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Short communication

Water transmission barrier properties of biodegradable films based on cellulosic whiskers and xylan

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ABSTRACT

The reinforcement of natural biopolymers with cellulosic whiskers has been shown to be beneficial for physical strength properties including xylan films. This study examines the water transmission properties of xylan films reinforced with cellulosic whiskers prepared from kraft pulp hydrolyzed with sulfuric acid. Measurements of water transmission rate (WVTR) were accomplished by a modification of wet cup method described by ASTM E 96-95. The results showed that films prepared by xylan reinforced by 10% sulfonated whiskers exhibited a 74% reduction in specific water transmission properties with respect to xylan film and a 362% improvement with respect to xylan films reinforced with 10% softwood kraft fibers.

1. Introduction

The majority of engineered plastic materials used today are made from synthetic polymers. The use of conventional petroleum-based polymer products creates many potential problems due to their non-renewable nature and ultimate disposal. Cellulose and its derivatives, when used in such applications, offers advantages with respect to sustainability, limited environmental impact and simplified end-of-life disposal issues (Petersson & Oksman, 2006; Ragauskas et al., 2006; Samir, Alloin, & Dufresne, 2005). Of growing interest is the use of polysaccharide derived films as an alternative to petro-based materials such as polyvinyl alcohol and polyvinylidene chloride. Early studies examined the application of chitosan, starch and cellulose derivatives which were shown have film forming properties (Krochta, Baldwin, & Nisperos-Carriedo, 1994). Glucuronoxylan isolated from aspen have been used to produce films (Gröndahl, Eriksson, & Gatenholm, 2004; Linder, Bergman, Bodin, & Gatenholm, 2003) that exhibit improved strength and oxygen barrier properties when plasticized with xylitol or sorbitol. Höije, Gröndahl, Tømmeraas, and Gatenholm (2005) has shown that arabinoxylan film can be prepared from the extracts of barley husks without the need for plasticizers. The resulting films were stiff and rather brittle with high water content. Dammström, Salmén, and Gatenholm (2005) prepared composite films of glucuronoxylan reinforced with bacterial cellulose and showed that this biocomposite could form transparent strong films. The use of xylan for the production of biodegradable composite films in combination with wheat gluten has been investigated (Kayserilioglu, Bakir, Yilaz, & Akkas 2003). The presence of xylan did not adversely affect the film forming quality or the water vapor transmission rate, though the mechanical and solubility properties depended on the quantity of xylan in the wheat gluten. Recently, studies by Ragauskas (2007) have reported that oat-spelt xylan, plasticized with sorbitol and reinforced with sulfuric acid generated cellulose whiskers exhibited enhanced strength properties. For example, the addition of 7% sulfonated whiskers increased the tensile energy absorption of the xylan films by 445% and the tensile strength of the film by 141%. As reviewed by Samir et al. (2005), the improvements in mechanical properties of the composite can be attributed to the formation of a rigid hydrogen-bonded network of cellulose whiskers that is governed by percolation mechanism. The objective of this study is to evaluate the effect of reinforcing xylan films with cellulose whiskers with respect to water transmission properties.

2. Experimental

2.1. Materials

Oat spelt xylan was obtained from Aldrich and was determined to contain 81% xylose, 9.8% arabinose, 7.6% glucose, 1.4% galactose and 0.2% of mannose. A dry, commercial, elemental chlorine-free (ECF) bleached softwood (SW) kraft pulp was employed for all

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studies. All other reagents and solvents were purchased from Aldrich and used as received.

2.2. Preparation of sulfonated cellulose whiskers

An aqueous suspension of cellulose whiskers was prepared following the literature procedures outlined by Yunqiao et al. (2007). A fully bleached ECF softwood kraft pulp, at 7% wet-basis moisture content, was ground with a Wiley mill to pass through a 0.5 mm mesh screen. The milled pulp (36.00 g, oven-dried weight) was hydrolyzed with 64 wt% sulfuric acid (700.00 ml) at 45 °C for 45 min, resulting in a milky colloidal suspension. The hydrolysis reaction was terminated by diluting the suspension with deionized water (7 L). After standing overnight, the water was decanted and the settled cellulosics were collected with a minimal amount of water. Excess acid was removed with a water wash (200 ml), centrifuged initially at 3000 rpm for 20 min and then at 11,000 rpm for 20 min. The aqueous phase was discarded and the wash cycle was repeated an additional two times. The solids sample was then dialyzed (Spectra/Por membrane, MWCO 50 K) against water for several days until the whisker slurry achieved a neutral pH. The suspension was then sonicated with a Heat Systems-Ultrasonic W-385 sonicator for 35 min and then allowed to stand over a mixed bed resin (Sigma TMD-8) for 48 h, filtered through hardened ashless filter paper and lyophilized. The average yield of cellulosic whiskers was 35%. The bulk charge on starting cellulose fibers and whiskers was determined using a method developed by Katz, Beatson, and Scallan (1984) and was found to be 3.82 mmol carboxylate groups/100 g and 9.73 mmol acid groups/100 g respectively.

2.3. Preparation of xylan–sulfonated whisker nanocomposite film

Xylan composite films were formed by adding an aqueous suspension (35.00 ml) of sulfonated whisker suspension to xylan (0.25 g). The solid whisker content in the whisker suspension used was 0.0, 5.0, 10.0, 15.0, 25.0, 50.0 wt% of the total mixture of sorbitol, xylan, and cellulose whiskers. Sorbitol (0.25 g, 1.37 mmol) was added to the mixture with stirring and then heated to 95 °C for 15 min. The solution was then poured into polystyrene 4.6 cm diameter petri dishes and allowed to dry at room temperature for three days. The resulting film thickness of sulfonated whisker was 0.091 mm with standard deviation of 0.002 mm.

2.4. Preparation of xylan–kraft softwood fiber reinforced films

Xylan composite films were prepared with the same procedure as described above except that the sulfonated cellulose whiskers were replaced with bleached softwood kraft fibers. The thickness of resulting composite films for xylan–5% softwood fiber film was 0.154 mm and for xylan–10% softwood fiber film was 0.244 mm with standard deviation of 0.005 mm.

2.5. Water vapor transmission rate (WVTR)

The technique used to measure water vapor transmission rate (WVTR) was a modification of the wet cup method described by ASTM E 96-95. The procedure involves using a Petri dish filled with distilled water and covered with a film. The mass of water lost from the dish was monitored as a function of time. Thickness measurements of the films were obtained with a digital gauge at a minimum of five positions on a test specimen. The glass petri dish was filled with distilled water (10.00 ml) and then the film was sealed to the petri dish with a 5-min epoxy adhesive. After allowing the epoxy to cure for 30 min, the sample dish was weighed and placed in a convection oven at a setting of 37.0 °C in the oven. The sample dish was periodically removed and weighed. The weight loss over a period of 24 h was determined. The water vapor transmission rate was calculated using: WVTR = mass of water lost/time - area = flux/area with units of g/hm^2. The percentage of error as determined by Percentage error = (Standard Deviation/Mean) $*$ 100 was less than 7%.

2.6. Optical microscopy analysis

The composite films were mounted on microscope slides and examined with Leica DMLM optical microscope. Bright-field images were collected with a transmitted light detector.

2.7. Electron microscopy

The composite films were analyzed by HITACHI S800, thermally assisted field emission (TFE) scanning electron microscope (SEM) with an accelerating voltage of 12 kV. The films were coated with a thin layer of gold prior to SEM observation.

3. Results and discussion

This study examines the reinforcement of xylan/sorbitol films with cellulose whiskers and its impact on water transmission. The films were prepared with varying amounts of cellulose whiskers (0–50% by mass) which were prepared by sulfuric acid hydrolysis of softwood bleached kraft fibers.

By AFM analysis the cellulosic whiskers were observed to have rod like structure with an average length of 150–200 nm and a width of less than 20 nm. Previous studies have indicated that AFM measurements of cellulose whiskers overestimated the width of the whiskers due to the tip broadening effects (Kvien, Tanem, & Oksman, 2005).

Prior studies have shown that the addition of 7% sulphonated whiskers increased the tensile energy absorption of the xylan films by 445% and the tensile strength of the film by 141% (Saxena & Ragauskas, 2009). To determine if cellulose whiskers impact water transmission properties a series of xylan composite films were prepared and analyzed using optical microscope and scanning electron microscopy. The specific water transmission rate (WVTR) of

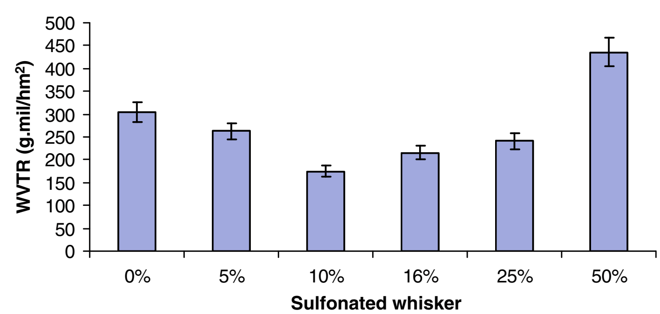

Fig. 1. Effect of sulfonated whisker dosage on specific water vapor transmission rate of xylan film.

Table 1
Specific water vapor transmission rate of xylan films.

Sample	Specific water vapor transmission rate (gmil/hm^2)
Control (Xylan)	304
Xylan + 5% softwood fiber	537
Xylan + 10% softwood fiber	807
Xylan + 10% sulfonated cellulose whiskers	174

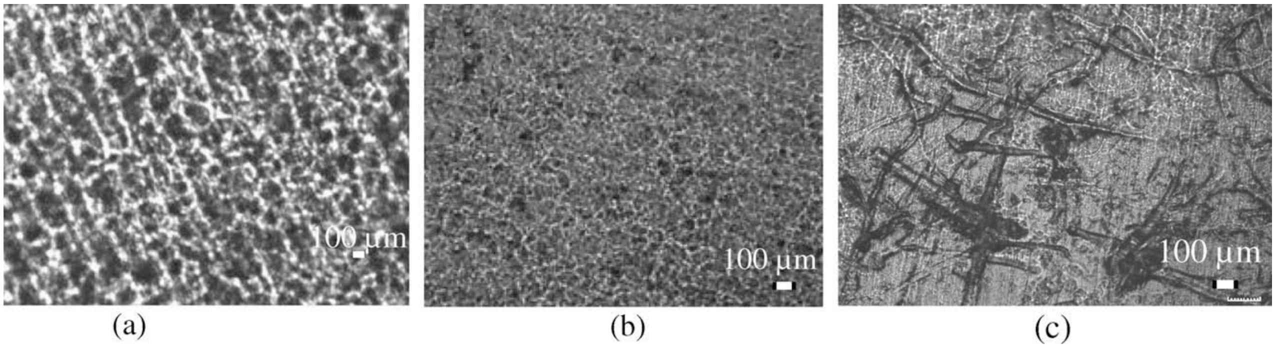

Fig. 2. Optical microscope image of (a) control xylan (b) xylan reinforced with 10% sulfonated cellulose whiskers (c) xylan reinforced with softwood fibers.

the xylan films are shown in Fig. 1. Because the thickness of the xylan–sulfonated whiskers and xylan–softwood fiber are different, the WVTR is sometimes normalized to film thickness (l) to obtain the specific water vapor transmission rate ($\acute{R} = \text{WVTR} * \text{l}$) with units of gmil/hm^2 (Hu, Topolkaraev, Hiltner, & Baer 2000).

The incorporation of sulfonated cellulose whiskers was found to reduce WVTR film properties. For example, the incorporation of 10% sulfonated cellulose whiskers into a xylan film decreased the specific WVTR value from 304 g/hm^2 of the control to 174 g/hm^2 of xylan–cellulose whisker films. The membrane with 16% sulfonated cellulose whiskers showed higher WVTR. This was contradictory to what was expected but was attributed to whisker agglomeration at higher dosages providing channels in the membrane that allow for more rapid permeation. Similar experiments were performed using a softwood kraft fiber as reinforcement in a xylan film and it was found that with 5% pulp fibers specific water vapor transmission rate increases which increases further on addition of 10% pulp fibers to xylan as summarized in Table 1.

Optical microscope images of xylan, xylan–softwood kraft fiber and xylan–cellulose whisker films were acquired both before and after the water transmission rate and these are summarized in Fig. 2. The specific density of xylan films was calculated and is summarized in Table 2. The data shows that the xylan–10% cellulose whisker films were denser than the control and the xylan–10% softwood films. The xylan control in Fig. 2a shows hexagonal platelets like pattern (Marchessault, Morehead, Walter, Glaudemans, & Timell 1961). The xylan–softwood kraft fiber films exhibited fiber aggregation as shown in Fig. 2c; this can be reason of higher barrier properties of xylan–sulfonated whisker than xylan–softwood kraft fiber films which have a more open structure.

Table 2
Specific density of xylan films.

Sample	Specific density of xylan films (g/cm^3)
Control (xylan)	0.7272
Xylan + 5% sulfonated cellulose whiskers	0.7560
Xylan + 10% sulfonated cellulose whiskers	0.7616
Xylan + 16% sulfonated cellulose whiskers	0.7451
Xylan + 50% sulfonated cellulose whiskers	0.6600
Xylan + 10% softwood fiber	0.1780

Lagaron, Catala, and Gavaa (2004) discussed the role of crystalline structure of plastics and emphasized that high crystallinity improves barrier properties. Cellulose whisker have high crystallinity (de Souza Lima & Borsali, 2004) which is more than 60% together with the dense network held together by rigid hydrogen-bonded network of cellulose whiskers which causes more tortuous path for water molecules to follow and less water molecules to penetrate the crystalline part of cellulose whiskers and this may lower the water transmission rate. SEM images of fractured membrane surface of control xylan in Fig. 3(a) and (b) showed rough texture in comparison to smooth surface of fractured surface of xylan reinforced with cellulose whiskers in Fig. 4(a) and (b). SEM images of control xylan film surface in Fig. 3(c) shows agglomeration in comparison to well dispersed sulfonated cellulose whiskers on xylan surface in Fig. 4(c). The uneven structure and agglomeration of the xylan can be the cause of higher water vapor transmission rate of control xylan film in comparison to xylan reinforced with sulfonated cellulose whiskers. It appears that pulp fibers cannot form an integrated matrix that cellulose whiskers can and this latter effect has a substantial benefit in the overall reduction of water transmission.

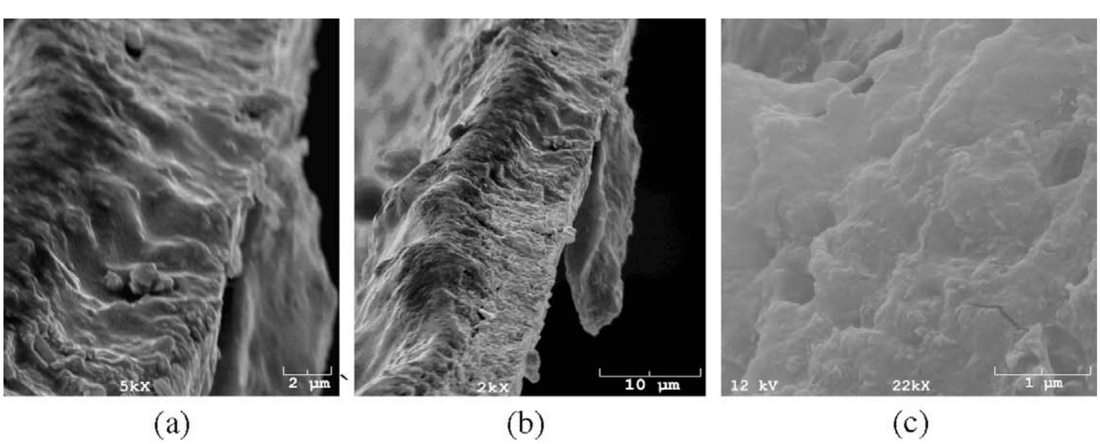

Fig. 3. Scanning electron microscopic images of control xylan film (a) and (b) cross section images (c) surface image.

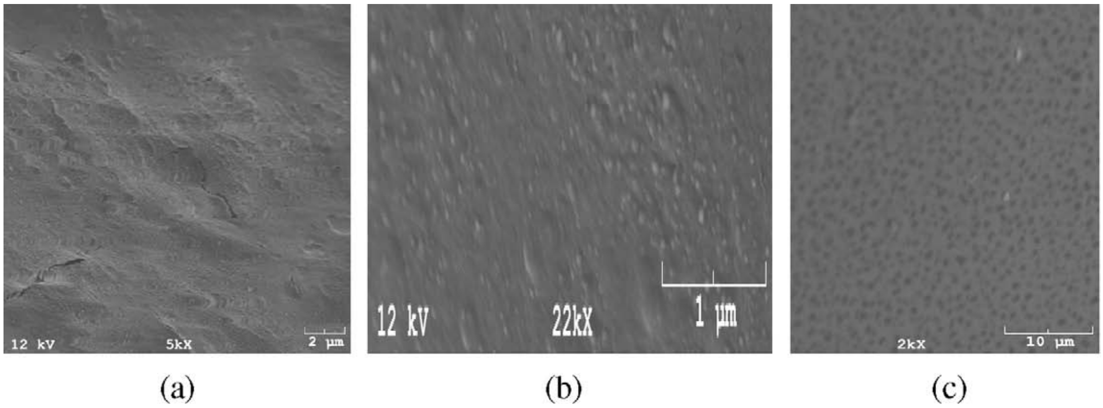

Fig. 4. Scanning electron microscopic images xylan film reinforced with 10% sulfonated cellulose whiskers (a) and (b) cross section image of xylan (c) surface image.

4. Conclusions

Xylan incorporated with low dosages of cellulose whiskers can be used to prepare films with improved water barrier properties. It appears that the high degree of crystallinity of cellulose whiskers, dense composite structure formed by the whiskers and a rigid hydrogen-bonded network of cellulose whiskers that is governed by percolation mechanism can cause cellulose whiskers to form integrated matrix which contribute to substantial benefit in the overall reduction of water transmission. The xylan–softwood kraft fiber films exhibited fiber aggregation; this can be reason of higher barrier properties of xylan–sulfonated whisker than xylan–softwood kraft fiber films which have a more open structure.

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