WATER PERMEATION IN POLYLACTIDE AND POLYLACTIDE/MONTMORILLONITE COMPOSITES

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Introduction

Recently bio-based polymers have raised their application due to potentials to achieve numerous environmental advantages compared to petroleum-based counterparts. Among all bio-based polymers, polylactide (PLA) is a promising material that is made from renewable sources such as corn or sugarcane. However, one of the major problems that prevents PLA from being competitive with petroleum-based polymers is its poor moisture barrier properties.

Some researchers have tried to improve moisture barrier properties in PLA is by chemical or physical modifications such as varying molecular weight, stereoisomerism, end group composition, blending, coating, copolymerization, adding microparticles or nanoparticles, chemical surface reaction and plasma treatment [1,2]. In this research, water permeation in neat poly(L-lactide) (PLLA) and PLLA-montmorillonite (PLLA-MONT) nanocomposites was studied to find out the effect of nanoparticles in improving the moisture barrier properties in PLA.

Experimental

Materials

Neat PLLA with a molecular weight of about 100,000 g/mol was commercially manufactured by NatureWorks and used as-received. The organically modified montmorillonite (MONT), Cloisite 30B was provided by Southern Clay Product Inc., Gonzales, TX and used as-received. The MONT was prepared by modifying natural montmorillonite clays with a quaternary ammonium salt. The extent of modification (ionic exchange) in Cloisite 30B is 90meq/100g clay. Thermal gravimetric analysis (TGA) technique showed that the percentages of inorganic and organic materials in MONT are 75% and 25%, respectively.

Composite Film Preparation

All studied samples were prepared by solution-casting method. Neat PLLA was dissolved in chloroform to form a 5 wt% solution which was cast on a petri-dish. To produce composite films with different wt% of MONT, a solution of neat PLLA and a suspension of MONT in dichloromethane were prepared. The PLLA solution and MONT suspension were stirred and sonicated separately before being stirred and sonicated together. The final mixture was cast on a petri-dish. All neat PLLA and PLLA-MONT composite samples were dried at room temperature over 2 days. Finally, the films were heated in a conventional oven at 70ºC overnight to sufficiently remove all the residual solvent. All films obtained had a thickness of about 100 microns.

Permeation Experiment Apparatus

Permeation of water in neat polymer and composite films were studied by a simple permeation experiment. Equipment used consists of an environmental chamber with constant temperature (24ºC) and relative humidity (40%). Twenty-ml vials with open-top caps and Teflon-lined septa with a 14-mm hole cut in the center of the septa are used. Membranes are cut into circles and placed inside the cap. Vials are filled with 10 ml of water, covered by the open-top cap with polymer membrane, and placed inside the environmental chamber. Vials are weighed every 24 hours to determine the mass loss with time. When the rate of mass loss stays constant, permeability of water through the membrane is calculated by the following equation:

$$P = \frac{L * VTR}{S * \left(P_1 - P_2\right)} \quad (1)$$

where S is the saturation vapor pressure at the test temperature, P_1 is the partial pressure or relative humidity on the challenge side, P_2 is the partial pressure on the exit side, L is the sample thickness, and VTR is the vapor transfer rate per unit area.

Results and Discussions

WAXS patterns (Fig.1) were obtained for as-received Cloisite 30B (MONT), neat PLLA and PLLA-MONT composite films. As-received MONT powder showed a very high intensity peak at a 2θ angle of 4.82º which is the main characteristic peak of MONT. The main peaks of PLLA were obtained at a 2θ angle of 16.7° and 19.1° which are characteristic of crystalline PLA. PLLA-MONT composite sample showed the evidence of a small peak at 4.62°, which corresponds to the presence of MONT. According to the results shown in Fig.1, the main characteristic peak of MONT shifted from 4.82° to 4.62°, which indicates an increase in the interlayer spacing of MONT when presenting in PLLA-MONT composite. This result suggests that the PLLA matrix was intercalated in between the layers of MONT.

Table 1 shows the water permeation rate in all tested neat PLLA and PLLA-MONT composite films According to this result, the water permeability in PLLA-MONT composites reduced with increasing MONT concentration. At 14.5 wt% of MONT, water permeation in PLLA-MONT composite reduced about 34% compared with neat PLLA. The addition of MONT particles increased the tortuosity of the pathway for water molecules to pass through the polymer membrane. This result showed that the presence of MONT particles has significantly improved the moisture barrier properties in PLA.

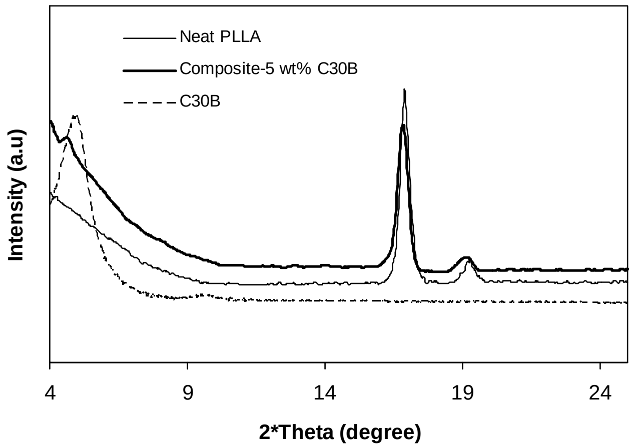

Fig. 1 WAXS pattern of as-received MONT, neat PLLA and PLLA-MONT composite with 5 wt% of MONT

Table 1 Water permeability in neat PLLA and PLLA-MONT composites

C30B wt fraction	Permeability 10^{-10}cm^3 (STP).cm/cm^2.s.Pa	P_{eff}/P_c
0	3.438	1.000
0.02	3.171	0.922
0.05	2.854	0.830
0.10	2.636	0.767
0.12	2.358	0.686
0.145	2.198	0.639

The Maxwell-Wagner-Sillars model (MWS) was applied to study the arrangement of MONT particles in the PLA polymer matrix [3].

$$P_{eff} = P_c \frac{nP_d + (1-n)P_c + (1-n)(P_d - P_c)\phi_d}{nP_d + (1-n)P_c - n(P_d - P_c)\phi_d} \quad (2)$$

P_c, P_d, P_{eff} and ϕ_d indicate the permeability of neat PLLA, MONT, PLLA-MONT composite and the volume fraction of MONT. n is the shape factor whose value is between 0 and 1. By using the water permeability in neat PLLA and PLLA-MONT composites with an assumption of $P_d = 0$ to fit to the MWS model, the shape factor (n) was determined to be 0.77, which indicates that MONT particles are of oblate ellipsoidal shape.

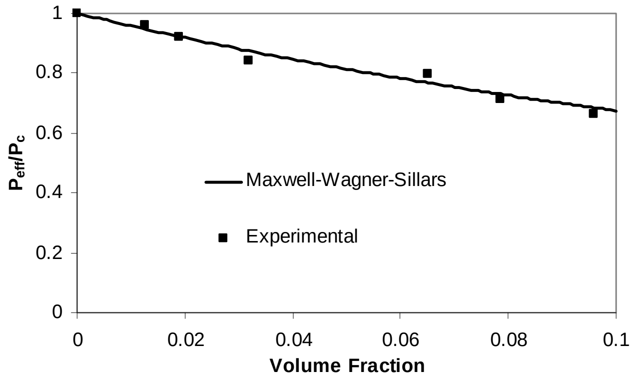

Fig. 2 Comparison of experimental water permeation rate and prediction from MWS model

Conclusions

Water permeability in neat PLLA and PLLA-MONT composites at different concentrations of MONT was studied. Results showed that water permeation rate reduced with the increase in MONT concentration. The Maxwell-Wagner-Sillars mixed matrix membrane model was applied to the permeation data for a curve fitting process to find out the shape of nanoparticles. It was found that MONT particles were oblate ellipsoids.

References

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