Carbohydrate Polymers 84 (2011) 1371–1377

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Moisture barrier properties of xylan composite films

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ARTICLE INFO

Article history:
Received 29 November 2010
Received in revised form 15 January 2011
Accepted 21 January 2011
Available online 28 January 2011

Keywords:
Composites
Xylan
Nanocrystalline cellulose
Moisture barrier

ABSTRACT

Moisture barrier properties of films based on xylan reinforced with several cellulosic resources including nanocrystalline cellulose, acacia bleached kraft pulp fibers and softwood kraft fibers have been evaluated. Measurements of water vapor transmission rate (WVTR) were performed by a modification of the wet cup method described by ASTM E 96-95, indicating that membranes with 10% nanocrystalline cellulose, prepared using a sulfuric acid, exhibited the lowest permeability value of 174 g mil/h m^2 among the composite films studied. Both the acacia and the softwood kraft pulp fibers when used for xylan film formation exhibited higher water vapor transmission rates at addition levels of 50% and no improvement at lower levels of 5% and 10%, in comparison to control xylan films. Reinforcement of xylan with hydrochloric acid made nanocrystalline cellulose yielded films that showed a reduction in water transmission but the reduction was not as significant as with the reinforcement of xylan with sulfuric nanocrystalline cellulose. The results showed that xylan films reinforced with 10% sulfuric nanocrystalline cellulose exhibited reductions in water transmission rates of 362%, 62% and 61% over films prepared with 10% softwood kraft fibers, 10% acacia fiber and 10% hydrochloric acid prepared nanocrystalline cellulose, respectively. The morphology of the resulting nanocomposite films was examined by SEM and AFM which showed that control films containing xylan and sorbitol had a more open structure as compared to xylan–sorbitol films containing sulfuric nanocrystalline cellulose. The results from FT-IR suggested strong interactions occurred between the nanocrystalline cellulose and the matrix.

1. Introduction

Petrochemically based polymers, such as polyolefins and polyesters, have been increasingly used as packaging materials due, in part, to their availability, low cost and favorable mechanical properties, but their non-biodegradability has generated environmental concerns (Tharanathan & Saroja, 2001). The advantages of using biopolymers to produce such packaging films include their renewability, availability, limited environmental impact and simplified end-of-life disposal issues (Petersson & Oksman, 2006; Ragauskas et al., 2006; Samir, Alloin, & Dufresne, 2005). Early studies examined the application of chitosan, starch and cellulose derivatives for their film forming properties (Krochta et al., 1994). Xylan is one of the most common hemicelluloses and is the most abundant polysaccharide in nature after cellulose (Coughlan & Hazlewood, 1993; Ebringerová & Heinze, 2000; Gabrielli & Gatenholm, 1998). Glucuronoxylan, isolated from aspen wood, when plasticized with xylitol or sorbitol has been used to produce films that exhibit improved strength and oxygen barrier properties with respect to control glucuronoxylan films (Gröndahl, Eriksson, & Gatenholm, 2004; Linder, Bergman, Bodin, & Gatenholm, 2003). Höije, Gröndahl, Tømmeraas, and Gatenholm (2005) have shown that arabinoxylan films can be prepared from the extracts of barley husks without the need for plasticizers. Dammström, Salmén, and Gatenholm (2005) showed that films based on glucuronoxylan reinforced with bacterial cellulose have tensile strength values ranging between 65 and 110 MPa. Xylan has also been used as an additive with wheat gluten for the production of biodegradable composite films (Kayserilioglu, Bakir, Yilaz, & Akkas, 2003). The xylan did not adversely affect the film forming quality or water vapor transmission rate, although mechanical and solubility properties were dependent on the quantity of xylan in the wheat gluten. Water vapor transmission rate is an important property for many film packaging applications influencing shelf life and product stability. Tock (1983) reviewed some of the permeability and water vapor transmission rate properties of commercial polymeric films and provided an overview of how structural changes, such as crystallinity, and the presence of plasticizers and lamination can influence the barrier properties of polymer films. Miranda, Garnica, Lara-Sagahon, and Cárdenas (2004) discussed water vapor transmission values of chitosan film plasticized with sorbitol, glycerol or polyethylene glycol reporting values from 1.3 to 1.5×10^{-3} [g/(m^2 h Pa)].

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doi:10.1016/j.carbpol.2011.01.039

Aydinli and Tutas (2000) determined WVP of $(6.3–11.6) \times 10^{-5}$ [g mm/(m^2 h Pa)] for polyethylene glycol-plasticized locust bean gum as compared to $(6.2–11.6) \times 10^{-5}$ [g mm/(m^2 h Pa)] reported by Mikkonen, Heikkilä, Helén, Hyvönen, and Tenkanen (2010). The WVP of sorbitol-plasticized oat spelt arabinoxylan films studied using a fan-equipped desiccator was 4.5×10^{-5} [g mm/(m^2 h Pa)] (Mikkonen et al., 2009), while Péroval, Debeaufort, Despré, and Voilley (2002) reported a value of 63.7×10^{-5} [g mm/(m^2 h Pa)] for corn arabinoxylan films. Saxena, Elder, Shaobo, and Ragauskas (2009) have shown that the addition of 7% sulfuric nanocellulose whiskers to xylan increased the tensile energy absorption of the resulting films by 445% and the tensile strength of the film by 141%. The improvements in mechanical properties of the composite film based on reinforcement with cellulose whiskers can be attributed to the formation of a rigid hydrogen-bonded network of cellulose whiskers that is governed by the percolation mechanism (Samir et al., 2005). Recent studies by Saxena and Ragauskas (2009) have also shown that xylan films reinforced with 10% sulfuric nanocrystalline cellulose exhibited a 74% reduction in specific water transmission properties with respect to control xylan film and 362% improvement with respect to xylan reinforced with 10% softwood kraft pulps. The objective of this study is to compare these previous results with xylan films reinforced with hydrochloric acid prepared nanocrystalline cellulose and films reinforced with acacia and softwood bleached kraft fibers. The bleached acacia kraft fiber was selected because it is one of the shortest commercially available pulp fibers with a weight-weighted length of 0.62 mm and width of ~0.02 mm and yet is approximately 4000 orders of magnitude larger than the cellulosic whiskers employed.

2. Experimental

2.1. Materials

Oat spelt xylan and sorbitol were obtained from Aldrich and used as received. The plant derived xylan was shown to consist of 81.0% xylose, 9.8% arabinose, 7.6% glucose, 1.4% galactose and 0.2% of mannose. For all studies, a dry commercial elemental chlorine-free (ECF) bleached softwood (SW) kraft pulp and fully bleached acacia kraft pulp were used as received. The arithmetic mean length and curl of acacia kraft fibers and softwood fibers were 0.653 ± 0.028 mm, 0.088 ± 0.005 and 2.276 ± 0.052 mm, 0.089 ± 0.006 mm respectively as determined using a fiber quality analyzer (FQA). Dialysis tubes were purchased from Spectrum Labs. All other reagents and solvents were purchased from Aldrich and used as received.

2.2. Preparation of sulfuric nanocrystalline cellulose

An aqueous suspension of nanocrystalline cellulose was prepared following the procedure outlined by Pu et al. (2007). In brief, softwood kraft pulp was ground in a Wiley mill to pass through a 20-mesh screen. The acid hydrolysis of the milled pulp was accomplished with 64 wt% sulfuric acid at 45 °C for 45 min with stirring. The reaction was halted by adding a 10-fold excess of deionized (DI) water. The sediment was centrifuged for 20 min at 11,000 rpm and the precipitate was collected, re-dispersed and re-centrifuged twice. The solids suspension was then dialyzed against DI water for 3 days using regenerated cellulose dialysis tubing (Spectra/Por membrane, MWCO 50K) until the pH of the solution was neutral. Sonication was then performed on the whiskers solution for 35 min while immersed in an ice bath. The average yield of cellulosic whiskers was 35%. The bulk charge for the 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 hydrochloride nanocrystalline cellulose

An aqueous suspension of hydrochloric nanocrystalline cellulose was prepared following the procedure outlined by Araki, Wada, Kuga, and Okano (1998). Fully bleached softwood kraft pulp with 7% wet-basis moisture content was Wiley milled to pass through a 0.5 mm mesh screen. A sample of this ground pulp (36.00 g, oven-dried weight) was treated with an aqueous 4.0 N HCl solution (2600 mL) at 80 °C for 8 h. The reaction was terminated by diluting the mixture with deionized water (8 L). After standing overnight, the clear supernatant was decanted and the settled cellulosics were diluted with deionized water (8 L) and then allowed to settle. This procedure was repeated until the pH of the supernatant was approximately 3. The cellulosics were then transferred to a series of dialysis tubes (Spectra/Por membrane, MWCO 50K) and dialyzed against deionized water for several days until the solution pH was >4 and the supernatant became turbid. The cellulosics were next sonicated with an Ultrasonic Processor GEX-500 for 2 min followed by centrifugation at 3000 rpm for 5 min. The turbid supernatant was decanted, the sediment was dispersed in deionized water, sonicated for 2 min and re-centrifuged. This procedure was repeated until the supernatant become clear. The cellulosic suspensions were concentrated by centrifugation at 11,000 rpm for 25 min and the clear supernatant was discarded, resulting in a final consistency of 1.57% for the whiskers. The concentrated whisker suspension was used directly to form nanocomposites. The gravimetric yield of HCl generated whiskers was 7–10%. The HCl generated whiskers had an absence of strong acid groups but weak acid groups of 1.4 mmol/100 g.

2.4. Preparation of xylan nanocomposite film

Xylan composite films were formed by adding an aqueous suspension (35.00 mL) of sulfuric nanocrystalline cellulose suspension to xylan (0.25 g). The solid nanocrystalline cellulose content in the suspension used was 0.0, 5.0, 10.0 and 50.0 wt% of the total mixture of sorbitol, xylan, and nanocrystalline cellulose. Sorbitol (0.25 g, 1.37 mmol) was added to the mixture with stirring and the mixture was heated to 95 °C for 15 min. The solution was then poured into polystyrene petri dishes (4.60 cm diameter) and allowed to dry at room temperature for three days. The resulting thickness of xylan films reinforced with sulfuric cellulose whiskers was 0.091 ± 0.002 mm thick.

Xylan composite films containing hydrochloride generated nanocrystalline cellulose, ECF bleached kraft softwood and acacia fibers were prepared with the same procedure used to form xylan–sulfuric nanocrystalline cellulose composite films. The thickness of resulting composite films for xylan–10% softwood fiber film was 0.244 mm, xylan–10% acacia fiber was 0.0886 and xylan–10% hydrochloride nanocrystalline cellulose was 0.096 mm, with standard deviation of 0.088 mm, 0.065 mm and 0.005 mm, respectively.

2.5. Water vapor transmission rate (WVTR)

The WVTR analysis was performed as described by ASTM E 96-95. Films were sealed to 4.60 cm diameter petri dish with a 5-min epoxy adhesive. The sample dish containing deionized water (10.00 mL) 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 to access the WVTR of the films. The water vapor transmission rate was calculated using: WVTR = mass of water lost/time × area = flux/area with units of g d^{-1} m^{-2}. The per-

centage 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

Differences in cross-section and surface morphology of the composite films were analyzed using a Hitachi S800, thermally assisted field emission (TFE) scanning electron microscope (SEM) with an accelerating voltage of 12 kV. The samples were sputter-coated with gold prior to examination.

2.7.1. Atomic force microscopy

Nanocrystalline cellulose and films were analyzed using a Dimension 3100 scanning probe microscope and Nanoscope III controller. The images were acquired in tapping mode in air using an etched silicon probe with the cantilever resonance frequency of 150 kHz. Scans were done at 2 μm.

2.8. Fourier transform infrared spectroscopy (FT-IR)

FT-IR analysis was performed in an absorbance range of 4000–500 cm^{-1}, to compare the control xylan films with the nanocomposite films using Bruker Vector 22 FT-IR.

3. Results and discussion

This study examines the reinforcement of xylan/sorbitol films with nanocrystalline cellulose, bleached acacia fiber and softwood kraft fibers and its impact on water transmission. By AFM analysis, nanocrystalline cellulose was observed to have rod like structure with an average length of sulfuric nanocrystalline cellulose in range of 150–200 nm and a width of less than 20 nm while hydrochloric nanocrystalline cellulose had an average length of 200–300 nm and a width slightly less than 20 nm. These results are consistent with the literature reported for nanocrystalline cellulose prepared from softwood kraft pulps using sulfuric acid and hydrochloric acid.

Recently, studies by Saxena et al. (2009) have reported that oat-spelt xylan, plasticized with sorbitol and reinforced with 7% sulfuric nanocrystalline cellulose increased the tensile energy absorption of the xylan films by 445% and the tensile strength of the film by 141% with respect to control xylan film. Saxena and Ragauskas (2009) have also shown that when xylan films are reinforced with 10% sulfuric nanocrystalline cellulose, WVTR reduces from 304 g/h m^2 for control to 174 g mil/h m^2 for xylan–sulfuric nanocrystalline cellulose films. To determine the impact of alternative cellulosic fillers on water transmission properties, a series of xylan composite films were prepared and analyzed using the water vapor transmission test. In the current work, similar experiments were performed using acacia fiber and hydrochloric prepared nanocrystalline cellulose as reinforcement in a xylan film. Because the thickness of the xylan–sulfonated nanocrystalline cellulose, xylan–softwood fiber and xylan–acacia fiber are different, the WVTR was normalized to film thickness (l) with units in mm to obtain the specific water vapor transmission rate (R = WVTR × l) with units of g mm/d m^2 (Hu, Topolkaraev, Hiltner, & Baer, 2000).

Xylan films reinforced with 10% acacia fiber and 10% hydrochloric nanocrystalline cellulose exhibited virtually no improvement in specific water vapor transmission rate in comparison to control. Xylan film reinforced with 10% sulfuric nanocrystalline cellulose exhibited lowest specific water transmission rate of 174 g mil/h m^2 and xylan film with softwood fiber exhibited highest water transmission rate as summarized in Table 1. The water transmission rate at other levels is summarized in Fig. 1. It was found that the addition of 5% softwood kraft pulp fibers yielded a xylan film with increased specific water vapor transmission rate and a significant high water vapor transmission rate at 50% dosage with respect to control. The addition of softwood kraft fibers in the xylan film causes a significant high specific water vapor transmission rate at any dosages (5%, 10% and 50%). The addition of hydrochloric acid prepared nanocrystalline cellulose to xylan films was also analyzed for specific water transmission rate. The specific WVTR values decreased as the content of HCl generated nanocrystalline cellulose in the xylan film increased from 0% to 5% and further decreases at higher dosage of 50% addition in the xylan. WVTR values of xylan–50% hydrochloric nanocrystalline cellulose are almost similar to the values of xylan–10% sulfuric nanocrystalline cellulose.

Table 1
Specific water vapor transmission rate of xylan films.

Sample	Specific water vapor transmission rate (g.mil/h.m^2)
Control (xylan)	304
Xylan + 10% acacia fiber	283
Xylan + 10% hydrochloric nanocrystalline cellulose	281
Xylan + 10% softwood fiber	807
Xylan + 10% sulfuric nanocrystalline cellulose	174

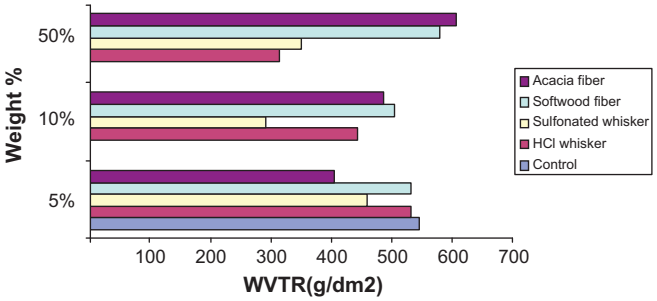

Fig. 1. Water vapor transmission rate for xylan films.

The rate of water transmission for the composite xylan and control films for first 24 h is summarized in Fig. 2. As can be seen, the control xylan film has a higher rate of weight of water loss per unit time whereas 10% sulfuric nanocrystalline cellulose and 50% hydrochloride generated nanocrystalline cellulose reinforced xylan films have the lowest weight difference loss per unit time. The rate increases initially then remains constant for control, sulfuric nanocrystalline cellulose and hydrochloric nanocrystalline cellulose reinforced film but for acacia and softwood fiber reinforced film, the rate shows an increase trend. The mechanism of water transmission can be attributed to a diffusion process in which water vapor condenses and dissolves on film surface and then liquid water diffuses through the membrane and finally water vapor evaporates from the other side of film. The low initial rate can be described as initial adsorption phase when water vapor condenses and dissolves on film surface and then liquid water diffuses through the membrane and finally water vapor evaporates from the other side of film.

The incorporation of sulfonated cellulose whiskers was found to reduce WVTR properties which can be attributed to the tortuous path the water molecules have to travel around the cellulose whiskers to diffuse through the film. Since, the filler material is crystalline together with the dense, rigid hydrogen bonded network, it acts as a physical barrier to the transport of the diffusing molecules.

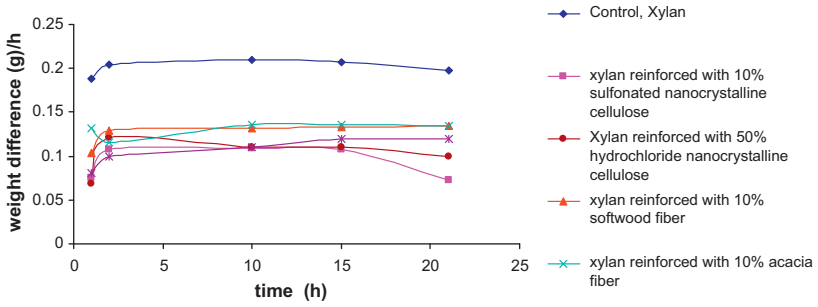

Fig. 2. Rate of water vapor transmission of xylan films for 24 h.

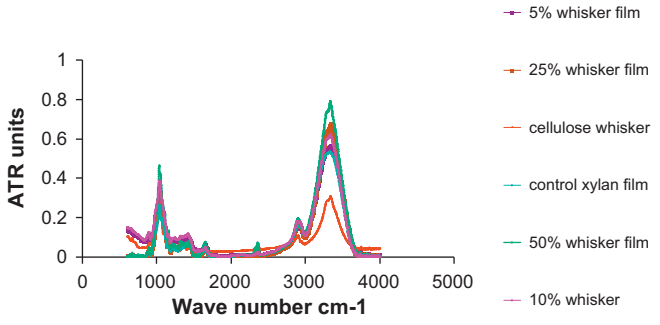

Fig. 3. FTIR of xylan–sulfuric nanocrystalline cellulose film.

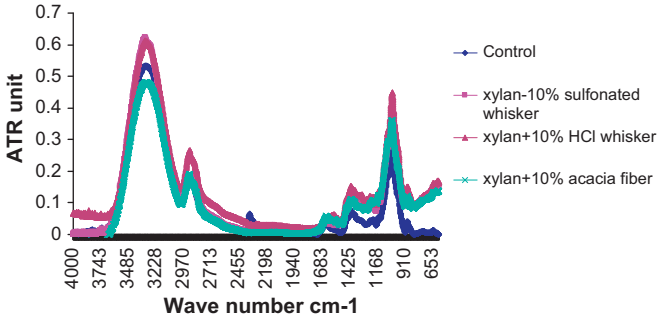

Fig. 4. FTIR of xylan–10% different fillers composite film.

Furthermore, since cellulose whisker and xylan are hydrophilic in nature, the diffusing water molecules could be absorbed via hydrogen bonding, which would also alter the flux. Once steady state equilibrium is attained, the flux remains constant. 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. The uneven structure and agglomeration of the xylan can be the cause of higher water transmission rate of control xylan film in comparison to xylan reinforced with sulfuric nanocrystalline cellulose. Figs. 3 and 4 show the FT-IR spectra of xylan films containing sulfuric nanocrystalline cellulose, acacia fiber, softwood kraft pulp fibers and hydrochloric nanocrystalline cellulose, respectively. Several characteristic bands of nanocrystalline cellulose can be readily assigned at 3340 cm^{-1} (OH stretch) and 2893 cm^{-1} (CH_2 stretch). A strong absorption band can be observed at 3330 cm^{-1} after addition of nanocrystalline cellulose for all concentrations, related to the typical O–H vibration of crystalline nanocellulose. The intensity of overall O–H band (3200–3450 cm^{-1}) increases with the nanocellulose whiskers concentration. This can be attributed to an increase of hydrogen bonding between xylan and nanocrystalline cellulose and the strong interactions between nanocrystalline cellulose surface and the matrix which is comparable to Khan's FT-IR study with whiskers and methylcellulose (Khan et al., 2010). Other bands 1160 and 1070 cm^{-1} have their intensity increased after nanocrystalline cellulose addition and these bands are specific to cellulose, and some of them have been studied in detail to determine the crystalline organization (Akeholm, Hinterstoisser, & Salmen, 2004). Strong peaks around 1100 cm^{-1} assigned to secondary alcohol. The peak at 1205 cm^{-1} is sulfate peak of cellulose nanocrystalline cellulose from the esterification reaction. The peak at (3200–3450 cm^{-1}) of the nanocomposite moved to higher wavenumbers suggesting a strong interaction occurred between the filler and the matrix (Li, Zhou, & Zhang, 2009). The interactions between cellulose and xylan in a model system consisting of bacterial cellulose/glucuronoxylan have been studied in the past that showed strong interactions existed between cellulose and xylan (Dammström, Salmén, & Gatenholm, 2009).

Optical microscope images of xylan, xylan–softwood kraft fiber and xylan–nanocrystalline cellulose films were acquired both before and after the water transmission rate studies and these results are summarized in Figs. 5–7. The xylan–sulfuric nanocrystalline cellulose film appears denser than control xylan film as seen in Fig. 5. Optical microscope images of xylan–acacia films were acquired before the WVTR test and immediately after and these results are summarized in Fig. 6. Xylan–acacia films appear swollen after the water vapor transmission study as can be seen in Fig. 6(a) and (b). All the films retain their shape after the water transmission test but the control film appears weaker than film reinforced with nanocrystalline cellulose. It appears that the mechanical properties of all the films deteriorated after water vapor transmission test which may be attributed to interference of water with the associated hydrogen bonding between matrix and fillers and this may make the films weaker. The specific density of xylan films was also calculated and the result shows that the xylan–10% nanocrystalline cellulose films were denser than the control xylan, xylan–10% softwood and xylan–10% acacia films with specific densities of 0.7616, 0.7272, 0.1780 and 0.1132 g/cm^3 respectively. The less dense structure of the control xylan, xylan–10% softwood and xylan–10% acacia films in comparison to the xylan–10% nanocrystalline cellulose film leads to lower water transmission rates for the xylan–sulfuric nanocrystalline cellulose films in comparison to the other films.

The xylan control film shown in Fig. 5(a) exhibits hexagonal platelets like pattern (Marchessault, Morehead, Walter, Glaudemans, & Timell, 1961).

The optical micrograph of xylan film reinforced with softwood kraft fibers, exhibited in Fig. 7(c), shows fiber aggregation which may provides channels in the membrane that allow for more rapid permeation of water.

Nanocrystalline cellulose have been reported to have crystallinity values greater than 60% (De Souza Lima & Borsali, 2004; Ioelovich, 2008). This property, together with the resulting rigid hydrogen-bonded network of nanocrystalline cellulose was attributed to cause an increase in tortuousity (Saxena, Elder,

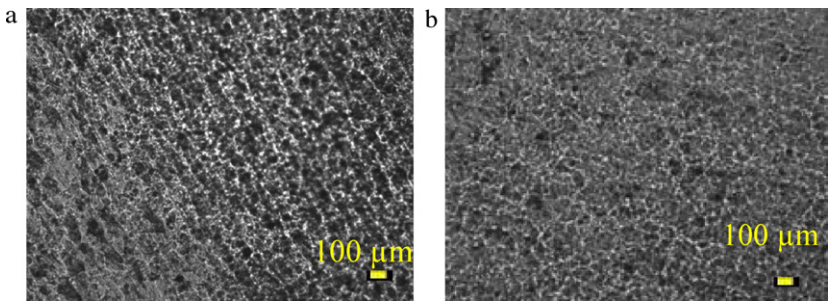

Fig. 5. Optical microscope image of (a) control xylan and (b) xylan reinforced with sulfuric nanocrystalline cellulose.

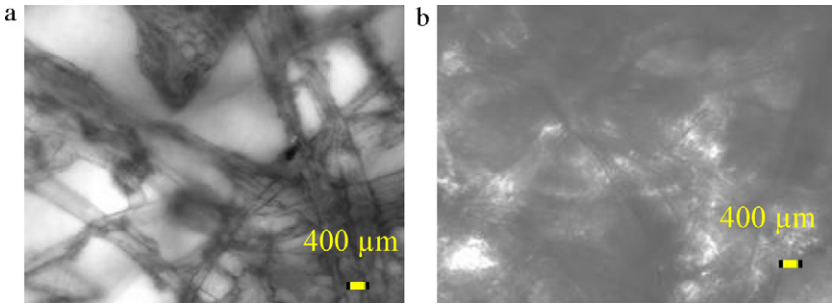

Fig. 6. . Optical images of (a) xylan reinforced with ECF bleached acacia kraft fibers before water vapor transmission rate showing more open structure and (b) dense swollen film of xylan–acacia fibers after water vapor transmission rate test.

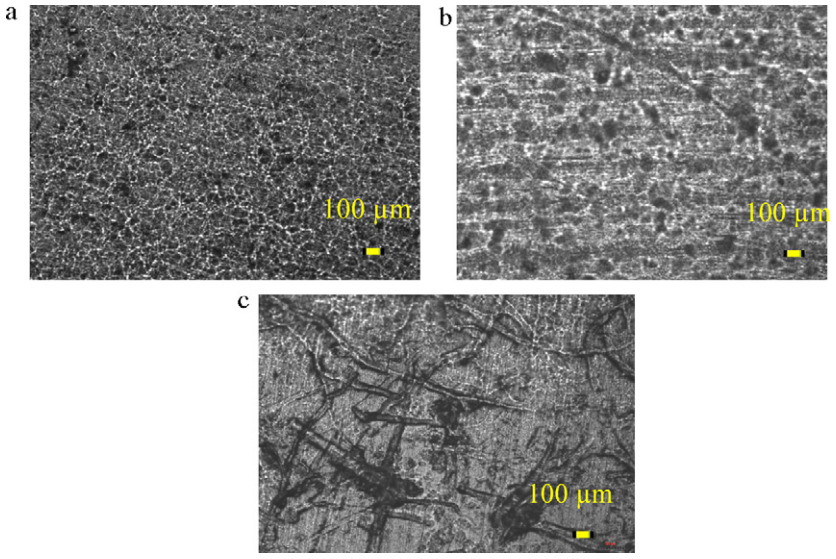

Fig. 7. Optical images of xylan reinforced with (a) sulfuric nanocrystalline cellulose, (b) hydrochloride nanocrystalline cellulose and (c) softwood fibers.

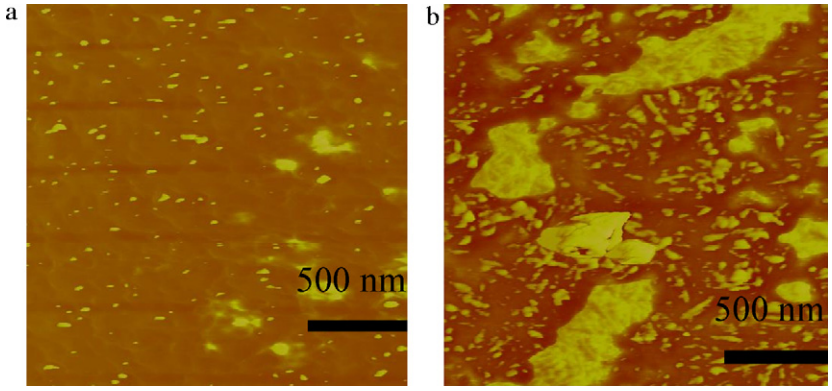

Fig. 8. AFM images of fractured surface (a) control xylan and (b) 10% sulfuric nanocrystalline cellulose film.

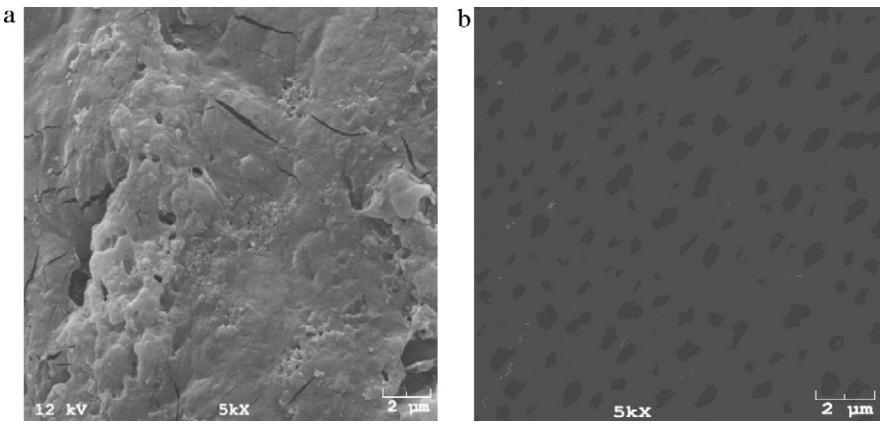

Fig. 9. Scanning electron microscopic images of (a) surface image of control xylan and (b) surface image of xylan sulfuric nanocrystalline composite film.

Kenvin, & Ragauskas, 2010) for water molecules to follow and the crystalline portion nanocellulose may further lower the water transmission rate as compared to more open structure of control xylan film as can be seen in Fig. 8(a) and (b).

SEM images of control xylan film surface in Fig. 9(a) shows agglomeration in comparison to well dispersed sulfuric nanocrystalline cellulose on xylan surface in Fig. 9(b). The uneven structure and agglomeration of the fibers can provide increase free volume of the matrix polymer leading to higher diffusivity of the permeating water molecules in the control xylan film which may cause higher water vapor transmission rate of control xylan in comparison to xylan reinforced with sulfuric nanocrystalline cellulose. It appears that pulp fibers cannot form an integrated matrix that nanocrystalline cellulose can and this latter effect has a substantial benefit in the overall reduction of water transmission.

4. Conclusions

Cellulose whiskers were incorporated into xylan slurry to prepare biodegradable films with improved water barrier properties. It appears that the high degree of crystallinity of nanocellulose, the dense composite structure of the formed films with nanocrystalline cellulose and xylan leads to a film that has reduced moisture transmission properties. These effects were attributed to a rigid hydrogen-bonded network of hydrogen bonded nanocellulose to form an integrated matrix as described by percolation theory. Optical microscopic images indicated that xylan incorporated with softwood kraft fiber and acacia fiber exhibit fiber aggregation in comparison to well dispersed sulfuric nanocrystalline cellulose on xylan surface as indicated in optical and SEM images of xylan–sulfuric nanocrystalline cellulose film. This provides more open structure for more rapid permeation in control xylan, xylan–softwood kraft fiber and xylan–acacia fibers leading to higher water vapor transmission rate as compared to xylan–sulfuric nanocrystalline cellulose films which have substantially lower water vapor transmission rate. The synergistic xylan–10% sulfuric nanocrystalline cellulose performed well and show potential for the development of improved biodegradable barrier membranes.

Acknowledgements

The authors wish to acknowledge the support of the member companies of IPST at the Georgia Institute of Technology and the IPST Fellowship. Portions of this work are being used by Amit Saxena as partial fulfillment of the requirements for graduation from the School of Chemistry and Biochemistry at the Georgia Institute of Technology, Atlanta, Georgia. AJR also wishes to thank the Gunnar Nicholson Foundation for support of his research efforts while in Sweden.

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