Creep Behavior of PLA-Based Biodegradable Plastic Exposed to a Hydrocarbon Liquid

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ABSTRACT: This study explores the effect of hydrocarbon liquid on creep behavior of polylactic acid (PLA)-based plastic. Evolution of the mechanical properties of the material was investigated experimentally by measurement of creep under tensile load. Tensile creep behavior was studied with a constant load over a temperature range from 30 to 50°C using specimens containing different levels of liquid. It was shown that the hydrocarbon liquid diffusion obeys the Fickian law of diffusion. The viscoelastic properties vary with temperature and these properties dramatically decrease above the glass transition temperature (T_g). Significant decreases in modulus and in the peak of tan δ were observed with an increase in liquid concentration at low temperatures. In contrast, at high temperatures, drier material recorded lower storage modulus. However, only small changes of T_g were recorded. Dependence of compliance on temperature was observed in the creep test at all levels of liquid content. With respect to drier samples, it was noted that the high liquid content material had a lower rate of increasing creep strain with temperature. Therefore, at elevated temperatures, higher creep strain of dry specimens was observed compared to those with a higher liquid content. The improvement of creep resistance and stiffening of material at high temperatures can be attributed to the significant increase of crystallinity fraction induced by liquid absorption. Understanding the effect of liquid diffusion in conjunction with temperature provides useful information for assessment of the potential use of this biodegradable plastic in load-bearing applications exposed to an organic liquid. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Biodegradable plastics have great potential as viable alternatives to petroleum-based materials because they consume less fossil fuel in their production and have better degradability properties. Polylactic acid (PLA) is one of the most promising biodegradable polymers made from renewable sources and has comparable mechanical and physical properties to those of some commercial thermoplastics.[1] PLA has various end-use applications because of its good mechanical properties such as high stiffness and high tensile strength, combined with good optical properties (transparency). Currently, it is being applied in biomedical implants, automotive interior components, durable consumer goods, and also for the flexible to rigid packaging required for a broad array of products. The disposable applications take advantage of the relatively fast degradation in an industrial composting environment. However, for application in wet environments, the performance behavior must be maintained for the lifetime of the product.

Under typical use conditions, PLA is very stable and will retain its molecular weight and physical properties for years. This is typified by its growing use for clothing and durable applications. However, changes in material properties might be observed after exposure to heat and humidity conditions.[2,3] A significant decrease in mechanical performance has been observed at high temperatures (more than 50°C) and in high humidity conditions (80–90% RH).[4] At high temperatures, absorbed water causes hydrolysis of the ester bonds, preferentially in the amorphous phase. Exposure to an aggressive environment, such as when chemical solvents and organic liquids are present, may also impact the morphological and thermomechanical properties of the polymer.[5] With any polymeric material, the absorption of a chemical compound can have one or more different effects, such as plasticization, solubilization, environmental stress cracking, and macromolecular chains breaking.[6] Therefore, evaluation of the performance of the polymer when exposed to a chemical solution is necessary to assess
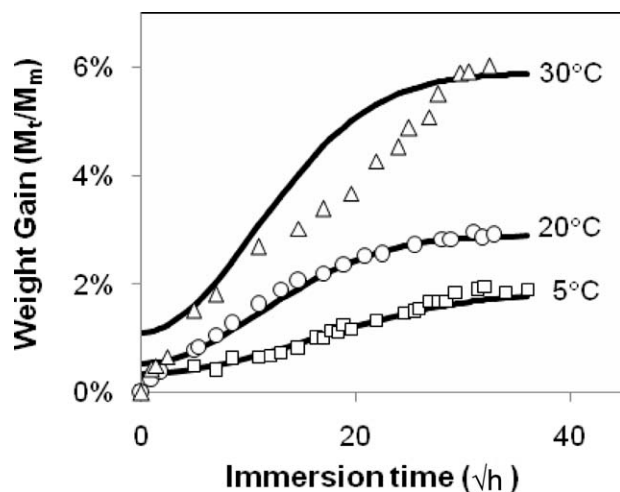
Figure 1. Percentage of liquid uptakes versus square root of immersion time for all materials at different immersion temperatures.

suitability and assure durability of the material during its service lifetime.

The resistance of PLA to chemical compounds, and its influence on thermomechanical performance, has attracted few studies to date.[7,8] The studies mainly focused on common food packaging solutions, such as acid solutions, vegetable oil, and organic aroma compounds, because the majority of existing commercial applications are for food packaging. Investigation by Auras et al.[7] showed that the exposure of acid solutions and vegetable oil for 7 days on oriented PLA resulted in minimal strength degradation. However, a decrease in the glass transition temperature of PLA, indicating plasticizing, was observed on the sorption of an organic compound after a 3-day exposure period.[8] For safe use during its lifetime, from production and storage to distribution and service, an assessment of the evolution of mechanical behavior is required, because of the sensitivity of plastic materials to applied load. Their viscoelastic behavior may produce physical distortion under external forces and heat. Creep measurement seems to be an excellent method to analyze the evolution of the viscoelastic properties after ageing with organic solvent. From an application point of view, this knowledge will be helpful in analyzing the compatibility of PLA-based plastics with chemical solvents for load-bearing applications. Therefore this study examines the short-term creep behavior of PLA-based material after liquid absorption. PLA samples with different liquid concentrations were prepared and studied. Hydrocarbon liquid was used to simulate the worst case of aggressive chemical solvent against a common polymer. Characteristics of the absorbed specimens on creep properties were investigated at various temperatures for a specified period.

MATERIAL AND METHODS

The biodegradable polymer used in this study was starch-based PLA resin produced by BIOTEC, a subsidiary company of

Biome Technologies, and supplied through BioPak Pty, Australia.[9] It was composed of 90% corn-derived PLA and reinforced with 10% potato starch.[1] The material in pellet form was converted into test samples according to the manufacturer's product manual, using a Battenfeld BA 350/75 injection molding machine. Immersion hydrocarbon liquid for conducting this experiment is gasoline, provided by a local fuel station. In varying levels of liquid concentration, different immersion temperatures were used to accelerate the level of liquid absorption. Unleaded gasoline was chosen as aggressive enough to accelerate the degradation that would occur in an application exposed to liquid and chemical solvent. Distilled water or moisture would be the most common media in evaluating the hygrothermal effects of polymer, but it is less aggressive and would require longer test duration. Samples were immersed to the point of saturation under three different conditions: (1) room temperature where the temperature was monitored with a digital thermometer at $20 \pm 3°C$; (2) a fridge set at $5 \pm 1°C$; and (3) a chamber set at $30°C$. Before immersion, the samples were placed in a vacuum oven for 3 h at $50°C$. The specimens were removed periodically for weight measurement until the saturation had occurred. The liquid absorption, M_t was calculated using the following relationship

$$M_t = \frac{m_t - m_0}{m_0} \times 100\% \qquad (1)$$

where m_t and m_0 are the mass of specimen before and during ageing, respectively.

Changes in the viscoelastic characteristics, i.e., the glass transition (T_g) and storage modulus (E') of the material, along with the immersion time in the fluids, were measured using a TA Instruments Dynamic Mechanical Analyser (DMA) 2980. Specimens of dimension $60 \times 10 \times 3$ mm were tested in a dual cantilever mode over a temperature range of 20–80°C, using a frequency of 1 Hz.
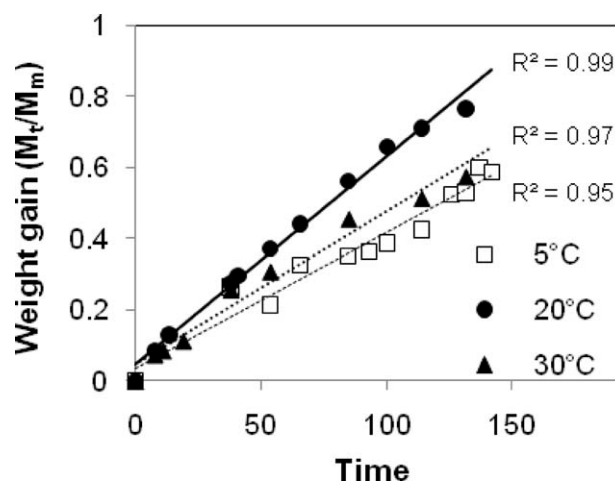

Figure 2. Plot of M_t/M_m values from the initial value (up to $t \approx 2$ weeks) of liquid absorption.
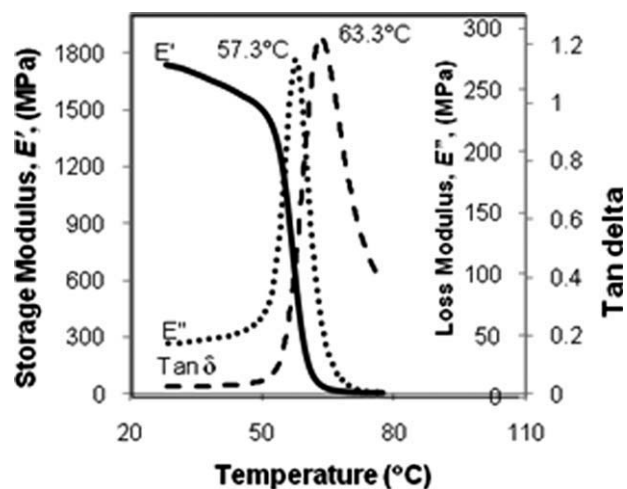
Figure 3. Thermomechanical analysis of dry specimens (0% liquid content) using frequency range 1 Hz.

Figure 5. Effect of liquid concentration on glass transition temperature determined from different methods: peak of tan δ and onset of loss modulus.

Creep experiments were conducted at isotherms at 30, 40, and 50°C in the film tensile creep mode. For each isotherm, a constant stress of 0.45 MPa was applied for 60 min, followed by a 10 min recovery period. The soak time, that is the equilibrium time to have the same temperature for all parts of the specimen, was set to 5 min. The sample dimensions were $\sim$ 50 mm $\times$ 12 mm $\times$ 2 mm.

RESULTS AND DISCUSSION

Liquid Absorption

Plotted points in Figure 1 show the weight gain variation, with immersion times at different temperatures. Determination of equilibrium weight gain during immersion is based on the standard method recommended by SAEJ1748, which compares data from two or more immersion periods. If no significant difference exists between the points, then it can be concluded that weight gain is in equilibrium.[10] The equilibrium plateau was obtained after 1152, 1008, and 888 hours for specimens immersed at temperature 5, 20, and 30°C, respectively.

The common approach used to describe diffusion of liquid into all types of polymer is by means of Fick's law, which shows the
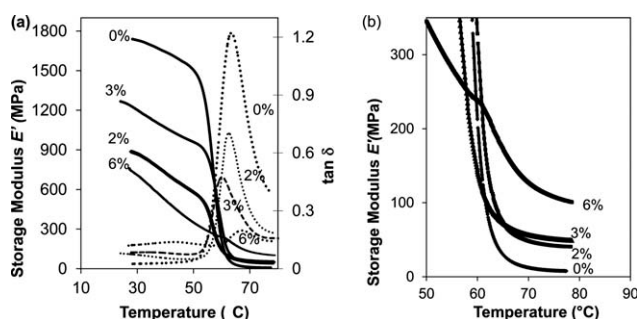
initial linear weight gain followed by a transition region, reaching saturation level at large values in time.[11] For Fickian diffusion, the equation for one dimension is given as follows[12]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (2)$$

where C is the concentration of diffusing substances (g/m^3), x is the space coordinate measured normal to the section (m), and D is called the diffusion coefficient (m^2/s). The analytical solution for eq. (2), which indicates the weight gain of the immersed sample on both sides, is given by Crank[12] as follows:

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 \pi^2 F_0}{4}\right] \qquad (3)$$

where Fourier number, $F_0 = \frac{D \cdot t}{(h/2)^2}$, M_t denotes the total amount of liquid, which has diffused into the specimen at time t, h is the thickness of the specimen, and M_m is liquid uptake in the material when the material is fully saturated, in equilibrium with its environment. Figure 1 also shows the comparison of experimental data with the fitting of the above Fick's equation, as indicated by a solid line.

Figure 2 shows the fitting of linear regression for the plot of M_t/M_m versus $\sqrt{t}$ at the initial stage of liquid absorption. It then supports the initial assumption that Ficks law can be applied to this type of diffusion process. This figure indicates a large value of correlation coefficient ($R^2 > 0.9$) of the regression lines. Therefore, the saturated weight gains at immersion temperatures 5, 20, and 30°C can be determined from the equilibrium plateau, which are observed at 1.90, 2.91, and 5.95%, respectively (as can be seen from Fig. 1).

Dynamic Mechanical Analysis

Using dynamic mechanical analysis, the viscoelastic properties observed were storage modulus (E'), loss modulus (E''), and mechanical damping (tan δ). The storage modulus indicates the

Figure 4. Effect of liquid concentration on viscoelastic properties (solid line is storage modulus whereas dot line is tan δ) at (a) low test temperature and (b) high test temperature.
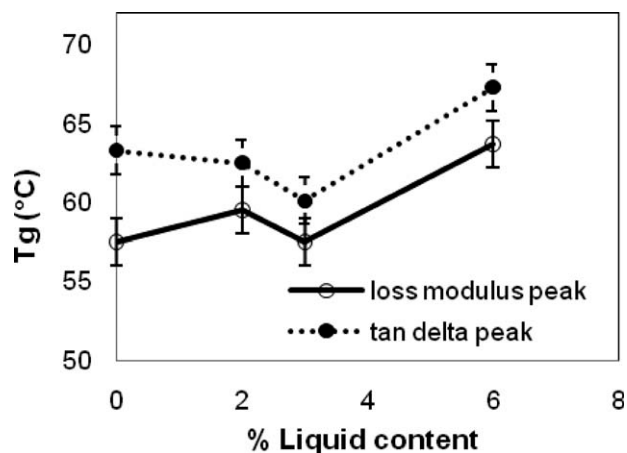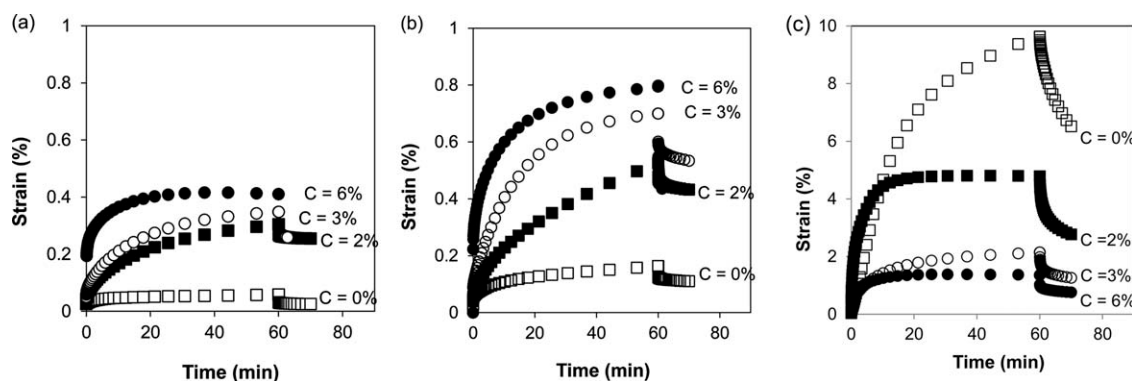
Figure 6. Creep strain versus time at 0.45 MPa with test temperature: (a) 30°C, (b) 40°C, and (c) 50°C for different level of liquid concentration.

inherent stiffness of the material under dynamic loading conditions. Dividing the loss modulus by the storage modulus gives tan δ. The loss modulus and tan δ curves help to identify one or more regions where the onset of specific types of molecular motion causes relatively large changes in properties over relatively narrow bands of temperature. These events are transitions and the most important of these is the glass transition.[13]

Figure 3 presents the results of the dynamic mechanical analysis of an unexposed PLA-based specimen. This curve consists of three zones: a glassy region, a sudden-fall region that corresponds to the respective relaxation in the PLA-based polymer, and a high-temperature region. In the range of temperature below 55°C, the material presents high mechanical stiffness (E' > 1500 MPa). In this region, the polymer is glassy and frequently brittle.[14] Following this is a sharp drop of modulus, a phenomenon of mechanical relaxation of the amorphous phase during the glass transition of the polymer. Above $T = 65°C$, the softening of the crystalline phase[5] can be observed, which means that the polymer is in the molten state. The glass-transition temperature, T_g, is identified as a peak in tan δ or loss modulus trace and it is around 57–63°C, which is comparable with the material property data released by NatureWorks LLC for their injection mould-grade PLA.[15]

Figure 4 shows the dynamic mechanical properties as a function of temperature for the PLA-based plastic specimens subjected to liquid absorption. The variation of the storage modulus (E') shows that it is affected by temperature and liquid concentration. At low temperatures (below 55°C), a reduction of E' with an increase in liquid content can be observed [Fig. 4(a)]. This figure also shows the reduction in the tan δ peak heights associated with the storage modulus plot. However, it is worth noting that a split on tan δ was observed in the 6% liquid containing sample, which suggests that an apparent phase separation had taken place in the material. Karad and Jones[16] suggested that the second peak was indicative of degradation of the resin molecular structure, which was believed to be assisted by the higher rate of liquid absorption. Above 55°C, the decreasing rate of E' was higher compared with those in the low temperature region. It should also be noted that in this high temperature region, a higher E' was observed for specimens with a higher liquid concentration [Fig. 4(b)].

The effect of absorbed liquid on changes of glass transition temperature (T_g) is displayed in Figure 5. As T_g is determined from the α peak of tan δ curve or loss modulus trace, only a small shift of the glass transition region was observed, except for specimens with 6% liquid content. This figure also shows error bars with standard deviation 2.9°C for both methods, with no trend displayed. In other words, it can be said that liquid absorption of PLA-based plastics does not result in significant changes in the glass transition temperature.

Creep Behavior

Plastics possess very temperature-sensitive creep behavior and exhibit significant creep even at room temperature.[14] To further characterize the rheological properties of the polymer, creep tests were undertaken. In a creep test, a constant load or stress is applied to the material, and the variation of deformation or strain with time is recorded. The effect of solvent absorption on creep behavior was explored in creep tests at 0.45 MPa conducted on specimens subjected to hydrocarbon liquid exposure, at different levels of concentration, at different test temperatures. The results of the creep tests are presented in Figures 6(a,b) and 7 for specimens tested at 30, 40, and 50°C, respectively.
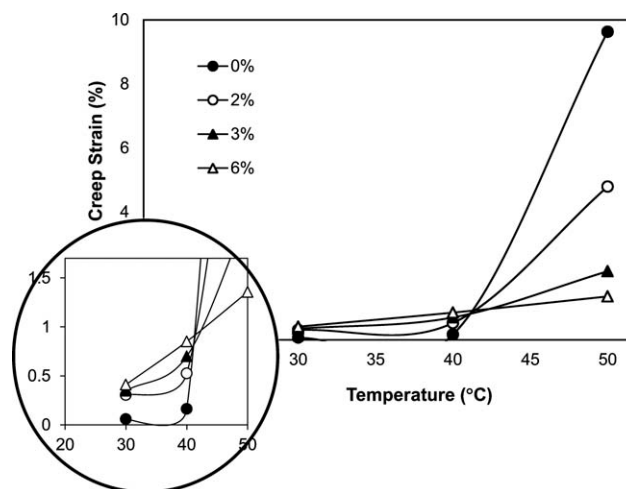

Figure 7. Creep strain accumulated at 60 min as a function of creep test temperature for different level of concentration.
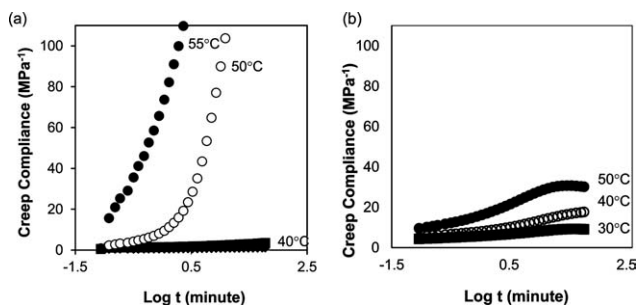
Figure 8. Creep compliance curves in time function at different test temperatures for (a) dry specimens and (b) specimens contain 6% liquid uptake.

The creep curves produced at all the test temperatures exhibited typical creep behavior for semicrystalline materials subjected to constant stress, which falls into three regimes: (1) instantaneous elastic response; (2) retarded viscoelastic response; and (3) permanent flow response.[17] As expected, at low temperatures (up to 40°C), the creep strain increased with an increase in liquid uptake [Fig. 6(a,b)]. This behavior can be explained considering that liquid uptake plays the role of a plasticizer, allowing more chain movement in the amorphous phase of the biopolymer. Therefore, it causes a higher strain, and the creep deformation of absorbed specimens will proceed more rapidly than that in the dry material.

Nevertheless, the creep behavior of specimens at 50°C follows a different trend. Figure 6(c) presents a significant decrease of creep strain as the liquid content increase. With respect to samples tested at 30 and 40°C, the drier samples at 50°C showed a lower creep strain rate in the initial part of the test but later in the test, the rate sharply increased and the final values were higher still. In other words, specimens with a higher liquid concentration have greater stiffening than those containing a lower liquid content. A similar finding with a different material was reported by Habas-Ulloa et al.,[5] who researched gas-oil exposure effects on high-density polyethylene (HDPE). They found that with only a short ageing time, the creep strain of the HDPE specimen containing a greater gas-oil uptake was higher than that containing a lower liquid uptake. However, with a longer gas-oil immersion time, a stiffening of the material containing a higher liquid concentration was observed. Papanicolaou et al.[18] also reported the anomalous creep behavior of glass epoxy composites in humid conditions. The creep strain of the material increased until the water uptake reaching a maximum value, but then rapidly decreased and after a long ageing time, the material became stiffer than the dry material.

To better understand this phenomenon, additional diagrams are presented. Figure 7 shows the creep strain accumulation of the samples at $t = 60$ min at different liquid concentrations. It displays different trends of creep strain with a liquid content at low and high temperatures, which confirms the findings explained by Figure 6. The magnified circle in Figure 7 shows the increasing creep strain with liquid uptake at a low temperature.

To evaluate the reciprocation law of viscoelasticity, creep compliance, $J(t)$, was calculated. Figure 8 shows the creep compli-

ance curves of the test specimens. Creep compliance is defined as the ratio of creep strain $\varepsilon(t)$ to the applied stress σ as given below[19]:

$$J(t) = \frac{\varepsilon(t)}{\sigma} \qquad (4)$$

Figure 8 shows that at the same value of imposed stress, the strain and creep compliance increase as the test temperature is raised. It can be seen that a higher mechanical flexibility is provoked by the enhanced chain mobility that results in increased creep deformation.[20,21] The figure for dry specimens [Fig. 8(a)] indicates a more significant increase of creep strain rate with increasing temperature compared to the specimens that absorbed liquid. However, as the liquid uptake inside the material increases, a decrease of creep strain rate with temperature can be observed [Fig. 8(b)]. In the case of dry material, creep compliance rapidly increases with temperature. In contrast, for material with a liquid content, the creep compliance is almost invariant with temperature, though an increased tendency can be observed. From these figures, it was assumed that the presence of liquid, particularly at elevated temperatures, induced physical structural changes of the polymeric material.

Differential scanning calorimetry (DSC) measurement was used to further investigate the structural changes of dry and immersed material after ageing at an elevated temperature
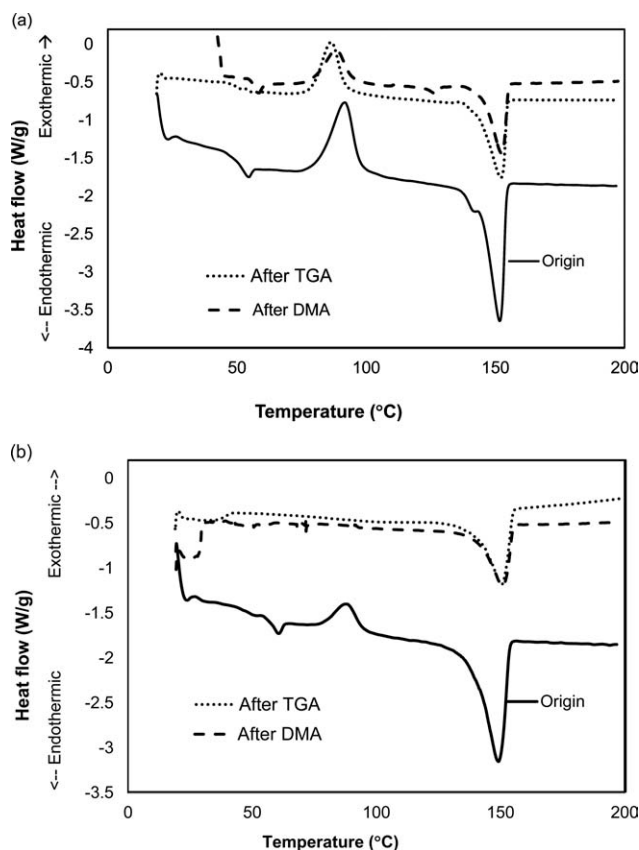

Figure 9. DSC curve of materials after 50°C DMA and TGA test compared with the origin samples for (a) dry specimens and (b) specimens with 6% liquid content.

Table I. Heat of Fusion and Degree of Crystallinity Before and After DMA Creep Test

Conditions	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_c (%)
Dry	151.65	13.96	19.11	5.74
Dry after 50°C creep test	152.68	8.69	17.34	9.64
6% Liquid	149.42	3.01	17.44	16.09
6% Liquid after 50°C creep test	149.59	–	20.00	22.30

typical for the creep test described earlier. The relative crystallinity, X_c, of the specimens was measured using DSC (TA Instrument). Heating runs were conducted from room temperature to 200°C at a heating rate of 3°C/min. The weights of the PLA specimens for DSC were 7–10 mg, taken from cross-sections of the creep test rectangular bars. Figure 9 shows the overlay DSC curves of specimens before and after the DMA creep test as a function of temperature. In the DSC profile of the original dry material before the creep test [Fig. 9(a)], endothermic and exothermic peaks derived from glass transition, crystallization of the amorphous phase, and the melting of the crystalline phase were detected at 56.5, 91.55, and 151.65°C, respectively. On the dry specimen, an exothermic peak of crystallization was detected before and after the 50°C tests. Nevertheless, the peak disappeared in the 6% liquid content samples after the creep test [Fig. 9(b)]. This DSC profile indicates that the crystallization process that occurs at 50°C had been completed.

In addition, another DSC test was run for specimens that had been previously conditioned at 50°C in a thermogravimetric (TGA) device to simulate the same heat conditions but without applied stress. Figure 9 indicates that the effect of low applied stress (0.45 MPa) to crystallinity behavior was negligible.

The percentage crystallinity of the specimen was determined using a value of 87.92 KJ/kg for the heat of fusion for the full crystallinity of the Bioplast GS2189 material[1] and calculated using the following equation:

$$\%\text{Crystallinity} = X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^\infty}$$

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 heat of fusion was obtained by integrating the area under the endothermic peak. The measured values of X_C are summarized in Table I.

The results indicate that the organic liquid absorption and heat condition have a significant effect on the degree of crystallinity. These results have also been reported by Naga et al.,[22] where a potential improvement in the PLA specimen crystallinity has been recorded due to organic solvent diffusion. Absorbed liquid plays the role of a plasticizer, which provokes movement in the amorphous phase that promotes a rearrangement of the structure and an increase in the crystallinity,[23] particularly at an elevated temperature. It is well known that the degree of crystal-

linity significantly affects the mechanical properties of polymeric materials. Earlier research has confirmed that the strength of semicrystalline polymers, including creep resistance, increases with an increase in the crystallinity ratio.[17,24] Therefore, the improvement in creep resistance of high-liquid content samples [Fig. 6(c)] and in the stiffness of the material at high temperatures [Fig. 4(b)] can be attributed to a significant increase in the degree of crystallinity of PLA-based specimens, as in indicated in Table I.

CONCLUSION

This article has described the effect of organic liquid absorption on the creep behavior of PLA based plastic. Although previous research has demonstrated the performance of PLA materials exposed to humidity[4,25,26] and food chemical compounds,[7] this study focused on the viscoelastic performance of the PLA compound used for load-bearing applications and exposed to gasoline. In this work, the polymer was exposed to gasoline, a well-known aggressive organic liquid, at various exposure temperatures to attain different levels of absorbed liquid.

Although the initial performance of PLA-based plastics meets the requirements for rigid application, its performance continually decreases as the temperature increases. A sharp drop of modulus was obvious above 50°C. The presence of hydrocarbon liquid greatly influenced the viscoelastic properties of this material. The results show a decrease of modulus with an increase in liquid content at low temperatures. However, at high temperatures, the modulus of the material with a high-liquid concentration was higher than that of drier material. A similar phenomenon of solvent absorption on PLA-based material was also observed in the creep behavior. At a lower temperature, creep compliance continuously increased with increasing liquid content, revealing the plasticization of the polymer. But, for higher temperatures, diffusion of the hydrocarbon solvent induced an improvement in creep resistance with liquid uptake. Investigation of the physical structure, using DSC, revealed a significant increase in the percentage of crystallinity, which leads to progressive stiffening of the polymer at high temperatures. Therefore, the competing processes of plasticization at low temperature and crystallization at high temperature limit changes in stiffness as a result of liquid absorption. For all applications, serious consideration must be given to the liquid absorption effect and it should be noted that the mechanical behavior of the polymer will not be stable.

ACKNOWLEDGMENTS

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