



Water vapor and oxygen barrier properties of extrusion-blown poly(lactic acid)/cellulose nanocrystals nanocomposite films

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ABSTRACT

This paper examined the effect of cellulose nanocrystal (CNC) content on water vapor permeability (WVP) and oxygen permeability (OP) of extrusion-blown poly(lactic acid) (PLA) films recorded at various temperatures and relative humidities. While both WVP and OP followed the Arrhenius equation, the WVP decreased with increasing temperature whereas an opposite trend was observed for OP, resulting in negative activation energy (E_p) for WVP but positive E_p for OP, regardless of CNC content. However, the E_p for both WVP and OP increased by adding CNC into PLA matrix. WVP was not affected by the relative humidity agreeing with Fick's law. Nanocomposite films had lower WVP (~40%) and OP (~75%) than neat PLA films because of the tortuosity effect created by the presence of highly crystalline CNCs in the nanocomposites, which increased PLA's degree of crystallinity. Indeed, the values of WVP and OP negatively correlated with increased crystallinity, irrespective of testing conditions.

1. Introduction

The global bioplastics market has been forecast to grow from US \$7.5 billion in 2013 to US\$43.8 billion in 2020 at a compound annual growth rate of 28.8% between 2014 and 2020 [1]. The key drivers of growth include growing environmental awareness in consumers and the changing legislative landscape wherein bio-based products are preferred to alleviate the problems associated with petroleum-based plastics [2]. This emerging bioplastic market is inspiring the industry and academia to develop environmentally friendly bio-based and biodegradable polymers [2].

Poly(lactic acid) (PLA) is a front-runner in the fast-growing bioplastics market because of its attractive properties such as excellent stiffness, reasonable strength, excellent flavor and aroma barrier, as well as good grease and oil resistance [3–8]. Despite these attributes, PLA's applicability as a food packaging material is limited due to several drawbacks such as brittleness, as well as poor water vapor and moderate gas barrier properties, amongst others [6–8]. The barrier properties of a film to water vapor and gas are critical properties for food packaging materials due to their role in food's deteriorative reactions and microbial growth.

Various attempts have been made to overcome the shortcomings of PLA in order to broaden its applicability [2–21]. For example, cellulose nanomaterials such as cellulose nanocrystals (CNCs) and cellulose

nanofibers (CNFs) are often added to the PLA matrix to improve its barrier properties by both increasing the crystallinity and acting as impermeable regions to increase tortuosity [9–12,17–19].

Several researchers have used solvent-casting techniques to manufacture PLA nanocomposite films with improved barrier performance by adding various amounts of unmodified and modified cellulose nanomaterials [9–12]. In one such effort, the addition of 1% CNCs modified with an acid phosphate ester of ethoxylated nonylphenol (s-CNCs) decreased the oxygen transmission rate (OTR) and water vapor permeability (WVP) of PLA films by 26% and 34%, respectively attributable to the tortuosity effect induced by well dispersed s-CNCs [9]. These results were consistent with those previously reported by Sanchez-Garcia and co-workers for nanocomposite films containing 1% nanowhiskers [11].

Past efforts on improving the barrier performance of PLA were focused on solvent-casting techniques (a batch process) instead of melt-processing which is an important processing method for introducing nanocomposite materials in the market where high-volume production is required [20]. However, limited studies have been reported on improving the barrier performance of PLA using melt-processing [17–19]. Improvements of 20% and 60% in water vapor and oxygen barrier of extrusion-cast PLA films were reported when 1% cellulose nanocrystals derived from coffee silverskin were melt-mixed with PLA in a twin-screw extruder [17]. Similar results have been reported for PLA/CNC-

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based cast films produced by a single-step reactive extrusion process [18]. Furthermore, our previous work successfully demonstrated that the incorporation of only 1% CNCs into the PLA matrix using a solvent-free approach improved the water vapor and oxygen barrier properties of extrusion-blown PLA films by 30% and 60%, respectively [19].

It is well-documented that different conditions of temperature and relative humidity (RH) strongly influence both the barrier properties of films and the food quality during distribution and storage [22]. Therefore, once a new plastic film for food packaging applications is developed, it is of utmost importance to characterize its barrier properties in different environment conditions in order to assess its effectiveness in extending food shelf-life throughout the supply chain.

Despite known effects of environmental conditions on the barrier performance of materials, no research has been carried out to examine the influence of temperature and RH on the barrier properties of nanocellulose-based PLA nanocomposite blown-films with various CNC contents, which was the objective of this study.

2. Experimental

2.1. Materials

Semi-crystalline PLA (4044D) from NatureWorks® LLC (Minnetonka, MN, USA) and freeze-dried cellulose nanocrystals (CNCs) obtained from Forest Products Laboratory (2012-FPL-CNC-043) with characteristics described in previous studies [8,19,23,24] as well as anhydrous calcium sulfate ($\geq 98\%$ CaSO₄, Drierite), the desiccant from Sigma-Aldrich were used. The CNCs were produced from dissolving wood pulp using the sulfuric acid process and have diameters around 5 nm and lengths around 100–300 nm [23,24].

2.2. Preparation of PLA/CNC nanocomposites and film manufacturing

PLA pellets were dried in an oven at 50 °C for at least 24 h before compounding. The PLA pellets were then compounded (dry-blended without heat) with varying amounts of CNCs (0; 0.5; 1; 1.5 and 2 wt%) in a high intensity mixer (Blender MX1050XTS from Waring Commercial, Calhoun, GA, USA) at 22,000 rpm for approximately 1 min. PLA pellets and PLA/CNC compounded materials were blown into films using a 19 mm single-screw extruder (C.W. Brabender Instruments, South Hackensack, NJ, USA) with a length-to-diameter ratio of 30:1 as previously described [5,7,8,19]. Starting from the hopper to the die, the temperature profile of the extruder was set at 180–180–180–180 °C. The speeds of the extruder's rotational screw and the pull-up rollers for film take off were set at 35 rpm and 40 rpm, respectively, while an air pressure of 0.517 kPa (0.075 psi) was used to inflate the film to a blow-up ratio of 5, leading to ~0.027 mm thick films, measured by digital micrometer and confirmed by the density method [25].

2.3. Property evaluation

2.3.1. Water vapor permeability (WVP)

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 at least 5, were mechanically sealed onto 3/4" depth vapometer cup assemblies, weighed and placed in a controlled humidity chamber set at various temperature and relative humidity (RH) conditions as described below. The cups were removed from the chamber and weighed to the nearest 0.0001 g after 24 h to determine the amount of water vapor permeating through the film and being absorbed by the desiccant (anhydrous calcium sulfate). The change in the weight of cups was used to calculate the water vapor transmission rate (WVTR) as follows [8,19]:

$$\text{WVTR} = \frac{\Delta W/t}{A} \quad (1)$$

where ΔW is the weight gain of the cups at time t (24 h); and A is the effective area of exposed film ($31.67 \times 10^{-4} \text{ m}^2$).

The influence of temperature was studied using four different temperatures (10 °C, 17 °C, 23 °C and 31 °C) at a constant RH of 85%, whereas the effect of RH content was evaluated at 23 °C in the range of 50–85% with 7% increments, both testing conditions generating different partial water vapor pressures.

The obtained WVTR values were normalized by the thickness (l) and difference in partial pressure of permeant across the sample (Δp) to calculate the WVP:

$$\text{WVP} = \frac{\text{WVTR} \times l}{\Delta p} = \frac{\text{WVTR} \times l}{p_1 - p_2} = \frac{\text{WVTR} \times l}{P_{\text{sat}} \cdot (\text{RH}_{\text{out}} - \text{RH}_{\text{in}})} \quad (2)$$

where p_1 and p_2 are the partial vapor pressures of the permeant (water vapor) on the outside and inside of the test film, respectively and can be given as $p_1 = P_{\text{sat}} \cdot \text{RH}_{\text{out}}$ and $p_2 = P_{\text{sat}} \cdot \text{RH}_{\text{in}}$, respectively. RH_{out} and RH_{in} are the relative humidities of the external (test RH) and internal sides ($\approx 0\%$) of the film; and P_{sat} is the saturated vapor pressure at the test temperature. For the temperatures tested, the saturated vapor pressures were 1227 Pa, 1938 Pa, 2812 Pa and 4498 Pa at 10 °C, 17 °C, 23 °C and 31 °C, respectively.

2.3.2. Oxygen permeability (OP)

Oxygen transmission rate (OTR) of PLA and PLA/CNC films was measured using VAC-V2 Gas Permeability Tester (Labthink International, Medford, MA, USA) in accordance with the procedures outlined in ASTM D3985. The influence of temperature was studied from 17 °C to 50 °C at 0% RH. At least three replicates were tested for each film sample. The OP was calculated from OTR values as follows:

$$\text{OP} = \frac{\text{OTR} \times l}{\Delta p} \quad (3)$$

where l is the thickness; Δp is difference in partial pressure of permeant (oxygen) across the sample (101,325 Pa).

2.3.3. Other properties

The surfaces of nanocomposite films were observed using a Keyence VHX-600E (Keyence Corporation, Osaka, Japan) microscope equipped with a Keyence VH-Z100R lens to monitor the distribution and dispersion of CNCs into the PLA film.

A Ultraviolet-Visible (UV-Vis) spectrophotometer Perkin-Elmer Lambda 25 (Perkin-Elmer Instruments, Beaconsfield, UK) recorded the transmittance of PLA and PLA/CNC nanocomposite films over a wavelength range of 200–900 nm at a scan rate of 240 nm/min in triplicates [19].

Differential scanning calorimetry (DSC) was performed on at least three samples for each film (6–10 mg) using a Q100 instrument (TA Instruments, New Castle, DE, USA) from 25 to 200 °C at a ramp rate of 10 °C/min under nitrogen atmosphere (flow rate: 70 ml/min) as described previously [19,26]. Generally, the first heating scan is used to assess the film's thermal properties in the as-molded conditions whereas the second heating scan is used to evaluate the material's intrinsic properties after erasing its thermal history. In this study, both heating scans were used to determine the percentage crystallinity ($\% \chi_c$) using the software Universal Analysis 2000, V4.5 (TA Instruments, Delaware, USA) [19]. DSC thermograms for PLA and PLA/CNC nanocomposite films are shown in Figs. S1 and S2 of Supplemental material.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.compositesa.2018.08.025>.

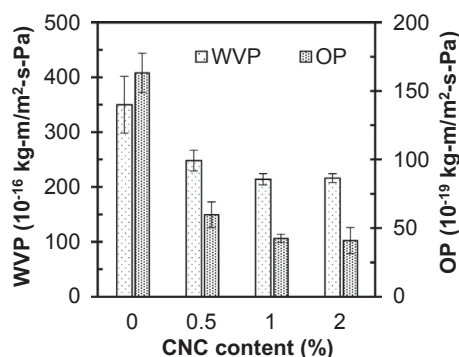


Fig. 1. Effect of CNC content on the WVP (23 °C and 85% RH) and OP (23 °C and 0% RH) of PLA films.

3. Results and discussion

3.1. Effect of CNC content on WVP and OP of films

Fig. 1 illustrates the effect of CNC content on the water vapor permeability (WVP) and oxygen permeability (OP) of PLA films. The WVP and OP decreased as the CNC concentration increased up to 1% and remained constant thereafter. Significant improvements of approximately 39% and 74% in WVP and OP, respectively, were observed by adding only 1% CNC into PLA matrix. This improved barrier performance of the nanocomposite films is likely due to the presence of highly crystalline CNCs which acted as efficient nucleating agent resulting in higher degree of crystallinity (Fig. 2) as well as impermeable regions in the matrix [6,9,13,19,27]. Other investigators have reported similar results for PLA nanocomposites with CNCs [19,28–31], microcrystalline cellulose [32], and cellulose nanofibers [33].

Because the permeant does not readily diffuse through crystallites [13,27], it is believed that the presence of nucleated crystals and CNCs increases the effective travel paths for water vapor and oxygen movements through the nanocomposites, making the path length more tortuous, which reduces the diffusion process, thus lowering permeation as reported by others [8,9,19,27].

Interestingly, the values of WVP and OP negatively correlated with the degree of crystallinity (Fig. 2) in the as-molded PLA films (1st heat) as well as their intrinsic crystallinity (2nd heat), in reasonable agreement with the work of Shogren [34] who asserted an improvement of 50% or higher in WVP of amorphous PLA by crystallizing it through annealing at 130 °C for 10 min in a vacuum oven. Similarly, the WVP of another biopolymer, poly(β -hydroxybutyrate-co-hydroxy-valerate) (PHBV) with various valerate contents (6, 12, and 18%), correlates well with the crystallinity. As valerate content of PHBV decreases, the crystallinity increases and WVP decreases. In other terms, highly crystalline PHBV with low valerate content (PHBV-6) had lower values of WVP in the range of temperatures investigated (6–49 °C) [34]. The

negative correlation between the degree of crystallinity and the permeability (WVP and/or OP) was also previously observed for solvent-cast PLA/nanocellulose films [9,11,35,36]. Investigators have reported a significant decrease in WVP of PLA film (~49%) by slightly increasing its degree of crystallinity from 9.1% to 10.7% with the addition of 3% solvent-exchanged cellulose nanowhiskers [11]. Likewise, increased crystallinity of PLA films from 5.5% to 6.2% by incorporating 3% CNCs reduced the WVP and OP of the films by 16% and 21%, respectively [35]. On the other hand, Oksman and Petersson reported a 13% decrease in PLA's crystallinity by adding 5% swollen microcrystalline cellulose (S-MCC) into the film, which resulted in 240% increase in the OP of the film due to less tortuous path for the gas molecules to travel [36]. Nevertheless, this trend also clearly supports the above-mentioned negative correlation.

The maximum increase in crystallinity occurred at 1% CNCs (see Fig. 2 caption), a CNC content that correlates very well with the optimum improvement in the barrier properties of the films (Fig. 1). It should be mentioned that the addition of more than 1% CNCs did not improve the crystallinity of PLA further (see Fig. 2 caption) probably due to the retarded crystal growth caused by CNC agglomerations at high loading levels [26,31].

Consequently, nanocomposite films with different CNC contents (0.5; 1 and 2%) were examined under a digital microscope to monitor CNC agglomerations at high loading levels (Fig. 3). A plot of the CNC agglomeration frequency as a function of their diameters is also shown. Homogenous distribution of CNCs was achieved in the PLA matrix, regardless of the CNC content. However, some agglomerates indicated by the micrometer-sized particle diameters recorded in Fig. 3(a-c) were still visible suggesting that nanoscale dispersion was not achieved as previously reported [19]. As expected, the PLA films with 2% CNCs slightly had higher number of particles with size 10 μ m or larger compared to the other concentrations [Fig. 3(d)].

Due to limited CNC dispersion, the light transmission of PLA films in the visible light wavelength range (380–720 nm) decreased by adding CNCs into the films, irrespective of the CNC content (Fig. 4). This deleterious effect could be attributed to the presence of nucleated crystals and micrometer-sized CNC agglomerations larger than the incident wavelength of light (nanometer) in the nanocomposite films, which scatter light [16,19,21]. The transparency of PLA films decreased from ~92% to ~86% with the addition of 0.5% CNCs, further decreased to ~78% with the addition of 1% CNCs and then levelled off with further addition of CNCs. Remarkably, the decreased light transmission of PLA films on the addition of CNCs did not affect their visual clarity (Fig. 5). It should be mentioned that the addition of CNCs into PLA reduced the light transmittance in the UV region of the spectra (250–380 nm) indicating that CNCs blocked light in this region, making the nanocomposite films attractive materials for packaging applications requiring UV light protection as reported by others for PLA nanocomposites with CNFs [16], CNCs [21,37] and S-MCCs [36].

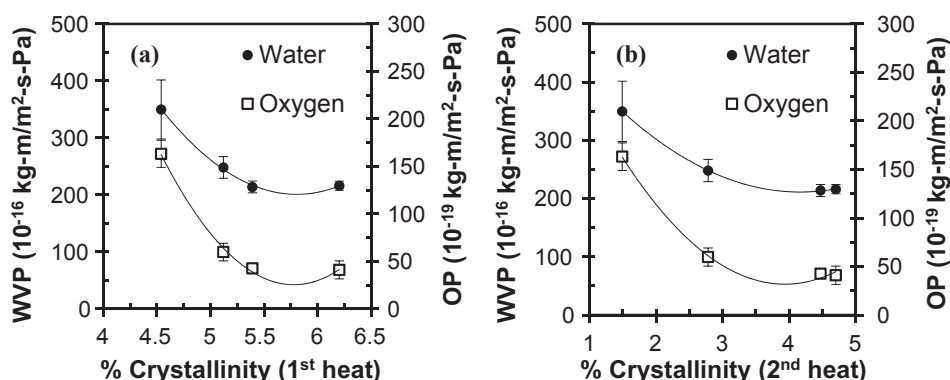


Fig. 2. WVP and OP of PLA and PLA/CNC nanocomposite films as a function of crystallinity obtained from (a) 1st heat and (b) 2nd heat. In the 1st heat the crystallinities were 4.5 ± 0.1 ; 5.1 ± 1.0 ; 5.4 ± 0.8 ; and 6.2 ± 0.2 whereas in the 2nd heat they were 1.5 ± 0.4 ; 2.8 ± 0.4 ; 4.5 ± 0.4 ; and 4.7 ± 0.4 for PLA with 0; 0.5; 1; and 2% CNC, respectively.

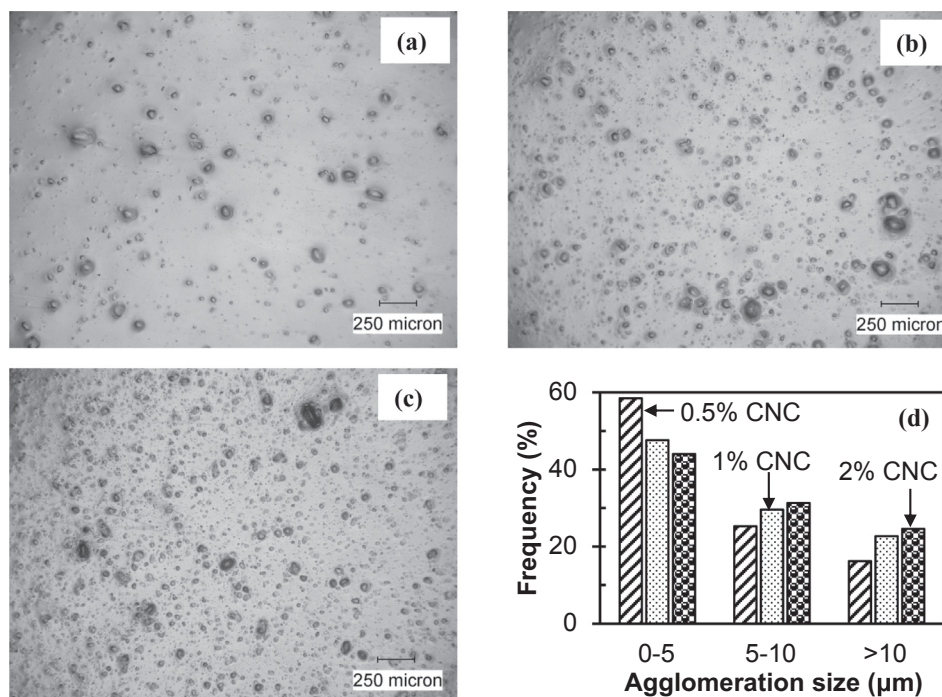


Fig. 3. Digital microscope images of PLA films with various CNC contents of (a) 0.5%; (b) 1%; and (c) 2% as well as (d) CNC agglomeration frequency as a function of their diameters in the nanocomposite films.

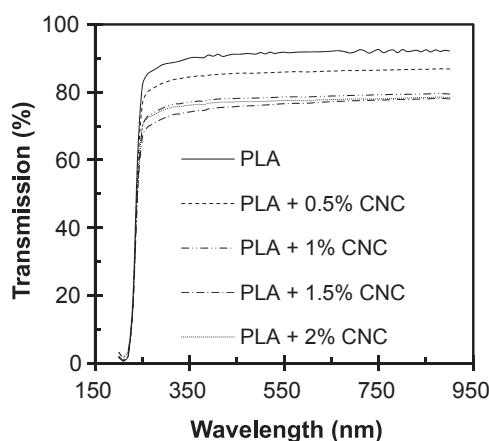


Fig. 4. Effect of CNC content on the transparency of PLA films.

3.2. Effects of temperature and/or RH on WVP and OP of PLA and nanocomposite films

Consider first the effects of CNC addition and testing temperature on the WVP [Fig. 6(a)] and OP [Fig. 6(b)] of PLA films. Increasing the temperature of the system led to an exponential decrease in the WVP but an exponential increase in OP for PLA and PLA/CNC nanocomposite films in agreement with results reported by other investigators [34,38–40]. However, the WVP decreased as the CNC content increased up to 1% and remained constant thereafter, irrespective of the testing temperature [Fig. 6(a)]. Since the optimum improvement in WVP was observed at 1% CNC content [Fig. 6(a)], the OP dependence on temperature was evaluated for neat PLA and PLA/1% CNC nanocomposite films only [Fig. 6(b)]. Overall, the nanocomposite films had better water and oxygen barrier properties than neat PLA counterparts, regardless of testing temperature due in part to the increased crystallinity (Fig. 7), which validates the negative correlation between the barrier properties (WVP and OP) and crystallinity discussed earlier.

The exponential relationships between the permeability (water and



Fig. 5. Visual clarity of neat PLA (top left) and PLA/CNC nanocomposites films with 0.5% CNC (top right); 1% CNC (bottom left) and 2% CNC (bottom right).

oxygen) and temperature shown in Fig. 6 can be described by the following Arrhenius relationship:

$$Y = A_0 \cdot \exp^{-E_p/RT} \quad (4)$$

where Y is the WVP or OP of the films; A_0 is the pre-exponential factor or Arrhenius constant, i.e., the WVP or OP of the film at very high temperature (approaching infinity) which has no physical meaning but represents permeability in the absence of polymer-polymer interaction [38]; E_p is the activation energy, i.e., the minimum energy barrier to be overcome by water vapor or oxygen to start permeating through the film; R is the universal gas constant ($0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$); and T is

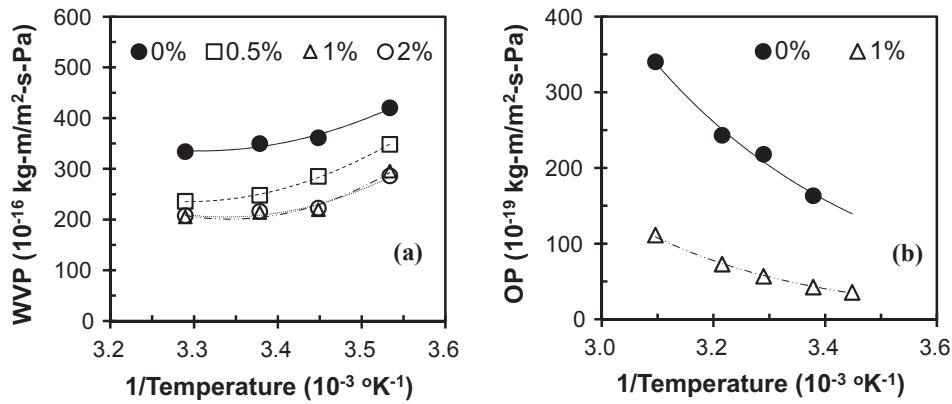


Fig. 6. Effects of (a) CNC content and testing temperature on the WVP of PLA films at 85% RH and (b) CNC addition and testing temperature on the OP of PLA films at 0% RH.

the temperature (K).

Table 1 summarizes the regression analysis results for the activation energy (E_p) and pre-exponential factor (A_0) of PLA and PLA/CNC nanocomposite films from the Arrhenius plots shown in Fig. 6. The activation energy for water vapor permeability is negative for the PLA and nanocomposite films. Negative activation energy values of -0.1 kJ/mol for semi-crystalline PLA [34], -3.93 kJ/mol for commercial PLA cast films [38], -9.8 kJ/mol for PLA 4030D with 98% L-Lactide [39] and -10.1 kJ/mol for PLA 4040D with 94% L-Lactide [39] have also been reported and attributed to the polarity of PLA [34,38], which affects the activation energies for diffusion (E_d) and sorption (or heat of solution, ΔH_s), two major components contributing to the overall activation energy for permeation given by:

$$E_p = E_d + \Delta H_s \quad (5)$$

Investigators have reported lower values of E_d for hydrophilic polymers due to their lower activation energy for water diffusion. Whereas, ΔH_s , which is controlled by two separate thermodynamic processes, is equal to the sum of the heats of condensation (ΔH_c) and mixing (ΔH_m). Polar polymers such as PLA, cellulose acetate (CA), cellulose acetate propionate (CAP) and ethyl cellulose (a hydrophilic polymer) have near-zero or negative values for ΔH_m [34,38]. Since ΔH_c is negative and equal to -42 kJ/mol for water vapor, ΔH_s becomes negative, resulting in negative values of E_p (Eq. (5)) [34,38].

The activation energy for water permeability (absolute E_p values in Table 1) slightly increased by adding CNCs into the matrix, regardless of CNC content, suggesting that more energy is required to initiate

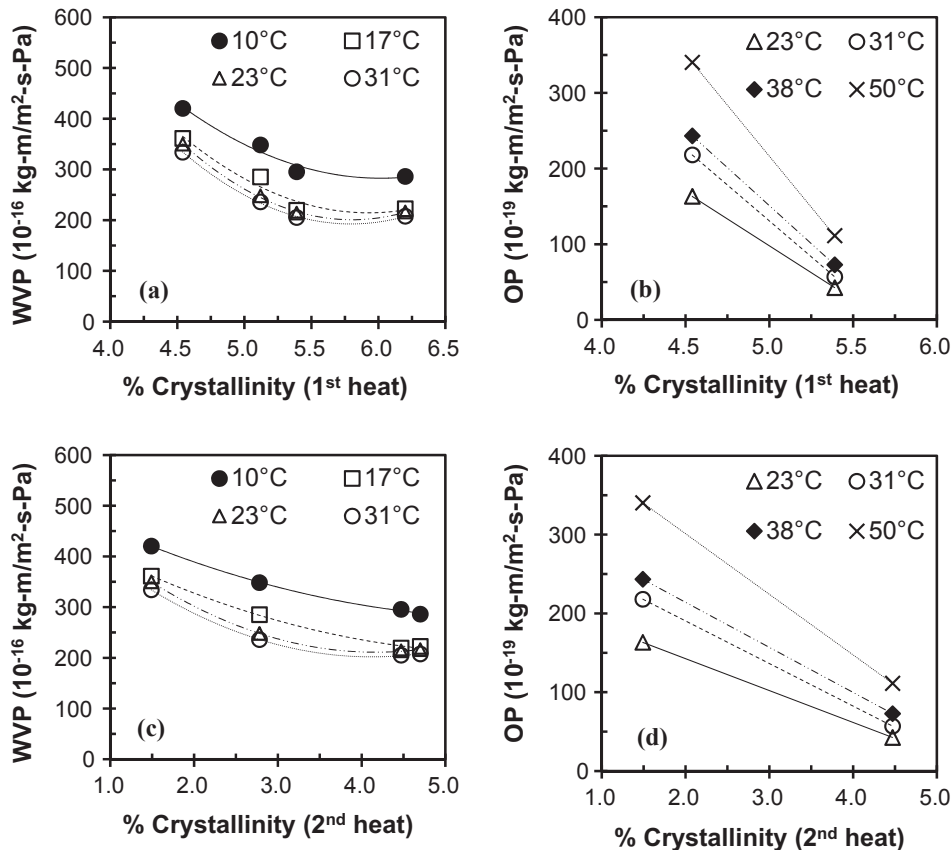


Fig. 7. WVP and OP of PLA and nanocomposite films at various temperatures as a function of percent crystallinity obtained from 1st heat [(a) and (b)] and 2nd heat [(c) and (d)].

Table 1Effect of CNC content on the water vapor and oxygen activation energy (E_p) and pre-exponential factor (A_0) of PLA films.

CNC content in PLA films (%)	WVP			OP		
	A_0 (10^{-16} kg m/m ² s Pa)	E_p (kJ/mol)	R^2	A_0 (10^{-14} kg m/m ² s Pa)	E_p (kJ/mol)	R^2
0	16.7	−7.5	0.88	8.5	21.0	0.99
0.5	1.1	−13.5	0.93	–	–	–
1	1.9	−11.7	0.76	26.5	27.1	0.99
2	3.3	−10.3	0.79	–	–	–

water vapor permeation through the nanocomposite films. Similar trend is observed for OP where the E_p slightly increased by adding 1% CNC into PLA matrix, owing to the excellent oxygen barrier of cellulose nanomaterials [13]. The activation energy for oxygen permeability of 21.0 kJ/mol obtained in this study for neat PLA films is consistent with the E_p values of 28.43 kJ/mol [39], 23.869 kJ/mol [40] and 24.9 kJ/mol [41] in the literature. It is worth mentioning that the Arrhenius equation parameters (A_0 and E_p) listed in Table 1 can be used in equation (4) to predict WVP and OP values of the PLA and PLA/CNC nanocomposite films at any absolute temperature (Kelvin).

Consider next the effects of CNC content and relative humidity (RH) on the WVTR and WVP of PLA films (Fig. 8). It is generally accepted that the WVTR through a polymeric film depends on the concentration gradient of the permeant and is described by the Fick's law [22,42]:

$$J = -D \nabla c \quad (6)$$

where J is the diffusion flux; D the diffusion coefficient; and ∇c the concentration gradient of the permeant in the film.

Since the diffusion coefficient (D) is independent of the permeant concentration at steady state, Eq. (6) can be combined with Henry's law ($c = S \times p$) and integrated to give [22,42]:

$$J_s = D \cdot \frac{c_1 - c_2}{l} = D \cdot S \cdot \frac{p_1 - p_2}{l} = P \cdot \frac{p_1 - p_2}{l} \quad (7)$$

where J_s is the diffusion flux at steady state (WVTR); l is the film thickness; c_1 and c_2 are the concentrations of the permeant (water vapor) on the external and internal sides of the test film; S is the solubility coefficient; and P is the permeability coefficient, i.e., product of D and S .

Eq. (7) can be rearranged as follows using $p_1 - p_2 = P_{\text{sat}} \cdot (RH_{\text{out}} - RH_{\text{in}})$:

$$J_s = \text{WVTR} = \frac{P \cdot P_{\text{sat}}}{l} \cdot (RH_{\text{out}} - RH_{\text{in}}) \quad (8)$$

It is clearly seen in Fig. 8(a) that WVTR increased linearly with increasing testing RH, irrespective of CNC content as expected from Fick's Law (Eq. (8)), in agreement with results reported for PLA [8] and other plastics [43].

The WVTR values of PLA and nanocomposite films were normalized by the film thickness and the difference in partial vapor pressures to obtain the permeability (Eq. (2)). A plot of the obtained WVP as a function of RH for PLA and nanocomposite films is shown in Fig. 8(b). Since the difference in partial vapor pressure in Eq. (2) [$\Delta p = P_{\text{sat}} \cdot (RH_{\text{out}} - RH_{\text{in}})$] increases linearly with increasing testing RH (i.e., increase in RH_{out} only since $RH_{\text{in}} \approx 0\%$), the normalized WVP of PLA and nanocomposite films did not vary with changes in testing RH, in agreement with the findings reported in the literature for PLA 4030D with 98% L-Lactide and PLA 4040D with 94% L-Lactide [39]. Nevertheless, all nanocomposite films were better barriers to water vapor than neat PLA films attributable to the increased crystallinity (Fig. 9), again validating the negative correlation between the WVP and crystallinity, insensitive to RH.

4. Conclusions

The effect of CNC content on the water vapor (WVP) and oxygen (OP) barrier properties of blown PLA films was evaluated at various temperatures and relative humidities. The following conclusions were drawn:

- Both WVP and OP of PLA and PLA/CNC nanocomposite films varied exponentially with temperature as expected from the Arrhenius equation, whereas the WVP remained constant with relative humidity as expected from Fick's law. However, two distinct trends were observed for the change in WVP and OP as function of testing temperature. WVP decreased with increasing temperature whereas an opposite trend was observed for OP, resulting in negative activation energy for water permeability attributed to PLA's polarity but positive activation energy for oxygen permeability, irrespective of CNC content. The activation energy for both water vapor and oxygen permeabilities increased by adding CNC into PLA matrix.
- The nanocomposite films were better barriers to both water and oxygen compared to PLA films irrespective of the testing temperature and relative humidity, attributable to the presence of highly crystalline CNCs, which increased the degree of crystallinity of the

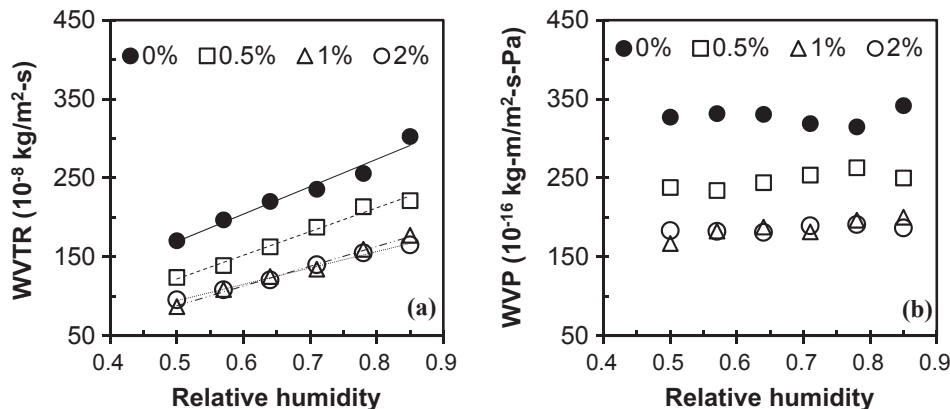


Fig. 8. Effects of CNC content and RH on the (a) WVTR and (b) WVP of PLA films at 23 °C.

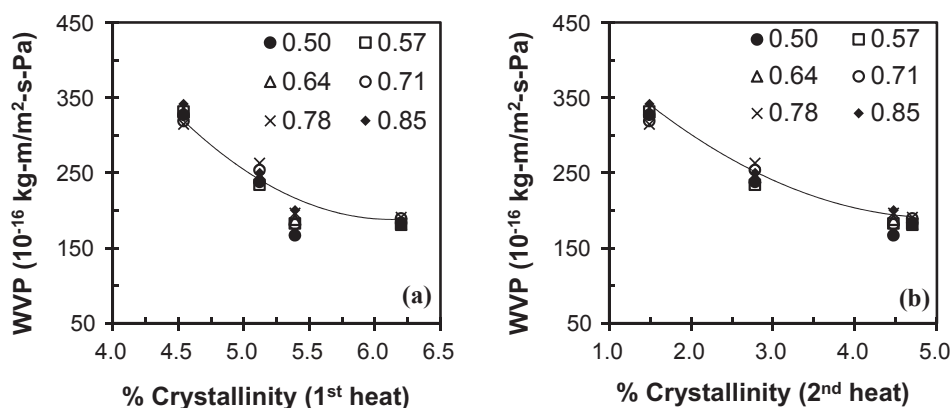


Fig. 9. WVP of PLA and PLA/CNC nanocomposite films tested at various relative humidities as a function of films' crystallinity obtained from (a) 1st heat and (b) 2nd heat.

nanocomposites and acted as impermeable regions in the matrix, thus creating a tortuosity effect.

- iii. The values of WVP and OP negatively correlated with the degree of crystallinity, i.e., as the crystallinity increased the WVP and OP decreased. In fact, depending on testing temperature or humidity, optimum improvements in WVP (30–40%) and OP (65–75%) of PLA films occurred at 1% CNCs, a CNC content that correlated very well with the maximum increase in crystallinity.
- iv. The combined effects of increased crystallinity and CNC agglomerations negatively affected the light transmission of nanocomposite films by scattering light without affecting their visual clarity.
- v. The transparent blown PLA/CNC nanocomposite films with better barrier performance developed in this study have tremendous potential for food packaging applications.

5. Declarations of interest

None.

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