

Effects of Aging on the Thermomechanical Properties of Poly(lactic acid)

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ABSTRACT: In this study, we examined the role of environmental parameters and physical structure in the aging process of poly(lactic acid) (PLA). The role of heating history on the aging behavior of the material was also investigated. PLA samples with a D-content of 4.25% were exposed to a relative humidity of 80% at three different temperatures, 20, 40, and 50°C (below the glass-transition temperature of the material), at various aging periods of 30, 60, 80, 100, and 130 days. Selected samples were subjected to two consecutive heating runs. The stability of PLA was monitored by a number of techniques, including size exclusion chromatography, differential scanning calorimetry, dynamic mechanical analysis, and tensile measurements. The initial thermal processing (150°C) of the

material resulted in an overall molecular weight reduction. A substantial lowering of properties was observed for PLA samples aged at 20°C for 30 days. No further loss of properties was observed for samples aged up to 40°C for several time intervals. A major portion (80–90%) of the induced changes in the tensile properties could be reversed after drying. At 50°C and 100 days of aging, a sharp decrease in the overall properties was noticed. The results seem to confirm the earlier finding that PLA degradation driven by hydrolysis needs a higher temperature (>50°C) in combination with ample time to take place. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 472–481, 2011

Key words: ageing; biodegradable; mechanical properties

INTRODUCTION

Poly(lactic acid) (PLA) is a (bio)degradable material with a wide range of medical, textile and packaging applications. The (bio)degradability of PLA, though, has both negative and positive aspects. The positive aspect is that (bio)degradation forms nonhazardous products when PLA polymers or articles are discarded or composted after their useful life is complete. The negative aspect is the degradation of PLA polymers during processing. Thus, the same properties that make PLA polymers desirable as replacements for nondegradable petrochemical polymers also create undesirable effects that must be overcome. For several applications, the degradation rate of PLA is still low compared to the waste accumulation rate. On the other hand, the fact that PLA degrades slowly (over a period of several weeks up to ca. 1 year) is advantageous for some other applications, as it leads to a relatively good shelf life.

PLA degrades during thermal processing or under hydrolytic conditions; this causes a reduction in the molecular weight that affects the final properties of the material, such as its mechanical strength.^{1–5} The degradation behavior depends strongly on the mo-

lecular weight and the crystallinity of the PLA.^{6,7} Previous studies have shown that degradation of PLA is enhanced by an increase in the temperature and relative humidity (RH).⁸ The temperature, in the presence of oxygen, triggers thermal oxidation, whereas moisture promotes hydrolytic degradation. PLA degradation driven by hydrolysis needs a higher temperature (>50°C) to take place.

Chemical hydrolysis of the hydrolytically unstable backbone is the primary mechanism for the degradation of the PLA polymer. Degradation occurs first by water penetrating the bulk of the polymer and hydrolyzing the ester bonds, preferentially those in the amorphous phase, and converting long chains into shorter water-soluble fragments.⁹

PLA has been known to degrade slowly because of its hydrophobic and semicrystalline structure, which does not allow fast water penetration. Although PLA is a hydrophobic polymer with great water resistance, differences in the RH affect the moisture content of the material.¹⁰ Water absorbed during aging at low temperatures [less than the glass-transition temperature (T_g)] act as an effective plasticizer, increasing the molecular mobility of PLA, which facilitates the aggregation of PLA chains and results in faster nucleation and crystallization of the PLA molecules.^{10,11} At high temperatures (> T_g), the absorbed water causes hydrolysis of the ester bonds, preferentially in the amorphous phase and converts long polymer chains into shorter ones,

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including oligomers and monomers. This explains the much faster hydrolysis rate of amorphous PLA (D,L) compared to semicrystalline PLA (L,L). The lactic acid oligomers, which result from hydrolysis, are known to catalyze the degradation reaction.¹² The degradation mechanisms can be affected by various factors, such as the chemical structure, molar mass and distribution, purity (e.g., water content, low-molecular-weight impurities, catalyst residues), morphology, shape, size, history of the specimen, and conditions under which the hydrolysis is conducted (e.g., aging time, temperature, presence of water).^{13,14}

The majority of previous art studies on the stability of PLA have been carried out in buffer solutions, primarily under physiological conditions, that is, at temperatures of 37°C with a pH of 7.4.^{7,9,12,15–26} A smaller number of articles has been dedicated to the effects of environmental conditions, such as humidity, pressure, UV radiation, temperature, aging time,^{8,10,27–30} and compost microorganisms.^{31–33} Only a fraction of the most recent studies have reported on the effects of environmental conditions on the mechanical properties of PLA.^{27,30,34,35} Only few of them have contained tensile measurements.^{7,27,35}

PLA has a T_g value of 50–60°C. Depending on its D-content and molecular weight, its cold crystallization temperature ranges between 95 and 110°C, whereas its melting temperature (T_m) ranges from 150 to 190°C.³⁶ The crystallizability of PLA is determined by its chain regularity and mobility. As lactic acid is chiral, the regularity of PLA chains is significantly affected by the ratio of L components over D components;³⁷ this leads to the suppression of the crystallizability when a small fraction of D is present in most L-chains. The PLA has insufficient flexibility, and plasticizers are used to increase its flexibility for use as, for example, packaging wrap films, stretch films, and agricultural mulch films. However, there is evidence that the mechanical properties of the plasticized material are eroded by aging.^{34,35} PLA is a slow-crystallizing polymer, like PET, and it has long mold cycle time. It can be quenched into a quasi-amorphous state or crystallized upon annealing and/or orientation. When crystallized quiescently from un-nucleated state, PLA generally becomes opaque as a result of light scattering due to the formation of large spherulites.³⁶

PLA is, therefore, a thermosensitive material prone to morphological and chemical changes by variations in the temperature, time, and water content, which can have a great impact on its thermomechanical properties. The inadequate thermal stability of PLA during service puts restrictions on the range of possible large-scale applications. In view of the scarcity of available experimental results on the effects of environmental conditions on the mechanical properties and, especially, the tensile properties of PLA, the aim

of this study was to supplement the existing literature with extra measurements and analysis on the effects of RH, aging time, and temperature (where the chosen temperature was below the T_g of the material) on the molar mass and thermomechanical properties of PLA having a D-content of 4.25%, as evidenced by size exclusion chromatography (SEC), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and tensile measurements.

EXPERIMENTAL

The polylactide resin (PLA) was supplied by NatureWorks LLC, Minnetonka, MN. The selected grade 2002D had a D content of 4.25%, a residual monomer content of 0.3%, and a density of 1.24 g/cm³. The material in pellet form was dried at 45°C for a minimum of 8 h before use in a desiccating dryer. The melt processing of PLA was performed in a Brabender mixer at a temperature of 150°C, whereas the rotation speed of the screws was 40 rpm. The temperature for melt mixing was kept as low as possible to minimize the effect of degradation. Hereafter, the material was compression-molded at 130°C with a thermopress and a special mold 2 mm thick. The material was then cooled slowly to ambient temperature. The PLA samples were put in an oven and exposed at 80 ± 2% RH in an ambient saturated solution of NH₄Cl, at three different temperatures, 20, 40, and 50°C (±0.5°C), and at time intervals of 0, 30, 60, 80, 100, and 130 days. The aging temperature range was chosen to be below the T_g of PLA. The various aged samples were annotated as PLA *x/y*, where *x* is the number of days and *y* is the temperature (e.g., PLA 30/50); the unaged material, which was processed in the Brabender mixer and the thermopress, was denoted PLA_{proc}. The raw material in pellet form was designated PLA_{pellet}.

The evolution of the molecular weight of the PLA and its crystallinity contents at different temperatures and aging time intervals were recorded by SEC and DSC, respectively. All aged and unaged samples were dissolved in tetrahydrofuran without any insoluble residues being visible to the naked eye; this suggested that no crosslinking took place.

Calorimetric measurements were carried out with a Setaram DSC 141 (Caluire, France) instrument, calibrated with an indium standard. Each PLA sample (aged and unaged) was heated at a constant heating rate of 10°C/min from 20 to 170°C, and the thermogram was recorded. A supplementary procedure was performed on selected samples, namely, those that were exposed for 130 days at 20 and 40°C. After they were heated to 170°C, the PLA samples were isothermally held for 2 min, subsequently cooled to 0°C, held there for 5 min, and heated again at a rate of 10°C/min to 170°C. Thermograms of

both the first and second heating runs were recorded. We calculated the degree of crystallinity by considering a melting enthalpy of 93.1 J/g for 100% crystalline PLA.³⁸ Three sheet specimens 2 mm thick were tested for every aging procedure. DSC samples were taken from both the center and the tip of every PLA sheet, and we found that the DSC results were repeatable, with an average scatter lower than 5%.

The molecular weights and molecular weight distributions of the PLA samples were determined by SEC (Milford, MA) with a Waters system composed of a Waters 1515 isocratic pump, a set of three μ -Styragel mixed bed columns with a porosity range of 10^2 – 10^6 Å, and a Waters 2414 refractive-index (RI) detector (at 40°C), operated/controlled through Breeze software. Tetrahydrofuran, containing 3% (v/v) triethylamine, was the mobile phase and was used at a flow rate of 1.0 mL/min at 30°C. The setup was calibrated with linear polystyrene standards having weight-average molecular weights in the range 1250 to 900,000 g/mol. The PLA samples were dissolved directly in the carrier solvent overnight at concentrations of about 0.1% w/v and characterized the next day.

DMA experiments were performed with a Perkin-Elmer (Norwalk, CT) DMA 7e instrument. The mode of deformation applied was the three-point bending system, and the mean dimensions of the sample plaques were $2 \times 4 \times 20$ mm². The temperature varied from -50 to 130 °C. We studied the temperature-dependent behavior by monitoring changes in the force and phase angle, keeping the amplitude of oscillation constant. The experiments were performed at a constant frequency of 1 Hz, and the heating rate was 5°C/min. The storage and loss moduli and loss tangent curves versus temperature were evaluated.

Tensile measurements were performed with an Instron (Buckinghamshire, UK) 1121 type tester at room temperature. The dumbbell-type specimens were at a gauge length of 30 mm, and the applied crosshead speed was 0.2 mm/min. This value corresponded to an effective strain rate of 1.1×10^{-4} s⁻¹. The deformation could be measured very accurately with an experimental procedure, which was based on a noncontact method with a laser extensometer and was described in detail in a previous article.³⁹ Therefore, the true stress–strain curves were then obtained up to the breaking point. Five specimens were tested for each aging procedure, and the standard deviation between the experimental data was lower than $\pm 5\%$.

RESULTS AND DISCUSSION

SEC

The raw material in pellet form had a number-average molecular weight (M_n) of 197,000 and a polydis-

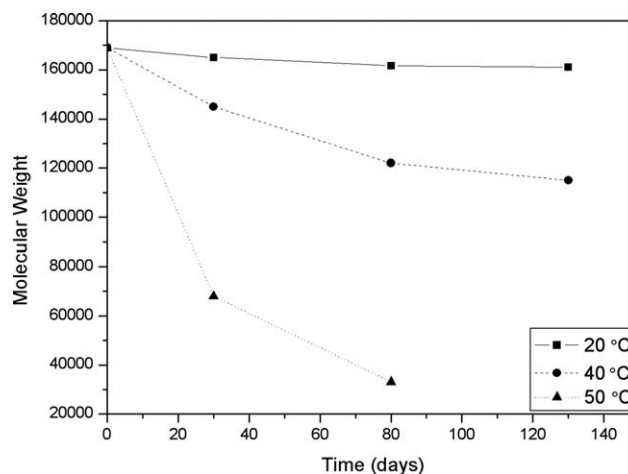


Figure 1 Variation of the PLA molecular weight with time at three different temperatures and 80% RH. Experimental data were obtained by SEC.

persity index (I) of 1.35. After melt processing, M_n was reduced to 169,000 and I was equal to 1.25. The drop in the molecular weight was attributed to the thermal oxidation of the PLA_{proc} sample during processing in the Brabender at a relatively low temperature (150°C).^{1,3,4}

The degradation of PLA was tested by examination of the molecular weight distribution after exposure to 80% RH at various temperatures, namely, 20, 40, and 50°C, for different time periods. The corresponding results of the molecular weight variation versus time are presented in Figure 1 as elution curves, and the M_n and I (M_w/M_n) values of the PLA samples measured by SEC are given in Table I.

As shown in Table I, after aging at 20°C for 130 days, PLA underwent little change in its molecular weight. Significantly lower molecular weights were measured for samples subjected to more intense degradation treatments. This is exemplified in Figure 2, which shows the elution curves of the PLA samples aged at 40 and 50°C for different time intervals. For comparison, the corresponding curve of the unaged sample (PLA_{proc}) is also presented. As shown in Figure 2, the elution peak shifted to a lower molecular weight with increasing temperature. Furthermore, the elution peaks of the aged samples displayed a higher contribution of low-molecular-weight fractions, which was attributed mainly to chain scission due to hydrolysis.

As shown in Table I, the M_n of PLA decreased dramatically when it was exposed for at least 80 days to 50°C at 80% RH; with a decrement on the order of 80%; after 130 days at the same temperature, the material was completely depolymerized. The reduction was much less pronounced at lower temperatures, namely, 4.8% at 20°C and 32% at 40°C after 130 days. As shown in Table I, the molecular

TABLE I
 M_n , M_w , and I Values of PLA Samples Measured by SEC Under Various Aging Conditions

Time (days)	20°C		40°C		50°C	
	M_n	$I = M_w/M_n$	M_n	$I = M_w/M_n$	M_n	$I = M_w/M_n$
0	169,000	1.25	169,000	1.25	169,000	1.25
30	165,000	1.25	145,000	1.55	68,000	1.56
80	161,700	1.26	122,000	1.56	33,100	5.59
130	161,000	1.26	115,000	1.56	—	—

The raw material in pellet form had an M_n value of 197,000 and an I value of 1.35.

weight of PLA was reduced with greater aging time at a given temperature. The effect of aging time became more pronounced at higher temperatures.

With regard to I , no dependence on the environmental conditions (aging time and temperature) was noticed, except for the temperature of 50°C, where $I = 5.59$ after 80 days.

The degradation process was very slow at temperatures equal or below 40°C, but the speed was greatly enhanced at 50°C. The degradation rate was quantified in terms of the average hydrolytic degradation rate constant (k_t). The k_t values were evaluated with the assumption of an exponential decrease of M_n with the following equation:⁷

$$\ln M_n(t_2) - \ln M_n(t_1) - k_t t$$

where t is the degradation time, $M_n(t_2)$ and $M_n(t_1)$ are the number-average molecular weights at the hydrolytic degradation times t_2 and t_1 , respectively. According to Figure 1, the M_n decrease rate was different depending on the time period of aging. Therefore, two different values for the constant k_t were evaluated. Apart from this, an average value of k_t for this constant was calculated over the entire period of aging. The estimated k_t values for the differ-

ent time intervals were 3.67×10^{-4} and 8.67×10^{-5} days⁻¹ at 20°C and 6.126×10^{-3} and 4.07×10^{-3} days⁻¹ at 40°C. The corresponding average values of k_t were 3.73×10^{-4} , 2.96×10^{-3} , and 20×10^{-3} days⁻¹ at 20, 40, and 50°C, respectively. The results show that the degradation rate was higher at the beginning (first 30 days) for every temperature and decreased significantly after 30 days. This finding was in agreement with previous results.^{1,15,22}

DSC

The DSC thermograms of the raw material (PLA_{pellet}), the unaged PLA samples (PLA_{proc}), and the aged PLA samples under various environmental conditions are presented in Figures 3–5. The DSC results, in terms of T_g , T_m , heat of fusion, and corresponding crystallinity content are summarized in Table II. As shown in Figures 3–5, the T_g region appeared at about 55°C, and in most cases, it was followed by an endothermic enthalpy relaxation, which was attributed to a secondary molecular reordering in the amorphous phase of the semicrystalline polymers. The T_g was defined from the endothermic peak position.

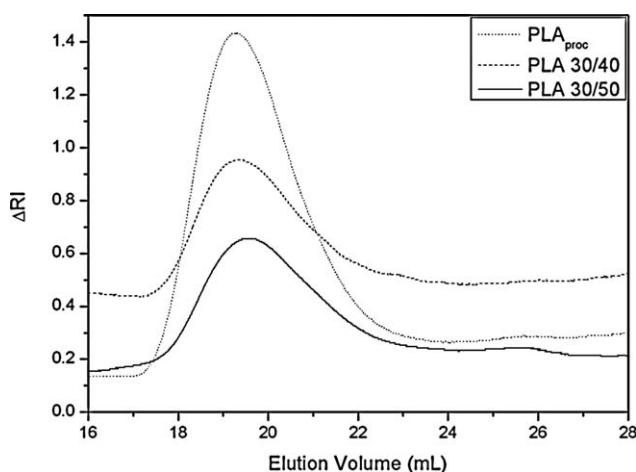


Figure 2 SEC chromatograms of PLA aged for 30 days at 80% RH and different temperatures.

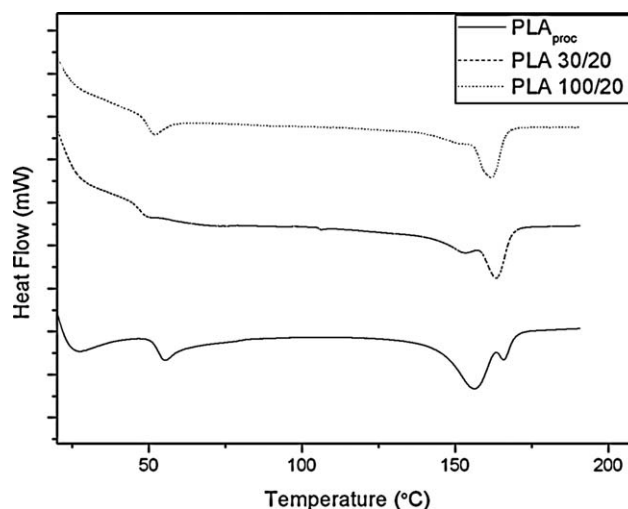


Figure 3 DSC results for PLA aged at 20°C and 80% RH for various time periods.

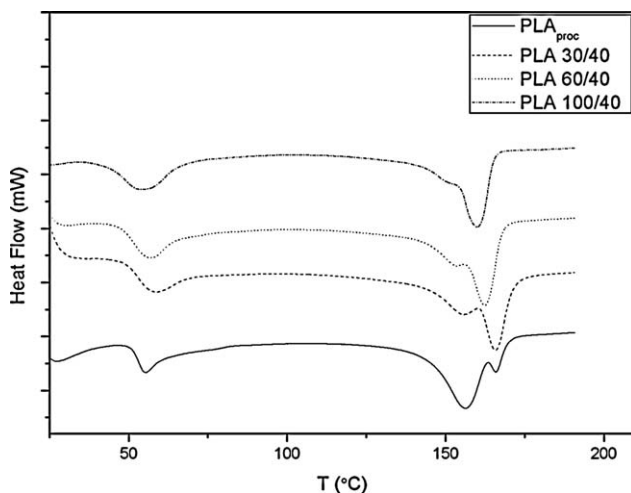


Figure 4 DSC results for PLA aged at 40°C and 80% RH for various time periods.

As shown in Figures 3 and 4, at temperatures of 20 and 40°C, respectively, T_g shifted slightly to lower temperatures with aging time. The dropping of T_g was attributed to the plasticization of the amorphous phase by the absorbed water, which penetrated between the polymer chains and increased their mobility. Two mechanisms were thought to be involved with the shift of T_g . The first was attributed to the plasticizing effect of the absorbed water, and the second was attributed to the degradation effect of water on the amorphous and crystalline fractions of the material. At 50°C, the shorter chains that arose by the degradation of PLA were reorganized in crystallites of lower melting points, which restricted the segmental mobility in the amorphous region.

As shown in Figures 3–5, the unaged sample (PLA_{proc}) showed a broad cold crystallization (exotherm) area extending from T_g up to T_m . When cold crystallization occurred, less perfect crystallites were formed, which melted during the DSC heating run. The exothermic area was attributed to the reorganization of the amorphous region into a crystalline one on account of the increased polymer chain flexibility and mobility as result of the thermal oxidation during processing. However, the total cold crystallization area was reduced by aging.

The PLA_{proc} sample also exhibited a bimodal melting peak, in which the first melting peak (T_{m1}) was lower than the second one (T_{m2}). With time, the T_{m1} peak diminished, with this effect being more pronounced at 20 and 40°C (Figs. 3 and 4), and eventually disappeared at 50°C (Fig. 5), whereas the magnitude of the T_{m2} peak increased, and the peak temperature shifted slightly to a lower temperature. The diminishing of the T_{m1} peak with time was attributed to the reorganization of the crystals, which arose from the cold crystallization during aging. Water absorbed during aging at temperatures

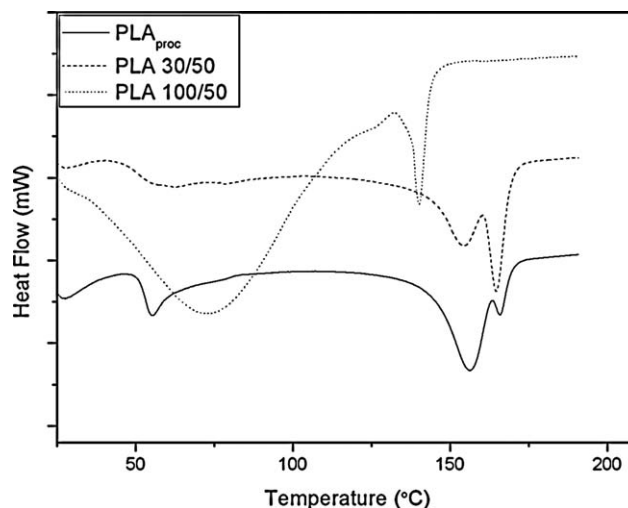


Figure 5 DSC results for PLA aged at 50°C and 80% RH for various time periods.

equal or lower than 40°C and acting mainly as a plasticizer promoted either the growth or perfection of already existing crystallites.^{10,40} The T_{m2} peak was attributed to the inherent crystallinity of the material. Alternatively, the T_{m2} peak resulted from the recrystallization of the crystallites of the T_{m1} peak according to the melt recrystallization model.⁴¹ This model suggests that the small and/or imperfect crystals changed successively to more stable crystals through the melt-crystallization process. The T_{m1} and T_{m2} peaks suppressed recrystallization, which was not revealed on the DSC thermograms. The slight shift to lower temperatures of the T_{m2} melting peak was attributed to the incurred degradation during the physical aging of the PLA samples at room temperature.

Samples aged at 50°C for 30 days showed an increase in crystallinity (see Table II). The lower molecular weight ($M_n = 68,000$) and effect of interactions with water were likely to have enhanced the mobility and, in combination with the formation of a

TABLE II
DSC Results

Sample type	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH^* (J/g)	Crystallinity (%)
PLA _{pellet}	60.0	153.4	26.5	28.5	
PLA _{proc}	55.4	156.9	165.9	33.8	36.3
PLA 30/20	49.0	153.5	163.7	34.1	36.6
PLA 60/20	49.2	153	162.2	32.0	34.3
PLA 100/20	51.5	—	161.3	27.8	29.9
PLA 30/40	58.0	156.0	165.7	28.7	30.8
PLA 60/40	56.4	153.1	162.6	39.9	42.8
PLA 100/40	54.0	150.0	159.8	38.7	41.6
PLA 130/40	55.7	155.1	164.6	30.8	33.0
PLA 30/50	54.0	154.0	165.1	35.4	38.0
PLA 100/50	—	140.0	12.70	13.6	

* Heat of fusion.

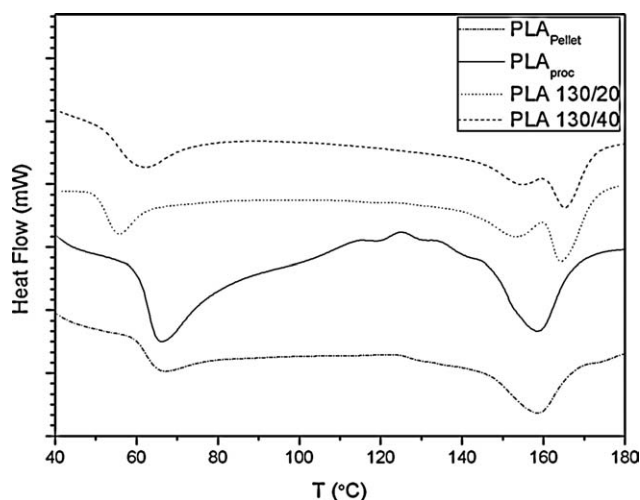


Figure 6 DSC results for the first heating scan of PLA aged for 130 days at 80% RH and two different temperatures.

higher number of crystallization centers that could have originated from the degradation products, could have led to the formation of crystallites with lower melting points.^{15,42}

The role of heating history on the aging behavior of the material was also investigated and is shown in Figures 6 and 7, which present the DSC thermograms of the first and second heating runs, respectively, of PLA in pellet form, PLA_{proc}, and the selected aged samples PLA/130/20 and PLA/130/40.

The T_g of the second run was lower than the T_g of the first run in all of the samples. This was attributed to the difference in the crystallinity between the two runs of the PLA_{proc} sample. The higher crystallinity of the first run was considered to restrict the segmental mobility in the amorphous region.

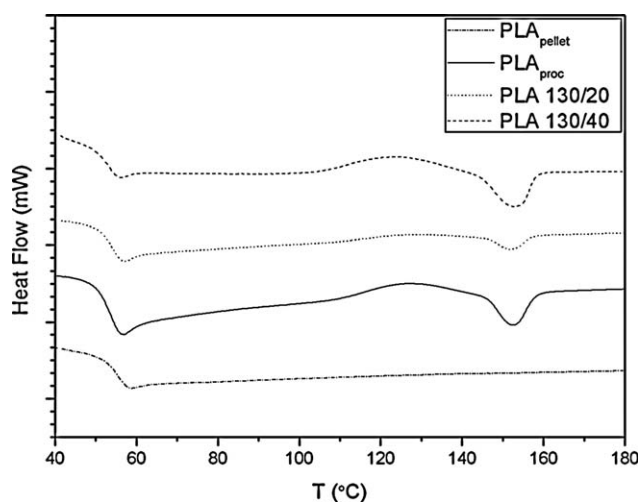


Figure 7 DSC results for the second heating scan for PLA aged for 130 days at 80% RH and two different temperatures.

T_m and the crystallinity content of the second run was always lower than the T_m of the first run in all of the tested PLA samples (cf. Figs. 6 and 7). The first heating run of the aged samples showed two melting peaks, which were reduced to one peak in the second run, which corresponded to the lower melting peak of the first run. The broad melting peak of the PLA_{proc} sample of the first run shifted to a lower temperature and decreased in size. Particularly, the first heating run of the PLA pellets showed an endothermic peak ($T_m = 158^\circ\text{C}$), which disappeared in the second heating run, where no endothermic or exothermic peak was detected at all. This behavior was in agreement with the reported slow crystallization rate of high-molecular-weight PLA, which did not allow the development of crystalline domains upon cooling.^{1,17} On the other hand, the appearance of an endothermic peak in the second run of the processed and aged samples was attributed to the increased molecular flexibility as result of the lower molecular weight, as observed by SEC, in combination with the enhanced mobility as result of the absorbed water, which favored the development of crystallites. The slow crystallization of PLA was a disadvantage for the processing of the material; very long cooling times of up to several minutes were necessary to obtain partially crystalline moldings having heat deflection temperatures above the T_g .

The induced morphological changes would significantly influence the material's performance during aging, and any application (e.g., packaging) needed to take into account such morphological changes and their effect on the material properties.¹⁵

DMA

The dynamic mechanical relaxation behavior of the aged and PLA_{proc} samples is presented by the temperature dependence of loss modulus in Figures 8–10. In these plots, the effect of aging time and temperature (80% RH) can be examined. In Figure 8, the effect of aging time (30 days) is presented for three temperatures, 20, 40, and 50°C. Figure 9 exhibits the effect of time for the same temperature of 20°C, whereas Figure 10 reveals the same effect for the temperature of 40°C. A single glass transition was observed, which was about 10°C higher than the T_g measured by DSC.

As shown in the loss modulus plot of Figure 9, a single peak at about 64°C was observed for samples aged at 20°C and 80% RH for 30 and 130 days. A slight shift of the peak to a lower temperature and a reduction of its intensity was observed only for the sample aged for 130 days. The decrease in loss modulus was correlated to the plasticization effect of water absorbed after 130 days of aging.

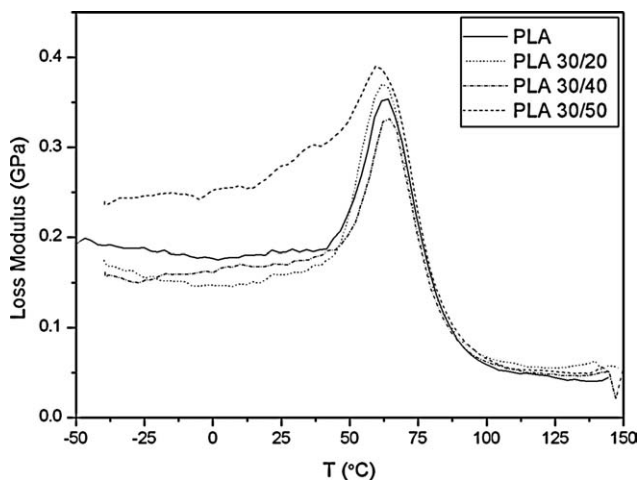


Figure 8 Loss modulus versus the temperature at the frequency of 1 Hz for PLA aged for 30 days at 80% RH and different temperatures.

The samples aged at 40°C and 80% RH also showed a slight shift of a few degrees of the peak to lower temperatures with a more pronounced reduction of its intensity after 130 days (Fig. 10).

As shown in Figure 8, the position and magnitude of the peak remained almost invariable for samples aged for 30 days at temperatures up to 40°C. Only at 50°C was a shift of the T_g to lower temperatures observed accompanied by a broadening of the peak. This was an indication that at up to 40°C, no substantial structural changes took place in the material.

Tensile results

The tensile results of the unaged sample and PLA samples exposed to 80% RH under different conditions of time and temperature are summarized in

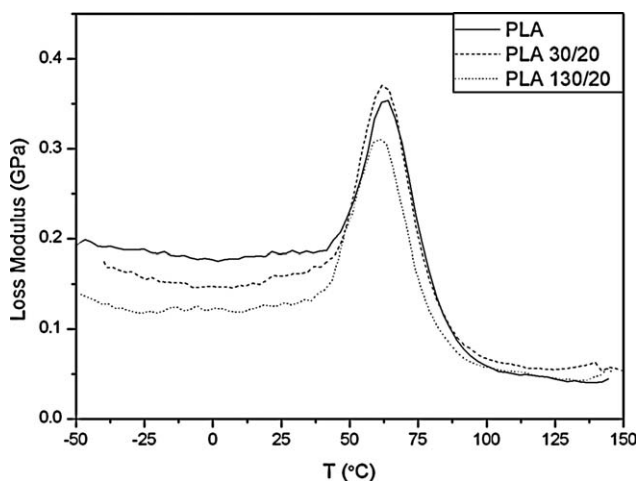


Figure 9 Loss modulus versus the temperature at the frequency of 1 Hz for PLA aged at 20°C and 80% RH for various time periods.

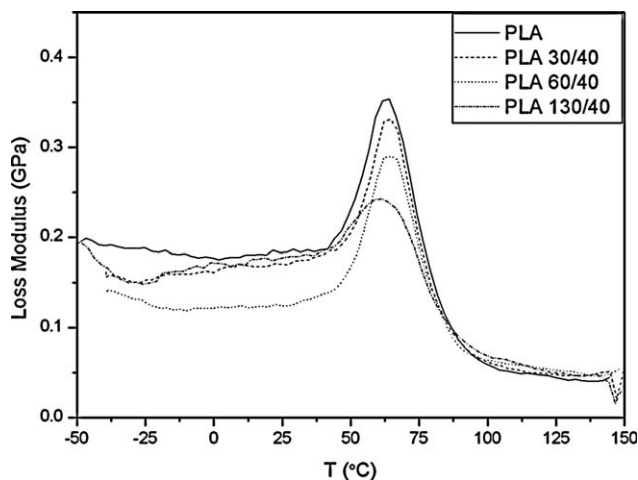


Figure 10 Loss modulus versus the temperature at the frequency of 1 Hz for PLA aged at 40°C and 80% RH for various time periods.

Table III. The corresponding stress–strain curves are plotted in Figures 11–13. In Figure 11, the tensile stress–strain curves are plotted to compare the PLA_{proc} sample with the aged samples exposed to 80% RH at three different temperatures for the same time period of 30 days. Figures 12 and 13 show the variation of the tensile curves at temperatures of 20 and 50°C, respectively, for various time periods. All of the tensile results confirmed the general knowledge⁴³ that PLA is a brittle material with a low possible elongation.

The unaged PLA sample displayed a yield stress manifested as a gradual slope change, which followed the initial linear part of the stress–strain curve. Yielding occurred at a strain about 2.6%. Thereafter, PLA_{proc} was driven to fracture at a strain equal to 3.5%. The tensile behavior of the PLA samples exposed to various conditions of degradation was gradually turned to lower values of Young modulus, tensile strength, and strain at break. After 100 days of aging at a temperature of 50°C, the tensile property decrement appeared to be the highest.

TABLE III
Tensile Results

Sample type	Young's modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
PLA _{proc}	3.2	57.0	0.035
PLA 30/20	3.0	49.0	0.018
PLA 130/20	2.6	42.3	0.016
PLA 30/40	2.6	40.5	0.016
PLA 30/50	1.9	39.1	0.032
PLA 100/50	1.5	20.0	0.013

Five specimens were tested for each aging procedure, and the standard deviation between experimental data was lower than $\pm 5\%$.

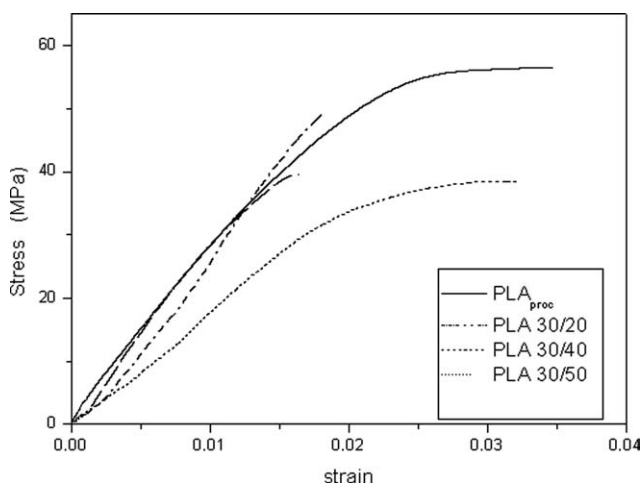


Figure 11 Tensile stress–strain results at a strain rate of $1.1 \times 10^{-4} \text{ s}^{-1}$ for PLA aged for 30 days at 80% RH and three different temperatures.

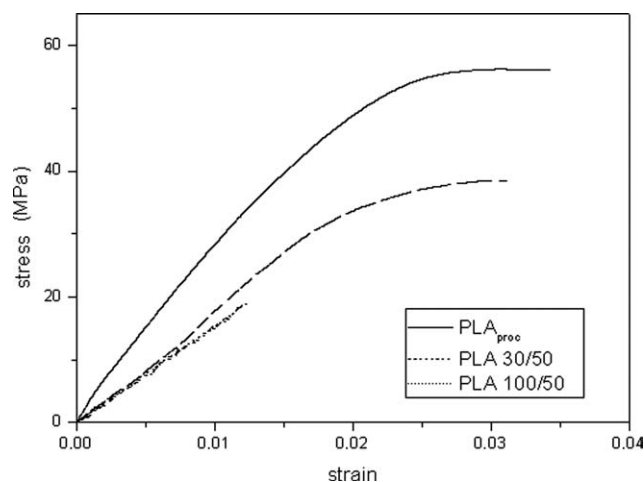


Figure 13 Tensile stress–strain results at a strain rate of $1.1 \times 10^{-4} \text{ s}^{-1}$ for PLA aged at 50°C and 80% RH for various time periods.

Namely, decrements of 51.4% for the Young's modulus, 65% for the tensile strength, and 67.5% for the strain at break were observed. With regard to exposure at 40°C for 30 days, the Young's modulus decreased 8%, whereas the tensile strength decreased 30%, which was a sufficiently lower degradation compared to that at 50°C. Lower values, on the order of a 20% decrement, were observed after 130 days at 20°C, whereas PLA embrittlement was more pronounced even at this ambient temperature.

With regard to the strain at break, after an initial decrease at 20°C, no further loss was observed for the aged samples, except for the sample exposed to 50°C for 130 days and 80% RH, where the strain at break decreased by 67.5%. Taking into account that the molecular weight did not change substantially when the PLA samples were aged at 20 and 40°C

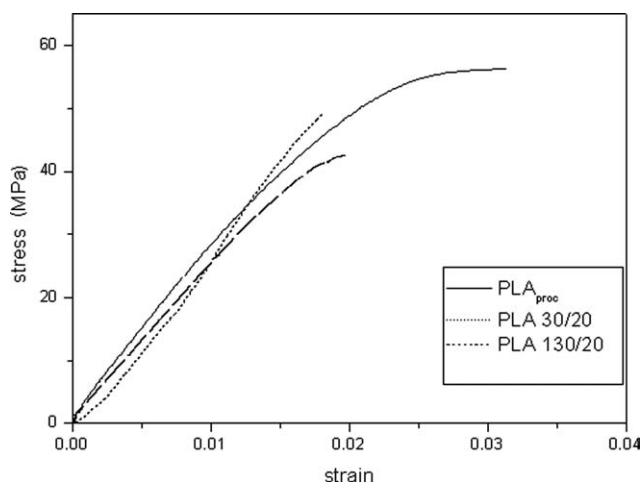


Figure 12 Tensile stress–strain results at a strain rate of $1.1 \times 10^{-4} \text{ s}^{-1}$ for PLA aged at 20°C and 80% RH for various time periods.

for up to 130 days (see Table I), we deduced that at this temperature range, the elongation at break was not affected by the hydrolytic degradation and/or plasticizing effect of the absorbed moisture. The plasticizing effect of water was somewhat analogous to the reported effects of other plasticizers. The sharp decrease in the elongation at break (67.5%) for samples aged at 50°C for 130 days and 80% RH was attributed to the irreversible change in the molecular structure toward a lower degree of polymerization caused by the hydrolysis of the PLA molecules in accordance with the SEC results shown in Table I and Figure 2. The PLA sample aged at 50°C for 30 days appeared to retain its ductility. This unusual behavior could be explained in terms of the extra plasticizing effect of the lactic oligomers, which resulted from the hydrolysis of the ester bonds of the backbone, on the remaining high-molecular-weight ($M_n = 68,000$) polymer chains.

The Young's modulus (rigidity) decreased in general with aging time and temperature. Between 20 and 40°C, the Young modulus decreased only slightly during the various aging periods. The Young's modulus of a semicrystalline material is related to the crystallinity content and its molecular weight. As the molecular weight was not substantially affected by the aforementioned aging conditions, it appeared that the rigidity of the material was slightly affected by the absorbed moisture. This behavior was not in full agreement with the typical behavior of a plasticized material, where a decrease in Young's modulus is expected with increasing moisture content.³⁰ The sharp decrease in the Young's modulus at 50°C was attributed to the induced hydrolysis of the PLA molecules in the amorphous and crystalline regions, in accordance with the SEC results shown in Table I.

The tensile strength decreased steadily with aging time and temperature. To distinguish the contribution of reversible versus irreversible changes toward the loss of the tensile strength, selected aged PLA samples were exposed to a low 25% RH for 80 days. Samples aged at 20 and 40°C regained almost 90 and 80% of their initial tensile strength, respectively, after exposure to dry conditions. This finding was in agreement with other results carried out on aged samples of PLA copolymers under similar conditions.³⁰ The mechanism proposed is that the absorbed moisture was removed during the drying, and the plasticization of samples aged at 20 and 40°C was nearly reversed. Samples aged at 50°C did not regain their initial strength, probably as result of the induced hydrolytic degradation of PLA.

CONCLUSIONS

The role of environmental parameters and physical structure in the aging process of PLA was investigated on a number of PLA samples with a D-content of 4.25% aged at temperatures below the T_g of the material for various aging periods. The initial thermal processing (150°C) of the material resulted in an overall molecular weight reduction. A substantial decrease in the properties was observed for PLA samples aged at 20°C for 30 days. No further loss of properties was observed for samples aged up to 40°C for several time intervals. A major portion (80–90%) of the induced changes in the tensile properties were reversed after drying. At 50°C and 100 days of aging, a sharp decrease in the overall properties was noticed. The results seem to confirm the earlier finding that PLA degradation driven by hydrolysis needs a higher temperature in combination with ample time to take place (>50°C).

The degradation process was very slow at temperatures equal or below 40°C, but the speed was greatly enhanced at 50°C. The results showed that the rate of degradation was higher at the beginning (first 30 days) and then decreased significantly over time. Three mechanisms were proposed for the interpretation of the experimental results. The initial drop in the molecular weight was attributed to the thermal oxidation of the material during processing in the Brabender. The decrease in the properties observed for the PLA samples aged at 40°C or lower for different time intervals was attributed to the plasticizing effect of the absorbed water, which increased the molecular mobility of PLA and resulted in faster nucleation and crystallization of the PLA molecules. The time required by water to permeate and plasticize the polymer structure was at least 1 month. At 50°C, water acted mainly as a degradation (hydrolysis) agent, and the shorter chains that arose by the degradation of PLA were

reorganized in crystallites with lower melting points. The hydrolysis of PLA at higher temperatures ($\geq 50^\circ\text{C}$) needed at least 3 months to complete. The calculated values were indicative because extra parameters, such as the size and shape of the sample, could influence the calculations.

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