sigma-Aldrich, were used as the solid support for HPX, and a 0.5 μL Hamilton syringe was used for the injection of water.

Preparation of Hydroxylpropyl Xylan. Hydroxylpropyl xylan (HPX) was prepared by reacting xylan with propylene oxide according to the method of Jain et al.[3] Xylan (5 g) was first dissolved in 20 mL of sodium hydroxide solution (pH 10) at ambient temperature and with constant stirring in a three-necked flask under nitrogen for 2 h. Upon the complete dissolution of xylan, the solution was cooled by placing the flask in an ice bath. While stirring under nitrogen, 10 mL of propylene oxide was added dropwise using an addition funnel. The reaction was left stirring under nitrogen for 12 h at ambient temperature. Then, the reaction was precipitated with 150 mL of acetone with brisk stirring. The suspension was let to settle and removed and then washed with fresh acetone. The precipitate was finally collected by filtration and dried in vacuum for 24 h.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) experiments were carried out to determine the glass transition temperatures of the neat HPX film and those with the addition of different amounts of sorbitol and CNC. All experiments were carried out using a DSC 2910 (TA Instruments, U.S.A.), calibrated with indium and zinc standards. Aluminum hermetic pans and lids were used for experiments with an empty pan used as reference. For preparing the films, HPX, sorbitol, and CNC were dissolved in distilled water according to the amounts described in Table 1. The solution was stirred for an hour and then was filtered to remove any insoluble materials. Fifteen milliliters of each solution was poured in a plastic Petri dish (diameter 9 cm) covered with Teflon papers. The films were left at ambient temperature and pressure for 1 week to dry. Approximately 2 mg of the dried films were sealed in the pans with the lid on top. To ensure that all samples had the same thermal history, each sample was heated to 150 °C with a heating rate of 10 °C/min under nitrogen, then it was cooled to room temperature. The same heating and cooling steps were repeated. Results of the third heating with a heating rate of 5 °C/min are reported and used for comparison. The first heating was used to get rid of the water in the films, while the second heating was carried out to ensure that the polymers went through the same thermal history without water. Midpoint temperatures were reported as the glass transition temperature for each sample. The measurements were repeated three times for each sample, and the corresponding means and standard errors are reported.

Table 1. Concentrations of HPX Solutions Used for Preparation of Films and Coating of Glass Beads

polymer solution	HPX (g)	sorbitol (g)	CNC (g)	water (mL)	wt % (HPX/sorbitol/CNC)
1	1	–	–	33	100
2	0.8	0.2	–	33	80/20/0
3	0.7	0.3	–	33	70/30/0
4	0.6	0.4	–	33	60/40/0
5	0.6	0.39	0.01	33	60/39/1
6	0.6	0.37	0.03	33	60/37/3
7	0.6	0.35	0.05	33	60/35/5

Inverse Gas Chromatography Procedure. Chromatographic measurements were carried by an Agilent 7890A Series GC equipped with a thermal conductivity detector (TCD). Helium was used as the carrier gas. The injector and TCD temperature were set 200 and 250 °C, respectively, (50 °C above the column temperature) to prevent condensation in the injector and detector.

The chromatographic columns were 90−100 cm long, 1/4 in. o.d., stainless steel tubes, and packed with glass beads (150−212 μm diameter) coated with HPX films. For preparing the column, the weighted quantity of the HPX, sorbitol, and/or CNC were dissolved in distilled water (Table 1) and stirred for an hour and filtered to remove insoluble materials. A known amount of glass beads (20 g) was added to a known amount of the solution (10 mL). Using the rotary evaporator, the solvent was evacuated, and the polymer film was coated on the glass beads. The percentage loading of the coating was <5% determined by thermal gravimetric analysis (TGA). The column was filled with the coated support and both ends were blocked with glass wool. The column characteristics are shown in Table 2.

Table 2. Specifications of Packed Columns

polymer coating	mass of glass beads in the column (g)	mass of coating in the column (g)	column length (cm)
solution 1	16.2	0.057	90
solution 2	17	0.062	90
solution 3	16.4	0.057	90
solution 4	17.9	0.064	100
solution 5	16	0.061	100
solution 6	16.2	0.055	100
solution 7	17.1	0.056	90

Small amounts of water vapor (0.01−0.05 μL) was injected in the column through the column injector using a 0.1 μL Hamilton syringe to have infinite dilution of the solvent. Changing the sample concentration would not change retention time when working in the infinite dilution region. A small amount of air was also injected with the sample to determine the dead volume of the column. Each measurement was repeated at least five times to verify infinite dilution conditions. Most of the retention times were reproducible with less than 5% difference with their average, meeting infinite dilution conditions. Measurements of the diffusion coefficient were done using the average of retention times and peak width for each flow rate. The diffusion data are presented with the standard deviations regarding the uncertainties from the slope of the Van Deemter curves. The experiments were carried out from 120 to 170 °C at a 10 °C interval.

The column temperatures were chosen to be higher than the T_g of HPX to minimize the adsorption of the injected water.

■ RESULTS AND DISCUSSION

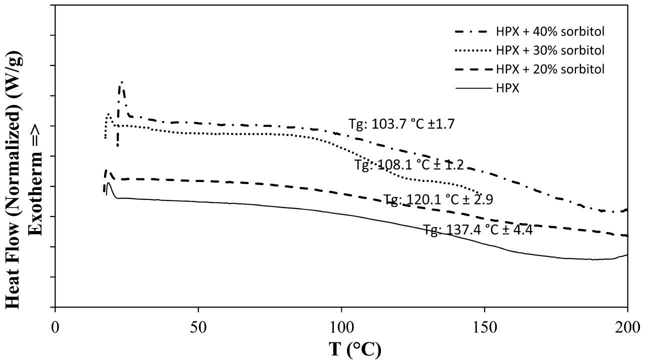

Figure 2. DSC curves for HPX films with sorbitol.

DSC curves of the third heating of HPX films containing various amounts of sorbitol are shown in Figure 2; the glass transition temperature (T_g) of each film is also given. As expected, addition of sorbitol to HPX films decreased their T_g, thereby increasing their flexibility. In particular, the T_g of the films decreased from 137.4 °C (no sorbitol) to 103.7 °C (40 wt % sorbitol). However, it is worth mentioning that the effect of sorbitol on the T_g (i.e., $dT_g/dC_{sorbitol}$) diminished with increasing sorbitol concentration, a somewhat expected observation, as some of the sorbitol molecules at high concentrations do not participate in breaking the HPX−HPX hydrogen bonds, a mechanism that increases the free volume and chain mobility of HPX, thereby decreasing the glass transition temperature.[23] There exist mathematical models that correlate T_g of a plasticized polymer with the plasticizer content. However, most of them are empirical and are only applicable over a narrow range of concentrations especially when the polymer and plasticizer have limited compatibility. Also, the kinetic aspect of the T_g measurements is not considered in such models that makes the results rough estimates of the plasticizer effect on the T_g of the polymer.[24] In the range of concentrations of interest in the present work, we used the results of two models to compare with our experimental results. One is the modified equation of Couchman and Karasz (C−K) that can be used for polymer−plasticizer mixtures when the ΔC_p of the polymer and plasticizer is not available.[25]

$$\ln\left(\frac{T_g}{T_{g1}}\right) = \frac{w_2 \ln\left(\frac{T_{g2}}{T_{g1}}\right)}{w_1\left(\frac{T_{g2}}{T_{g1}}\right) + w_2} \tag{8}$$

The other model is the simple empirical model that predicts glass transition temperatures that yielded results that are less than 5% difference from our the experimental results[24]

$$\frac{1}{T_g} = \frac{1}{T_{g1}} + \left(\frac{1}{T_{g2}} - \frac{1}{T_{g1}}\right)\sqrt{w_2} \tag{9}$$

In the above equations, T_g is the glass transition temperature of the plasticized polymer; T_{g1} is the glass transition of plasticizer; T_{g2} is the glass transition of the bare polymer; and w_2 is the weight fraction of the polymer. As shown in Figure 3, eq 8 yielded results that are significantly lower than the experimental results. However, eq 9 shows a much better agreement.

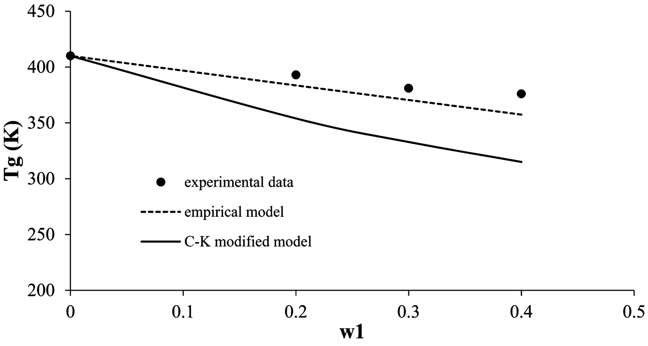

Figure 3. T_g of plasticized films as a function of weight fraction of sorbitol compared with two mathematical models.

Figure 4 shows the effect of adding CNC to the plasticized HPX films with 20−40 wt % of sorbitol. As expected, adding CNC to the plasticized films increased their T_g except in the case in which 1 wt % of CNC was added to the film with 60 wt % HPX and 39 wt % of sorbitol. Compared to the film with 60 wt % HPX and 40 wt % of sorbitol, the T_g decreased from 103.7 to 98.6 °C. In fact, similar behavior was observed for plasticized starch-based composites where the addition of CNC up to 3.2 wt % decreased the T_g of the composite.[26] The reason is not known, and further investigation is needed. Nevertheless, our data show that the effect of adding 1 wt % of CNC on the T_g of the plasticized HPX films depends on the amounts of HPX and sorbitol. In general, adding CNC to a hydrophilic polymer such as HPX reduces its chain mobility and free volume, thereby increasing T_g. This is because there are strong interactions between the hydroxyl groups of CNC and those of HPX.[27] It seems that the effect of such interactions on the T_g (i.e., dT_g/dC_{CNC}) is more or less linear over the range from 1 to 5 wt % and independent of the sorbitol concentration.

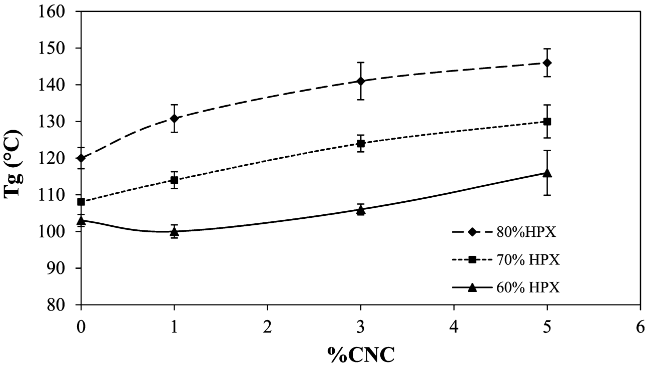

Figure 4. Effect of adding 1−5% CNC to plasticized HPX films on T_g (Data is presented as mean + standard error for n = 3).

To quantify the water diffusivity for the aforementioned HPX films, IGC was used. It should be pointed out that the profile of the elution peaks is not perfectly symmetrical as required by eq 5. In fact, the peaks tend to have a long tail (due to the adsorption of water molecules). The same phenomenon has been reported for cellulosic type of materials.[28] To reduce the adsorption effect, high flow rates but without severe pressure drop were used.

The van Deemter equation plots of plate height (H) versus carrier gas linear velocity (u) over the temperature range of 120−170 °C for the neat HPX film are shown in Figure 5. We omit the corresponding plots of the HPX films with different amounts of sorbitol and/or CNC as they resemble to those of neat HPX. It is obvious from Figure 5 that the carrier gas flow rate used met the condition that the first two terms of the van Deemter equation could be ignored. Estimated diffusion coefficients of water in different HPX films are listed in Table 3. It shows that the diffusion coefficient at infinite dilution increases with increasing temperature, as expected, in all cases. Also, the diffusion coefficient varies with the concentration of additives, sorbitol, and/or CNC added to the HPX film. However, all such changes are more or less within the same order of magnitude.

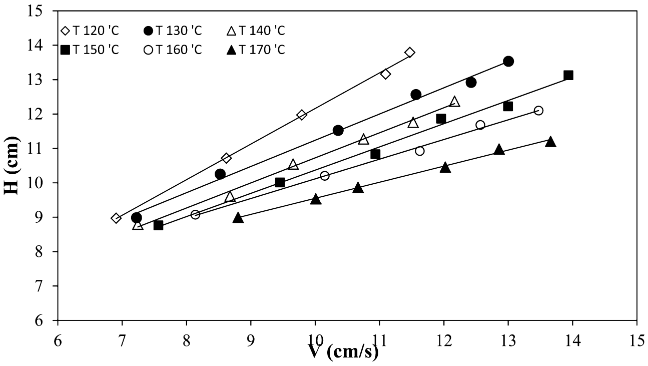

Figure 5. Van Deemter plots for the neat HPX film at various temperatures from 120 to 170 °C.

As mentioned earlier, sorbitol molecules reduce the number of hydrogen bonds between the HPX chains leading to more free volume available for the diffusion of water.[23] In fact, in Figure 6, logarithmic plots of diffusion coefficient versus the sorbitol concentration in HPX over the range of 0 to 40 wt % support such an idea. According to the free volume theory, there exists a logarithmic relationship between the diffusion coefficient and free volume. However, other researchers proposed that increasing the mobility of HPX chains due to the increasing amount of sorbitol would lead to higher rates of free volume redistribution, thereby increasing the rate of diffusion.[22]

Adding a small amount of CNC to the plasticized films decreases the diffusion coefficient. Generally, an increase in barrier properties of polymers due to the addition of nanosized fillers is attributed to three reasons: (1) induced crystallization of the polymer, (2) increase in tortuosity due to fractionation and alignment of crystals in the diffusing direction, and (3) decrease in the free volume of the amorphous phase.[19] Several studies have related the reduction in water transport through biocomposites filled with CNCs (with average aspect ratios of 10−50) to the increase in the tortuosity in the films.[12,13,15−18] Our DSC results did not suggest the existence of a crystalline phase in HPX films upon addition of CNC. On the other hand, Figure 7 suggests that it is the decrease in the free volume that leads to the decrease in the water diffusivity as the data shows a linear relationship between logarithm of diffusion versus concentration of CNC in the films (i.e., the free volume theory). Cellulose-based fillers are able to form strong hydrogen bonds with a hydrophilic biopolymer resulting in a less mobile structure (i.e., lower free volume) and therefore reduce the diffusivity of water in the composite environment.[15] In the present study, interaction of CNC with HPX decreased the diffusion coefficient by 10−50% at different temperatures as

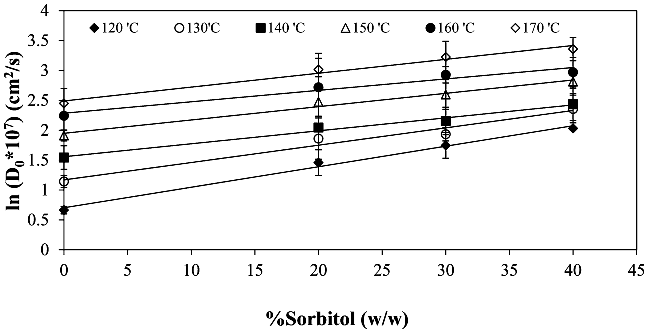

Figure 6. Effect of sorbitol concentration on the diffusion coefficient of water at various temperatures.

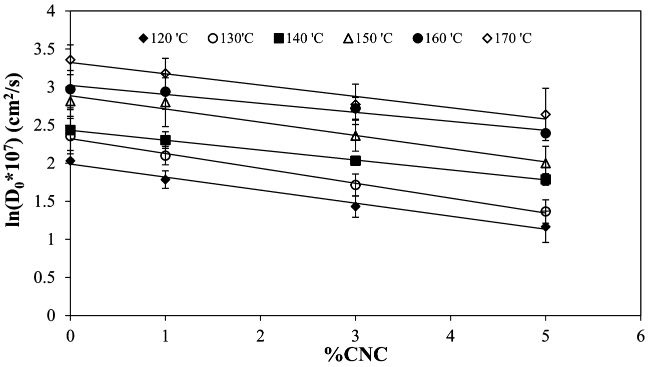

Figure 7. Effect of adding CNC to HPX films with 60% w/w HPX on the diffusion coefficient of water at various temperatures.

Table 3. Infinite Dilution Diffusion Coefficients of Water in HPX Films with Different Amounts of Sorbitol and CNC at Various Temperatures

	D^{∞} ($\times 10^7$ cm^2/s)						
T (K)	HPX	20% sorbitol	30% sorbitol	40% sorbitol	1% CNC	3% CNC	5% CNC
394	1.94 ± 0.12	4.30 ± 0.95	5.74 ± 1.28	7.63 ± 0.23	5.96 ± 0.69	4.19 ± 0.59	3.21 ± 1.85
404	3.13 ± 0.29	6.43 ± 1.46	6.91 ± 0.55	10.55 ± 2.15	8.16 ± 0.25	5.55 ± 0.61	3.92 ± 0.33
414	4.68 ± 0.94	7.72 ± 0.49	8.63 ± 2.06	11.42 ± 3.27	10.01 ± 1.11	7.63 ± 0.3	5.97 ± 0.45
424	6.77 ± 0.95	11.89 ± 2.1	13.44 ± 1.19	16.70 ± 1.36	16.48 ± 0.57	10.61 ± 0.81	7.39 ± 0.78
434	9.41 ± 2.4	15.16 ± 0.87	18.68 ± 3.12	19.53 ± 2.87	18.91 ± 3.60	15.20 ± 2.21	10.99 ± 1.56
444	11.58 ± 2.41	20.40 ± 3.01	25.15 ± 4.06	28.74 ± 1.63	24.08 ± 2.9	16.01 ± 1.08	14.03 ± 3.56

a result of a reduction in free volume and chain mobility. This is somewhat unexpected as the CNC added did not increase the tortuosity of the water molecules. However, Dufresne et al. had a similar observation that adding 30% CNC to starch-based biocomposites reduced the diffusion coefficient of water only by about 65% in their study.[29] It seems that sorbitol increases, while CNC decreases, the free volume in the HPX matrix leading to the result that the water diffusivity of the HPX film with 35 wt % sorbitol and 5 wt % is comparable to that of the neat HPX film.

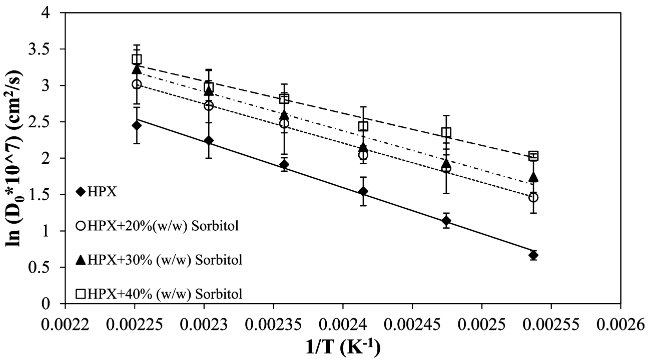

Figure 8. Inverse temperature dependence of the diffusion coefficient of water in HPX films with various concentrations of sorbitol.

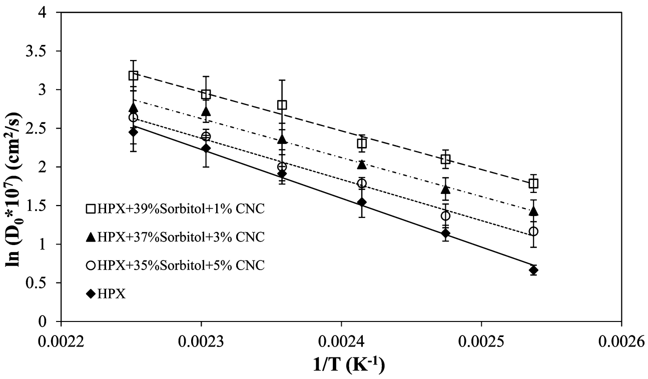

Figure 9. Inverse temperature dependence of the diffusion coefficient of water in HPX films with 60 wt % of HPX and various concentrations of sorbitol and CNC.

Figures 8 and 9 show the inverse temperature dependence of the logarithm of the diffusion coefficient of water for the HPX films at various concentrations of sorbitol and CNC. Obviously, the data follow a linear relationship in the two plots, indicating that the data follow the Arrhenius equation of the temperature dependency of diffusion coefficient (D)

$$D = D_0 e^{-E_a/RT} \tag{10}$$

where D_0 is the pre-exponential constant, and E_a is the activation energy. R and T are the universal gas constant and temperature, respectively. Here, the activation energy signifies the energy required for free volume hole formation against the attractive forces between the polymer chains as well as that required for the water molecules to jump from one free volume hole to a nearby one.[22] Following the Arrhenius behavior simply suggests that the water molecules exhibited a hopping diffusion mechanism as described in the free volume theory.[21]

Table 4. Dependence of Activation Energy of Water Diffusion in HPX Films on Sorbitol and CNC Concentrations (films contained 60 wt % HPX)

sorbitol % (w/w)	E_a (kJ mol^{-1})	CNC % (w/w)	E_a (kJ mol^{-1})
0	52.6 ± 0.3	0 (40% sorbitol)	36.8 ± 0.4
20	44.9 ± 0.2	1 (39% sorbitol)	41.6 ± 0.3
30	44.8 ± 0.4	3 (37% sorbitol)	41.9 ± 0.3
40	36.8 ± 0.4	5 (35% sorbitol)	44.4 ± 0.3

Table 4 summarizes the activation energy values determined based upon the data shown in Figures 8 and 9. Over the temperature range of interest, activation energy decreases with increasing concentration of sorbitol. As discussed before, adding sorbitol reduces interchain interactions, thereby decreasing the activation energy required for the free volume hole formation and for the hopping of the water molecules.[22]

On the other hand, adding CNC to plasticized films increases activation energy. Once again, the increase in the activation energy is attributed to the adsorption of HPX chains on to the CNC surfaces. It is obvious that the most significant increase in the activation energy occurs at 1 wt % CNC. Further increase in the CNC concentration does not increase the activation energy much. This means that increasing the CNC concentration reduces the diffusion coefficient by reducing the fractional free volume but not by decreasing the corresponding activation energy. This is probably due to an insignificant change in the environment experienced by water molecules.

■ CONCLUSION

To determine the suitability of using HPX as an internal layer for packaging material, the effect of adding sorbitol, a commonly used environmentally friendly plasticizer, and a nanosized filler, namely, cellulose nanocrystals, on the film glass transition temperature (T_g) and water diffusivity was studied. Adding sorbitol to the HPX film decreased T_g as a result of increasing free volume in the material. This is because sorbitol reduces the number of hydrogen bonds formed between the HPX chains. The diffusivity of water in such plasticized HPX films was increased 2−5 times by adding 20−40 wt % of sorbitol. The concentration dependence of the water diffusivity indicates that the diffusion of water follows the free volume theory. Adding CNC to the plasticized films increased the T_g of the films while decreasing the water diffusivity. Once again, the free volume theory is able to explain the data, and the expected increased tortuosity due to the presence of CNC with high aspect ratios did not slow the diffusion of water molecules. The addition of 5% CNC to plasticized films would neutralize the effect of sorbitol on the increase of the diffusion coefficient.

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Notes

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