Durability of Polylactide-Based Polymer Blends for Injection-Molded Applications

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ABSTRACT: The durability of polylactide (PLA) blended with polycarbonate (PC) was assessed by exposure to conditions of elevated temperature and humidity over a period of several weeks. Mechanical performance, moisture absorption, chemical composition, and thermal properties were monitored as a function of continuous conditioning at 70°C and 90% relative humidity (RH). All PLA and PC/PLA blends showed significant moisture absorption and hydrolysis, resulting in degradation of properties. Furthermore, while the addition of PC was intended to improve the durability of the blend over neat PLA, it was found that the hydrolysis products of PLA accelerated the degradation of PC itself. This study shows for the first time the hydrolysis behavior of PC/PLA blends in an increasingly acid environment during heat and humidity conditioning. These injection-molding grades of PLA-based resins are currently not suitable for use in applications that require long-term durability in environments subject to elevated temperature and humidity, such as automotive interiors. Further material formulation work is required before use in injection-molded applications for automotive. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

As the use of bio-based polymers and composites continues to expand beyond disposable and packaging applications, the long-term durability of the materials becomes more important. For polylactide (PLA), in particular, applications that currently exist use its compostability—biomedical implants, drug delivery, packaging, and single-use items. More durable applications are currently being investigated. An understanding of the degradation behavior is of utmost importance.

The degradation of PLA occurs primarily through hydrolysis of the ester bond when exposed to moisture.[1–6] The rate of hydrolysis is dependent on many variables, including temperature, moisture level, material thickness and geometry, microstructure, and the presence of basic or acidic environments, to name a few, and has been the subject of numerous investigations.[7–11] In addition, degradation in a composting environment has been studied for single-use applications such as packaging.[3,12–15] In these types of applications, a relatively high-degradation rate is desirable.

Medical applications including implants and drug-delivery devices require a very controlled degradation rate in a specific *in vivo* environment. Research in this area of injection-molded

PLA has focused on materials with extremely high levels of optical purity and crystallinity.[16–23] Although these studies provide much information on hydrolysis behavior *in vivo* or *in vitro*, durable applications for consumer goods and automotive components are exposed to significantly different environments. Limited studies and uses for durable, molded consumer goods exist, including those for laptop and mobile phone casings.[24,25]

Automotive applications require durability under much harsher environments than for laptop and phone applications. Interior applications are exposed to an extremely large range in temperature, from −40°C in cold climates to 80°C in hot environments with heavy sun load. In addition, high-humidity levels are also possible. Furthermore, automotive applications require mechanical and durability performance throughout the lifetime of the vehicle (>10 years in service). Previous work by the authors showed the effects of crystallinity on the performance of molded PLA parts as well as their durability during high heat and humidity conditioning.[26,27] These studies showed that while initial properties of PLA have potential to meet automotive requirements, the commercial injection-molding grades of PLA still lack the long-term durability required for interior vehicle applications. Because of this shortcoming, many material suppliers of PLA have developed injection-molding grades of PLA

blended with petroleum-based resins such as polycarbonate (PC). The potential of these PLA blends is that the petroleum-based resin could help improve the overall performance and durability, and yet the overall material would still possess significant biocontent. However, once a petroleum-based polymer is mixed with the PLA, the material is no longer fully compostable. The current study addresses the durability of the same commercially available material as in the previous study as well as these developmental PC/PLA blends exposed to heat and humidity over time.

All PLA and blend samples were injection-molded and continuously exposed to heat and humidity at 70°C and 90% relative humidity (RH) for durations of up to 28 days. Flexural properties, moisture absorption, chemical composition, and crystallinity were monitored as a function of conditioning time through quasi-static mechanical testing, infrared spectroscopy (IR), and differential scanning calorimetry (DSC). This study shows for the first time the long-term durability behavior of PC/PLA blends in high heat and humidity levels.

EXPERIMENTAL

Materials

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

Developmental grades of PLA blended with PC/PLA were obtained from three different material suppliers. Because of the proprietary nature of the material formulations, only the PLA and PC contents are known. Additive packages and the individual grades of PLA and PC used in the formulations are unknown.

A commercial, automotive injection-molding grade of PC blended with acrylonitrile–butadiene–styrene (PC/ABS, Cycoloy XCY620) was obtained from Sabic Innovative Plastics. PC/ABS was molded and evaluated for this study as a control, because while it is also sensitive to hydrolysis, material formulations have been optimized to be durable in automotive interior environments. Sample descriptions and abbreviations are provided below in Table I.

Sample Preparation

Pellets of PLA and the PC/PLA blends were dried at 60°C for 3 days to remove residual moisture before injection molding. The pellets were injection-molded into ASTM flexural specimens on an 80-ton BOY (BOY 80M) injection-molding machine. The

Table I. Sample Descriptions

Sample	Resin	PLA content (%)	Supplier
PLA-100	Neat PLA	100	NatureWorks
PLA-45	PC/PLA	45	1
PLA-30	PC/PLA	30	2
PLA-25	PC/PLA	25	3
PCABS	PC/ABS	0	Sabic

barrel temperature ranged from ~200–205°C, with a nozzle temperature of 205°C. The mold temperature was maintained at 25°C.

PC/ABS pellets were dried at 80°C overnight to remove moisture before molding. The barrel temperature ranged from 240°C in the rear to 255°C at the nozzle. PC/ABS was molded into ASTM specimens in a heated mold at 60°C.

All molded specimens containing PLA were annealed in an oven at 80°C for 120 min to increase crystallinity uniformly throughout the specimens, as confirmed through DSC analysis. Previous studies have shown that samples with higher percent crystalline content exhibit improved performance.[26,27]

Conditioning

Injection-molded flexural specimens were placed in a Test Equity 1000H Series temperature/humidity chamber. All samples were conditioned at a temperature of 70°C and 90% RH. The samples were evaluated initially before conditioning and again after 1, 2, 4, 7, 14, 21, and, in some cases, 28 days of continuous conditioning. Save for moisture absorption, all other characterization testing were performed on samples dried at 60°C for 3 days. Drying is an important step before mechanical property characterization in order to separate out the plasticizing effects of excess moisture in the molded samples.

Characterization

Mechanical Properties. Injection-molded flexural specimens (nominal dimensions 3.2 mm × 12.6 mm × 125 mm) were evaluated under 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.

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

$$\% \text{ Moisture} = \frac{\text{Final Part Weight} - \text{Initial Part Weight}}{\text{Initial Part Weight}} \times 100\%,$$

(1)

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

Chemical Composition. The chemical composition of each sample before and after conditioning was evaluated using IR spectroscopy. IR spectra were taken of injection-molded samples using a BIORAD FTS 175 FTIR (Fourier transform IR) spectrometer coupled with a UMA 500 FTIR microscope. Spectra of the sample surfaces were collected using reflection mode. An FTIR sampling accessory equipped with a germanium crystal was used to measure the attenuated total reflectance (ATR) spectra.

Thermal Properties and Crystallinity. DSC was used to examine the crystallization behavior of the materials as a function of conditioning time. Degree of crystallinity (X_{ci}), melt

temperature (T_{mi}), and glass transition temperature (T_{gi}) were determined during the initial heating scan for the materials before and after heat and humidity conditioning, using a Mettler Toledo DSC30 with TC15 TA Controller. For nomenclature purposes, subscript "i" refers to the component polymer phase such as PLA, PC, or ABS. 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 equations were used to calculate the degree of crystallinity within the samples:

$$\% \text{ Crystallinity (polymer component)} = X_{c_i}$$
$$= 100\% \times \frac{\Delta H_{m_i} - \Delta H_{c_i}}{\Delta H_{m_i}^{\infty} W_i}, \quad (2)$$

$$\text{Total } \% \text{ Crystallinity} = X_{c_{Total}} = \sum_i X_{c_i} W_i, \quad (3)$$

where i is the polymer component, ΔH_m the measured endothermic enthalpy of melting, ΔH_c the exothermic enthalpy that is absorbed by the crystals formed during DSC heating scan, ΔH_m^{∞} the theoretical melting enthalpy of 100% crystalline polymer, W_i the weight fraction of component i, X_{ci} the percent crystallinity of component i, and $X_{c_{Total}}$ the overall crystallinity of total sample.

The theoretical melting enthalpy of 100% crystalline PLA was taken to be $\Delta H_m^{\infty} = 93 \text{ J/g}$.[4] The theoretical melting enthalpy of 100% crystalline PC was taken to be $\Delta H_m^{\infty} = 134 \text{ J/g}$.[28] The DSC was calibrated periodically with indium standards.

RESULTS AND DISCUSSION

The initial properties of all samples, including flexural strength, crystallization behavior and content, chemical composition, and initial specimen weight, were evaluated before conditioning. These conditions were chosen to be aggressive enough to accelerate the degradation that would occur in an application such as an automotive interior. A cyclic test alternating between elevated and depressed heat and humidity levels would better simulate the real automotive interior 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 petroleum-based polymeric materials that are susceptible to hydrolysis.[1,29,30] Many of these use cumulative damage models in order to accelerate the testing at constant elevated temperature and humidity levels for applications requiring more than 10 years durability. These models take into account the rate of water diffusion into and out of the polymeric material in addition to the hydrolysis reaction rate during cyclic temperature and humidity conditions and correlate them to noncyclic conditioning by cumulating the amount of degradation over time. Based on the data from Bauer et al.[31] on petroleum-based polymers, conditioning at 70°C and 90% RH for 1500 h is approximately equivalent to 10 years of exposure in southern Florida for an automotive interior application. Although accelerated
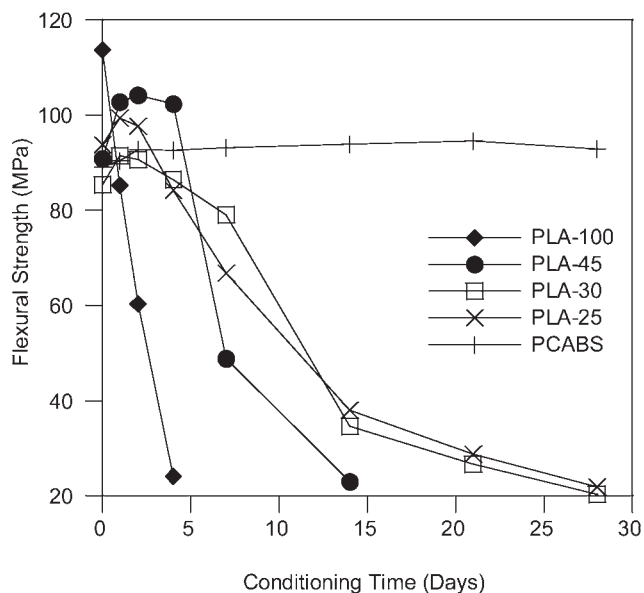

Figure 1. Flexural strength as a function of conditioning time.

testing of PLA hydrolysis is not yet widely available in the literature, a similar method can be applied by knowledge of the moisture absorption and hydrolysis kinetics during durability conditioning. Although previous research by the current authors show the durability behavior of neat PLA at 50°C and 90% RH, the same cumulative damage method has been applied to further accelerate the testing.[26]

Flexural properties, crystalline content, and moisture absorption were measured as a function of continuous conditioning time to assess the long-term durability performance. For all PLA-containing samples, the specimens exhibited extreme degradation by 14 days of conditioning, resulting in either loss of mechanical integrity or formation of large amounts of liquid residue on the sample surfaces.

Mechanical Performance
The effect of moisture and heat conditioning on mechanical performance was monitored through flexural testing per ASTM D790. Figure 1 shows the flexural strength of all PLA samples as a function of conditioning time. Also included in the plot are the data for the automotive grade of PC/ABS subjected to the same conditioning environment. Although the PC/ABS maintains its flexural strength throughout the duration of the conditioning, the flexural strength of the PLA-based samples decreased significantly, due to the decrease in molecular weight. As conditioning time of the PLA-based specimens increased, the samples became extremely brittle. After only 7 days of continuous conditioning, all three PC/PLA samples began to experience a severe loss in flexural strength, while the neat PLA specimens lost enough mechanical integrity to cease testing after 4 days.

For use in a durable application, a material must maintain a specified mechanical performance with exposure to its in-use environment throughout the entire lifetime of the item. In an automotive application, the level of mechanical performance, as well as its environmental conditions, will depend upon the
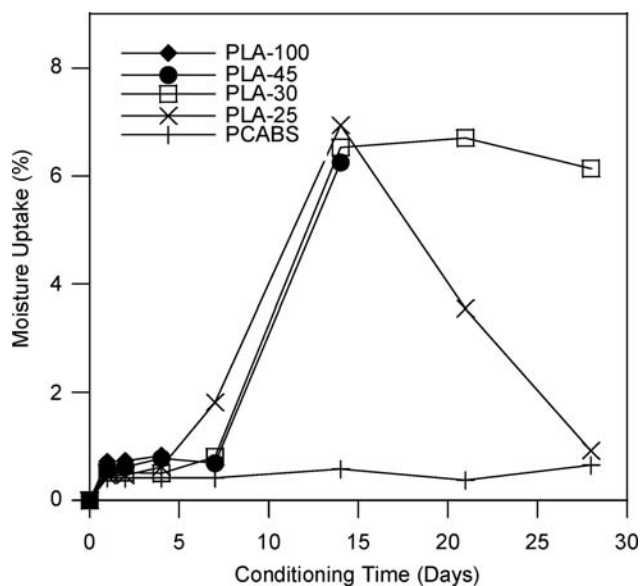
Figure 2. Moisture uptake (%) as a function of conditioning time (days).

Figure 4. Hydrolysis reaction of polycarbonate.

Moisture Absorption

Moisture content was monitored as a function of conditioning time for all samples (see Figure 2).

All samples, except for the PC/ABS, were observed to absorb moisture during the course of the heat and humidity conditioning. Neat PLA lost mechanical integrity and could not be transported out of the chamber after 4 days, and so data are only shown until that point. PC/PLA blends exhibited a slow initial uptake of moisture followed by a rapid uptake between 7 and 14 days of conditioning. The moisture content increases up to a maximum of 7% in the PC/PLA samples, followed by a decrease. This decrease is an artifact due to the loss of mass as opposed to a real decline in the moisture content. At day 14, a sticky brown residue was observed on the surface of the PC/PLA samples. The composition of the residue was later examined by IR and will be discussed further in the next section.

Degradation of PLA in the presence of elevated heat and humidity occurs through hydrolysis.[1–6] Moisture attacks the ester linkages, causing chain scission and a decrease in molecular weight.[26] Figure 3 shows the hydrolysis reaction for PLA, which produces carboxylic acid end groups.

Contrary to many hydrolysis studies available in the literature, the specimens in the current study were not immersed in phosphate-buffered solutions of constant pH.[7,9–12,15–19] Therefore, as the hydrolysis proceeded, the PC/PLA was exposed to an increasingly acidic environment due to the formation of carboxylic acid hydrolysis products. The effects of heat and humidity conditioning on blends of PC with PLA in an increasingly acidic environment have not been previously reported.

PC is also an ester-based polymer and is therefore susceptible to hydrolysis as well. Although PC is more likely to hydrolyze at higher temperatures, it remains more resistant to hydrolysis at room temperature.[32] According to Chow,[32] the solubility of liquid water in PC is low, but water vapor can easily dissolve into the PC matrix. Once the PC is exposed to conditions of high heat and high humidity, hydrolysis and ultimately chain scission occur. The presence of additives as well as acids or bases can further reduce the overall resistance of PC against steam. The hydrolytic degradation of PC is illustrated in Figure 4. Bisphenol-A (BPA), shown in Figure 5, is the initial product resulting from the PC hydrolysis reaction. Upon further conditioning,

specific part location and function. Overall durability for all automotive applications is expected to be at least 10 years or >100,000 miles. Interior durability is quite demanding for materials that are susceptible to hydrolysis. This is due to the greenhouse-like environment caused by high sun load and humidity in regions such as southern Florida. Because this region has the highest hydrolytic dose within the continental United States, it is often chosen as a benchmark for correlating in-field durability to laboratory-conditioning tests for interior, exterior, and underhood applications for various materials including PC/ABS, polyamides, and polyesters, to name a few.[1,29,30] By using a cumulative damage model,[1,26,31] we estimate that for an interior application, 10-year exposure in southern Florida is approximately equivalent to 1500 h of continuous conditioning at 70°C and 90% RH. As such, the durability test protocol used in the current study would require properties to be maintained at least 62 days. The automotive grade PC/ABS used in this study indeed shows no degradation in flexural strength over 30 days of continuous conditioning, as expected. PLA-based samples, however, show mechanical durability of just less than 1 year, at best. Although the neat PLA does show the most extreme drop off in performance over time, the blends do not behave in the expected manner. One would expect PLA-25, which contains the highest PC content of the blends, to have the best performance of the blends owing to the durability of the petroleum-based PC. It in fact decreases more quickly compared to the other PC/PLA blends. This will be discussed further in the following sections.
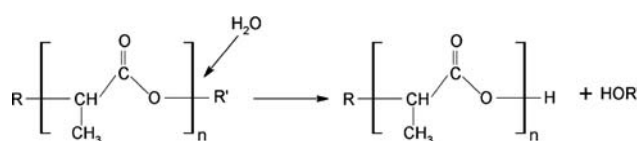
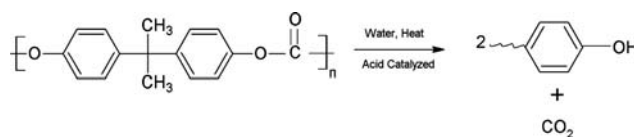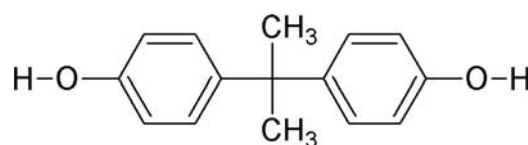

Figure 3. Hydrolysis reaction of PLA.

Figure 5. Chemical structure of bisphenol-A (BPA).

Figure 6. IR spectra of as-molded PLA and PC/PLA samples.

Figure 7. IR spectra of PC/PLA samples conditioned for 14 days.

BPA breaks down further to produce shortened chains with phenolic end groups and ultimately phenol.

The hydrolysis of PC alone has been well studied (see, e.g., Bair et al.[33] and references therein). Bair et al.[33] reported that elevated temperatures and humidity exposure of injection-molded PC specimens resulted in a decrease in molecular weight and impact strength. Similar to the current study, Bair et al.[33] also observed the presence of a brown liquid on the surface of conditioned PC specimens. According to their analysis, the brown liquid was composed of 70 wt % BPA, with the balance comprising BPA oligomers and water.

Chemical Composition

IR was used to determine the chemical composition of the degradation products in the current study. IR spectra were taken of the surfaces of injection-molded samples before and after conditioning. The IR spectra of the conditioned samples were taken once the brown residue was visible in significant quantities.

IR spectra of the as-molded samples are plotted in Figure 6 below. PLA-100 shows the fingerprint of the neat PLA sample. A comparison of the spectra of PC/PLA blends to the neat PLA shows that there is not a significant difference in the main features. There are two distinguishing regions of which to take note: the —CH— stretch (3000 cm^{-1}), corresponding to the methyl end groups, and the —C=O ester carbonyl stretch (1750–1765 cm^{-1}).

After the samples were conditioned for 14 days at 70°C and 90% RH, residue began appearing on the surface of the PC/PLA samples. The residue on the surface was brought into contact with the germanium crystal attachment on the FTIR microscope to collect the ATR spectra (shown in Figure 7). Conditioning was stopped after 4 days for the neat PLA specimens due to the loss of mechanical integrity at which point no residue was
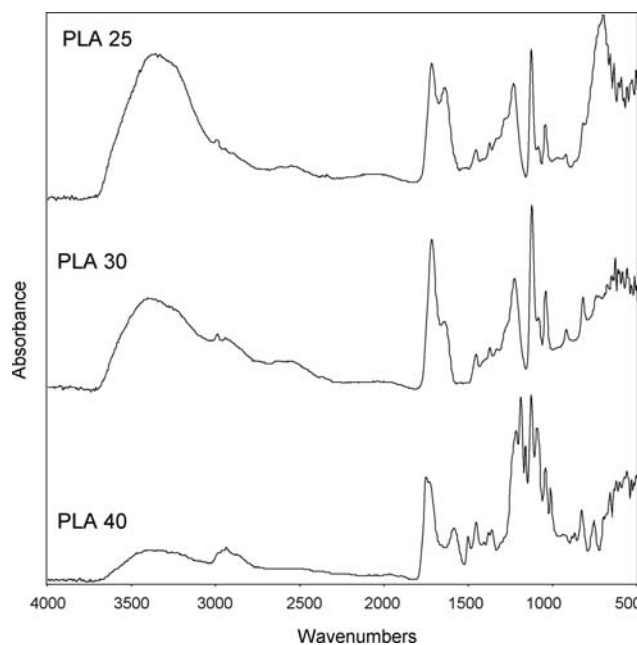
visible on the surface; therefore, its spectrum is not included in Figure 7.

The most significant changes are the evolution of two broad peaks. The first and most prominent is the development of the peak between wavenumbers 3000–3500 cm^{-1}. Stretching in this region indicates the presence of an —OH bond of an alcohol. Given what is known of the hydrolysis products, the —OH bond that is detected is indicative of phenol. This is in agreement with Bair et al.[33] that the brown residue contains BPA. An interesting trend is also observed when looking at this peak; the peak is strongest for PLA-25, the sample with highest PC content and weakest for PLA-45, and the sample with the least amount of PC. At higher PC content, a larger amount of BPA is produced during hydrolysis.

Another broad peak is found at ~2450–2650 cm^{-1} over the course of conditioning. This is caused by stretching of another —OH bond from a carboxylic acid group. At the same time, the —C=O ester carbonyl experiences a shift to a lower wavenumber range from about 1760 cm^{-1} to 1720 cm^{-1}, corresponding to the —C=O stretch of the carboxylic acid group, rather than that of an ester at 1760 cm^{-1}. These peaks indicate the carboxylic acid hydrolysis products from the PLA degradation.

Because of the formation of carboxylic acid within the PC/PCA specimens during PLA hydrolysis, the environment becomes increasingly acidic. The rate of PC hydrolysis is acid-catalyzed, and so the reaction occurs at a higher rate due to the interaction with PLA's hydrolysis products. Between 7 and 14 days of conditioning, the PC chains experience significant chain scission, resulting in decreased molecular weight PC, BPA, BPA oligomers, and phenol. This effect is more pronounced in samples with higher initial amounts of PC. Although the PC component was initially blended in to help stabilize the PLA and improve the overall durability, the final durability of the blend
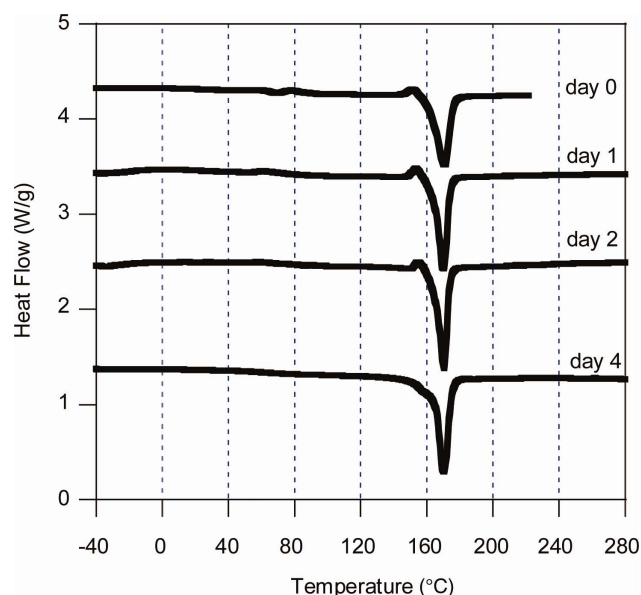
Figure 8. DSC traces of neat PLA at various conditioning times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. DSC traces of PC/ABS at various conditioning times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is only marginally improved, because the PC itself is susceptible to the acid produced from hydrolysis of the PLA.

Thermal Properties and Crystallization Behavior

The crystallization behavior of each material at various conditioning times was evaluated by using DSC. 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 specimen. For conditioned materials, specimens were thoroughly dried of residual moisture content before DSC measurements to determine crystalline content. DSC samples were heated at 10°C/min from −40 to 280°C. The data from this initial heating ramp was used to determine specimen crystallinity information.

For the neat PLA samples, a small amount of amorphous material was present, shown by the glass transition temperature (T_{gPLA}) at ~65°C (see Figure 8). The melting endotherm (denoted T_{mPLA}) was observed at 165°C. Figure 8 shows the DSC traces during the initial heating ramp for each of the conditioned specimens over 4 days of conditioning. DSC measurements in the current study were performed on dried specimens in order to accurately determine crystalline content, such that changes in T_{gPLA} due to moisture plasticization were not measured. Some examples from literature, however, do show significant decreases in T_{gPLA} during heat and humidity conditioning. Copinet et al.[3] 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.

The neat PLA sample shows an increase in crystalline content from 43% initially to 56% after 4 days of conditioning. This increase can be attributed both to secondary crystallization as well as induced new crystallization from decreased molecular weight PLA chains.[34]

DSC was also performed on the PC/ABS samples as a control. Scans were performed during the conditioning period from day
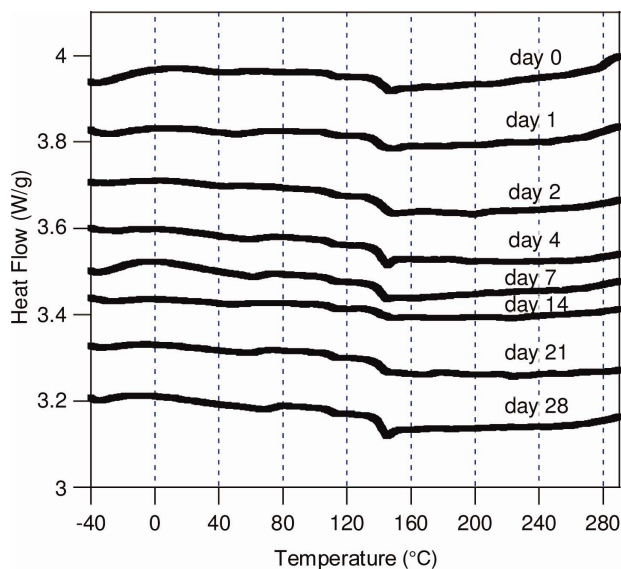
0 to day 28. Figure 9 shows the DSC traces during the initial heating ramps. Two glass transitions can be seen at $T_{gABS} = 110°C$ and $T_{gPC} = 142°C$.[2] There was very little change in the T_gs as a function of conditioning time. No melting endotherm was observed as PC/ABS is an amorphous polymer blend.

DSC heating scans on the PC/PLA blend with 45% PLA content (PLA-45) were performed on as-molded and conditioned samples up to day 14. After day 14, conditioning was stopped in order to prevent potential contamination of the humidity chamber with the brown residue. Figure 10 shows the DSC traces during the initial heating ramps. The PLA glass transition temperature (T_{gPLA})
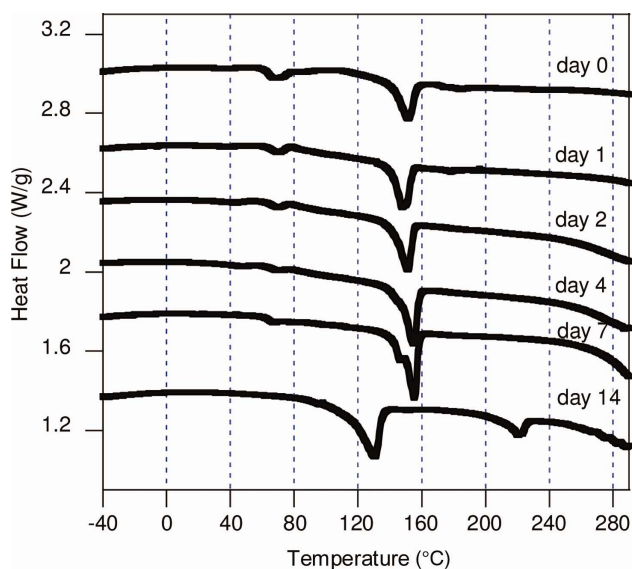
Figure 10. DSC traces of PLA-45 at various conditioning times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
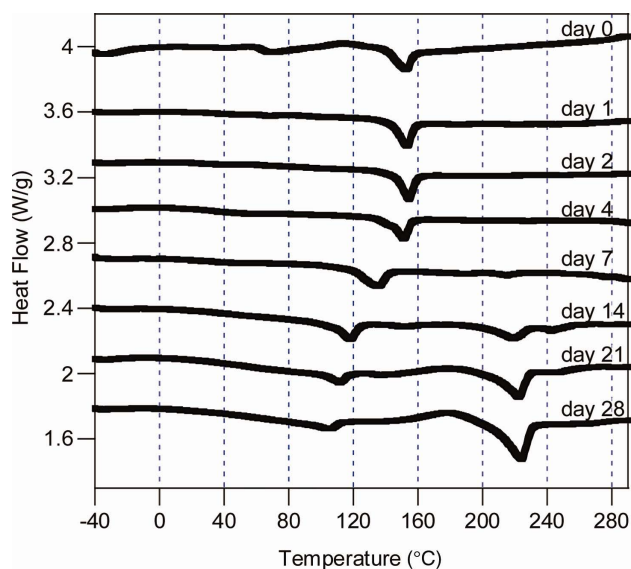
Figure 11. DSC traces of PLA-30 at various conditioning times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
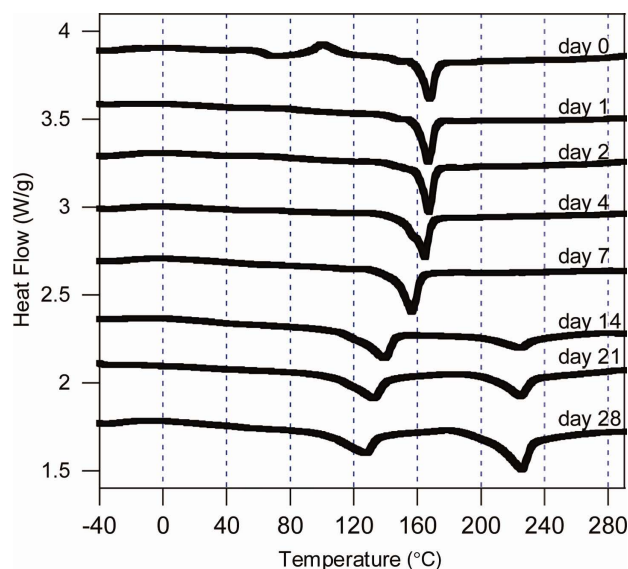

Figure 12. DSC traces of PLA-25 at various conditioning times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

could be seen at ~65°C until day 14 when T_{gPLA} could no longer be detected due to the decreasing amorphous content.

The melting endotherm of PLA component, T_{mPLA}, was observed initially at 152°C. As the material began to break down during conditioning and the molecular weight decreased, a large shift in the melting point occurred. By day 14, the PLA component melting endotherm was observed at 130°C, a decrease of 22°. Further at day 14, another melting endotherm, T_{mPC}, was observed at 220°C for the PC component in the blend.[2] Although PC is typically amorphous, the reduction in molecular weight due to chain scission was great enough to induce crystallization in the lower molecular weight chains.

DSC heating scans were also performed on the PC/PLA blend with 30% PLA content, PLA-30, (shown in Figure 11) from initial time up to day 28. The glass transition temperature of the PLA component was again observed at ~65°C for the initial sample. After only 1 day of conditioning, the amorphous phase decreased so much that T_{gPLA} could no longer be detected.

The melting endotherm of PLA was observed initially at T_{mPLA} = 170°C. This value is significantly higher than those of samples PLA-45 and PLA-25 (see Figure 12). Because of the proprietary nature of the formulations in the developmental grades, one can only assume that this is due to the use of a different grade of PLA with a higher molecular weight. Despite the higher initial value, PLA-30 also experienced a large shift in the PLA melting point. By day 28, the PLA melting endotherm was found to be 129°C, a decrease of 41°. At day 14, the PC melting endotherm, T_{mPC}, was observed at 227°C. From day 14 to day 28, the PC melting endotherm increased and was more defined as the hydrolysis progressed. Further crystallization of the PC phase occurred as the chain scission increased. The crystalline content of the PC phase was found to increase from 0% at time 0–27.6% after 28 days of conditioning.

Finally, Figure 12 shows the DSC heating scans for PLA-25, with PLA content of 25%. Again, the PLA glass transition temperature is shown at 65°C initially and was no longer detectable at day 2.

The melting endotherm of PLA was observed initially at 153°C. Again, the material starts to degrade causing a large shift in the melting point of the PLA phase. By day 28, the PLA melting endotherm had decreased by over 46° to a final value of 107°C. The appearance of the PC melting endotherm (T_{mPC} = 220°C) was found to occur much earlier for this sample, at day 7, compared to day 14, due to its higher PC content. As the conditioning progressed, the PC melting endotherm became larger and more defined to a final crystalline content of 24.8% after 28 days of continuous conditioning.

The crystalline contents of PLA and PC phases are shown in Figure 13 as a function of conditioning time for PLA-45. The overall crystalline content (see Equation 4) was found to increase from 15 to 35% over from day 0 to day 14. The increase in crystallinity is attributed to two factors. First, secondary crystallization occurs in the amorphous phase upon heating with the formation of new crystals between the pre-existing lamellar crystals or by adding to the pre-existing crystals themselves. This occurs first and accounts for the initial rise until day 2. Second, as the PLA undergoes chain scission during hydrolysis, the polymer chains become shorter and are therefore even more mobile, leading to further crystallization. This accounts for the later rise in crystallinity. The PC phase has no contribution until day 14, when the PC chains start to crystallize.
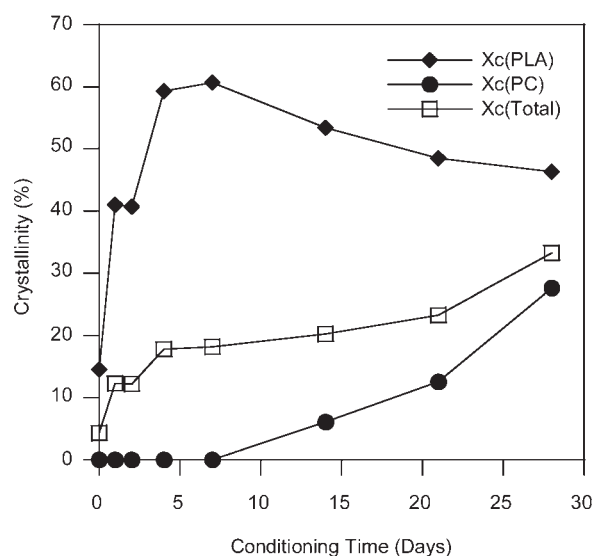
Figure 14 shows the crystalline contents of PLA and PC phases as a function of conditioning time for PLA-30. The PLA crystallinity, $X_{c(PLA)}$, at day 0 was found to be 15%. This value was slightly lower than those for PLA-45 and PLA-25, again due to the difference in PLA grade used in the developmental blend formulation. However, the trends are similar, showing the initial increase from the secondary crystallization, followed by the new
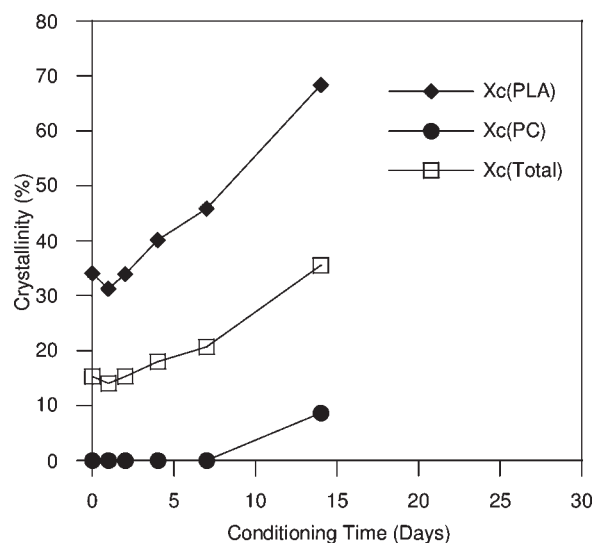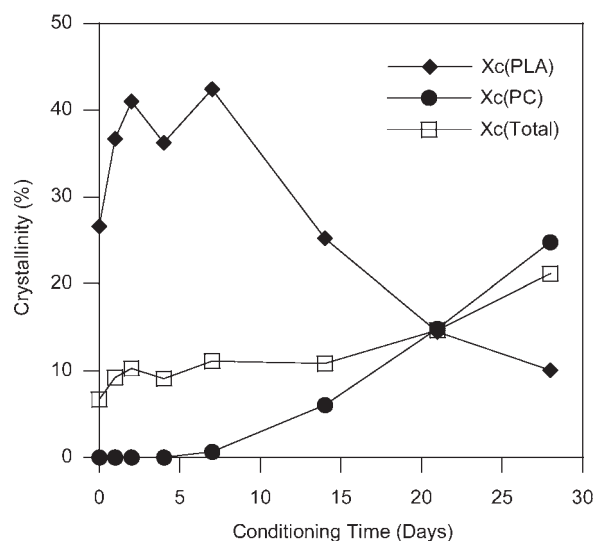
Figure 13. Crystalline content as a function of conditioning time for PLA-45.

Figure 15. Crystallinity of PLA-25 as a function of conditioning time.

crystallization from shorter PLA chains to a maximum of 61% after 7 days, and finally a decrease to 46%. This decrease can be attributed to loss in overall mass of the PLA portion. This would most likely have been observed in sample PLA-45 as well had the conditioning time continued past day 14. The PC component starts to crystallize after 7 days of conditioning and continues to a value of 28% after 28 days. The total crystallinity of PLA-30 blend increases from 4 to 33%.

The component crystallinities as a function of time for PLA-25 are shown in Figure 15. The PLA had an initial crystallinity of 27%, increasing first from secondary crystallization until day 2, then from new crystals to a maximum of 42% after 7 days. The reason for the decrease in crystallinity at day 4 is unclear, but may be due to loss of mass in the solid component. The crystal-

line content then decreases to a final value of 10.4%, again due to loss in overall mass of the PLA portion. Unlike PLA-30, after 28 days, the crystallinity of the PC component was greater than the PLA component, due to the higher content of PC at low-molecular weight. The total crystallinity increased from 7% at day 0 to 21% at day 28.

CONCLUSION

The current study shows for the first time the durability behavior of PC/PLA blends, subjected to elevated temperature and humidity conditions. Neat PLA and an automotive grade of PC/ABS were also included in the study as control samples. Although PC itself can undergo hydrolysis, blends with ABS, such as the automotive grade used in the current study, are shown to be resistant under conditions of elevated temperature and humidity. The conditions chosen for the study were extremely harsh, such that the correlation to in-field exposure for an automotive interior component in a southern Florida climate could be considerably accelerated. Using a cumulative damage model, 10 years of in-field exposure was correlated to ~62 days of continuous conditioning at 70°C and 90% RH.

Although the results indicate that the presence of PC does improve the long-term performance of the blends over neat PLA, the durability has only increased to 1 year of in-field exposure, at best. Furthermore, an unexpected result was found in the effect of PC content in the blend formulations. Although PC was added to the PLA blends to slow the hydrolytic degradation, the blend with the highest PC content was found to degrade more quickly of the three blends investigated. It was found that as the PLA hydrolyzed during exposure, the solvation of the hydrolysis products decreased the pH of the environment enough to result in an acid-catalyzed hydrolysis of the PC phase. This interaction does not occur in the PC/ABS blend due to the hydrolytic stability of ABS.

Figure 14. Crystalline content of PLA-30 as a function of conditioning time.

The hydrolysis of the PC phase was significant, resulting in the appearance of a brown residue on the surface of the injection-

molded specimens. This residue was found to be a mixture of low-molecular weight PC, BPA, BPA oligomers, and phenol. The presence of these components indicates that a significant amount of chain scission had occurred. Although PC is normally an amorphous polymer, there was enough decrease in molecular weight and plasticization from the hydrolysis products to induce its crystallization. As the degradation continued, more PC crystallization occurred.

Overall, the blends performed slightly better than the neat PLA only because of the reduced proportion of PLA in the blend. The hydrolysis behavior of the PLA phase in the blends was not affected by the addition of PC. The PC, however, showed worse hydrolysis behavior than when blended with other hydrolysis resistant polymers such as ABS.

This study shows that while the approach of blending a durable polymer resin with PLA can enhance the overall durability, the selection of resin is critical. The interactions of the resins with one another as well as with any degradation products need to be considered and understood. The results here indicate that PC/PLA blends will not be durable enough for automotive applications, regardless of PC content. Developmental PLA blends with other resins such as ABS or PMMA could have better long-term performance.

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