Absorption and Diffusion in Bio-Based Polymer Films

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Thin bio-based polymer films have been shown to have potential uses in a variety of applications, such as medical coatings, food packaging, and textile fibers. In order to optimize their use, it is essential to understand how these films interact with their environment and how these interactions effect changes in the properties of these films. This paper presents experimental measurements of moisture transport in polylactide (PLA), obtained using a combined Quartz Crystal Microbalance and Heat Conduction Calorimeter (QCM/HCC) and Dynamic Vapor Sorption (DVS). Measurements of moisture sorption in PLA, a moderately hydrophobic aliphatic polyester, versus relative humidity and temperature show that moisture sorption increases with degradation but is only weakly dependent on crystallinity. These results contradict the common assumption that water is excluded from crystalline domains. The composition of the end groups in PLA were modified and no significant end group effect was observed.

1. Introduction

Despite the significant and growing interest in *bio-based polymers* derived from renewable resources, bio-based polymers have had limited success competing against petroleum-based plastics in the commodity plastics markets due to several reasons including economics, inferior properties and environmental performance. Some of the major technical challenges to widespread acceptance of bio-based polymers are difficulties achieving mechanical and barrier properties comparable to conventional synthetic polymers while maintaining biodegradability. The current leading bio-based polymer is polylactide or polylactic acid (PLA, Figure 1), which is being produced commercially by NatureWorks (formerly Cargill Dow) in the USA, and other companies worldwide [2, 3]. The main application areas for PLA are food packaging, bottles, films, and serviceware with a number of PLA products now commercially available. A barrier to effective commercialization of PLA for the applications described above is inferior moisture barrier properties compared to synthetic polymers. Fundamental knowledge of moisture transport in PLA will help in the following aspects: drying of bio-based polymer pellets during production (melt-processed pellets are quenched in water), moisture regain (i.e. equilibrium moisture content) and degradation during processing, water losses through products, industrial composting and degradation kinetics, and life cycle assessment of bio-based polyester products.

Despite the importance of moisture penetration in evaluating the performance, degradation, and life cycle of polymer products, there have been few published papers on moisture transport in renewable polymers [4-6]. However, there is some disagreement about the dominant mechanisms of moisture transport.
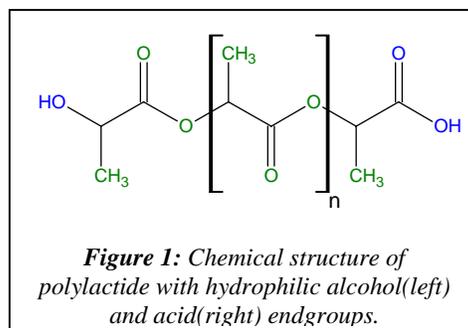

Figure 1: *Chemical structure of polylactide with hydrophilic alcohol(left) and acid(right) endgroups.*

2. Results

QCM/HCC: Sorption isotherms were measured by QCM/HCC in PLA films [7, 8]. The QCM measures changes in the frequency of an oscillating quartz crystal coated with a polymer film in order to calculate the amount of moisture absorbed into the film over time by using the Sauerbrey equation[9]. The HCC uses the inverse Peltier effect to generate a measurable voltage correlated to the amount of heat flow in the film as a result of the absorption. Crystalline and amorphous films

Figure 2: *Sorption Isotherms for amorphous PLA films after being degraded at 80ºC and 85% relative humidity. Isotherms measured by DVS at 40ºC.*

have been prepared and tested with little difference between their sorption properties. The sorption isotherms are nearly linear, and are fit well by the Flory-Huggins theory with a high interaction parameter. Stereocomplexed PLA samples exhibited somewhat smaller moisture sorption even though both samples were amorphous; heat treatment did not affect the sorption isotherms. Whether the smaller sorption in stereocomplexed PLA is due to molecular conformation or due to slight differences in molecular weight is unknown and deserves further investigation.

DVS: Sorption isotherms have also been measured using DVS [7, 8]. The sorption isotherms for amorphous and crystalline PLA from DVS are comparable to those from QCM/HCC. The sorption isotherms show that crystallinity has a small influence on moisture sorption in PLA. For films that are 40% to 50% crystalline, the amount of water absorbed decreases by less than 20% compared to the amorphous films; this result is independent of sample thickness and the type of crystalline structure. The insensitivity of sorption to crystallinity is unexpected and inconsistent with results for other semicrystalline polymers. For sorption to be independent of crystallinity in PLA, the sites for water sorption in PLA must be largely *excluded* from the crystalline domains, because it is commonly though that water cannot enter into the crystalline domains (and it has been established that crystallinity does not change during sorption/desorption). Based on these observations, we hypothesized that moisture sorption is controlled by hydrophilic end groups in PLA.

Degradation (and molecular weight) is known to have a significant effect on moisture sorption and transport in PLA. Measurements of sorption isotherms on partially degraded PLA films (of amorphous 4060 PLA) show a rapid increase in sorption with degradation (Figure 2). Films were exposed to high humidity (85%) and high temperature (80ºC) prior to being tested with DVS. After one day of degradation, the change in sorption is small; this may be due to a time-lag for the sample chamber to rise to an elevated humidity or it may be due to the reported autocatalytic effect for PLA degradation. The amounts of moisture absorbed after 2 days and 3 days of degradation are about twice and ten times as much, respectively. The increase in moisture sorption with degradation is consistent with the hypothesis of end groups controlling sorption because more end groups are present in a degraded sample.
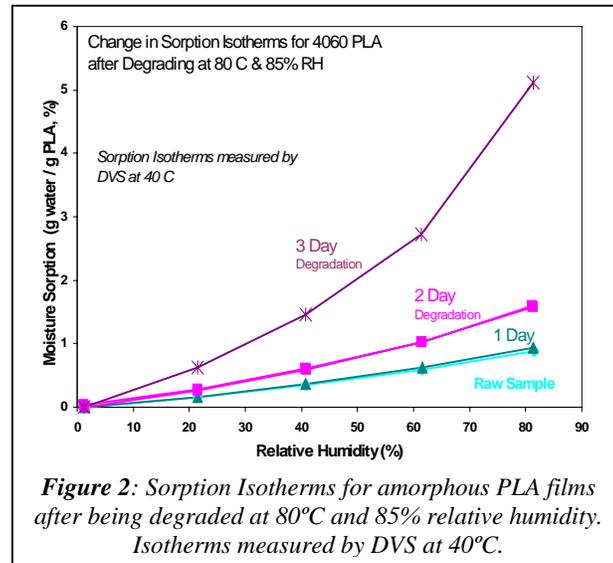
3. Effect of Varying End Group Composition on Sorption

To test the hypothesis that the end groups in PLA controlled the amount of moisture sorption in amorphous and crystalline PLA samples, several samples of varying end group composition were synthesized. These samples were synthesized by Nate Lynd in Marc Hillmyer's laboratory in the Chemistry Department at the University of Minnesota.

The modified PLA samples were synthesized with a benzyl-methyl-aluminum catalyst that initiates a living polymerization reaction with lactide:
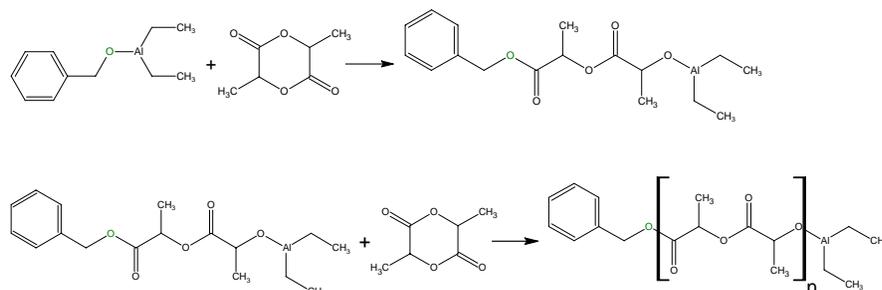
The polylactide produced by this polymerization scheme has a hydrophobic aromatic group at the initiated terminus and an aluminum catalyst group at the living terminus.

After producing a polymer solution of moderate molecular weight, the reaction batch was divided into two half-batches and the reaction in each half-batch was terminated by a different technique. To produce a hydrophilic alcohol end group, the reaction was terminated by addition of an acid (aqueous HCl). To produce a hydrophobic acetate end group, the reaction was terminated by addition of acetic anhydride.

Figure 3 shows sorption isotherms for the four synthesized PLA samples (with molecular weights about 10,000 and varying end groups) and for high molecular weight
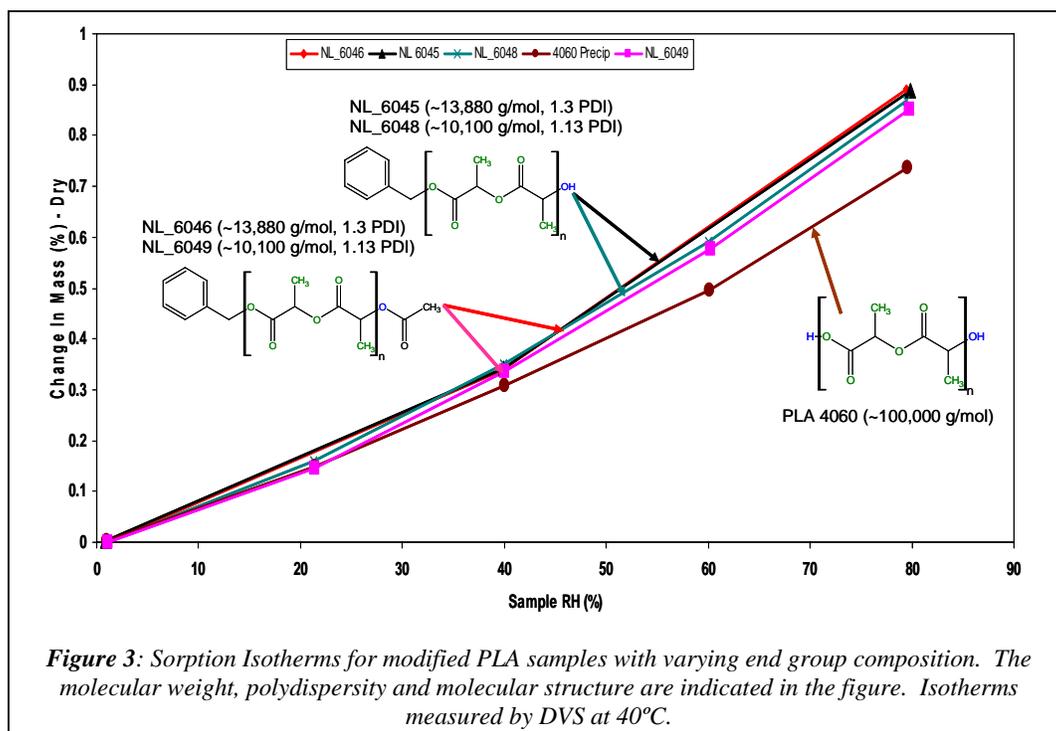

Figure 3: *Sorption Isotherms for modified PLA samples with varying end group composition. The molecular weight, polydispersity and molecular structure are indicated in the figure. Isotherms measured by DVS at 40ºC.*

PLA from Natureworks (PLA 4060 which was purified by dissolving in chloroform and precipitated in methanol). Within the accuracy of the experimental data, the sorption isotherms are nearly identical with a slightly higher amount of moisture sorption in the low molecular weight synthesized PLA compared to the Natureworks PLA. There was not a discernable difference between the sorption isotherms of PLA with two hydrophobic end groups and the PLA with one hydrophilic and one hydrophobic end group. These results are inconsistent with the hypothesis that end groups control sorption in PLA. Consequently there is a need to determine an alternative mechanism that explains the insensitivity of sorption in PLA to crystallinity.

4. Discussion

Several experimental techniques were used to characterize sorption in polylactide (PLA) films. The measured sorption isotherms were relatively insensitive to differences in molecular weight, crystallinity, and stereocomplexation. However hydrolytic degradation did lead to a significant rise in sorption, presumably due to the formation of low molecular weight oligomers of lactic acid. A hypothesis was proposed that the hydrophilic end groups in PLA controlled moisture sorption, but synthesis of PLA with hydrophobic end groups did not alter the sorption isotherms. Additional studies of the end group affect are underway, but at this point it appears that another mechanism must be responsible for the insensitivity of sorption isotherms to crystallinity.

5. Acknowledgments

5 References

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