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Hydrophobic-modified nano-cellulose fiber/PLA biodegradable composites for lowering water vapor transmission rate (WVTR) of paper

Zhaoping Song [a,*], Huining Xiao [a,b,**], Yi Zhao [b]

[a] Department of Chemical Engineering, University of New Brunswick, Fredericton, NB, Canada E3B5A3
[b] School of Environmental Science & Engineering, North China Electric Power University, Baoding, China 071003

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ABSTRACT

New biodegradable nanocomposites have been successfully prepared by incorporating modified nano-cellulose fibers (NCF) in a biodegradable polylactic acid (PLA) matrix in this work. The hydrophobic-modified NCF was obtained by grafting hydrophobic monomers on NCF to improve the compatibility between NCF and PLA during blending. The resulting NCF/PLA composites were then applied on paper surface via a cast-coating process in an attempt to reduce the water vapor transmission rate (WVTR) of paper. The WVTR tests, conducted under various testing conditions and with different coating weights, demonstrated that the modified NCF/PLA composites coating played a critical role in lowering WVTR of paper. The lowest WVTR value was 34 g/m^2/d, which was obtained with an addition of 1% of modified NCF to PLA and the composites coating weight at 40 g/m^2 and substantially lower than the control value at 1315 g/m^2/d. The paper coated with the modified biodegradable composite is promising as green-based packaging materials.

1. Introduction

The environmental awareness imposed to packaging films is to design or synthesize polymers that are biodegradable to be used as packaging materials. For the application in a number of areas such as food packaging and containers, the benefits of using biodegradable packaging materials are obvious. Biodegradable polymers derived from sugars, natural fibers, renewable forest resources, and protein are able to reduce or replace the usage of the fossil-based materials thus reducing the pollution caused by conventional plastic packaging.

Paper products made of cellulose fiber have been widely used as packaging materials, due to their favorable properties such as biodegradability, sustainability and low environmental impact. However, the hydrophilic properties of the cellulose fiber creates a low water vapor barrier property of the paper-based packaging materials, which is insufficient to meet the requirements for high-barrier applications or extended application in packaging. Over the past few decades, a number of approaches, including chemical modification of cellulose fibers or handsheets, have been attempted to improve the hydrophobic properties of cellulose fibers or fiber networks (Pan, Xiao, & Song, 2013; Rodionova & Lenes, 2011). However, there are still several issues or challenges remaining, including how to achieve a high efficiency of grafting and tailored barrier properties of the paper products. Therefore, one of the factors of the massive use of conventional plastic in the food packaging industry is largely contributed by its water permeation barrier ability, i.e., the satisfying low water vapor transmission rate (WVTR). The WVTR, which indicates the amount of water vapor that can permeates per unit area of the packaging material and time (Siracusa, Rocculi, Romani, & Dalla Rosa, 2008), is also an important indicator in the barrier properties of paper and paper products. Therefore, increasing the hydrophobic properties of paper products and improving the water vapor barrier properties (Aulin & Strom, 2013), like lowering WVTR, is of great importance and high fundamental research value to the development of packaging materials.

In order to develop paper products with higher water vapor barrier properties and maintain the green features of packaging materials, we intended to incorporate biodegradable materials into the paper products, typically via a coating process. Among various

* Corresponding author. Tel.: +1 506 452 6373; fax: +506 453 3591.
** Corresponding author at: Department of Chemical Engineering, University of New Brunswick, 15 Dineen Drive, Fredericton, NB, Canada E3B 5A3. Tel.: +1 506 453 3532; fax: +1 506 453 3591.
E-mail addresses: m748i@unb.ca (Z. Song), hxiao@unb.ca (H. Xiao), zhaoyi9515@163.com (Y. Zhao).

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biodegradable polymers, polylactic acid (PLA) has been mostly used as a food-packaging polymer for short shelf life products such as drinking cups, salad cups, containers, and overwrap and lamination films (Sedlarik et al., 2012). PLA has been studied extensively due to its well-established biodegradability and biocompatibility (Tsourapas, Rutten, Briggs, Davies, & Shakesheff, 2006). PLA is easily made and obtained from 100% renewable resources such as corns, maize and wheat, wood residues or other biomass (Plackett et al., 2006). Its production consumes carbon dioxide which makes it more eco-friendly. PLA is of interest not only because of the need to ultimately replace many synthetic polymers but also because of PLA's useful physical and mechanical characteristics (Auras, Singh, & Singh, 2005). Therefore, PLA has attracted extensive research interests. Making composites through reinforcing PLA with different kinds of cellulose fiber has been a popular research topic (Frone, Berlioz, Chailan, Panaitescu, & Donescu, 2011; Jonoobi, Harun, Mathew, & Oksman, 2010; Sanchez-Garcia & Lagaron, 2010; Shi et al., 2012). In addition to its advantages, PLA also has some shortcomings which restrict its applications, one of which is that the gas and water vapor barrier properties are not sufficient for some uses (Ljungberg & Wesslen, 2002). Therefore, the preparation of nanocomposites has also been considered as a promising method for PLA property improvement (Petersson, Kvien, & Oksman, 2007; Petersson, Oksman, & Mathew, 2006; Sanchez-Garcıa, Gimenez, & Lagaron, 2008). Furthermore, cellulosic nanocomposites are currently considered as one of the most promising areas of scientific and technological development in the field of plant products (Chinga-Carrasco, 2011). Iwatake, Nogi, and Yano (2008) reported the reinforcement of PLA using microfibrillated cellulose (MFC) and explored the potential of reinforcement by a nanofiber network, with the goal of making sustainable 'green-composites'. In terms of combining MFC with PLA, Okubo, Fujii, and Thostenson (2009) and Okubo, Fujii, and Yamashita (2005) reported an effective technique for improving the mechanical properties of PLA-based bamboo fiber composites. The fabrication of MFC/PLA nanocomposites based on a papermaking-like process has been presented as an industrially practical method by Nakagaito, Fujimura, Sakai, Hama, and Yano (2009).

However, due to the hydrophilic nature of cellulose, MFC or NCF is not easily uniformly dispersed in most non-polar polymer matrix. Consequently, much attention has been paid to MFC modification in order to improve the compatibility with a wider variety of the hydrophobic matrices. Many methods have been tried for cellulose surface modification, such as acetylation, silylation, grafting and use of coupling agent (Abdul Khalil, Bhat, & Yusra, 2012). Wang, Sain, and Oksman (2007) applied chemically treated cellulose nanofibers extracted from hemp to prepare PLA and PHB nanocomposites containing 5 wt% nanofibers. These nanocomposites were prepared by melt blending the polymer with the fiber followed by granulating and injection molding steps. Plentiful techniques for modifying natural fiber surfaces to improve the interaction between the fibers and polymers matrix have been reported (Juntaro, Pommet, Mantalaris, Shaffer, & Bismarck, 2007; Lu, Askeland, & Drzal, 2008; Pommet et al., 2008; Siró & Plackett, 2010). Much attention has been paid to the preparation of nanocomposites and related film products, but it has been seldom reported on the application of nanocomposite coating on paper for packaging materials.

In this work, the composites based on PLA reinforced with hydrophobic-modified NCF were prepared; the WVTR of paper coated with the resulting composites were also investigated. NCF was chosen prior to other types of cellulose since the composite materials containing NCF are a promising class of new materials (Eichhorn et al., 2010; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). The NCF was modified by grafting hydrophobic monomers via free radical polymerization to improve compatibility with the PLA matrix. The hydrophobic modification of NCF facilitated its dispersion in tetrahydrofuran (THF), a solvent used to dissolve PLA. After modification, the NCF-PLA composites were made by a solvent casting method; the properties of composites as well as the WVTR of paper coated with the composites were determined. The key objectives in this work were to improve the compatibility of PLA and NCF via hydrophobic modification and to lower the WVTR of paper via PLA-NCF composite coating.

2. Experimental

2.1. Materials

Nano-cellulose fiber (NCF, 5.4% suspension in water made from purified wheat straw, see images in Fig. 1) was purchased from the Center for Biocomposites and Biomaterials Processing, University of Toronto, Canada. Hydrophobic monomer, butyl acrylate (BA, ≥99%) used for fiber modification via grafting, and ammonium ceric (IV) nitrate (CAN) as initiator, were purchased from Sigma–Aldrich (USA)and were used as received. Polylactic Acid (PLA, Ingeo™ 2003D)was purchased from NatureWorks® LLC, USA, is a thermoplastic resin derived from annually renewable resources and is specifically designed for use in fresh food packaging and food service ware applications.

2.2. Methods

2.2.1. Hydrophobic modification of NCF

The hydrophobic modification of NCF was conducted via a free radical polymerization. The initial NCF suspension in water (5.4%, w/w) was washed and centrifuged with acetone and anhydrous ethanol several times in order to remove the water as much as possible. After the centrifugation at 5000 rpm and 20 °C for 5 min and the removal of the supernatant, the NCF was then re-dispersed in 200 ml of anhydrous ethanol in a three-necked round-bottomed flask equipped with a magnetic bar. After stirring and nitrogen purging to reduce the inhibiting effect of the oxygen in the radical polymerization reaction, a certain amount of hydrophobic monomer BA and initiator CAN were added via a dropping funnel. The system was maintained at 50 °C under constant stirring for 5–6 h as well as nitrogen purging until the end of the reaction. After termination of the reaction, the mixture was filtrated and the sediment was purified by Soxhlet extraction in the mixture of acetone and ethanol at 60 °C for 24–48 h to remove the residual monomers and ungrafted copolymers. The grafting ratio was calculated by the weight change of the paper sheets before and after the modification. And the formula used is shown in Eq. (1).

$$\text{Grafting ratio} = \frac{w_2 - w_1}{w_1} \times 100\% \quad (1)$$

where, w_1 is the weight of NCF before modification, w_2 is the weight of NCF after modification.

2.2.2. Composites/films preparation

The solvent-casting composites were prepared by dissolving PLA pellets in tetrahydrofuran (THF) (10%, w/v) and mixed with hydrophobic modified NCF. The modified NCF was added into the PLA solution after the PLA pellets were dissolved completely, and the mixture was thoroughly stirred for 2 h. For reference, pure PLA films were made by dissolving PLA pellets in THF and those solutions were cast onto Petri dishes. Similarly, the composite films with 0, 1, 5, 7, 10% (w/w) of modified NCF in PLA matrix were also prepared subsequently before being coated on handsheets. The suspension mixture of PLA and NCF were also casted onto glass Petri dishes and left in a fume hood overnight to evaporate the solvent. The films were removed from the Petri dishes by dipping them into

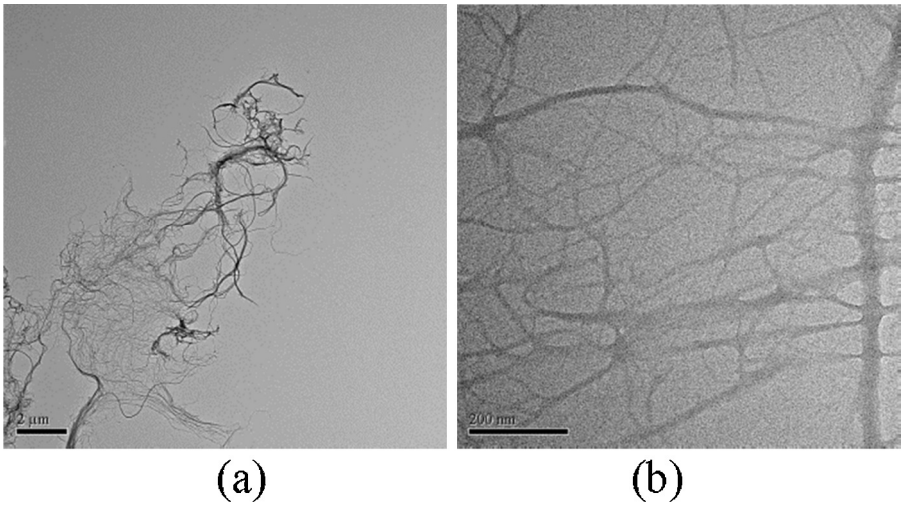

Fig. 1. TEM images showing NCF and nanofiber bundles. Scale bars correspond to 2 μm (a) and 0.2 μm (b).

a glass bowl with deionized water for 10 s and then the films were carefully peeled off from the glass and stored in a vacuum desiccator until use.

2.2.3. Coating

Different amounts of the resulting composites formulations were coated onto the surface of the handsheets (60 g/m^2) made in lab. The solvent was allowed to evaporate at room temperature by putting the coated handsheets in a fume hood for at least 24 h, and the resulting products were dried in a vacuum oven at 50 °C for 48 h to remove the residual solvent (Hossain et al., 2012).

2.3. Sample characterization

The Fourier transform infrared spectroscopy (FT-IR) spectra of modified NCF were recorded using a Spectrum 100 Series (PerkinElmer Ltd, Beaconsfield, BUCKS, United Kingdom) equipped with an attenuated total reflectance (ATR) device for solids analysis and a high linearity lithium tantalite (HLLT) detector, in transmission mode, at 2 cm^{-1} resolution and 32 scans. The surface properties of the composites were observed on a scanning electron microscope (SEM) (JEOL 6400 SEM, JEOL Ltd., Japan) after being carbon coated with 10 kV accelerating voltage.

The WVTR measurements were performed using the 120 mm^2 sample to seal an impermeable container containing saturated potassium nitrate solution at 90% relative humidity (RH) or magnesium nitrate solution at 50%RH and then were placed in micro-gravimetric chamber kept at 0% relative humidity. The WVTR determination was according to TAPPI T464 om-12 at 37.8 °C (100 °F) and 90%RH & TAPPI T 448om-09 at 23 °C (73 °F) and 50%RH. The decrease in weight was measured by a microbalance of gravimetric apparatus (IGA-003, Hiden Analytical Ltd., UK). The WVTR values were calculated from the slope of weight change versus time. The experiments were done in duplicate. The setup for WVTR testing is shown in Fig. 2 (Bedabe, Huang, Xiao, & Eić, 2012).

The WVTR values were calculated from the slope of the weight change against time using the exposed surface area of the sample, and the equation shown in (2):

$$\text{WVTR} = \frac{\text{Sample weight change}}{\text{Area} \times \text{time}} \text{ (g/m}^2\text{/d)} \quad (2)$$

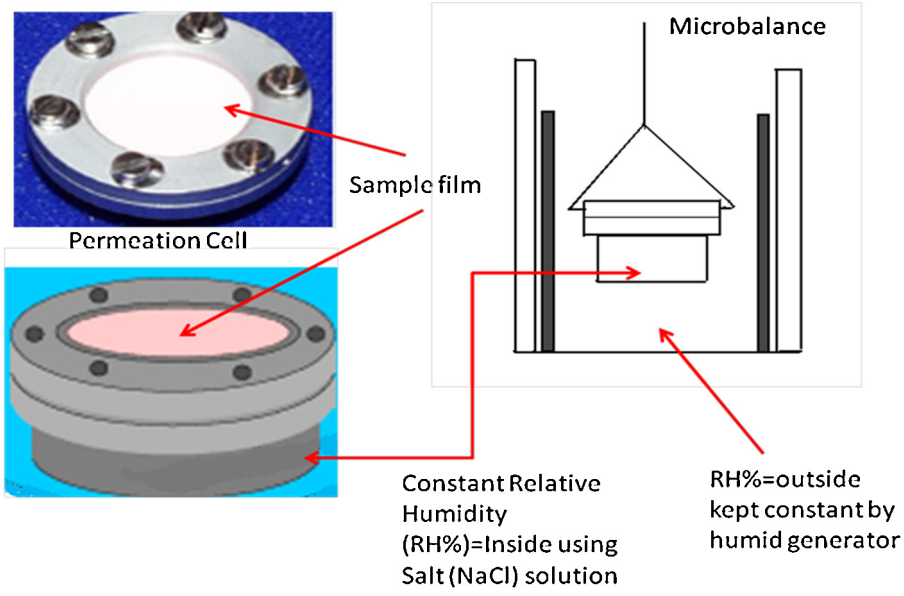

Fig. 2. Schematic of the set-up of WVTR testing.

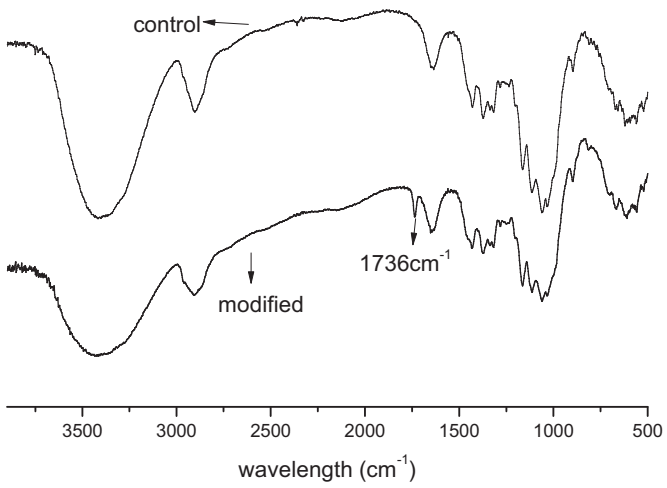

Fig. 3. FT-IR spectrum for control and modified NCF.

3. Results and discussion

3.1. FT-IR spectroscopy for NCF

The FT-IR was employed to investigate the changes of the functional groups on NCF after hydrophobic modification by free radical polymerization. The spectra of both modified and control samples are presented in Fig. 3.

The effect of grafting hydrophobic monomers onto NCF can be assessed by observing the evolution of changes in absorption bands. There is a new absorption peak at around 1736 cm^{-1} on the modified sample compared to the control sample, which is attributed to the absorption peak of carbonyl groups from the hydrophobic monomers. This literally demonstrated that a certain amount of monomers have been grafted onto the NCF fibers to form grafted polymer chains. The grafting ratio, estimated based on Eq. (1), was approximately 3–5%.

3.2. Surface morphology of composites

In order to investigate the physical properties of the composites made of modified NCF and PLA, films were first prepared prior to the coating of the composites on the handsheets. The film was formed well, but sometimes the dispersion of NCF in the film was not optimal. One of the drawbacks of NCF is the poor dispersibility in organic (hydrophobic) solvents and their propensity to aggregation because of the large number of hydroxyl groups on the surface (Favier, Chanzy, & Cavaille, 1995). To overcome this problem, the hydrophobic monomer, butyl acrylate, was grafted on the NCF via a free-radical polymerization. SEM was employed to determine the morphology and microstructure of samples. Both the surface and cross sections of films of various ratios of modified NCF and PLA were tested and the morphologies are shown in Figs. 4 and 5.

As can be seen from the SEM images shown in Fig. 4, there is some difference on the surface morphologies of the films made of NCF and PLA. The films based on modified NCF and PLA appear to be smooth and homogeneous, suggesting that casting is a viable method for preparing PLA/NCF composite films. Moreover, the hydrophobic modification has improved the compatibility between the cellulose and the PLA matrix, compared to the unmodified cellulose. In the similar work, Sanchez-Garcia and Lagaron (2010) found that detrimental fiber agglomeration was clearly observed to take place for samples with fiber contents in excess of 5 wt%. It is of interest that the more homogenous surface structure was obtained even with the higher NCF content in the composites in the current work.

Correspondingly, as can be seen from the cross section shown in Fig. 5, morphologies varied significantly with different ratios between NCF and PLA. When the ratios of NCF were equal or lower than 5%, the composite films were very compact and homogenous; whereas those with NCF higher than 5% appeared to be porous and the NCF fibrils and porous structure could also be observed from the cross section images. The presence of ordered dispersed NCF (see Fig. 5b and c) in the cross sections means that there is no aggregated NCF in the films and the modified NCF showed good compatibility with the PLA matrix. Moreover the porous structure

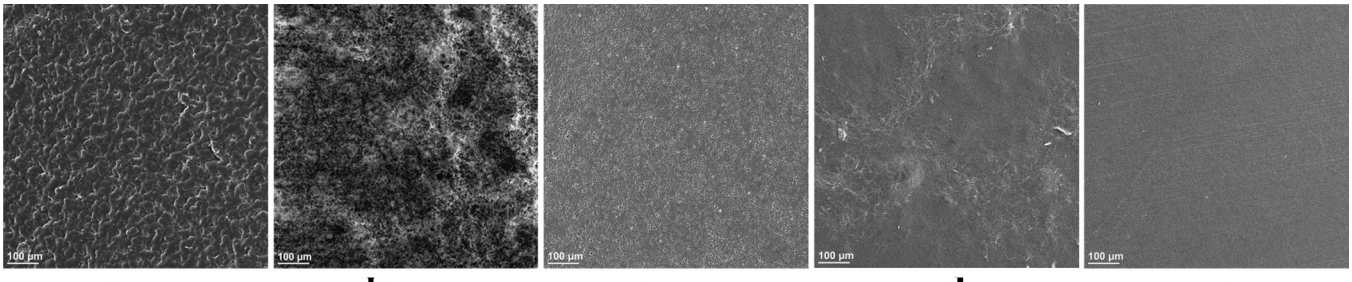

Fig. 4. SEM morphology of PLA/NCF composite film (surface). PLA:NCF = 100:0 (a); 99:1 (b); 95:5 (c); 93:7 (d); 90:10 (e).

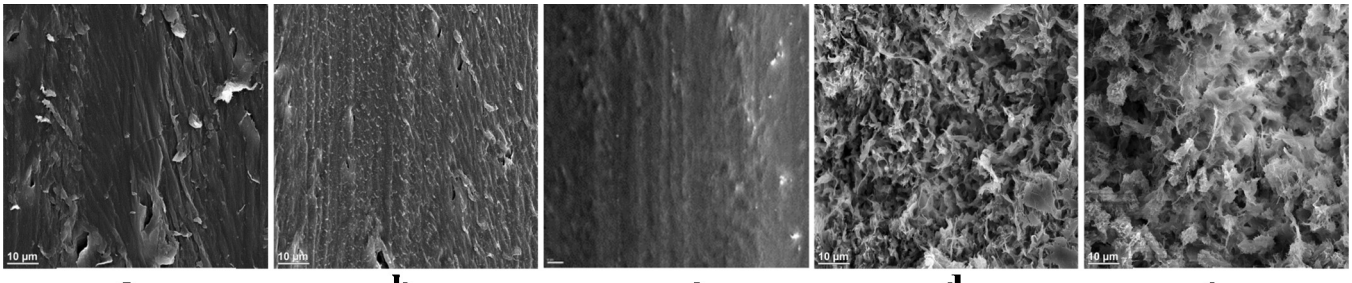

Fig. 5. SEM morphology of PLA/NCF composite film (cross section). PLA: Modified NCF = 100:0 (a); 99:1 (b); 95:5 (c); 93:7 (d); 90:10 (e).

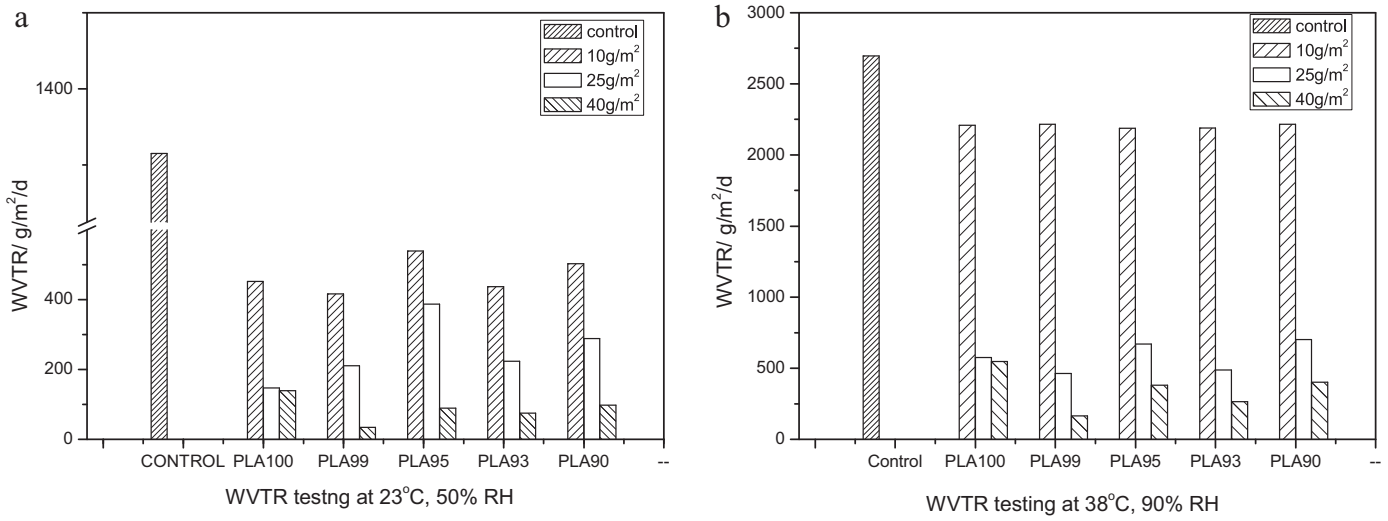

Fig. 6. WVTR of PLA/NCF nanocomposites coating paper.

in the composite films tends to have a negative impact on lowering WVTR.

3.3. WVTR characterization

The composites used for coating were made of pure PLA, PLA/NCF = 99/1, PLA/NCF = 95/5, PLA/NCF = 93/7 and PLA/NCF = 90/10 (mass ratio), marked as PLA_{100}, PLA $_{99}$, PLA_{95}, PLA_{93}, and PLA_{90} here and below, and the coating weight were controlled at 10, 25, and 40 g/m^2, respectively. The WVTR values of the paper treated by composites, measured by IGA-003, are shown in Fig. 6. The WVTR testing was conducted at 23 °C and 50%RH and also performed at 37.8 °C and 90%RH in accordance with TAPPI standards.

The comparison of the results presented in Fig. 6 suggested that the WVTR is sensitive to environmental temperature and RH, as well as the coating weight. High temperature and high humidity conditions promote the transferring of water vapor, thus leading to much higher WVTR values at 37.8 °C and 90%RH compared to those at 23 °C and 50%RH. Both the coating weight and the testing conditions played important roles in WVTR results. Fig. 6 shows that, when the coating weight was at the low level of 10 g/m^2, the coating layer hardly showed the positive effect on lowering the WVTR of coated paper when tested at 37.8 °C and 90%RH; whereas the WVTR at 23 °C and 50%RH decreased dramatically. The higher the coating weight, the further lower WVTR values were achieved. The main reason is that the higher coating weight of the composites provided higher chances covering porous structure on the surface of the handsheets.

Besides, as shown in Fig. 6, the WVTR values fluctuated with the changing of the content of NCF in the composite coating layer. However, the WVTR values of the samples coated with nanocomposites containing hydrophobic-modified NCF were lower than those of the control samples. When the content of NCF in composites was kept at a low level of 1%, the minimum WVTR of the samples was comparable with that of the other samples. And the lowest WVTR values at 23 °C, 50%RH and 38 °C, 90%RH were 34.6 g/m^2/d and 164.9 g/m^2/d, respectively, which were obtained when the coating weight was 40 g/m^2 of composites containing 1% modified NCF (named PLA_{99} in Fig. 6). Among the nanocomposites coated paper samples, when the NCF content was lower than 5%, the coated samples showed better water vapor barrier properties or lower WVTR values. In the compact interfaces, the transport of water vapor is believed to be retarded due to the compact and homogenous coating layer (See SEM image in Fig. 5b and c), and leads to a decreased mass transport rate through the composites coating layer, which then demonstrated a lower water transmission rate. Due to the hydrophobic modified NCF, which showed good compatibility with PLA matrix, the WVTR of the composites was further decreased, compared to the pure PLA film. For the composites containing 5% modified NCF or higher, the WVTR values increased as the fiber content became higher. Owing to the hydrophobic properties of the modified NCF, the bonding among hydrophobic fibers was weakened, which resulted in the porous structure as revealed by SEM observation (See SEM images in Fig. 5d and e). Therefore, the porous structure makes it easier for the water vapor to transmit inside and the water vapor can transport larger distances in the porous interfaces, thus leading to the higher permeability observed and further resulted in higher WVTR. This is also supported by the SEM morphologies in Fig. 5. Another explanation for the increasing WVTR values is that, there should be abundant hydroxyl groups left after the modification, since the surface hydroxyls were only partially replaced by the functional group (Mukherjeea, Sanib, & Kaoa, 2013) or PBA hydrophobic chains in this work. From the work of Etzael Espino-Pérez et al. on preparing bio-nanocomposite based on PLA and hydrophobic modified cellulose nanowhiskers, it was found that the water vapor permeability of the grafted nanocomposite was lower than that of ungrafted one. The conclusion was the hydrophobic grafting and improved compatibility could counteract the effect of enhanced water vapor permeability because of inclusion of hydrophilic structures in the matrix (Espino-Pérez et al., 2013), which is consistent with the findings in this work.

Moreover, the explanation could be based on the water vapor transmission pathway. In composites, a tortuous pathway (Ray & Okamoto, 2003; Yano, Usuki, Okada, Kurauchi, & Kamigaito, 1993) was induced by adding nanofillers or nanofibers in the PLA matrix, because the fillers acted as impermeable physical barriers and forced water molecules to wiggle around them to follow longer and more tortuous paths, leading to a strong enhancement of water barrier properties. The passage of diffusing molecules through composite films is consequently limited. Similar effects on barrier PLA/cellulose nanowhisker composites (Paralikar, Simonsen, & Lombardi, 2008) were also reported in the literature. The water permeability and diffusion appear to match the well-known tortuous path for the appearance of fibers (Sanchez-Garcıa et al., 2008),

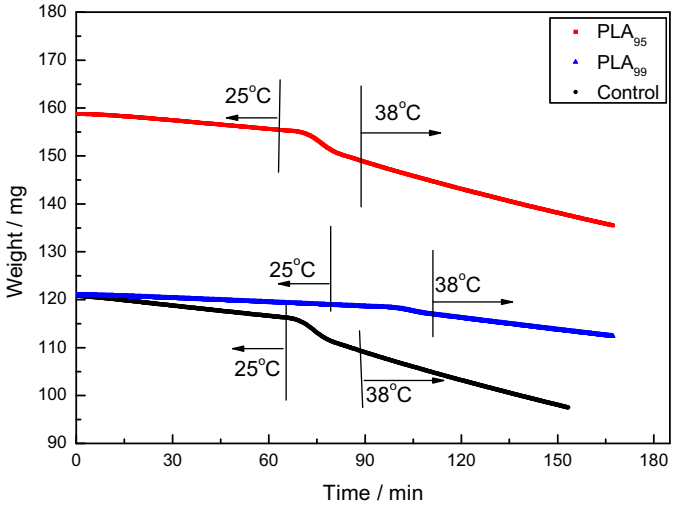

Fig. 7. Effect of temperature on WVTR test (90%RH).

which was also suggested by Sanchez-Garcia and Lagaron (2010). The interpretation based on tortuous pathway is adoptable for our current systems.

3.4. Effects of testing temperature on WVTR

To further reveal the factors influencing WVTR results, the testing temperature was varied from 23 to 38 °C at the same humidity (90%RH). The corresponding changes in water vapor transmission rate were recorded and analyzed in this work (see Figs. 7 and 8). Clearly, the testing temperature has significant impact on WVTR.

The three samples tested in this work included handsheets without coating, samples coated with the composites at two fiber/PLA ratios (i.e., PLA_{95} and PLA_{99}). As addressed previously, at constant temperature and ΔRH (%), a steady state will be reached where WVTR values were calculated from the slope of sample weight change versus time. Various samples with different changing trends for temperature changed from 23 to 38 °C are marked in Fig. 7 and the slope for each sample is shown in Fig. 8a and b. For the control sample, when tested at 23 °C (Fig. 8a), the sample weight changed from original 120.8–116.6 mg in the duration from 0.5 s to 60.9 min, and the slop of weight change versus time came to 0.0704. For the testing period at 38 °C starting from 90.1 min to 155.7 min in Fig. 8b, the sample weight changed from 109.3 to 97.5 mg with the slope of 0.183, which is much higher than that of at 23 °C. Similar results were obtained for the composite-coated paper. For PLA_{99}, the two slopes at 23 and 38 °C were 0.0259 and 0.0819. For PLA_{95}, the two slopes at 23 and 38 °C were 0.0543 and 0.170, respectively. The results showed that there was significant higher water vapor transfer ratio induced by the higher temperature at 38 °C compared to 23 °C. The results also proved that the WVTR is indeed sensitive to the testing temperature.

When the water vapor transferred under a higher temperature, the transport behavior of water vapor is controlled by the molecule diffusion and Knudsen diffusion among the pores of the cellulose network and the PLA films, where the diffusivity is nearly independent of relative humidity because these samples were tested at same relative humidity. At a high temperature, the water vapor has a higher diffusion coefficient according to the diffusion theory, thus promoting its transmission cellulose fiber network or composites. Therefore, lowering WVTR at a relatively high temperature is still a challenge in developing completely green-based packaging materials. The utilization of the composite coating is a promising approach

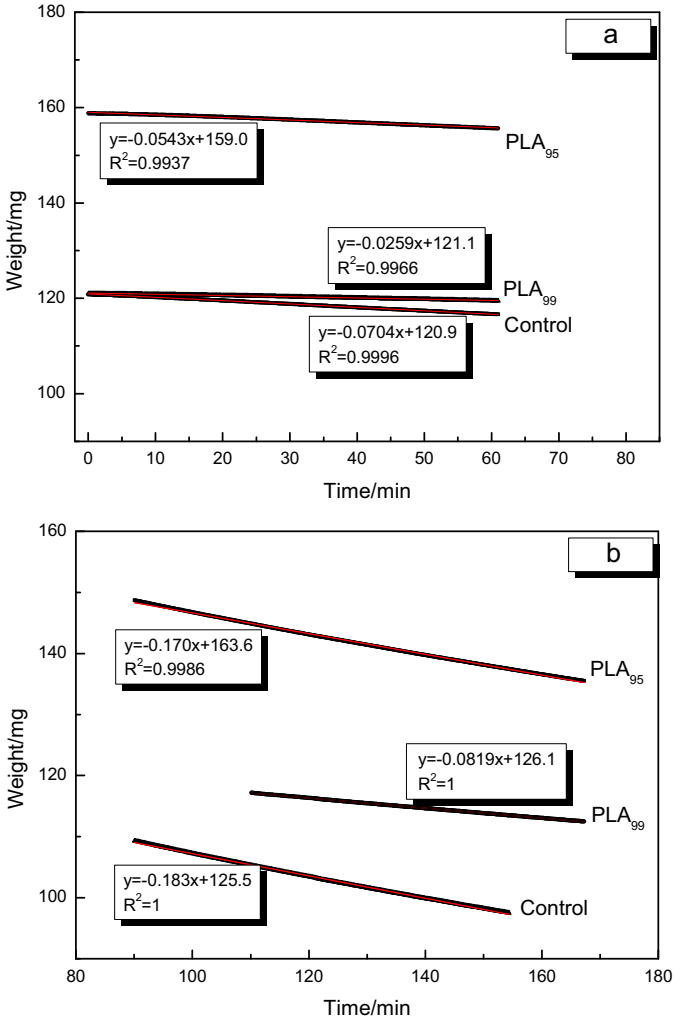

Fig. 8. Weight change slope for samples at23 °C (a) and 38 °C (b).

in enhancing water vapor barrier property of paper for packaging application, though further research in this area is definitely required.

4. Conclusions

Novel biodegradable and environmental friendly nanocomposites were successfully prepared by incorporating nano-cellulose fibers in biodegradable PLA matrix. The hydrophobic-modified NCF were obtained by grafting hydrophobic monomers via a free-radical modified and mixed with PLA. The resulting NCF/PLA composites were applied on paper surface by a cast coating method. The WVTR tests, conducted under various testing conditions and with different coating weights, demonstrated that the modified NCF/PLA composites coating played a critical role in lowering WVTR of paper. The work on revealing the relationship between temperature and WVTR suggested that WVTR is sensitive to surrounding temperature. The lowest WVTR value was 34 $g/m^2/d$, which was obtained with an addition of 1% of modified NCF to PLA and the composites coating weight at 40 g/m^2 and substantially lower than the control value at 1315 $g/m^2/d$. As a result, the paper coated with the modified biodegradable composite is promising as green-based packaging materials, thus minimizing the environmental concerns.

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