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Moisture Sorption, Transport, and Hydrolytic Degradation in Polylactide

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Abstract

Management of moisture penetration and hydrolytic degradation of polylactide (PLA) is extremely important during the manufacturing, shipping, storage, and end-use of PLA products. Moisture transport, crystallization, and degradation in PLA have been measured through a variety of experimental techniques including size-exclusion chromatography, differential scanning calorimetry, and X-ray diffraction. Quartz crystal microbalance and dynamic vapor sorption experiments have also been used to measure moisture sorption isotherms in PLA films with varying crystallinity. A surprising result is that, within the accuracy of the experiments, crystalline and amorphous PLA films exhibit identical sorption isotherms.

Index Entries: PLA; biodegradable polymers; bio-based polymers; polylactic acid; diffusion; hydrolysis.

Introduction

Even though there is a significant growing interest in *bio-based polymers* derived from renewable resources, these polymers have had limited success competing against petroleum-based plastics in the commodity plastics markets owing to several reasons including economics, inferior properties, and environmental performance. One of the major technical challenges to widespread acceptance of bio-based polymers is difficulties achieving mechanical and barrier properties comparable with conventional synthetic polymers while maintaining biodegradability. The leading bio-based polymer is currently polylactide or polylactic acid (PLA), which is being produced commercially by NatureWorks (formerly Cargill Dow) in the United States and other companies worldwide (1,2). The main application areas for PLA are food packaging, bottles, films, and serviceware, with a number of PLA products now commercially available. Bio-based polymers

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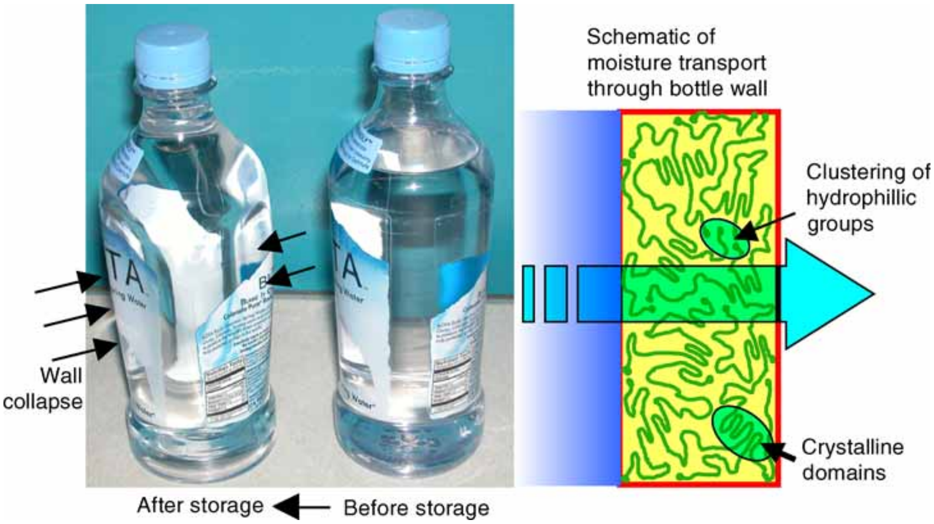

Fig. 1. Photo showing buckling of polylactide (PLA) water bottle owing to moisture loss through walls and schematic of moisture transport through a PLA film.

and biodegradable polymers are also popular for biomedical applications. Polylactides and copolymers of lactic acid with other monomers, such as glycolic acid, are leading candidates for degradable drug-delivery devices, tissue scaffolds, and other biomedical applications *(3)*.

A barrier to effective commercialization of bio-based polyesters is their inferior moisture barrier properties compared to those of synthetic polymers. Fundamental knowledge of moisture transport in bio-based polyesters will help the polymer's life cycle 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 (e.g., water bottles shown in Fig. 1), 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. In the published literature, there is some disagreement about the dominant mechanisms of moisture transport. Sharp et al. (2001) proposed that the equilibration time of glassy polymers such as PLA lead to non-Fickian diffusion effects, which is inferred by thickness-dependent diffusion coefficients *(4)*. Siparsky et al. (1997) suggested that for many samples (especially thick samples), it is not possible to separate the diffusion process from hydrolytic degradation, so accurate measurement of transport properties requires analyzing the simultaneous diffusion/reaction processes *(5)*. Auras et al. (2002) measured water vapor permeability in PLA at various temperatures and relative humidities; surprisingly, the permeability was independent of relative humidity and decreased with increasing temperature *(6,7)*. Shogren (1997) also reported that PLA permeability to water decreases with increasing temperature, although permeability to both CO_2 and O_2 increased with temperature *(8)*. Diffusion coefficients of water in PLA and other biopolymers were measured by gravimetric techniques and changes in solubility were correlated with hydrophobicity of biopolymers and related to formation of clusters of water molecules *(5,9)*.

The literature is also inconsistent about how crystallinity affects moisture sorption and moisture transport. One study suggests that the mass of water that absorbs into PLA at equilibrium is essentially independent of crystallinity *(5)*. Other studies show that the mass of water that absorbs into PLA at equilibrium scales the percent crystallinity *(8,9)*. In most studies on other semicrystalline polymers, crystallinity does affect water transport with lower solubility and lower diffusion coefficients at higher crystalline fraction *(10,11)*. Vert (1998) showed that changing the catalyst used for ring-opening polymerization of PLA can have a significant impact on moisture sorption, and this was attributed to transesterification reactions of impurities in the catalyst, leading to more hydrophobic end groups *(3)*. A systematic study of the influence of end groups (Fig. 2) on moisture sorption in bio-based polyesters is needed and will help to explain why the published data are inconsistent.

Degradation of bio-based polyesters is commonly understood to occur in two steps: (1) hydrolytic degradation of ester bonds into lower molecular weight polymers and oligomers followed by (2) biological degradation to carbon dioxide and water. Several researchers show that hydrolytic degradation must reduce molecular weight of PLA to 15,000–40,000 before biodegradation can take over *(2,12)*. Hydrolytic degradation of PLA can either occur randomly within the polymer or from the ends (unzipping); the ratio of these reactions is pH-dependent *(13–16)*. In semicrystalline PLA, degradation can lead to bimodal molecular weight distributions through hydrolytic cleavage of the polymer tie chains spanning among crystallites *(17)*. The kinetic studies on PLA have shown the reaction to be pseudo-first-order with an autocatalytic effect owing to production of acidic end groups by the hydrolytic reaction *(14,16)*. Autocatalysis also leads to faster degradation inside of PLA specimen immersed in water because soluble oligomers are trapped on the interior of the specimen and raise the interior pH relative to the surface *(3,16,18)*.

Experiment

Three different samples of polylactide were provided by NatureWorks LLC: 4032, 4060, and stereocomplex. The 4032 grade of PLA is synthesized from a high percentage of L-lactic acid and can be amorphous or crystalline, depending on heat treatment. The 4060 grade of PLA is synthesized from a mixture of lactic acid stereoisomers and does not crystallize.

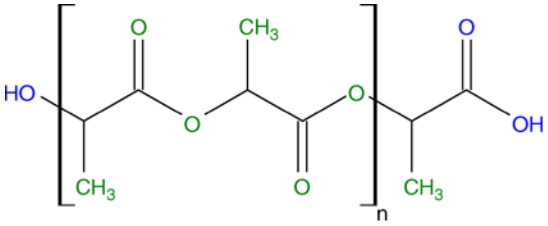

Fig. 2. Chemical structure of polylactide with hydrophilic acid and alcohol end groups.

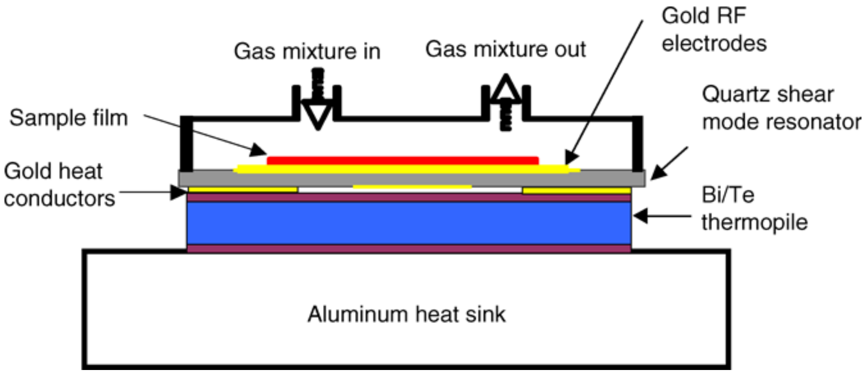

Fig. 3. Schematic of quartz crystal microbalance heat conduction calorimeter (QCM/HCC) mass/heat flow sensor and gas sample chamber.

The stereocomplex samples are a 50/50 blend of PLLA and PDLA (homopolymers prepared from nearly pure L- or D-lactic acid); the stereocomplex sample crystallizes rapidly into a different, higher-melting-point crystalline structure than homopolymer PLA.

Quartz Crystal Microbalance Heat Conduction Calorimeter

The quartz crystal microbalance heat conduction calorimeter (QCM/HCC) combines a *quartz crystal microbalance* coated with a thin polymer film in intimate thermal contact with a *heat-flow sensor* mounted on a heat sink (Fig. 3). Using QCM/HCC, Smith and co-workers *(19–21)* have been able to measure simultaneously the change in mass per unit area (to ±2 ng/cm^2) and the resulting heat flows (to ±1 µW) when the polymer on the sample QCM surface takes up or releases solvent vapor. When the gas composition above a polymer film is changed, the resulting change in mass and the integrated thermal power signal gives the enthalpy of sorption, $\Delta_{\mathrm{sorp}}H$, of the vapor in the polymer at a specific vapor activity. The combination of heat and mass measurements enables both $\Delta_{\mathrm{sorp}}H$ and $\Delta_{\mathrm{sorp}}G$ to be measured, so $\Delta_{\mathrm{sorp}}S$ can also be determined. Thus, a single set of experiment at a constant temperature is sufficient to determine all three thermodynamic properties characterizing the polymer/solvent interaction. Recently, Masscal Co. (Chatham, MA) developed a commercial version of QCM/HCC, the Masscal G1™, which was used for the results in this article by special arrangement with Masscal. Humidity was controlled by combining a dry nitrogen gas stream and a water-saturated nitrogen gas stream at various ratios. The saturated stream was prepared by bubbling nitrogen through water, and the humidity produced by this system was verified using a Buck Research CR-4™ chilled mirror hygrometer.

PLA films were prepared for QCM by dissolving PLA in chloroform (stereocomplex sample was dissolved in hexafluoroisopropanol) and spin coating. Films were air-dried for 2 d at ambient conditions, and then dried at 60°C and 80°C for at least 1 d, each in an inert nitrogen atmosphere. Amorphous films were prepared by heating to above the melting temperature for 2 h under dry nitrogen and cooling rapidly to room temperature.

Dynamic Vapor Sorption

Dynamic vapor sorption (DVS) is a gravimetric sorption method that combines a highly sensitive (i.e., lower detection limit of 0.1 μg) electrobalance with a controlled-humidity gas handling system in controlled-temperature environment. DVS is an ideal system for measuring sorption isotherms (i.e., mass uptake vs relative humidity at constant temperature). For moderately hydrophobic bio-based aliphatic polyesters, sorption isotherms can be measured with sample sizes as small as 5 mg. The DVS measurements in this paper were measured using a surface-measurement-systems DVS instrument located in Gary Reineccius's laboratory in the Food Science and Nutrition Department at the University of Minnesota (St. Paul, MN).

PLA films were prepared for DVS by melt-pressing with a heated hydraulic press at 200°C (for 4032 and 4060) or 250°C (for stereocomplex) under dry nitrogen. PLA pellets were inserted between sheets of cleaned aluminum foil, connected to a supply of dry nitrogen, and inserted into the press. After pressing for approx 5 min at approx 100 lb of force, the sample was removed and cooled quickly by pouring water over the outside of the aluminum foil surrounding the sample.

Crystallinity Measurements

Crystallinity of PLA films was determined using differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Wide-angle XRD was performed on the films prepared for QCM/HCC and DVS using a Bruker-AXS rapid XRD™ microdiffractometer in the Characterization Facility at the University of Minnesota. Sharp, crystalline, broad, and amorphous peaks were identified in the plots of intensity vs 2θ, and the areas under crystalline and amorphous peaks were calculated using the JADE™ software package to obtain a qualitative percent crystallinity.

DSC was performed on melt-pressed films using either a Perkin Elmer TGA 7™ in Ted Labuza's laboratory in the Food Science and Nutrition Department at the University of Minnesota (St. Paul, MN) or a TA Instrument

Q1000™ in the Polymer Characterization Lab in the Chemical Engineering and Materials Science Department at the University of Minnesota. Crystallinity was determined by integrating the areas under the crystallization and melting peaks, subtracting them, and dividing by the enthalpy of fusion for 100% crystalline PLA (taken to be 93 kJ/kg for 4032 PLA, and 135 kJ/kg for stereocomplex PLA).

Results

Quartz Crystal Microbalance Heat Conduction Calorimeter

Figures 4–6 display data measured by QCM/HCC for moisture sorption in PLA films. The raw QCM/HCC data in Fig. 4 show that sorption of water closely follows changes of water partial pressure (or relative humidity) within the sample chamber through two cycles of stepwise humidity changes from zero to approx 25% at 40°C. The frequency of the QCM decreases as water absorbs into the film, and the mass change is calculated by the Saurbrey equation. The thermal power (heat flow through HCC) exhibits spikes whenever the humidity changes and mass sorbs into or desorbs out of the film. The motional resistance is a measure of the damping properties of the film, and as water absorbs into PLA films, the motional resistance increases, which indicates that water acts as a plasticizer in PLA. The frequency and motional resistance are reproducible over the two cycles of humidity, indicating that degradation of PLA during the experiment is negligible.

Sorption isotherms in PLA films can be estimated from the mass absorption data from QCM (Fig. 5). Crystalline and amorphous films have been prepared and tested with little difference observed among their sorption properties. Figure 5 displays a comparison among moisture sorption into amorphous PLA films from 4032 PLA and stereocomplex PLA. The sorption isotherms are nearly linear and are fit well using the Flory-Huggins equation with a high interaction parameter. The stereocomplex PLA sample exhibited somewhat smaller moisture sorption, and even though both samples were amorphous; heat treatment did not affect the sorption isotherms.

Simultaneous measurement of mass changes and heat flow (thermal power) with QCM/HCC enables calculating a sorption enthalpy directly from the experimental data. Figure 6 shows measured values of sorption enthalpy vs moisture content for PLA films at 40°C. There is considerable scatter in the data because the low levels of sorption (less than 0.2%) lead to heat flows that are close to the limit of accuracy for the equipment. However, there is a general trend of decreasing sorption enthalpy with increasing moisture content, and the sorption enthalpy for 4032 PLA appears slightly lower than stereocomplexed PLA. All of the measured sorption enthalpies are higher than the heat of vaporization of pure water (approx 44 kJ/mol); such high sorption enthalpies have been related to formation of water clusters when water absorbs into a hydrophobic polymer *(5,9)*.

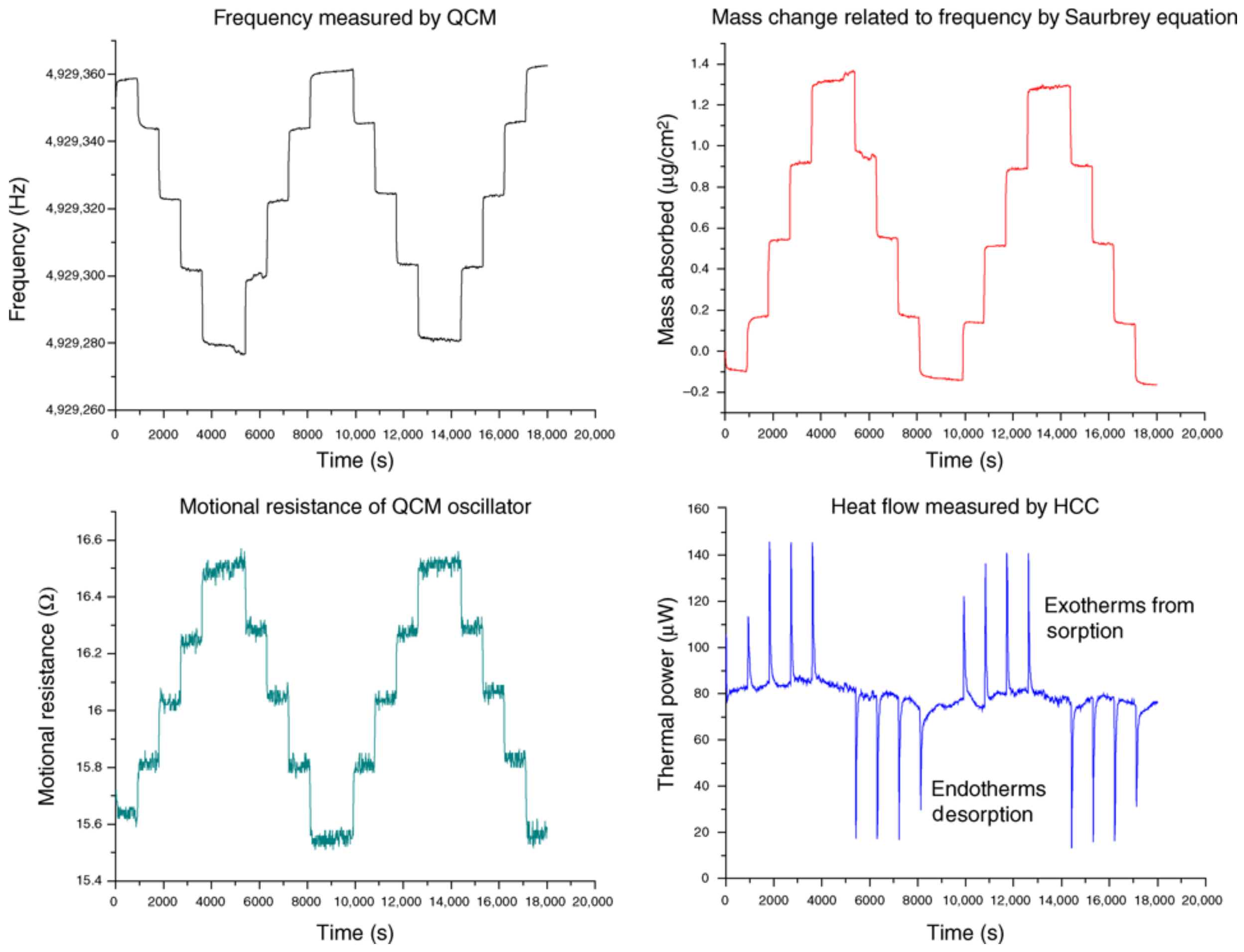

Fig. 4. Quartz crystal microbalance heat conduction calorimeter (QCM/HCC) measurements of frequency, mass of water absorbed, thermal power, and motional resistance for a PLA film subjected to a cycle of humidities at 40°C.

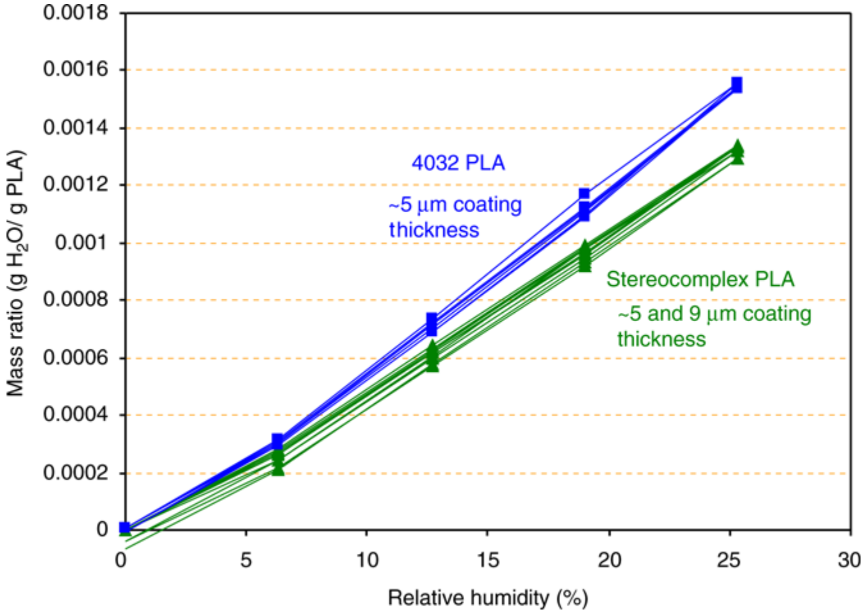

Fig. 5. Sorption isotherms for amorphous PLA films measured by quartz crystal microbalance heat conduction calorimeter (QCM/HCC) at 40°C.

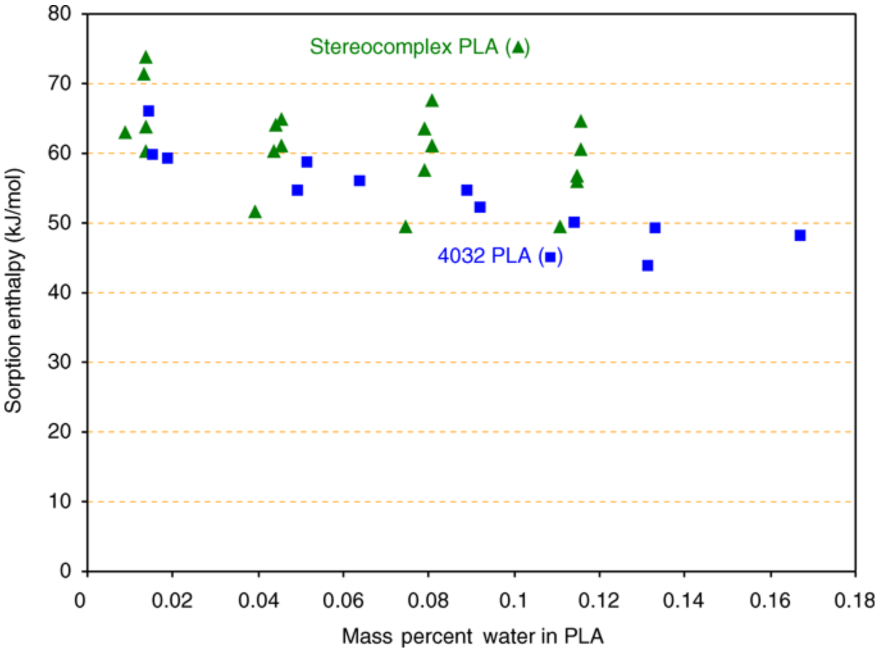

Fig. 6. Sorption enthalpies for amorphous polylactide (PLA) films measured by quartz crystal microbalance heat conduction calorimeter (QCM/HCC) at 40°C.

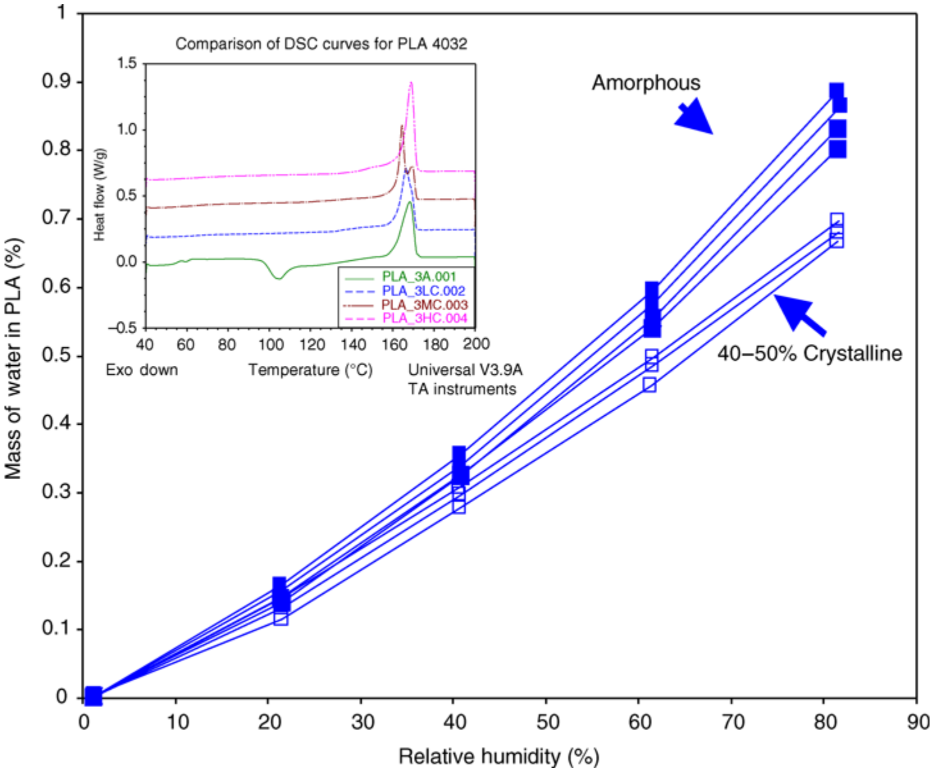

Fig. 7. Moisture sorption isotherm for polylactide (PLA) at 40°C at several different crystallinities. Inset shows differential scanning calorimetry (DSC) measurements used to determine crystallinity.

Dynamic Vapor Sorption

Sorption isotherms were also measured using DVS (Figs. 7–9). The sorption isotherms for amorphous and crystalline PLA plotted in Figs. 7 and 8 from DVS are comparable with those from QCM/HCC. The sorption isotherms for both 4032 PLA (Fig. 7) and stereocomplexed PLA (Fig. 8) show that crystallinity has a small influence on moisture sorption in PLA. For films that are 40–50% crystalline, the amount of water absorbed decreases by less than 20% compared with the amorphous films; this result is independent of sample thickness and the type of crystalline structure.

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. Films were exposed to high humidity (85%) and high temperature (80°C) before being tested with DVS. After 1 d degradation, the change in sorption is small; this may be owing to a time-lag for the sample chamber to rise to an elevated humidity or owing to the reported autocatalytic effect for PLA degradation. The

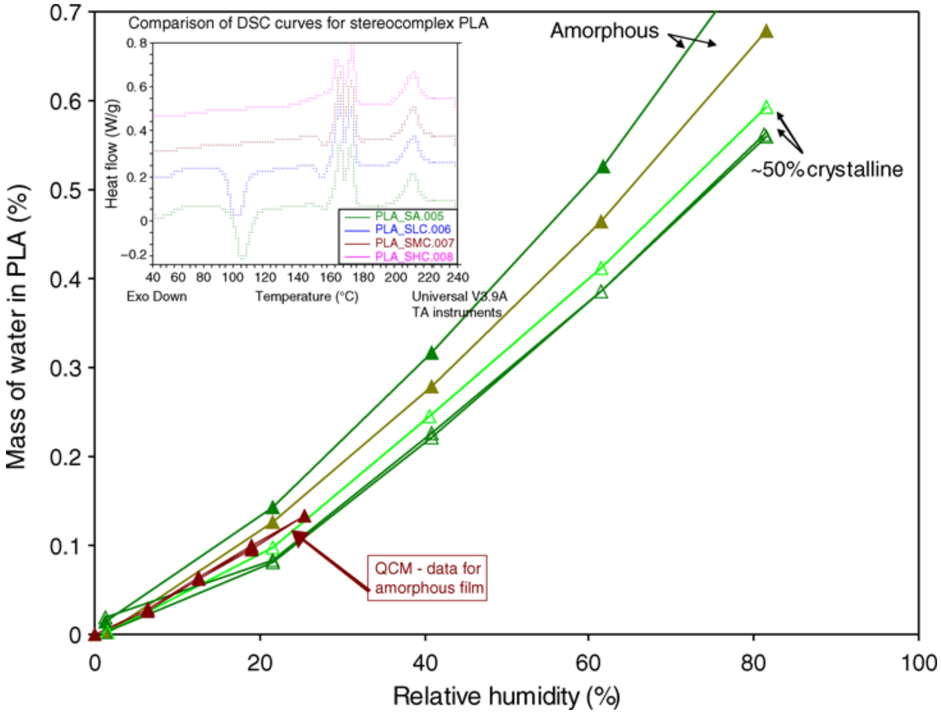

Fig. 8. Moisture sorption isotherms for a stereocomplex blend of polylactide (PLA) at 40°C measured by dynamic vapor sorption (DVS). Inset shows differential scanning calorimetry (DSC) measurements used to determine crystallinity.

amounts of moisture absorbed after 2 and 3 d 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.

Discussion

With the growing interest in bio-based and degradable polymers, there is a need for a more fundamental understanding of moisture transport within these polymers. A goal of the US Department of Energy and the US Department of Agriculture is to increase the fraction of chemicals and materials produced from biomass from the 2001 level of 5–12% in 2010 and 25% in 2020 *(22)*. Achieving this goal requires the development of a number of enabling technologies for converting biomass into chemicals and materials and for processing materials into useful, competitive products.

The results presented in this article suggest that molecular structures of bio-based polymers affect moisture transport and barrier properties in a way not discussed previously. 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

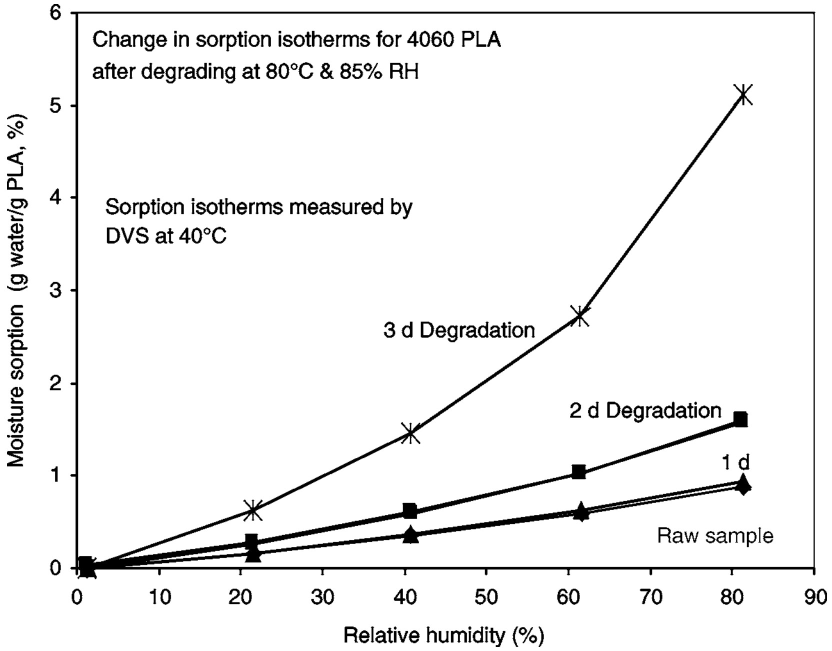

Fig. 9. Sorption isotherms for amorphous polylactide (PLA) films after being degraded at 80°C and 85% relative humidity. Isotherms measured by dynamic vapor sorption (DVS) at 40°C.

domains, because it is commonly thought 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 hypothesize that moisture sorption is controlled by hydrophilic end groups (and as indicated in Fig. 1) in PLA. Future experiments will investigate the effect of molecular weight and chemical modification of the end groups on sorption in PLA.

There are several open issues raised by research described in this article, such as why sorption and diffusion in hydrophobic polyesters are apparently insensitive to crystallinity, the role of the hydrophilic end groups on sorption, whether dynamic sorption follows Fickian kinetics, and whether water absorbs as clusters in bio-based polyesters. Also, the published literature on sorption and diffusion in PLA is inconsistent; so there is a need for systematic research focused on molecular and structural factors affecting sorption and diffusion.

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