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**Moisture Sorption, Transport, and Hydrolytic Degradation in
Polylactide**

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Management of moisture penetration and hydrolytic degradation of polylactide (PLA) is extremely important during 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 (SEC), Differential Scanning Calorimetry (DSC), and X-Ray Diffraction (XRD). Quartz Crystal Microbalance (QCM) and Dynamic Vapor Sorption (DVS) experiments have also been used to measure moisture sorption isotherms in PLA films with varying crystallinity. A surprising result is that crystalline and amorphous PLA films exhibit identical sorption isotherms, within the accuracy of the experiments.

1. Introduction

Even though there is a significant 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

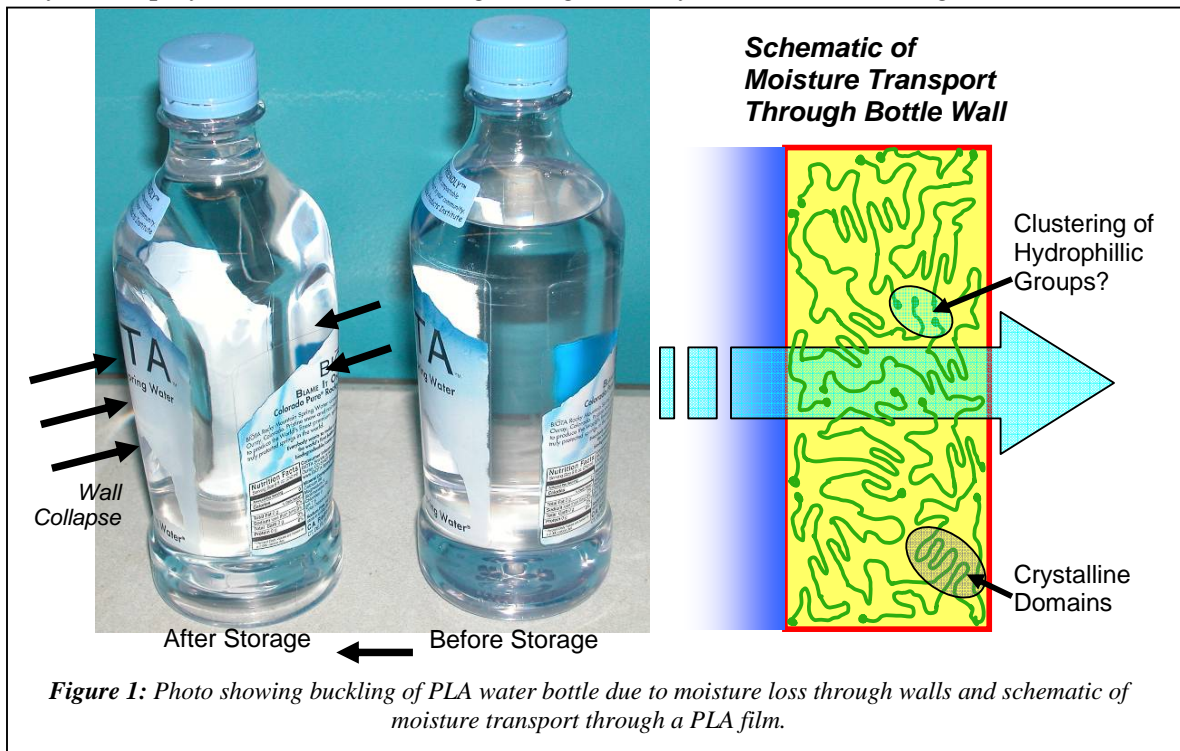


Figure 1: Photo showing buckling of PLA water bottle due to moisture loss through walls and schematic of moisture transport through a PLA film.

polymer is polylactide or polylactic acid (PLA), which is being produced commercially by NatureWorks (formerly Cargill Dow) in the USA, and other companies worldwide (4, 6). 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 and biodegradable

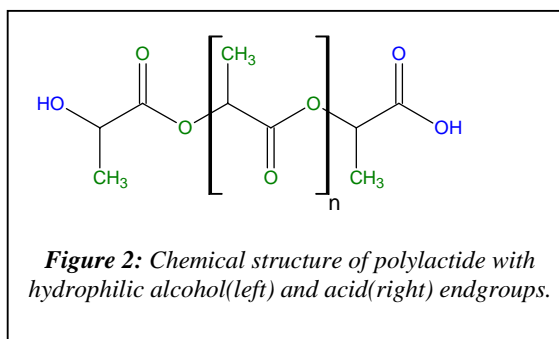


Figure 2: Chemical structure of polylactide with hydrophilic alcohol(left) and acid(right) endgroups.

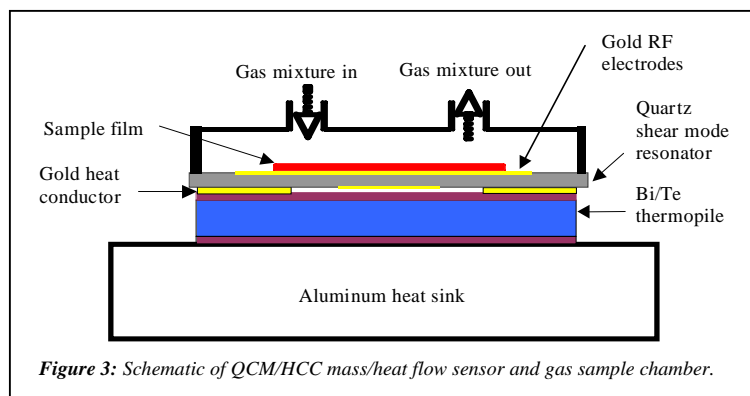
polymers are also popular for biomedical applications. Polylactides and copolymers of lactic acid with other monomers, such as glycolic acid, are leading candidates for degradable drug delivery devices, tissue scaffolds, and other biomedical applications (21). This project focuses on the class of bio-based aliphatic polyesters which included polylactides, polyhydroxyalkanoates and combinations or modifications of bio-based polyesters. A barrier to effective commercialization of bio-based polyesters for the applications described above is inferior moisture barrier properties compared to synthetic polymers – properties that are currently poorly understood in this class of materials. Fundamental knowledge of moisture transport in bio-based polyesters 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 (e.g. water bottles shown in Figure 1), industrial composting and degradation kinetics, and life cycle assessment of bio-based polyester products.

Aliphatic bio-based polyesters such as polylactide (PLA) are *moderately hydrophobic* but not as hydrophobic as traditional synthetic polymers such as PET. The research described in this paper indicates that the presence of hydrophilic end groups in PLA plays a key role in determining moisture sorption, transport properties and degradation performance.

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; moisture transport in polylactides (PLA) and blends or copolymers of PLA (especially with glycolic acid) have received the most attention for biomedical applications. However, there is some disagreement about the dominant mechanisms of moisture transport. Sharp, et al. (2001) propose that the equilibration time of glassy polymers such as PLA lead to non-Fickian diffusion effects, which is inferred by thickness-dependent diffusion coefficients (12). Siparsky, et al. (1997) propose 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 (15). 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 (2, 3). Shogren (1997) also reported that PLA permeability to water decreases with increasing temperature although permeability to both CO₂ and O₂ increased with temperature (14). 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 (15, 22).

The literature is also inconsistent about how crystallinity affects moisture sorption and moisture transport. Several studies suggest that the mass of water that absorbs into

PLA at equilibrium is essentially independent of crystallinity (15) whereas it is expected to scale with the percent crystallinity as was observed by some studies (14, 22). Conversely, crystallinity does affect water transport in PHB and PEG with lower



solubility and lower diffusion coefficients at higher crystalline fraction (8, 9). Based on this literature and our preliminary data, we hypothesize that differences in observations of sorption in bio-polyesters is largely controlled by the molecular architecture and particularly by differences in hydrophobicity of the main chain and chain ends of the polymer. 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 (21). A systematic study (as proposed here) of the influence of end groups on moisture sorption in bio-based polyesters is needed and will help to explain why the published data is 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 shows that hydrolytic degradation must reduce molecular weight of PLA to 15,000-40,000 before biodegradation can take over (1, 6). Hydrolytic degradation of PLA can either occur randomly within the polymer or from the ends (unzipping), and the ratio of these reactions is pH dependent. (5, 11, 13, 19). In semi-crystalline PLA, degradation can lead to bimodal molecular weight distributions through hydrolytic cleavage of the polymer tie chains spanning between crystallites (20). The kinetic studies on PLA have shown the reaction to be pseudo-first order with an autocatalytic effect due to production of acidic end groups by the hydrolytic reaction (11, 19). 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 (7, 19, 21).

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. There are several open issues raised by research described in this paper, 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.

2. Experimental

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 upon heat treatment. The 4060 grade of PLA is synthesized from a mixture of lactic acid stereoisomers and does not crystallize. The stereocomplex samples are a 50/50 blend of

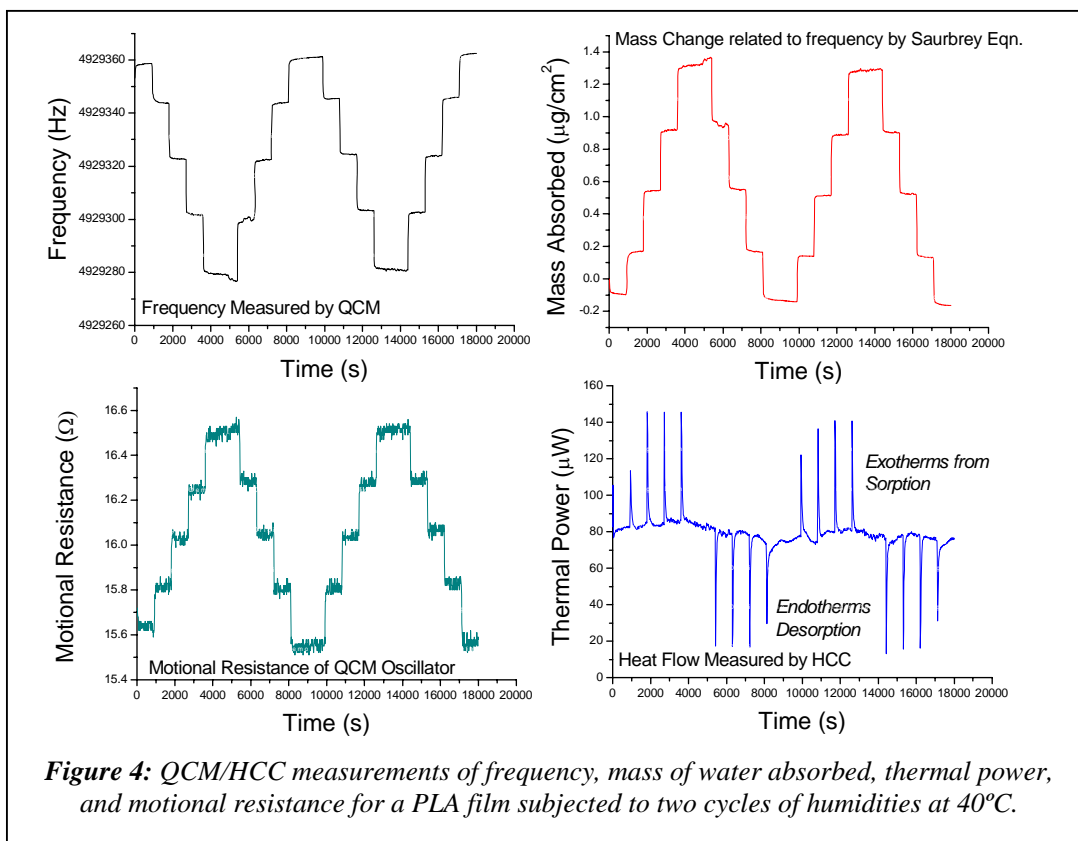


Figure 4: QCM/HCC measurements of frequency, mass of water absorbed, thermal power, and motional resistance for a PLA film subjected to two cycles of humidities at 40°C.

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.

QCM/HCC: 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 (Figure 3). Using QCM/HCC, Smith and coworkers(17, 18) have been able to measure simultaneously the change in mass per unit area (to $\pm 2 \text{ ng/cm}^2$) and the resulting heat flows (to $\pm 1 \text{ } \mu\text{W}$) 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 $\Delta_{\text{sorp}}H$ of the vapor in the polymer at a specific vapor activity. The combination of heat and mass measurements enables both $\Delta_{\text{sorp}}H$ and $\Delta_{\text{sorp}}G$ to be measured, so $\Delta_{\text{sorp}}S$ can also be determined. Thus, a single set of experiments at a constant temperature is sufficient to determine all three thermodynamic properties characterizing the polymer/solvent interaction. Smith and coworkers have used QCM/HCC to study absorption and adsorption into a number of thin-film systems. The enthalpies, Gibbs energies, and entropies of sorption of water and viscoelastic damping were measured for 10 volatile organic solvents in aliphatic polyurethane films of thickness $0.8 \mu\text{m}$ to $8 \mu\text{m}$ (16). The measured enthalpies of sorption are all comparable to condensation enthalpies of the vapor (to $\pm 30\%$). Sorption isotherms and sorption enthalpies were measured for water in a thin lysozyme film ($1 \mu\text{m}$ thick, 0.3 mg in mass)(17). As the protein film dries out, the enthalpy of sorption increases, because the water being removed is bound to the protein rather than to the surrounding aqueous phase.

Recently Masscal Co. developed a commercial version of QCM/HCC, the Masscal G1, which was used for the results in this paper 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 two days at ambient conditions, then dried at 60°C and 80°C for at least one day each in an inert nitrogen atmosphere. Amorphous films were prepared by heating to above the melting temperature for 2 hours under dry nitrogen and cooling rapidly to room temperature.

DVS: Dynamic Vapor Sorption is a gravimetric sorption method which combines a highly-sensitive (0.1 µg) electrobalance with a controlled-humidity gas handling system in controlled-temperature environment. DVS is an ideal system for measuring sorption isotherms (mass uptake versus 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 experiment located in Gary Reineccius' lab in the Food Science and Nutrition Department at U. Minnesota.

PLA films were prepared for DVS by melt pressing with a heated hydraulic press at 200°C (for 4032 & 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 about 5 minutes at about 100 pounds of force, the sample was removed and cooled quickly by pouring water over the outside of the aluminum foil surrounding the sample.

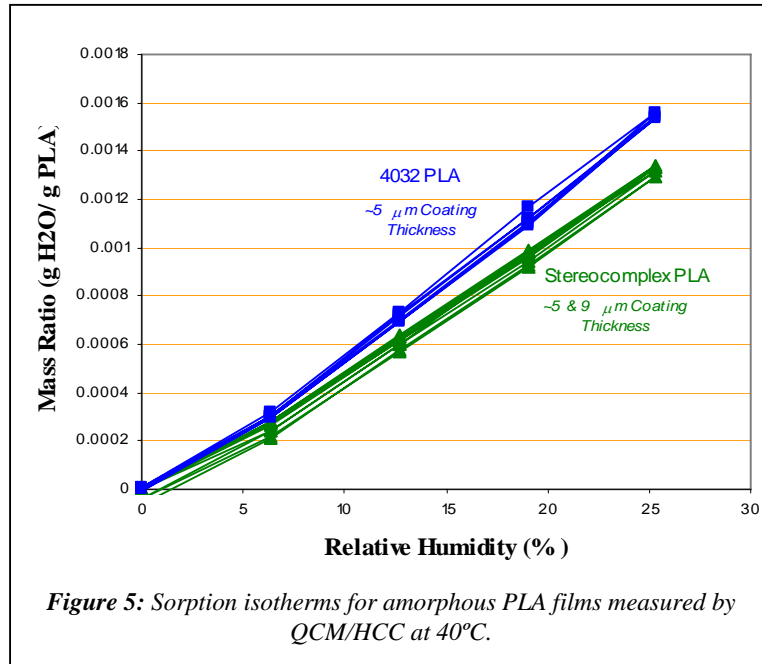
Crystallinity Measurements: Crystallinity of PLA films was determined using DSC and XRD. Wide angle X-ray diffraction (XRD) was performed on both QCM/HCC films and DVS films using a Bruker-AXS Rapid XRD Microdiffractometer in the Characterization Facility at the University of Minnesota. Sharp crystalline and a broad amorphous peak were identified in the plots of intensity versus 2-theta and the areas under crystalline and amorphous peaks were calculated using the Jade software package to obtain a qualitative percent crystallinity.

Differential Scanning Calorimetry (DSC) was performed on melt-pressed films using a Perkin Elmer TGA 7 in Ted Labuza's lab in the Food Science and Nutrition Department at the U. of Minnesota and a TA Instruments Q1000 in the Polymer Characterization Lab in the Chemical Engineering and Materials Science Department at U. 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).

3. Results

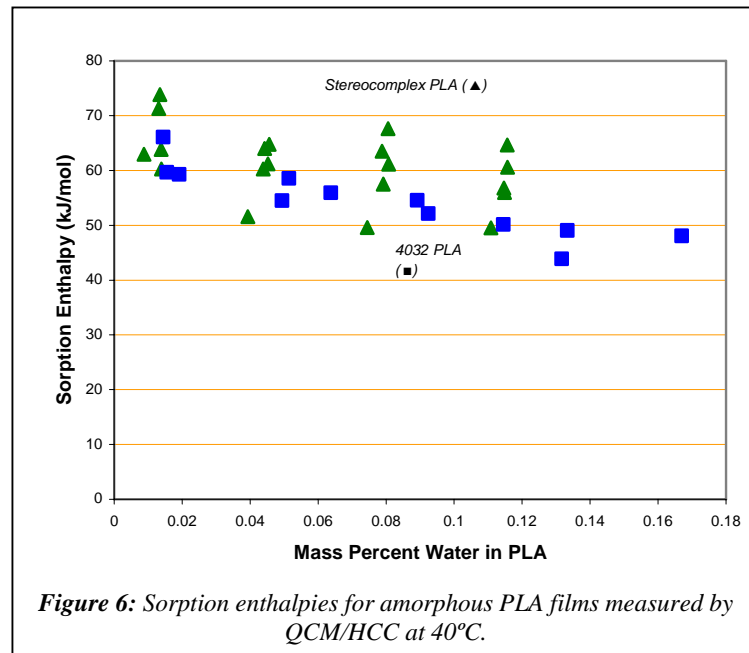
QCM/HCC: Figures 4-6 display data measured by QCM/HCC for moisture sorption in PLA films. The raw QCM/HCC data in Figure 4 shows that sorption of water closely follows changes of water partial pressure (or relative humidity) within the sample chamber through two cycles of humidity changes in steps from zero to about 25% at 40°C. The frequency of the QCM decreases as water absorbs in to 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 shown here 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 (Figure 5). Crystalline and amorphous films have been prepared and tested with little difference between their sorption properties. Figure 5 displays a comparison between moisture sorption into amorphous PLA films from 4032 PLA and stereocomplex PLA. The sorption isotherms are nearly linear, and are fit well by the Flory-Huggins theory with a high interaction parameter. The stereocomplex PLA sample 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.

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 displays measured values of sorption enthalpy versus 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 (~44 kJ/mol); such high sorption enthalpies have been related to formation of water clusters when water absorbs into a hydrophobic polymer (15, 22).

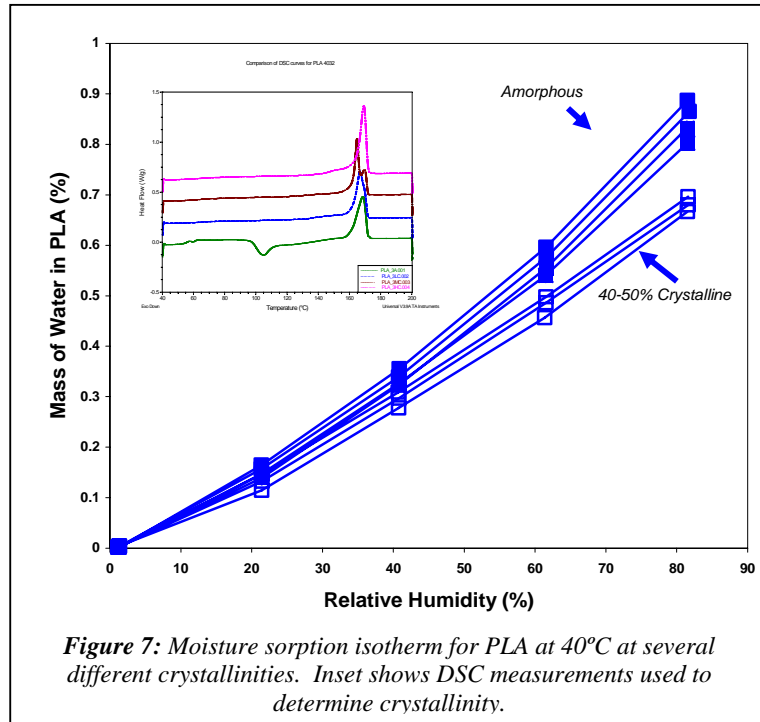


Figure 7: Moisture sorption isotherm for PLA at 40°C at several different crystallinities. Inset shows DSC measurements used to determine crystallinity.

DVS: Sorption isotherms have also been measured using DVS (Figures 7-9). The sorption isotherms for amorphous and crystalline PLA displayed in Figures 7 and 8 from DVS are comparable to those from QCM/HCC. The sorption isotherms for both 4032 PLA (Figure 7) and stereocomplexed PLA (Figure 8) 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 thought that water cannot enter into the crystalline domains (and it has been established that crystallinity does not change during sorption/desorption).

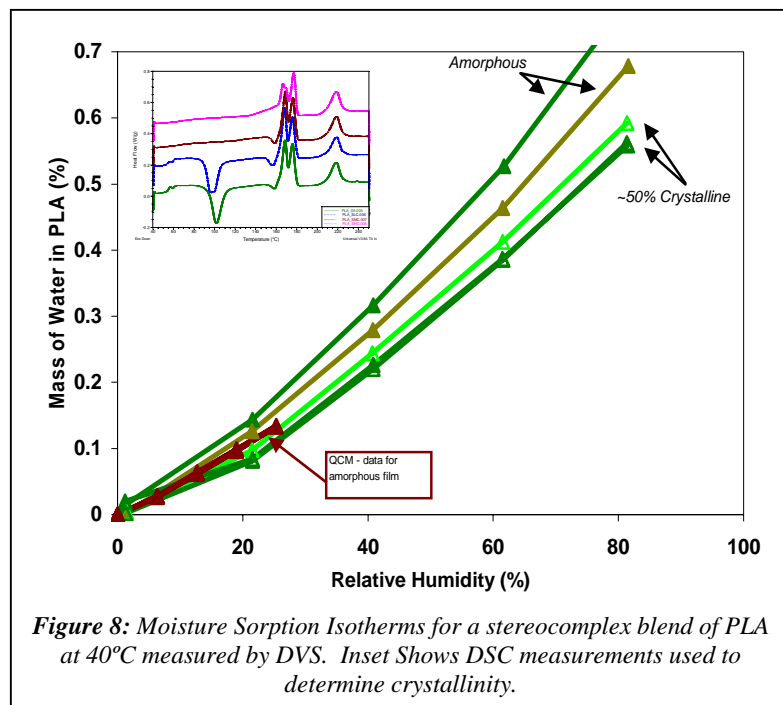


Figure 8: Moisture Sorption Isotherms for a stereocomplex blend of PLA at 40°C measured by DVS. Inset Shows DSC measurements used to determine crystallinity.

Based on these observations, we hypothesize that moisture sorption is controlled by hydrophilic end groups (and as indicated in the cartoon of Figure 1) in PLA. Future experiments will investigate the effect of molecular weight and chemical modification of the end groups on sorption in PLA.

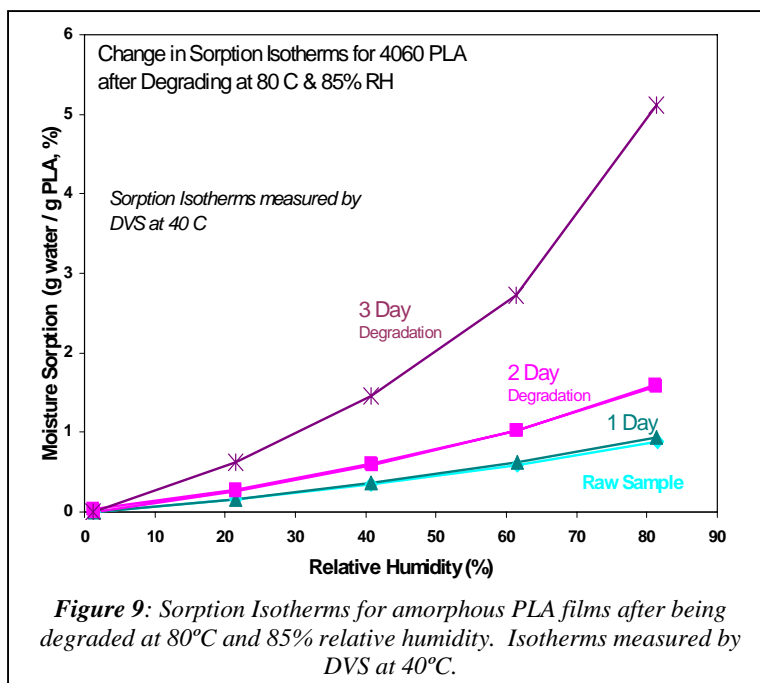
Degradation (and molecular weight) is known to have a significant effect on moisture sorption and transport in PLA. Measurements of sorption isotherms on partially degraded PLA films (of amorphous 4060 PLA) show a rapid increase in sorption with degradation. Films were exposed to high humidity (85%) and high temperature (80°C) 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.

4. 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 DOE and USDA is to increase the fraction of chemicals and materials produced from biomass from the 2001 level of 5% to 12% in 2010 and 25% in 2020 (10). To achieve 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 paper suggest that molecular structures of bio-based polymers affect moisture transport and barrier properties in a way not discussed previously.

Bio-based polymers have potential for a number of environmental benefits relative to their petroleum-based competitors. A major benefit is reduced use of solvents during synthesis and processing, leading to fewer volatile organic compounds and less emissions of toxic and greenhouse gases. The raw materials for bio-based polymers are less toxic than

petroleum-based feedstocks. Most bio-based polyesters are degradable – first by hydrolytic degradation and later by biological degradation; so with proper waste management (i.e. industrial composting), it will be possible to significantly reduce the amount of polymeric material entering into municipal solid waste (MSW) and landfills. Packing material is



one of the leading sources of plastics in MSW and bio-based polyesters have properties comparable to petroleum-based plastics commonly used for packaging. Moisture management is a key factor in degradability. The bio-based products revolution needs fundamental research aimed at producing products with properties competitive with traditional materials while having the benefits of bio-based products – i.e. production from renewable resources and degradable.

5. Acknowledgments

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