Heat and Humidity Performance of Injection Molded PLA for Durable Applications

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ABSTRACT: The durability of a commercially available injection molding grade polylactide (PLA) was assessed by exposure to conditions of elevated temperature and humidity over a period of several weeks. Moisture absorption, molecular weight, and mechanical performance were monitored over time and as a function of crystallinity level. At 50°C and 90% relative humidity, both amorphous and crystalline samples of PLA showed significant moisture absorption, allowing hydrolysis to occur. The study showed that while crystalline content had an effect on the initial moisture absorption behavior, the overall longer term effects on degradation were surprisingly minor. A cumulative damage model was used to relate the overall degradation due to moisture uptake and hydrolysis to long-term durability in environments typical of automotive interiors. The study showed that the injection molding grade PLA resins that are currently commercially available are not suitable for use in applications that require long-term durability in environments subject to elevated temperature and humidity. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1380–1389, 2010

Key words: durability; conditioning; injection molding; crystallization; biopolymers

INTRODUCTION

Interest in developing polymers from renewable resources has grown dramatically due to increased environmental sensitivity to continued depletion and rising costs of petroleum. Applications of these types of bioderived polymers can range from biomedical implants to packaging to durable consumer goods. Of particular interest is poly(lactic acid) or polylactide (PLA), a thermoplastic polyester that can be processed into many forms from fibers to films to molded components. PLA can be derived completely from a renewable feedstock and has several end-of-life options including both chemical and mechanical recycling, as well as compostability. Furthermore, increased large-scale production of the resin has made it more attractive to use PLA as a commodity thermoplastic, replacing petroleum-based plastics in many disposable and packaging applications. These consumable applications take advantage of the relatively fast degradation in an industrial compositing environment. However, for durable applications, the performance behavior must be maintained over the lifetime of the product.

Degradation of PLA occurs with exposure to heat and moisture. The primary mode of degradation is through hydrolysis of the ester bond,[1–6] shown in Figure 1. The degradation rate depends highly on several factors including microstructure, part geometry and thickness, moisture and heat exposure, the presence of microbes, and so on. Much research has been performed on PLA durability and degradation. Numerous research groups have documented the hydrolysis behavior of PLA films typically used for packaging applications either through immersion in phosphate buffered solutions (PBS)[7–16] or as a function of temperature and humidity conditioning.[3,17–19] Because of the relatively low performance requirements for packaging and other disposables, the studies mainly focused on molecular weight and the mechanical integrity of the films. In addition to degradation and hydrolysis, mass loss was also monitored for studies in which dissolution of oligomeric hydrolysis products occurred.

Use of PLA for durable applications requires the assessment of long-term performance. Whereas a fast degradation rate is desirable for disposable applications, long-term durability (i.e., slow degradation rate) is required for durable goods. Although numerous researchers have studied compostability behavior and how to increase the degradation rate of disposable items,[12,20–23] the bulk of the literature on the durable, injection molded PLA is focused on the performance of surgical implants. In these studies, PLAs with high optical purities and high crystallinity levels were conditioned *in vitro,* in

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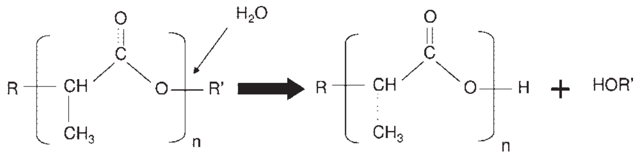

Figure 1 Hydrolysis reaction of PLA.

either phosphate buffered or enzymatic solutions, as well as *in vivo*.[8,13,24–27] Several studies were also performed on the hydrolytic degradation of PLA micro and nanospheres.[14,28,29] These environments are significantly different than that which would apply to the long-term performance for durable applications such as automotive interiors.

Very limited research and applications exist for rigid PLA in durable goods. NEC Corporation and Unitika introduced a kenaf fiber-reinforced PLA composite (Terramac) for mobile phone components in 2006,[30] Samsung has recently announced the use of PLA blends in their own branded mobile phone components as well as by Sony in Walkman parts, and Fujitsu has introduced a laptop computer with a PLA-based casing.[31] Apart from these, the majority of existing commercial applications continue to be for clothing and linens, packaging, and disposable products. The main challenge of utilizing PLA for injection molded, durable applications stems from the need to mediate between improved durability while maintaining compostability at the end of life.

Furthermore, the properties of PLA can vary greatly based on the stereochemical makeup, whether one is using homopolymers, copolymers, or blends. As a semicrystalline polymer, PLA's crystalline content not only depends on the stereochemistry but also on the presence of nucleating agents, additives, solvents, shear, and cooling rate, among other factors.[2,32–47] Semicrystalline forms, which generally possess higher thermal stability, stiffness, and durability, are suitable for injection molding or rigid applications, while amorphous forms are ideal for film and packaging applications.[1,15,25,42,47]

For use in automotive applications, not only does the material need to meet mechanical performance specifications in a newly molded part, but it must maintain its performance throughout the lifetime of the vehicle (>10 years). In an earlier publication, the authors investigated the processability of a commercial injection molding grade of PLA through its crystallization behavior.[45] The work also described the effect of crystallinity on the properties and behavior of PLA. The current study addresses the durability of the same commercially available materials exposed to heat and humidity over time. This is the first time data have been reported for the durability behavior of a commercial grade of injection molded PLA in an environment of elevated heat and humidity. Because of the differences in their microstructural and mechanical performance, both amorphous and crystalline samples of injection molded test specimens were exposed to heat and humidity for durations of up to 12 weeks. Crystallinity, molecular weight, moisture absorption, and flexural properties were monitored as a function of conditioning time through differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and quasi-static mechanical testing. The molecular weight degradation kinetics, as well as a correlation between mechanical performance and molecular weight, were also determined.

EXPERIMENTAL

Materials

Commercially available, injection molding grade poly(lactic acid) (PLA, NatureWorks® 3001D) was obtained from NatureWorks LLC (Minnetonka, MN). The PLA had high optical purity, containing mainly L-lactic acid, with 1.4% ± 0.2% D-lactic acid.

Sample preparation

PLA pellets were dried at 60°C for 3 days to remove any moisture present before injection molding. The pellets were injection molded into flexural bars per ASTM D790 on an 80-ton BOY (BOY 80M) injection molding machine. The barrel temperature ranged from ~ 200 to 205°C, with a nozzle temperature of 205°C.

To evaluate the effect of crystallinity on the durability of the bioresin samples, specimens injection molded into a room temperature mold were annealed in an oven at 80°C for 60 min. The annealing process produced samples with spatially uniform crystallinity, as confirmed through DSC analysis.

Conditioning

Both as-molded and annealed samples were placed in a Test Equity 1000H Series temperature/humidity chamber. All samples were conditioned at a temperature of 50°C and 90% relative humidity (RH). The samples were evaluated initially before conditioning and again after 1, 4, 8, and, in some cases, 12 weeks of continuous conditioning. Save for moisture absorption measurements, all other characterization testing was performed on samples dried at 60°C for 3 days. Drying is an important step before mechanical property characterization to separate out the plasticizing effects of excess moisture in the molded samples.

Characterization

Moisture absorption

Moisture absorption of the PLA samples was calculated after each conditioning period. The specimens were each weighed before conditioning (Initial Part Weight) and then weighed after conditioning (Final Part Weight). Moisture uptake was calculated using the following equation:

$$\% \text{ Moisture} = \frac{\text{Final Part Weight} - \text{Initial Part Weight}}{\text{Initial Part Weight}} \times 100\%. \quad (1)$$

Moisture absorption data were reported as an average of five specimens.

Gel permeation chromatography

Molecular weight distributions (MWD) of PLA before and after processing and conditioning were measured using GPC (Waters 2695 Separations Module, Styragel guard, Styragel HR4E, and Styragel HR5 columns, with a Waters 2410 RI detector). For comparing data in graphical form, molecular weight data are also reported as weight averaged molecular weights (M_w). Monodisperse polystyrene (PS) standards (Polymer Laboratories) were used for the calibration with tetrahydrofuran (THF, Fisher Scientific) as the eluent at 30°C and a flow rate of 1 mL/min. Because optically pure PLA homopolymers are insoluble in THF, samples were first dissolved in a small amount of chloroform (Fisher Scientific) and then diluted with THF. The refractive index increment (dn/dc) and solvent quality parameters for the mixed solvent were assumed to be close to that of pure THF because of the small ratio of chloroform to THF. Molecular weights of PLA specimens were determined through universal calibration using the Mark-Houwink relationship:

$$[\eta] = KM^a, \quad (2)$$

where [η] is the intrinsic viscosity, M is the molecular weight, and K and a are the Mark-Houwink coefficients. For PS in THF, $K_{\mathrm{PS}} = \times 10^{-4} > 1.4 \times 10^{-4}$ dL/g and $a_{\mathrm{PS}} = 0.7$, while $K_{\mathrm{PLA}} = \times 10^{-4}\ 1.74 \times 10^{-4}$ dL/g and $a_{\mathrm{PLA}} = 0.736$ for PLA in THF. Mark-Houwink coefficients for PS and PLA, in THF at 30°C, were obtained from the literature.[1,48] The percent uncertainty in the GPC data was found to be ±1% based on multiple calibrations and measurements on specimens of known molecular weight.

Thermal properties/crystallinity

The crystallization behavior of PLA subjected to durability exposure was examined through DSC. Degree of crystallinity (X_c), melt temperature (T_m), cold crystallization temperature (T_c), and glass transition temperature (T_g) were determined during the initial heating scan for the PLA materials before and after annealing, and again after heat and humidity conditioning, using a Mettler Toledo DSC30 with TC15 TA Controller. Unless otherwise noted, DSC samples ranged from 4 to 10 mg in mass and were taken from cross sections at the center of injection molded flexural bars. The specimens were placed in aluminum pans and run under a flow of nitrogen. The following equation was used to calculate the degree of crystallinity within the samples:

$$\% \text{ Crystallinity} = X_c = 100\% \times \frac{\Delta H_m - \Delta H_c}{\Delta H_m^{\infty}}, \quad (3)$$

where ΔH_m is the measured endothermic enthalpy of melting and ΔH_c is the exothermic enthalpy that is absorbed by the crystals formed during the DSC heating scan. The theoretical melting enthalpy of 100% crystalline PLA was taken to be $\Delta H_m^{\infty} = 93$ J/g.[2] The DSC was calibrated periodically with indium standards.

Mechanical properties

Injection molded flexural specimens (nominal dimensions 3.2 mm x 12.6 mm x 125 mm) underwent quasi-static three-point bend testing according to ASTM D790 at a crosshead speed of 1 mm/min at room temperature on an Instron Model 3366. Results from flexural testing were reported as averages from five specimens per sample.

RESULTS AND DISCUSSION

Two sets of PLA samples were prepared for conditioning and durability testing. The samples denoted as "amorphous" had a nominal crystallinity of <10%. To obtain the "crystalline" samples, as-molded specimens were annealed for 60 min at 80°C, and had a final crystallinity level of ~ 45%. The initial properties of both amorphous and crystalline samples, including crystallization behavior and content, flexural modulus, molecular weight, and initial specimen weight, were evaluated before conditioning. Crystalline and amorphous samples were conditioned together in a humidity chamber that was maintained at 50°C and 90% RH. These conditions were chosen to be aggressive enough to accelerate the degradation that would occur in an application such as an automotive interior, yet at a temperature below the glass transition temperature of PLA, which was measured for the as-received PLA to be 63°C. The temperature was maintained below the glass transition temperature to limit secondary crystallization in the amorphous samples. A cyclic test alternating between elevated and depressed heat and humidity conditions would better simulate the actual environment for the injection molded materials, but is less aggressive and would require longer test duration.

Much work has been done on relating elevated temperature and humidity conditioning to in-vehicle, in-field exposure for various polymeric materials that are susceptible to hydrolysis.[5,49,50] Many of these use cumulative damage models to accelerate the testing at constant elevated temperature and humidity levels for applications requiring more than 10 years durability. Based on the data from Bauer and coworkers on petroleum-based polymers, 1 week exposure at 50°C and 90% RH is approximately equivalent to 2 months of exposure in Florida for an automotive interior application.[51] Although accelerated testing of PLA hydrolysis is not yet available in the literature, a similar method can be applied by knowledge of the moisture absorption and hydrolysis kinetics during durability conditioning.

Crystallization, flexural, and moisture absorption properties, as well as molecular weight, were monitored at 1, 4, and 8 week intervals to follow the long-term durability performance. At 12 weeks, the specimens lost mechanical integrity, such that only molecular weight measurements were performed.

Moisture absorption

Both crystalline and amorphous PLA samples were observed to absorb moisture during the course of the heat and humidity conditioning. Figure 2 shows that the moisture absorption as a function of conditioning time has a shape typical of Fickian diffusion. Comparing the two sample sets shows that because the crystalline regions act as barriers to the diffusion of moisture, the amorphous material initially gained significantly more weight due to water uptake than did the crystalline PLA samples. However, after 4 weeks, the moisture taken up by the amorphous sample fell slightly and subsequently decreased after 8 weeks. On the other hand, for the crystalline sample, an initially rapid increase in moisture content was observed, followed by a much slower uptake. Although initial moisture absorption was less for the crystalline samples, the amorphous and crystalline data began to converge at 8 weeks exposure time. This is due to the crystallization of some of the amorphous regions of the samples, which was enhanced both by the plasticization effect and the decreasing molecular weight in the conditioned samples. Although this phenomenon was observed for both amorphous and crystalline samples, the effect was much more pronounced for the amorphous samples. Detailed crystallization data will be discussed in a forthcoming section.

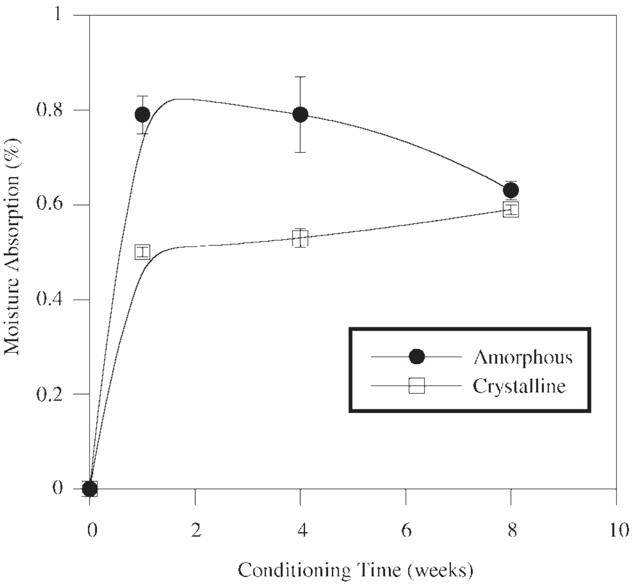

Figure 2 Moisture absorption as a function of conditioning time for amorphous and crystalline PLA (lines added to guide the eye).

Molecular weight

The molecular weight was monitored as a function of conditioning time to assess the amount of degradation of the material through hydrolysis and chain scission. The molecular weight distribution for the unconditioned PLA is a symmetrical, single modal distribution with a polydispersity index (PDI = M_w/M_n) of 1.66 [see Fig. 3(a), 0 week sample]. Figure 3(a) shows the molecular weight distribution of the amorphous PLA series as a function of conditioning time, from initial time (0 weeks) to 12 weeks. After 1 week, the molecular weight distribution remained largely unchanged. By week 8, however, a significant decrease in molecular weight had occurred, as shown by a shift and a broadening of the MWD. After 12 weeks, enough chain scission had occurred that the MWD shows a bimodal distribution as well as a significant shift in peak molecular weight. A similar progression is shown in Figure 3(b) for the molecular weight distributions of the crystalline PLA series. For the crystalline samples, the rate of degradation was observed to occur more slowly. By week 12, a slight shoulder appears. Both amorphous and crystalline samples show the development of bimodal molecular weight distributions at long conditioning times. In the amorphous sample, the peak molecular weights in the bimodal distribution are separated by a factor of two. This implies nonrandom, mid-chain scission, which would

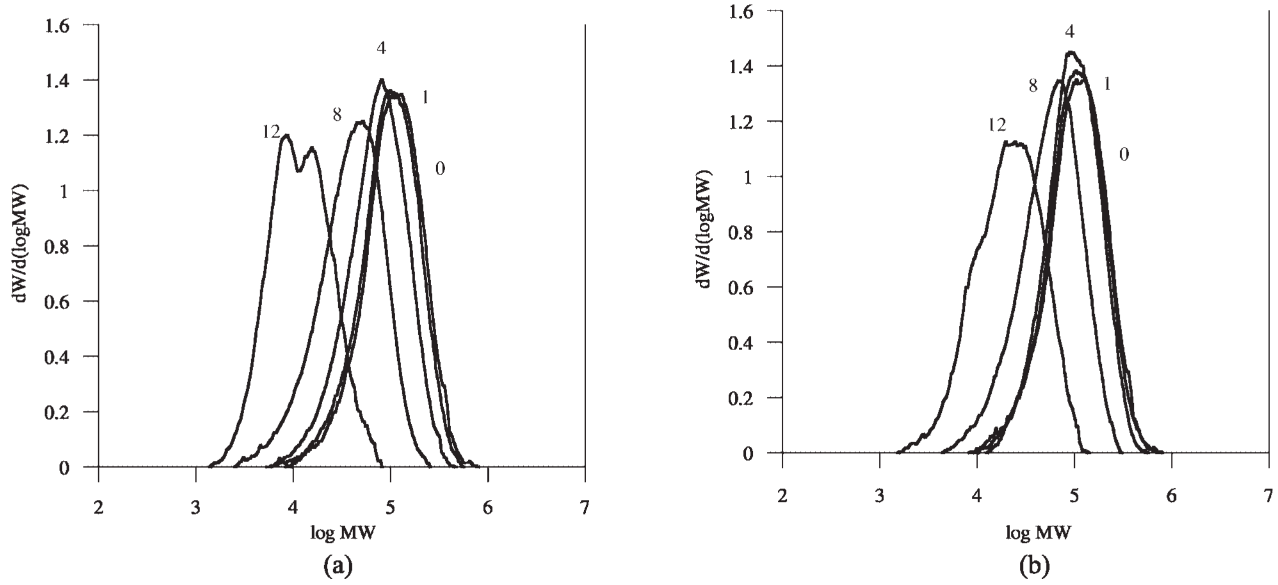

Figure 3 Molecular weight distribution of injection molded amorphous (a) and crystalline (b) PLA samples: as-molded, conditioned for 1 week, conditioned for 4 weeks, conditioned for 8 weeks, and conditioned for 12 weeks. Denoted as 0, 1, 4, 8, and 12, respectively.

produce a significant population of chains at half the molecular weight. This is in contrast to the results of De Jong et al., who showed that chain end scission was preferred at low pH.[7] Because the specimens were not immersed in phosphate buffered solutions of constant pH, the PLA was exposed to an increasingly acidic environment due to the formation of carboxylic acid groups during hydrolysis. A similar behavior was observed for the crystalline sample, although because the degradation rate was slower, only a shoulder at lower molecular weight was observed by week 12.

Weight averaged molecular weights were calculated from the MWDs and are shown as a function of conditioning time in Figure 4. A linear regression for the amorphous data shows that the rate of degradation is ~ 6600 g mol^{-1}/week. On the other hand, the crystalline PLA has a slightly slower degradation rate at ~ 5900 g mol^{-1}/week. The slight difference in the degradation rate can be attributed to the crystallites acting as barriers to the diffusion of moisture within the specimens. These degradation rates are significantly slower than those found by Ho et al., who reported rates between 28,000 and 63,000 g mol^{-1}/week for different grades of PLA films.[18] While small differences in rate may be due to material grade and stereochemical make up, the significant contributions are due to crystalline structure and geometry. Degradation rates reported by Ho and coworkers are for amorphous samples of PLA films (both mono and trilayer). On the other hand, the compression molded disks used by Lyu et al. are similar in geometry to the current study, but they performed the conditioning in buffered testing solutions of various pH levels.[52] Accordingly, their reported degradation rate was lower than those reported here, at ~ 5000 g mol^{-1}/week, due to both the increased thickness and a constant neutral pH level.

The hydrolysis kinetics of PLA are autocatalytic or self-catalytic[6,53] due to the participation of the carboxylic acid end group in the reaction. Looking at the hydrolysis reaction in Figure 1, a general reaction rate can be written as the following:

$$\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{H}_2\text{O}][\text{ester}], \qquad (4)$$

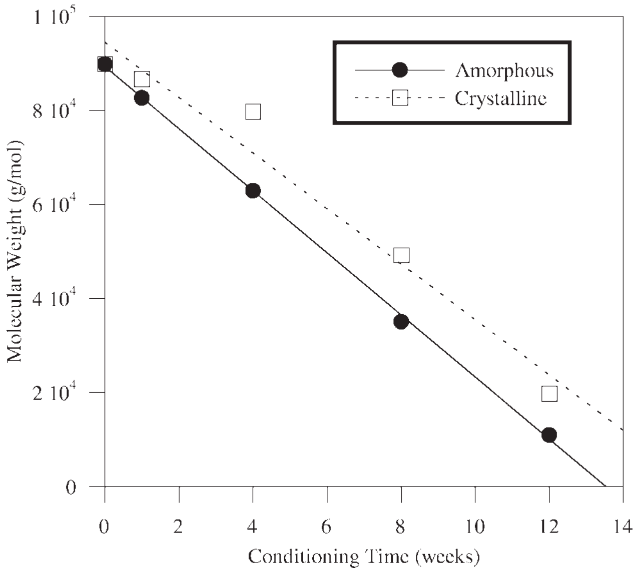

Figure 4 Dependence of molecular weight on conditioning time for amorphous and crystalline PLA.

where [COOH] is the concentration of carboxylic acid end groups, $[H_2O]$ is the concentration of water, and [ester] is the concentration of ester linkages in the sample. At low extents of degradation, the ester concentration can be approximated as a constant. Because of the thickness of the samples, the diffusion and hydrolysis processes cannot be separated but rather occur simultaneously. At short times, the degradation is limited by the diffusion of moisture into the injection molded samples, limiting much of the initial hydrolysis to the skin surface of the specimens. An examination of the moisture absorption data (see Fig. 2) shows that at times longer than approximately two 2 weeks, diffusion has progressed enough such that the hydrolysis reaction is the degradation limiting step. Therefore, the water concentration cannot be taken as constant in eq. (4). Although the moisture absorption follows Fickian diffusion, a much more simplified model can be developed for kinetics by dividing the moisture absorption into two regimes. In the first regime, for $t < 2$ weeks, the moisture uptake can be approximated to occur linearly with time, giving:

$$[H_2O] = Ct, \tag{5}$$

where C is a constant describing the rate of moisture uptake. Substituting eq. (5) into eq. (4), and taking the ester concentration as a constant, yields the following:

$$\frac{d[\mathrm{COOH}]}{dt} = k'[\mathrm{COOH}]t. \tag{6}$$

The rate constant now includes the ester concentration and moisture uptake rate, $k'=kC[\mathrm{ester}]$. The concentration in the early time regime is thus given by:

$$[\mathrm{COOH}] = [\mathrm{COOH}]_0 \exp\left(\frac{k't^2}{2}\right) \tag{7}$$

Because the carboxylic acid concentration is proportional to the number of chain ends, which goes as the inverse of the number-averaged molecular weight, eq. (7) can be rewritten as:

$$M_n = M_{n,0} \exp\left(-\frac{k't^2}{2}\right). \tag{8}$$

In the second regime at longer conditioning times, for $t > 2$ weeks, the water concentration can be approximated as a constant. The hydrolysis rate can then be written as:

$$\frac{d[\mathrm{COOH}]}{dt} = k''[\mathrm{COOH}], \tag{9}$$

where $k''=k[H_2O]_\infty[\mathrm{ester}]_\infty$. Equation (9) now simplifies into the pseudo first-order reaction:

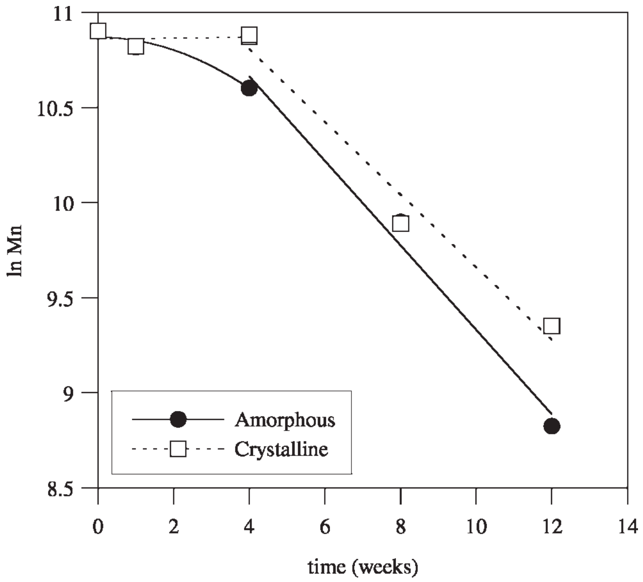

Figure 5 Natural log of the molecular weight as a function of conditioning time.

$$[COOH] = [COOH]_0 \exp(k''t) \tag{10}$$

or

$$M_n = M_{n.0} \exp(-k''t). \tag{11}$$

A plot of $\ln(M_n)$ as a function of conditioning time is shown in Figure 5. When the conditioning time is less than 2 weeks, $\ln(M_n)$ goes as the square of time. At times longer than ~ 2 weeks, $\ln(M_n)$ becomes linear with time, with the slope of the line equal to the rate constant k''. A comparison shows that the rate constant for the amorphous sample is slightly faster than the crystalline sample, with $k''_{\mathrm{amorphous}} = 0.22$ and $k''_{\mathrm{crystalline}} = 0.19$. Because the crystallites in the semicrystalline sample act as barriers to the diffusion of water into the samples, and because hydrolysis occurs in the amorphous regions, the overall degradation of the higher crystallinity samples is shown to be slower.

Crystallization behavior

The crystallinity levels of the PLA materials at various conditioning times were evaluated by using dynamic scanning calorimetry (DSC) measurements. Samples were taken from the entire cross section of the molded test specimens, such that the thermal and crystalline properties observed were those averaged across the thickness of the test bar. For conditioned materials, test specimens were thoroughly dried of residual moisture content before DSC measurements to determine crystalline content. DSC samples were heated at 10°C/min from −50°C to 220°C.

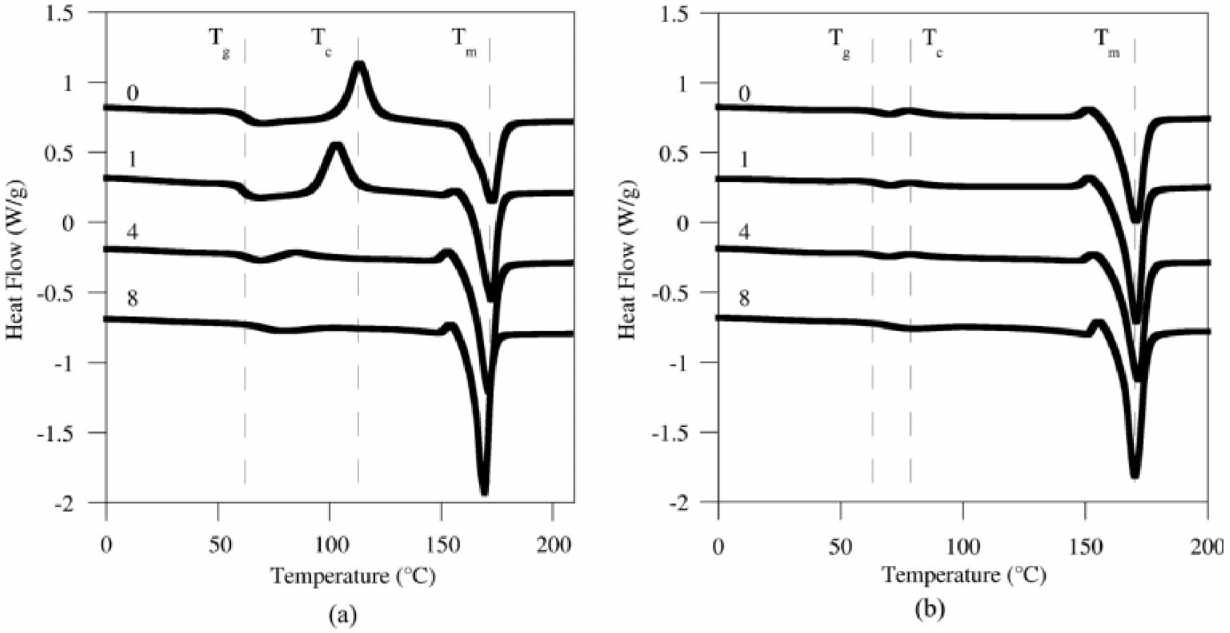

Figure 6 DSC heating scans of (a) injection molded amorphous PLA specimens: as-molded, conditioned for 1 week, conditioned for 4 weeks, and conditioned for 8 weeks. Denoted as 0, 1, 4, and 8, respectively; (b) injection molded crystalline PLA specimens: molded and then annealed, conditioned for 1 week, conditioned for 4 weeks, and conditioned for 8 weeks. Denoted as 0, 1, 4, and 8, respectively.

The data from this initial heating ramp were used to determine the specimen crystallinity information.

For the as-molded, amorphous sample before conditioning, a cold crystallization exotherm was observed before the melting endotherm during the heating ramp [see for example 0 week curve in Fig. 6(a)]. The crystallization peak indicates that the PLA had not reached maximum crystallinity during the injection molding process. The peak of the crystallization exotherm was denoted as T_c, while the melting endotherm was denoted T_m. For the annealed, crystalline sample, on the other hand, only an extremely small cold crystallization peak was observed in some samples during the heating ramp [see Fig. 6(b)]. For both crystalline and amorphous samples, small steps denoting the glass transition temperature (T_g) could also be seen at approximately 65°C.

The crystalline content of the conditioned samples were monitored over time for both amorphous and crystalline samples. Figure 6(a) shows the DSC traces during the initial heating ramp for each of the conditioned amorphous specimens over 8 weeks of conditioning, while Figure 6(b) shows the same for the crystalline specimens. One can immediately see in Figure 6(a) that the crystalline content in the amorphous samples increases with conditioning time by the disappearance of the cold crystallization peak and the increased size of the melting endotherm. Quantitatively, the crystalline content increases from 10.8 to 51%. The growth in crystalline content is shown as a function of conditioning time in Figure 7. This has been observed by several researchers[6,10,11] and is due to the preferential hydrolysis of the amorphous material, the increased crystallization of the shorter chains, and the plasticization by moisture. These results imply increased chain moblility during conditioning. DSC measurements in this study were performed on dried

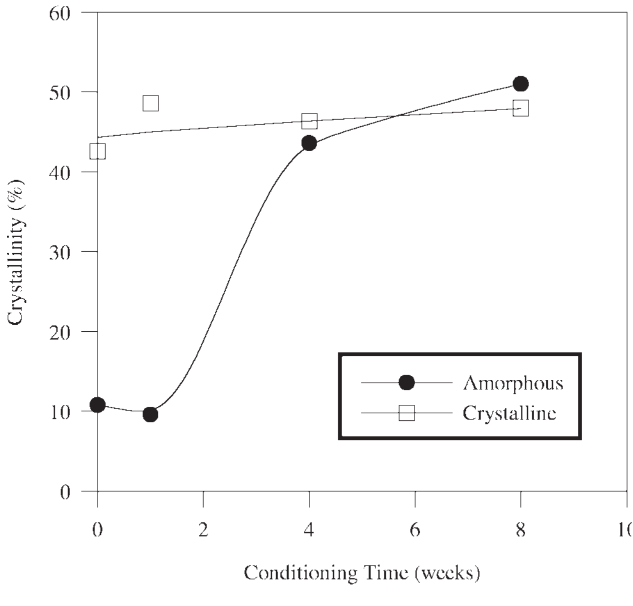

Figure 7 Crystallinity as a function of conditioning time for amorphous and crystalline PLA (lines added to guide the eye).

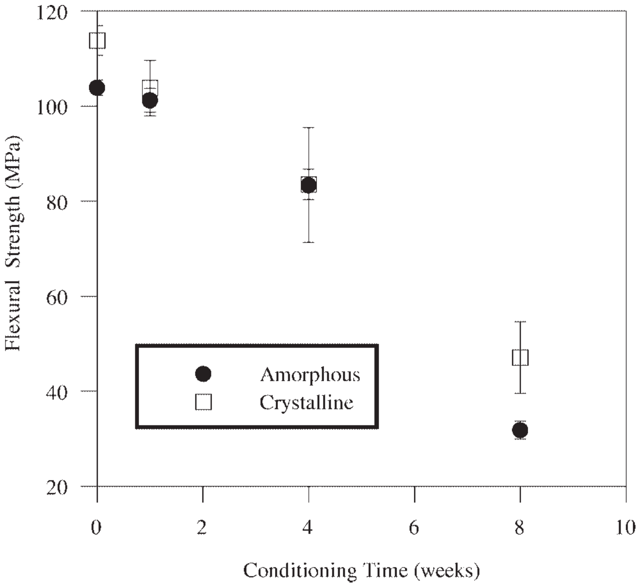

Figure 8 Dependence of flexural strength on conditioning time for amorphous and crystalline PLA.

specimens to accurately determine crystalline content, such that changes in T_g due to moisture were not measured. Some examples from literature, however, do show significant decreases in T_g during heat and humidity conditioning. Copinet et al. observed a negative shift in the glass transition by 19.4°C of a PLA film specimen exposed to 60°C and 100% RH for 4 weeks.[3] One must note that although a slight increase in T_g was observed in this study, these measurements were made on dried samples and do not reflect changes due to plasticization by moisture.

The crystalline sample series also shows a slight increase in crystalline content from 42.3 to 48%. This slight change can be attributed to the decrease in molecular weight that occurs during conditioning, which in turn induces further crystallization. Similar to the amorphous series, the dried crystalline samples also show a slight increase in T_g over time, indicating a decrease in amorphous content.

The significant change in the crystallinity of the initially amorphous samples had an appreciable effect on the moisture absorption and mechanical performance. The presence of moisture during the conditioning exposure enhanced the crystallization, allowing it to occur due to an apparent shift in glass transition temperature.

Mechanical performance

The effect of moisture and heat conditioning on mechanical performance was measured through flexural testing per ASTM D790. Figure 8 shows the flexural strength of the amorphous and crystalline samples as a function of conditioning time. Before conditioning, at time $t = 0$ weeks, the flexural strength of the crystalline sample was slightly higher than that of the amorphous sample, as expected. Over the duration of the conditioning, the flexural strength of both samples decreased significantly. This is due to the decrease in the molecular weight, a result of hydrolysis in the highly plasticized amorphous regions. As conditioning time of the PLA specimens increased, the samples became more brittle, accounting for much of the reduction in flexural strength. After only 8 weeks of conditioning, both amorphous and crystalline samples had lost significant amounts of strength. Samples conditioned for 12 weeks did not retain enough mechanical integrity to allow flexural testing.

Figure 9 shows the flexural strength of the PLA samples as a function of molecular weight. As the molecular weight decreases, we observe a correlated decrease in the mechanical performance. A linear regression of the data shows that flexural strength approaches zero at a weight averaged molecular weight of ~ 11,500 g/mol. This is in close agreement with the molecular weights of the 12-week conditioned samples. Furthermore, Lyu and coworkers relate the functional time of a PLA component to maintain mechanical properties to the entanglement molecular weight, which is ~ 8,000 to 10,000 g/mol.[52]

In order to be used for durable applications, a material must maintain a specified mechanical performance over the entire exposure or use time. The level of mechanical performance and the exposure or use time will be determined by the specific

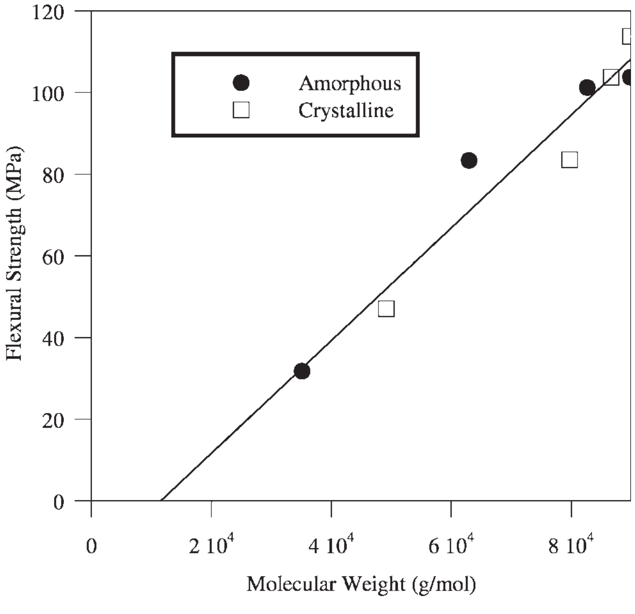

Figure 9 Flexural strength as a function of molecular weight for amorphous and crystalline PLA.

application requirements. In the case of automotive, applications are designed for at least 10-year or 100,000-mile durability. Furthermore, because south Florida has the highest hydrolytic dose within the continental U.S., it is often chosen as a worst case location for correlating the exposure data. Researchers at Ford Motor Company have extensively studied the correlation between Florida exposure and laboratory exposure tests for interior, exterior, and underhood automotive applications[5,49,50] for various materials including PC/ABS blends, polyamides, and polyesters, to name a few. Using their data, we estimate that 1 week of conditioning at 50°C and 90% RH would be roughly equivalent to 2 months exposure in Florida for an interior application.[51] A material used for an interior automotive application would thus need to maintain mechanical performance for at least 60 weeks at these exposure conditions to meet 10-year durability requirements.

CONCLUSIONS

This study shows for the first time the durability behavior of a commercially available, injection molded PLA exposed to high temperature and humidity. While previous research has shown the durability performance of PLA materials for packaging films and disposable applications exposed to heat and humidity, as well as the durability of highly crystalline PLA immersed in PBS, this study focused on the temperature and humidity durability performance of crystalline and amorphous forms of rigid injection molded PLA. The conditions for the durability exposure were chosen to simulate an environment found in automotive interiors.

As expected, the flexural strength and molecular weight of the PLA samples decreased over conditioning time. After 12 weeks at 50°C and 90% RH, the materials could no longer be tested mechanically. Somewhat surprisingly, however, was the lack of significant differences between the behavior of the initially amorphous and crystalline samples. Although flexural strength was slightly higher in the crystalline sample at time $t = 0$, there was not an appreciable difference in its ability to retain strength over extended conditioning times. In fact, some researchers have reported that there was no dependence of crystallinity on the degradation rate of PLA.[11] A significant growth in the crystalline content of the initially amorphous sample during the heat and humidity conditioning was also observed. The crystallization of the amorphous PLA was facilitated both by the plasticization effect of the moisture and the decrease in the molecular weight. Over the course of conditioning exposure, the amorphous samples equalized with the crystalline samples, with only slightly advanced molecular weight degradation.

While the initial performance of rigid, injection molded PLA approaches the requirements for select durable applications, its durability in humid and elevated temperature environments remains inadequate for automotive use. Even with the improved performance of crystalline over amorphous PLA, the properties of the conditioned samples were not maintained to an acceptable degree.

Several strategies exist to improve the durability performance of PLA-based materials. One method may be to combine PLA with another resin that is not susceptible to hydrolysis. Blending or alloying the resins could reduce the hydrolysis to an acceptable level, while encapsulating the PLA with a moisture impermeable resin could eliminate contact with water. A second approach is to eliminate the hydrolysis reaction itself. This could be achieved by the addition of scavengers or sacrificial compounds that react with moisture before hydrolysis can occur, as well as capping functional end-groups. Improvements such as these will need to be made by material suppliers before more widespread durable use in automotive applications.

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