



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



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ARTICLE INFO

Keywords:

- A. Biocomposite
- A. Nano-structures
- B. Permeability
- E. Extrusion

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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<https://doi.org/10.1016/j.compositesa.2018.08.025>

Received 19 June 2018; Received in revised form 16 August 2018; Accepted 18 August 2018

Available online 20 August 2018

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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]:

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

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:

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

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 $p_1 = P_{\text{sat}} \cdot RH_{\text{out}}$ and $p_2 = P_{\text{sat}} \cdot RH_{\text{in}}$, 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:

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

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>.

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