

Cellulose Nanocrystals as Barrier Performance Enhancer of Extrusion-Blown PLA Films for Food Applications

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ABSTRACT

This paper examined the effect of cellulose nanocrystal (CNC) addition on the water vapor and oxygen transmission rates of extrusion-blown poly(lactic) acid (PLA)/CNC nanocomposite films recorded at various temperatures and relative humidities (RH). Experimental results indicate that the addition of CNCs into PLA matrix through a melt processing approach improves the barrier properties of PLA, irrespective of RH or temperature. The addition of only 1% CNC into PLA matrix improved the water vapor and oxygen barrier performance of nanocomposite films by 33% and 62% respectively due to the tortuosity effect caused by cellulose nanocrystals-induced crystallinity in the matrix. Both RH and temperature had less influence on water vapor barrier properties when CNCs were added into the films. This implies that novel bio-based composites with improved barrier properties suitable for packaging applications could be developed by combining CNCs with PLA.

Keywords: Cellulose nanocrystals (CNCs), PLA, blown film, water and gas barriers

1 INTRODUCTION

Bio-based plastics from sustainable resources such as biomass are the best alternative to petroleum-based polymers because they provide solutions for reducing the general dependency on oil availability and environmental concerns about the use of common petroleum-based plastics. One bio-based plastic that has become an attractive alternative to petroleum-based polymers because of its physical properties (high stiffness, reasonable strength, excellent flavor and aroma barrier) and favorable degradation characteristics is poly(lactic acid) (PLA), a plastic that comes from fermented plant starch such as corn and sugar beets [1-4].

Despite these attractive properties, PLA has relatively few commercial applications, concentrating mainly in textile and specialty biomedical niches such as sutures and drug delivery devices. Additionally, it is being used as a commodity polymer for packaging food and consumer goods where the physical properties of PLA make it suitable for manufacture of rigid containers and bottles [1-

4]. However, the widespread applicability of PLA in flexible sheets and films is limited because of its poor water and oxygen barrier properties, brittleness, lower impact resistance at room temperature, and narrow processing window [4]. PLA has very low melt strength compared to other plastics currently in the market, making it difficult to melt-process. Additionally, the use of PLA films to package water and/or oxygen sensitive food products is avoided because of its poor barrier properties that can significantly shorten the products shelf life and quality. All these factors greatly limit its applicability. Therefore, it is of paramount importance to overcome these difficulties in order to broaden the range of PLA's commercial applications.

Cellulose nanocrystals and cellulose nanowhiskers have been shown to improve the barrier properties of PLA films [5-8] and other plastics [9-12]. However, most of the research reported in the literature used solvent casting techniques (a batch process) [6,8,12] instead of melt-processing (a continuous process). Melt-processing is industrially viable for processing many types of packaging materials, such as films, sheets, bottles or containers that are often melt-blown or molded [1,7,13].

Essentially, no research has been reported on the barrier properties of extrusion-blown PLA film and its composites with CNCs. Therefore, the objective of this work was to evaluate the barrier properties of melt-processed PLA/CNC nanocomposites. The effect of CNC addition on the water vapor and oxygen transmission rates of extrusion-blown PLA/CNC nanocomposite films recorded at various temperatures and relative humidities were examined.

2 EXPERIMENTAL

2.1 Materials

Semi-crystalline PLA (4044D) from NatureWorks® LLC (Minnetonka, MN, USA) was used in this study. The characteristics of the resin are: melt flow rate of 3.95 g/10 min (190°C, 2.16 kg), density of 1.24 g/cm³, and melting temperature of 145-160°C. Anhydrous calcium sulfate (≥98% CaSO₄, Drierite) from Sigma-Aldrich was used as the desiccant. Cellulose nanocrystals (2012-FPL-CNC-043) were prepared by sulfuric acid hydrolysis at Forest Products Laboratory (FPL), in Madison, Wisconsin, USA.

2.2 Film Manufacturing

Film manufacturing was performed following previously described approach [3]. PLA pellets were dried in an oven at 50°C for about 24 hours and blown into films using a 19 mm single-screw extruder (C.W. Brabender Instruments Inc.) with a length-to-diameter ratio of 30:1. This extruder was powered by a 3.73 kilowatt (5 hp) Prep Center® D52 (C.W. Brabender Instruments Inc.) and fitted with a blown film die 25.4 mm in diameter with 0.889 mm (0.035") extrudate wall thickness (A vertical one-inch blown film assembly from C.W. Brabender Instruments Inc.). Starting from the hopper to the die, the temperature profile of the extruder was set at 180-180-180-180°C.

Processing parameters such as the extruder's rotational screw speed, the speed of the pull up nip rollers, and the air pressure inside the inflated plastic have strong effects on the blow up ratio (BUR) and the thickness of the films [3]. All these variables were kept constant throughout the experiments. Specifically, the speeds of the extruder's rotational screw and the pull up rolls for film take off were set at 35 rpm and 40 rpm, respectively, while 0.517 kPa (0.075 psi) was the air pressure used to inflate the film during the extrusion process. The blow up ratio of blown films calculated from equation (1) was approximately 5, leading to ~0.027 mm thick films. The average thickness was measured using a digital micrometer (model 49-70 from TMI, Ronkonkoma, NY, USA) with a resolution of 0.001 mm at 10 random locations around the film.

$$BUR = R_f / R_o \quad (1)$$

where R_o and R_f are the radius of the annular die and the radius of the final tubular film, respectively.

2.3 Property Evaluation

Water vapor transmission rate

The water vapor transmission rate (WVTR) of the films was measured gravimetrically, according to the desiccant method in ASTM E 96. Film samples, in replicates of 5, were mechanically sealed onto 3/4" depth vapometer cup assemblies (Thwing-Albert Instrument Co., West Berlin, NJ, USA) and placed in a controlled humidity chamber (Model LH 1.5 from Associated Environmental Systems, Ayer, MA, USA) set at various temperature and RH conditions as described below. The cells contained anhydrous calcium sulfate to maintain 0% RH inside the cells. The cells were periodically removed from the chamber and weighed to the nearest 0.0001 g to determine the amount of water vapor permeating through the film and absorbed by the desiccant. The change in the weight of the cups was monitored as a function of time and then plotted. Linear regression was used to calculate the slope of the fitted straight line, which represents the water vapor transmission rate as follows:

$$WVTR = (W/t)/A \quad (2)$$

where W is the weight gain at time t , A is the effective area of exposed film ($31.67 \times 10^{-4} \text{ m}^2$), and W/t the slope of the straight line.

The influence of the temperature was studied at 10°C-38°C with 85% RH, whereas the effect of RH content was evaluated at 23°C in the range of 46% to 85% with 13% increments.

Oxygen transmission rate

Oxygen transmission rate (O_2TR) was measured using Ox-Tran Module 2/21 (Mocon Inc, Minneapolis, MN), in accordance with the procedures outlined in ASTM D3985. Two replicates were tested at 23°C subjected to 0% RH.

3 RESULTS AND DISCUSSION

3.1 Effect of CNC Content on WVTR

Figure 1 illustrates the effect of CNC content on the WVTR of PLA-based films. The WVTR decreased as the CNC concentration increased up to about 1% and remained constant thereafter. A significant decrease of approximately 33% in WVTR was observed by adding only 1% CNC into PLA matrix.

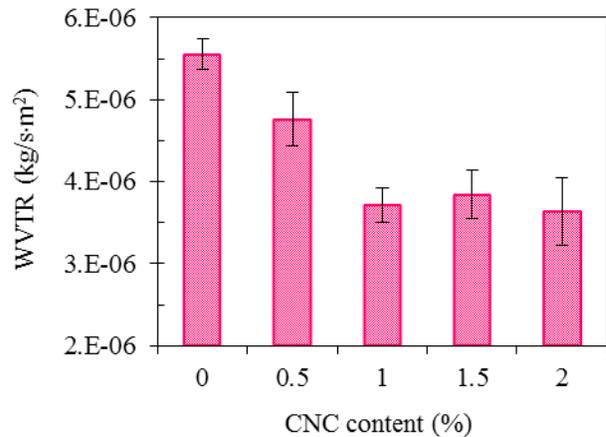


Figure 1: Effect of CNC content on the WVTR of PLA films measured at 38°C and 85% RH.

This improved barrier performance of nanocomposite films is likely due to increased crystallinity in the nanocomposite films. Because the permeant does not diffuse through the crystallites [14], the presence of cellulose nanocrystals increased the tortuosity in the nanocomposite films. This leads to slower diffusion processes since the crystals increase the effective travel path for permeants (vapor or gas) movement through the composite, thus a lower permeation as reported by others [6,7,12,14]. Moreover, several investigators have demonstrated that the addition of cellulose nanofibers into PLA matrix increases its degree of crystallinity because

nanofibers induce crystal nucleation and facilitate subsequent crystallization of the matrix [6,8,12].

3.2 Effects of RH and Temperature on WVTR

The WVTR values of the PLA and PLA/CNC nanocomposite films at 23°C and different RH are shown in Fig. 2. It is clearly seen that WVTR is a function of RH. As expected from Fick's Law, the WVTR values of the tested films increased linearly with vapor content over the RH range studied, i.e., with increasing RH, irrespective of the addition of CNC. Similar results have been reported by other investigators for PLA [15] and other plastics [16]. Interestingly, the addition of CNC significantly reduced the WVTR of PLA films, regardless of the RH value, attributable to the tortuosity effect.

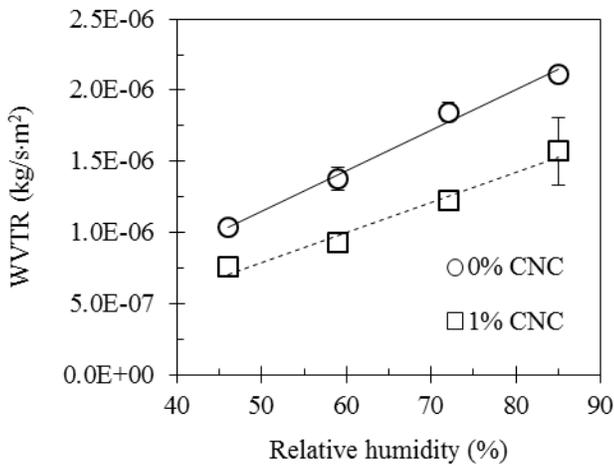


Figure 2: Effect of CNC addition on the WVTR of PLA films measured at 23°C in the range of 46% to 85% RH.

Figure 3 shows the WVTR values of the PLA and PLA/CNC nanocomposite films at constant RH (85%) and different temperatures. Increasing the temperature of the system led to an exponential increase in the WVTR of the tested films, regardless of CNC fibers. However, the nanocomposite films presented lower values of WVTR compared to PLA film.

This result was corroborated by the temperature dependence of WVTR given by the Arrhenius equation (Eq. 3) and also shown in the Arrhenius plot (Fig. 4) used to determine the activation energy (E_a) of the transmission process and pre-exponential factor or Arrhenius constant (A_0) for both PLA and nanocomposite films.

$$WVTR = A_0 \cdot e^{-E_a/RT} \quad \text{or} \quad \ln WVTR = \ln A_0 - \frac{E_a}{R} \cdot \frac{1}{T} \quad (3)$$

Where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T the temperature in degree Kelvin.

The E_a was obtained from the slope of the natural logarithm of WVTR versus the reciprocal temperature ($1/T$) plot whereas the A_0 was obtained from the intercept (Fig. 4). The activation energy and pre-exponential factor of PLA/CNC nanocomposite films ($E_a = 3.67 \times 10^4 \text{ J/mol}$ and $A_0 = 4.85 \text{ kg/s}\cdot\text{m}^2$) were smaller than those of PLA film ($E_a = 4.13 \times 10^4 \text{ J/mol}$ and $A_0 = 43.84 \text{ kg/s}\cdot\text{m}^2$), implying that the temperature had less influence on the WVTR for the nanocomposite films [17].

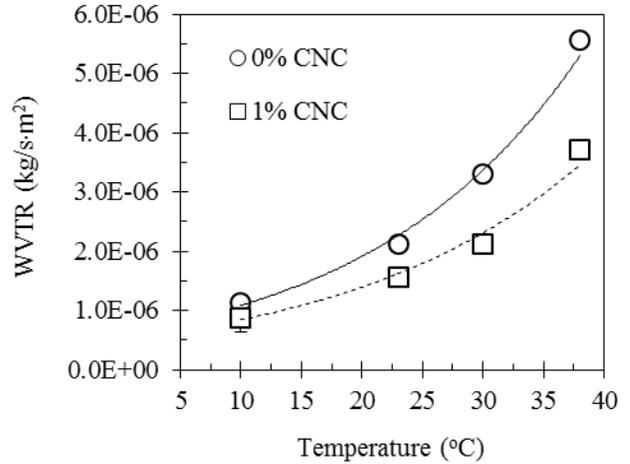


Figure 3: Effect of CNC addition on the WVTR of PLA films measured from 10°C to 38°C at 85% RH.

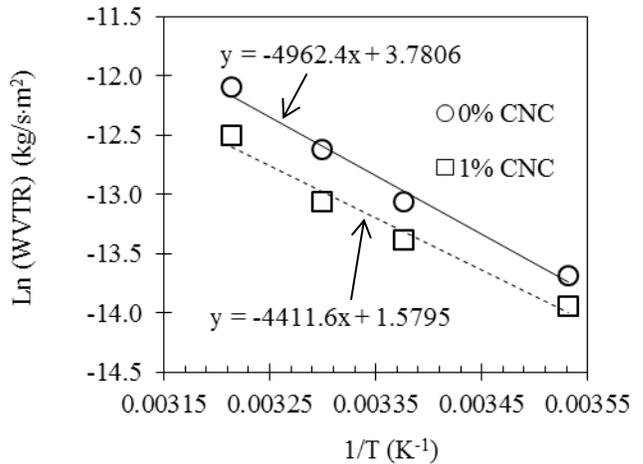


Figure 4: Arrhenius plots of PLA and nanocomposite films.

The following Arrhenius equations were derived from the data, which could be used to predict WVTR values of the PLA films (Eq. 3) and PLA/CNC nanocomposite films (Eq. 4) at any absolute temperature (Kelvin):

$$WVTR = 43.84 \cdot e^{-4.13 \times 10^4 / RT} \quad (3)$$

$$WVTR = 4.85 \cdot e^{-3.67 \times 10^4 / RT} \quad (4)$$

3.3 Effect of CNC Addition on O₂TR

The presence of CNC into PLA had a significant effect on the O₂TR of the films (Table 1). Incorporation of CNC significantly improved the oxygen barrier property of the PLA/CNC nanocomposite film showing a 62% decrease in O₂TR due to only 1% CNC addition, owing to the tortuosity effect.

Table 1: O₂TR of unfilled PLA and PLA filled with 1% CNC.

CNC content (%) in PLA films	Oxygen transmission rate at 23°C, 0% RH (10 ⁻⁸ ×m ³ /s·m ²)
0	2.75 ± 0.56
1	1.05 ± 0.09

4 CONCLUSIONS

The water vapor transmission rates (WVTR) of PLA and PLA/CNC nanocomposite films increased linearly with increasing relative humidity (RH) but exponentially with increasing temperature. However, the nanocomposite films presented lower values of WVTR compared to PLA films, irrespective of RH and temperature. Incorporation of CNC significantly improved the water vapor and oxygen barrier properties of the PLA/CNC nanocomposite film showing a 33% decrease in WVTR and a 62% decrease in O₂TR due to only 1% CNC addition into PLA matrix. This improvement is due to enhanced crystallization of the matrix attributable to the presence of nanocrystals from CNC, which increased the tortuosity in the nanocomposite films. Both RH and temperature had less influence on water vapor barrier when CNC was added into the films. These results indicate that PLA/CNC nanocomposite films with improved water and oxygen barrier properties have a potential for packaging applications.

Further study is needed to determine the impact of CNC addition on the carbon dioxide transmission rate of extrusion-blown nanocomposite films as well as the ability of these films to prolong the shelf life of packaged food.

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