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Internal Motions in Polylactide and Related Polymers

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ABSTRACT: Polylactide (~95% L-isomer), polyglycolide, and a 1:1 copolymer were studied by differential scanning calorimetry, dynamic mechanical analysis, and dielectric relaxation. In addition to the previously known glass transitions, all of these polymers exhibit a relaxation similar to the β-relaxation which occurs in many other materials. This relaxation, which occurs near 200 K at 1 kHz, is attributed to noncooperative local motions. Another new relaxation near 15 K was found in polyactide and the copolymer but not polyglycolide and hence is attributed to motions of the methyl side groups. The effect of increased humidity on polylactide was also investigated. The weight gain of the samples depends strongly on the relative humidity and continues over extended periods of time. Changes in the dielectric relaxation spectra were consistent with substantial decreases in molecular weight.

Introduction

Polyglycolide, polylactide, and their copolymers are of interest for biomedical applications because of their ability to decompose over a period of time. Polyglycolide has been reported to have a glass transition temperature, T_g, of 35–45 °C and a melting point, T_m, from 210 to over 233 °C.[1–5] Poly(L-lactide) has been reported to have a glass transition temperature of 55–64 °C and a melting point of 159–215 °C,[1,4–11] while poly(D,L-lactide) is an amorphous polymer with a glass temperature of 50–57 °C.[4,8,12] Polyglycolide, poly(L-lactide), and their copolymers can all be quenched to an amorphous state, and copolymers with 25–70 mol % glycolide remain amorphous on annealing.[1] The internal motions of these materials were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and dielectric relaxation (DR) measurements. The effect of humidity on polylactide was investigated via weight gain and DR measurements.

Experimental Section

Sample Preparation and Differential Scanning Calorimetry. Polylactide (~95% L-isomer), polyglycolide, and a 1:1 copolymer were received from Dr. Thomas M. Ford of this laboratory made from the cyclic diesters shown schematically in Figure 1. Lactic acid has an asymmetric carbon atom which is retained in both rings and linear polymers. The mixed lactide–glycolide leads to a 1:1 copolymer and, since the ring can open at either of the two ester groups, the copolymer is not expected to be strictly alternating. This is consistent with the fact that this copolymer is amorphous in contrast to the homopolymers.

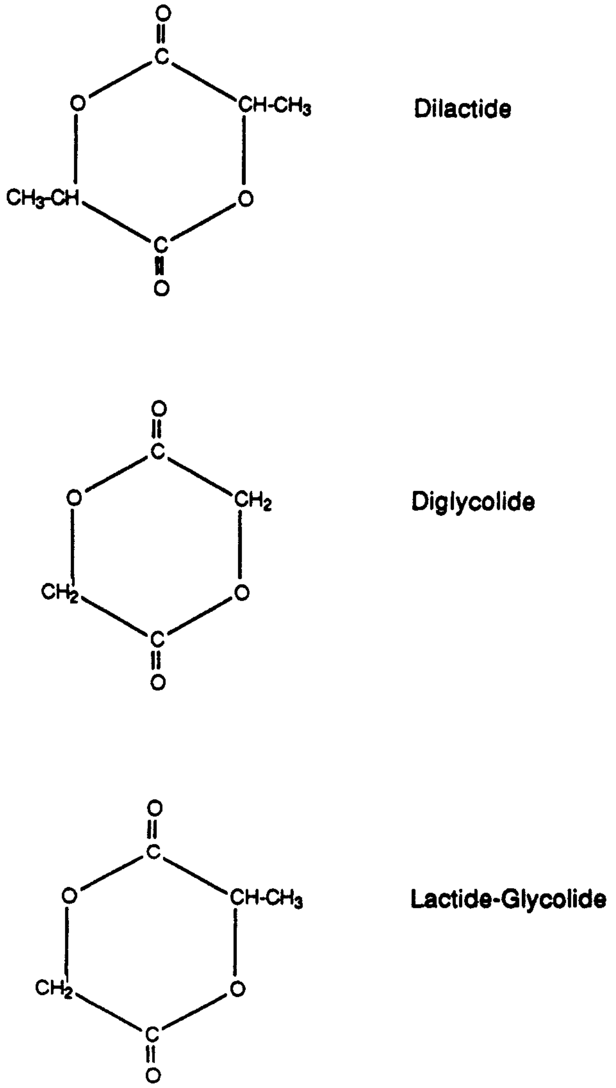

Figure 1. Intermediates.

All DSC scans were run on a TA Instruments (formerly Du Pont Instruments) Model 910 machine, at a scan rate of 10 °C/min. Three samples of polylactide were prepared at different levels of crystallinity. Sample 1 was molded at 185 °C and air cooled on the bench. The data for this sample showed a crystallization exotherm at T_c and a melting endotherm at T_m which were of equal magnitude, within experimental uncertainty, and so the sample was assumed to be amorphous. Sample 2 was molded at 175 °C, cooled to 105 °C, and held there for 45 min. The DSC scan showed a crystallization exotherm and a melting endotherm of different magnitudes, and the difference between the heat of fusion, ΔH_f, and the heat of crystallization, ΔH_c, was 20.7 J/g. Some of this material was then annealed under vacuum at 110 °C for 30 min to maximize the crystallinity, and this was

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Table I. DSC Data on Polylactide

	sample 1	sample 2	sample 3
T_g, °C	55	52	48
T_c, °C	111	106	
ΔH_c, J/g	5.2	2.5	
T_m, °C			
peak	149	141, 149[a]	(131), 148, 153
end	152	153	156
ΔH_f, J/g	5.0	23.2	46.9
net ΔH_f, J/g	nil	20.7	46.9

[a] In the case of multiplet endotherms, the temperature of the largest peak is underlined and that of the smallest is in parentheses.

Table II. DSC Data on Polyglycolide

	sample 4	sample 5
T_g, °C	44	
T_c, °C	75	
ΔH_c, J/g	27.4	
T_m for peak, °C	222	222
ΔH_f, J/g	29.1	56.7
net ΔH_f, J/g	1.7	56.7

designated as sample 3. The heat of fusion for sample 3 was 46.9 J/g, and there was no crystallization exotherm. A summary of the results of analysis of the DSC is given in Table I.

Two samples of polyglycolide were studied. Both were molded at 240 °C, but sample 4 was quenched in water at room temperature, whereas sample 5 was cooled to 180 °C under pressure, held for 30 min, and then cooled to room temperature at atmospheric pressure. Values for the heat of fusion of 100% crystalline polyglycolide in the literature vary between 180 and 202 J/g.[14,15] Assuming an average value of 190 J/g, the calculated crystallinities of samples 4 and 5 were 1 and 30%, respectively. A summary of the results of analysis of the DSC data are given in Table II. As expected, the 1:1 lactide glycolide copolymer showed a DSC scan typical of an amorphous material. The glass transition temperature is 43 °C.

Dynamic Mechanical Properties. Dynamic mechanical measurements were carried out at a frequency of 1 Hz using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA). Plots of the storage modulus, E' (in Pa), and tan δ vs temperature for the three polylactide samples (samples 1–3) discussed above are shown in Figure 2. Softening at the glass transition near 50 °C is observed for all three samples, and increases in the modulus due to crystallization near 100 °C are clearly seen for samples 1 and 2. The magnitude of these effects decreases as the crystallinity of the sample increases. Finally, the modulus begins to decrease as the melting point near 150 °C is approached. Similar observations have been reported in the literature.[11,16] There is also evidence in the tan δ plot of a broad secondary relaxation near −50 °C.

Dielectric Properties. Electrical relaxation measurements were performed as described previously[13] using 17 frequencies from 10 to 10^5 Hz. Typical results in the form of a tan δ vs temperature plot at 10^2, 10^3, and 10^4 Hz for sample 1 of polylactide are shown in Figure 3. The α-relaxation associated with the glass transition is observed near 340 K (67 °C) as well as the broad β-relaxation near 220 K (−53 °C). There is also a well-defined shoulder at about 15 K. Since there is no maximum, its temperature–frequency relationship is not clear from the data, although the dissipation factor appears to increase with increasing frequency. This is in contrast to the discussion of Celli and Scandola[16] on poly(L-lactic acid). They stated that they saw no secondary relaxations below the glass transition although their plots of dielectric results at frequencies from 0.3 to 50 kHz and dynamic mechanical data show a weak, broad maximum in tan δ near 220 K (−53 °C).

Electrical relaxation data at 1 kHz for polylactide, two polyglycolide samples, and a copolymer sample are shown in Figure 4. Not surprisingly, the height of the β-peak is larger in the quenched polyglycolide sample than for the annealed sample. The reason is that the quenched sample is more amorphous. In addition, the β-peak for the copolymer sample which is highly amorphous is also strong. In the region of the 15 K relaxation, the shoulder in the tan δ curve is most obvious for the polylactide sample, smallest in polyglycolide, and intermediate for the copolymer. This is consistent with assigning this relaxation to motions of the methyl side groups. The fact that this motion, although very weak, is dielectrically active is attributed to the distortion of bond angles or the sympathetic motion of adjacent ester groups.

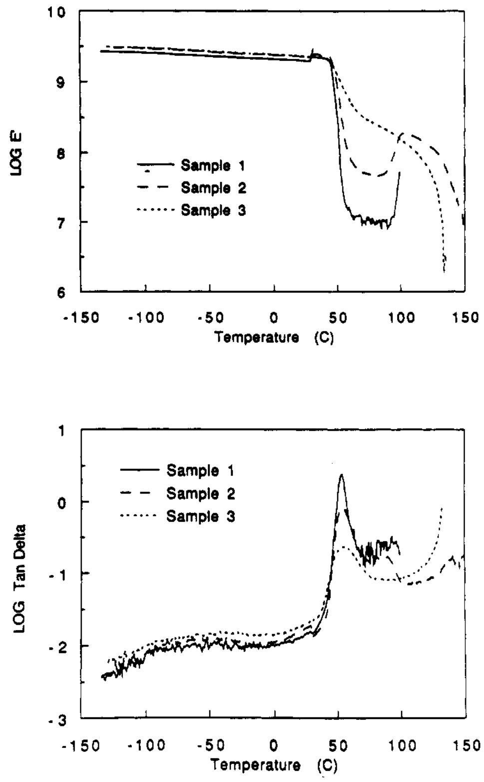

Figure 2. Dynamic mechanical properties of polylactide.

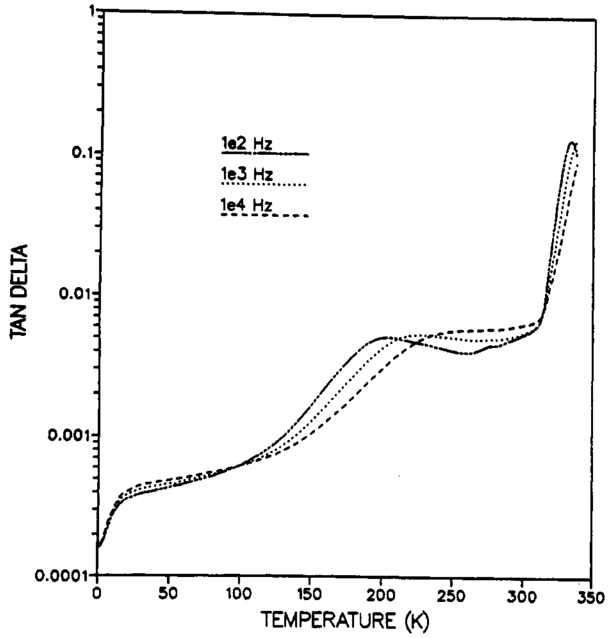

Figure 3. Dielectric tan δ of polylactide.

The properties of the α- and β-relaxations are summarized in Table III. The presence of the methyl groups apparently shifts the α-relaxation to slightly higher temperatures. The apparent Arrehnius activation energies of the α-relaxations, E_a, of 71–74 kcal/mol (297–310 J/g) are lower than the value of 420 J/g reported by Celli and Scandola[16] for poly(L-lactic acid).

The temperature and the activation energy for the β-relaxation are somewhat higher for polyglycolide than for polylactide and the copolymer. This may reflect a more cooperative character for this internal motion. For polylactide and the copolymer, the

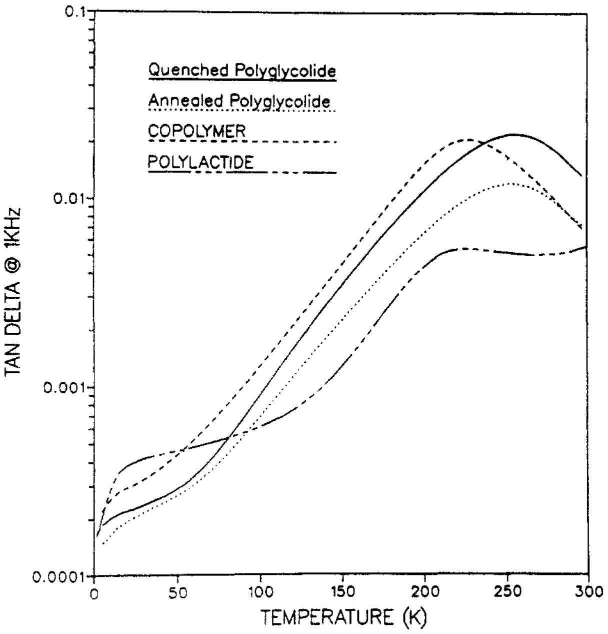

Figure 4. Comparative low-temperature dielectric behavior.

Table III. Dielectric Relaxations

	polylactide	polyglycolide[a]	1:1 copolymer
	α-Relaxation		
temp (K) at 1 kHz	341	332	338
E_a (kcal/mol)	74	74	71
E_a (kJ/mol)	310	310	297
	β-Relaxation		
temp (K) at 1 kHz	228	255	224
E_a (kal/mol)	8.7	12	9.2
E_a (kJ/mol)	36	50	38.5
$\Delta F^{\ddagger}$ (kcal/mol)	9.2	10.4	9.0
$\Delta F^{\ddagger}$ (kJ/mol)	38.5	43.5	38

[a] In the quenched and annealed samples of polyglycolide, these properties are very similar.

Arrhenius activation energy was about 9 kcal/mol, and the Eyring activation free energy defined by

$$\Delta F^{\ddagger} = RT[\ln(k/2\pi h) + \ln(T/f)]$$

was essentially independent of temperature. This means that the activation entropy is close to zero, a characteristic of a simple, noncooperative process.[17,18]

Effect of Humidity. Most of the interest in polylactide is related to its ability to degrade, with major decreases in molecular weight occurring within a few months at room temperature and moderate levels of relative humidity (RH). We followed the gain in weight at room temperature and 23, 43, and 97% RH. The data are plotted in Figure 5. The most striking feature is that the weight continued to increase with time with no tendency to level off. After about 140 days, the weight gains were 0.2% at 23% RH, 0.9% at 43% RH, and 27% at 97% RH. At this point, the sample which had been exposed to 97% RH was very brittle. The effects of these treatments are summarized in Table IV.

Electrical relaxation data at higher temperatures for the 43% and 97% RH samples and a dry control sample are shown in Figure 6. The dry and 43% RH samples show single features in the region of the α-relaxation and broad relaxations in the vicinity of the β-relaxation. In contrast, the 97% RH sample has several features above 280 K and a substantial peak at about 180 K with a shoulder on the high temperature side. Figure 7 shows a complex plane plot for the three samples at a frequency of 1 kHz. The difference in the value of ϵ' from one side of a peak in ϵ'' to the other gives the strength, $\epsilon'_r - \epsilon'_u$, of the relaxation. Estimates of the strengths of the α- and β-relaxations in the three samples are given in Table IV, showing that the strength of the β-relaxation in the 97% RH treated sample is almost as large as those of the α-relaxations in other samples. However, the activation energy remains low and the activation entropy is close to zero as for the other β-relaxations. This effect is presumably related to the decrease in the molecular weight of the polymer as decomposition progresses, presumably by increasing the number of dipoles able to reorient.

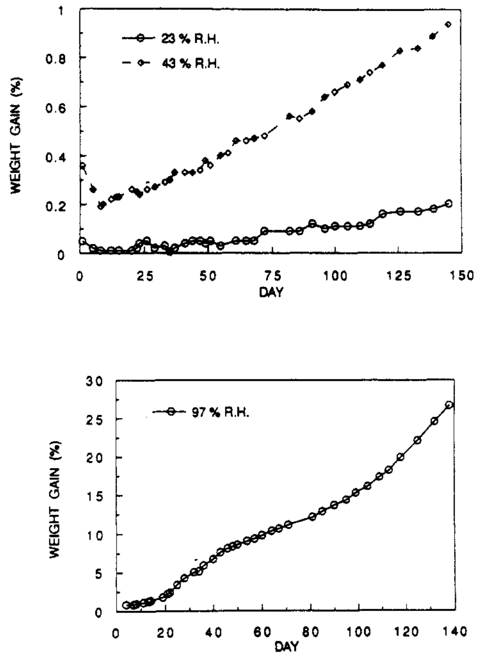

Figure 5. Weight gain of polylactide at various humidities.

Table IV. Effect of Humidity on Polylactide (ca. 140 days)

relative humidity (%)	dry	43	97
weight gain (%)		0.89	27.05
α-relaxation			
T (K) at 1 kHz	341	337	
ϵ_r	7.43	6.29	
ϵ_u	3.51	2.96	
$\epsilon_r - \epsilon_u$	3.92	3.33	
β-relaxation			
T (K) at 1 kHz	229	219	183
E_a (kcal/mol)	8.9	8.4	7.8
E_a (kJ/mol)	37	35	33
$\Delta F^{\ddagger}$ (kcal/mol)	9.5	8.7	7.3
$\Delta F^{\ddagger}$ (kJ/mol)	40	36	30.5
ϵ_r	3.51	2.96	5.18
ϵ_u	3.14	2.20	2.23
$\epsilon_r - \epsilon_u$	0.37	0.76	2.95

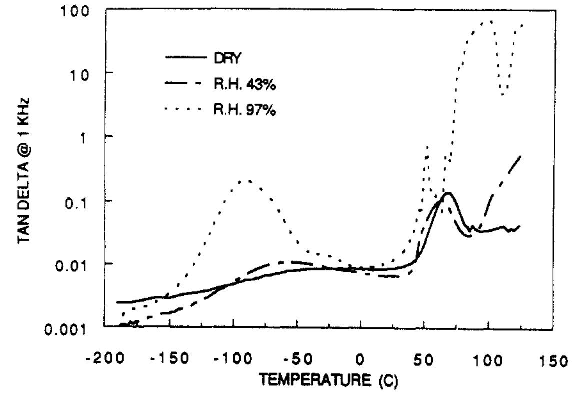

Figure 6. Effect of humidity on the dielectric tan δ of polylactide.

Conclusions

Like many other polymers, polylactide, polyglycolide, and a 1:1 copolymer exhibit secondary relaxations at temperatures below the glass transition. The β-relaxation near 220 K has an activation entropy which is extremely small and hence the relaxation is attributed to noncooperative local motions. An additional relaxation near 15 K

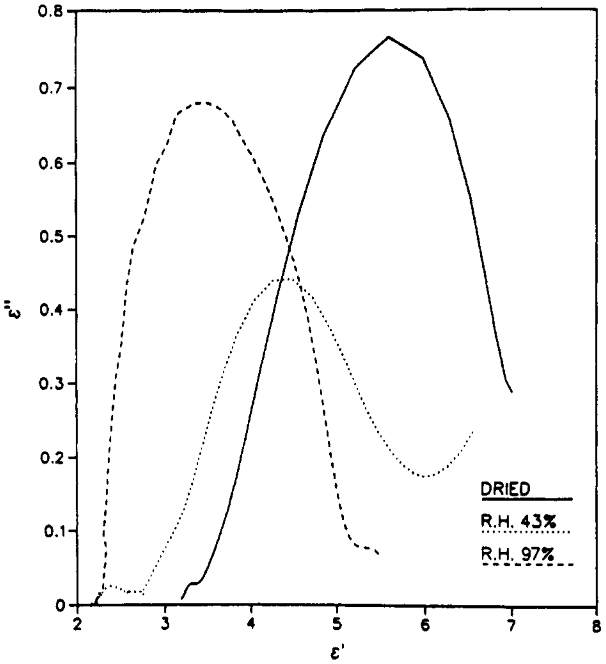

Figure 7. Isochronal complex plane plot for dielectric data taken at 1 kHz on polylactide at three humidity levels.

in polylactide and the copolymer, but not polyglycolide, and is probably associated with the methyl side groups.

The sorption of water by polylactide samples continues for extended periods of time. The sorption of small amounts of water shifts existing peaks to lower temperatures. The sorption of large amounts of water causes the complication of the dielectric relaxation spectra for polylactide samples by introducing new peaks at high temperatures and dramatically increasing the strength of the β-relaxation peak.

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