Thermomechanical Film Properties and Aging of Blends of Poly(lactic acid) and Malonate Oligomers

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ABSTRACT: Malonate oligomers were synthesized as plasticizers for poly(lactic acid) (PLA). Esterification reactions were performed between diethyl bishydroxymethyl malonate (DBM) and either adipoyl dichloride or succinyl dichloride. Two molar masses were obtained within each series. Blending was carried out with PLA and the four oligomers as well as the monomeric unit from the syntheses (DBM). Dynamic mechanical analysis and differential scanning calorimetry were used to investigate the viscoelastic mechanical and thermal film properties of the blends. All the investigated plasticizers reduced the glass-transition temperature of PLA, and the plasticization effect was better for the plasticizers of low molar mass. However, the amorphous domains of PLA became saturated with plasticizer at a certain concentration, and phase separation occurred. A higher molar mass of the plasticizer caused this saturation to occur at lower plasticizer concentrations. Subsequently, the aging of the blends at the ambient temperature for 4 months induced phase separation in the blends containing DBM, whereas those with an oligomeric plasticizer were stable and remained compatible with PLA within the aging period. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2140–2149, 2004

Key words: ageing; compatibility; oligomers

INTRODUCTION

Poly(lactic acid) (PLA), a thermoplastic that can be produced from renewable resources, is an interesting polymer for producing packaging materials.[1] It has a number of remarkable properties, including biodegradability, biocompatibility,[1,2] good mechanical properties, and processability.[3,4] Presently, mainly polyolefins are used for packaging applications, and so it would be of great benefit to the environment if PLA could replace polyolefins in this area. However, the film extrusion of PLA would be required because many packaging materials contain polymer films, and this remains a difficult process because of the brittleness and thermal instability of PLA.[5]

The flexibility of PLA can be improved through the physical modification of the polymer, such as the copolymerization[6–13] or blending of PLA with a plasticizer or a second polymer. Various substances have been blended with PLA and investigated as potential modifiers of its physical properties. Such polymers include thermoplastic starch,[14] poly(ethylene oxide),[7,15,16] poly(ε-caprolactone),[6,7,17–23] poly(vinyl acetate),[24] poly(hydroxyl butyrate),[25–28] poly(cellulose acetate),[29] poly(butylene succinate),[30,31] and poly(hexamethylene succinate).[32] As plasticizers for PLA, poly(ethylene glycol),[8,14,33–36] oligomeric lactic acid,[14] glycerol,[14] triacetine,[37,38] and low-molar-mass citrates[37,39] have been investigated.

The requirements of packaging applications drastically limit the possible choices of polymers or plasticizers to be used as modifiers for PLA. It is essential that the selected substances be nontoxic and approved for food contact. Other important requirements include that the plasticizer be miscible, or at least compatible, with PLA, thus creating a reasonably homogeneous blend. In addition, the plasticizer should not be too volatile because this would cause it to evaporate at the elevated temperatures used during processing. Nor should migration of the plasticizer occur, as this would contaminate the food or beverage in contact with the plasticized PLA. Migration would also cause the blended material to regain the brittleness of neat PLA.

It was previously observed[37] that low-molar-mass plasticizers such as tributyl citrate (TbC) and triacetine caused a drastic decrease in the glass-transition temperature (T_g) of PLA, thus creating a homogeneous and flexible film material. Although it was also observed that the plasticizers migrated to the film surface after the aging of the materials at the ambient
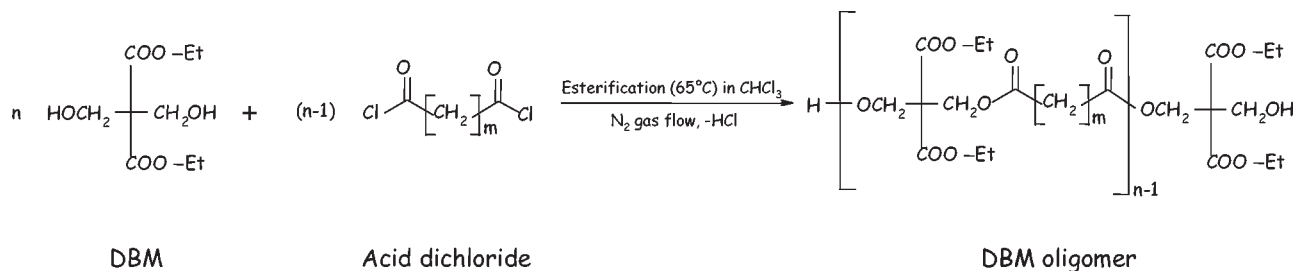
Figure 1 Synthesis path for the esterification of DBM with either AdCl ($m = 4$) or SuCl ($m = 2$).

temperature for 1–4 months, such a migration was successfully prevented[40] by an increase in the molar mass of the plasticizers. However, the higher the molar mass was of the plasticizer, the lower the concentration was at which phase separation started to occur.[41]

This study was conducted to obtain PLA films with increased flexibility via blending with potential plasticizers. For improved compatibility with PLA, two series of syntheses were performed. The main building block was diethyl bishydroxymethyl malonate (DBM), an ester with a solubility parameter very close to that of PLA. To produce esters with various molar masses and hydrophobic chain lengths, we reacted DBM with either adipoyl dichloride (AdCl) or succinyl dichloride (SuCl). The study was largely focused on the dynamic mechanical and thermal film properties of PLA/malonate oligomer blends and on their stability upon aging under ambient conditions. An investigation of the plasticization of PLA with oligomeric malonate ester amides will be presented in a separate article.[42]

EXPERIMENTAL

Materials

DBM, AdCl, and SuCl were purchased from Aldrich (Steinheim, Germany). All the reactants, along with other chemicals and solvents, were used as received.

PLA, with a weight-average molecular weight (M_w) of approximately 100,000 g/mol and a polydispersity index of 2.4, was supplied by Fortum (Keileniemi, Finland). The melting temperature (T_m) and T_g, as given by the supplier, were 175 and 52°C, respectively. The enantiomeric form of PLA was 100% L. The polymer was dried for 30 h at 40°C in a Piovan (Venice, Italy) H31M drier with a Piovan DS403 control unit and then was stored in sealed polyethylene (PE) bags wrapped in aluminum foil in a desiccator at the ambient temperature.

Oligomer synthesis

Two series of syntheses were performed that were based on DBM, and the main reactants were either DBM and AdCl or DBM and SuCl. In all cases, the reactants were added to obtain approximately 20 g of the product. Chloroform ($CHCl_3$) was used as a solvent, and the polymerization was performed in a reaction vessel equipped with a magnetic stirrer and an oil bath thermostated at 60°C. There was a constant flow of N_2 gas through the reaction vessel. Hydrochloric acid (HCl) was emitted from the reaction mixture and collected in a trap device containing distilled water. Figure 1 displays the synthesis path for the esterification reactions of DBM with the acid dichlorides, that is, AdCl and SuCl.

Two reactions were carried out with DBM and AdCl to synthesize short and long oligomers. These are called DBM-A oligomers. In the first case, 14.8 g (0.067 mol) of DBM was dissolved in 20 mL of $CHCl_3$ and charged to the reaction vessel; 7.8 mL (0.054 mol) of AdCl in 20 mL of $CHCl_3$ was slowly added to the reaction mixture through a funnel. The reaction was run for 7 h at 60°C, and the remaining $CHCl_3$ was then evaporated *in vacuo* (20 mmHg) in a Rotavapor-R from Büchi (Flawil, Switzerland). For the long DBM-A oligomer, the reaction vessel was charged with 13.9 g (0.063 mol) of DBM dissolved in 20 mL of $CHCl_3$. The reaction was run for 7 h at 60°C after 9.1 mL (0.062 mol) of AdCl in 20 mL of $CHCl_3$ was added to the reaction vessel. Excess $CHCl_3$ was removed *in vacuo* in the Rotavapor-R.

Two other reactions were carried out with DBM and SuCl to prepare short and long oligomers denoted DBM-S. For the short oligoester, the vessel was charged with 15.4 g (0.07 mol) of DBM dissolved in 20 mL of $CHCl_3$, and 6.2 mL (0.054 mol) of SuCl in 20 mL of $CHCl_3$ was slowly added to the mixture through a funnel. The reaction was run for 15 h at 60°C, and the remaining $CHCl_3$ was then evaporated *in vacuo* in the Rotavapor-R. For the long DBM-S oligomer, 14.6 g (0.066 mol) of DBM was dissolved in 20 mL of $CHCl_3$ and charged to the reaction vessel. After the addition of 7.2 mL (0.065 mol) of SuCl in 20 mL of $CHCl_3$, the reaction was run for 14 h at 60°C. Excess $CHCl_3$ was removed *in vacuo* in the Rotavapor-R.

Sample preparation

Blending

Blending experiments were performed in a Midi 2000 corotating twin-screw extruder from DSM Research (Heerlen, The Netherlands). It was equipped with a chamber volume of 15 cm^3 and was chosen because the effective blending of small volumes was especially important, in that the syntheses only produced limited amounts of the oligomeric plasticizers. The temperature profile ranged from 220°C in the feeding zone down to 180°C in the die, and the screw speed was 100 rpm.

PLA and the plasticizers were mixed and fed into the extruder, in which blending was carried out for 2 min. The blend composition was 15 wt % plasticizer and 85 wt % PLA for all four oligomers. Reference blends with the monomer from the syntheses, that is, DBM, were prepared at concentrations of 5, 15, and 25 wt % DBM. The blended material was extruded as a strand through a single-filament die. The strand was wound and cooled on a glass cylinder with a diameter of 15 cm and stored at the ambient temperature in sealed PE bags.

Film preparation

Films were prepared from the blends via heat pressing at 200°C. Short strands of the blends were placed in a template frame to ensure a constant film thickness and were covered with aluminum foil sheets to prevent sticking to the press plates. This assembly was then placed between the press plates for 3.5 min, without pressure, until the material was properly melted, and then was pressed for 30 s under a pressure of 9×10^5 Pa. The samples were removed from the press plates and cooled in air until they reached the ambient temperature (ca. 20 s). The specimens were then stored in sealed PE bags under the ambient conditions of the laboratory until their analysis.

Characterization

Size exclusion chromatography (SEC)

The oligomers from the synthesis were characterized by SEC. SEC analyses were run at room temperature in tetrahydrofuran (Labscan, Ltd., Ireland; concentration = 1–2 wt %) on Waters Styragel columns (10^5, 10^4, 10^3, 500 Å) or two Waters Ultrastyragel linear columns with differential refractive-index and viscometry detectors (model 250 dual detector, Viscotek).

Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR)

FTIR and ^{1}H-NMR analyses were carried out to study the molecular structure of the oligomers. FTIR spectra were recorded with a Bruker (Ettlingen, Germany) IFS 66 FTIR spectrometer. Small droplets of the liquid oligomers were placed between two ZnSe crystals, and the samples were then analyzed in the transmission mode. Each spectrum corresponded to an average of 32 scans at a resolution of 4 cm^{-1}. ^{1}H-NMR spectra were recorded with a Bruker 400-MHz spectrometer with chloroform-d_6 solutions with concentrations of 10 g/L of the synthesized products. The spectrometer was calibrated with tetramethylsilane as a reference, and each spectrum corresponded to an average of 16 scans.

Differential scanning calorimetry (DSC)

DSC was conducted on a Q1000 from TA Instruments (New Castle, DE). Scans were run on neat plasticizing agents from −90 to 50°C at 10°C/min to determine the glass transitions of the oligomers. Scans were also run on films from −60 to 210°C (heating rate = 10°C/min) and back down to −60°C (cooling rate = 10°C/min) to characterize the thermal film properties of the blends. During the heating ramp, the glass transition, cold crystallization, and melting of the material occurred successively. During the cooling, the crystallization of the PLA chains could be observed. The T_g's, fusion enthalpies, crystallization temperatures, and T_m's were evaluated from the DSC traces. All the scans were carried out in hermetic pans under an N$_2$ atmosphere on approximately 5 mg of the material.

Dynamic mechanical analysis (DMA)

The investigation of the α-relaxation process of PLA, which was associated with its glass transition, and of the cold crystallization was performed with DMA on a DMA 2980 from TA Instruments. The experiments were conducted in the tensile mode under isochronal conditions at a frequency of 1 Hz. Thermograms displaying the storage and loss moduli were recorded between −60 and 150°C at a heating rate of 3°C/min. The amplitude was 5 μm, a preload force of 0.010 N was applied, and the autostrain was set to 115%. The shape of the film samples was rectangular, approximately 15 mm × 5 mm × 0.35 mm.

Aging

The films of the blends were kept in sealed plastic bags for 4 months under the ambient conditions of the laboratory. The aging was carried out to determine the stability of the flexible PLA-based materials during storage.

	δ (J/cm^3)[a]	M_n (g/mol^{-1})[b]	M_w (g/mol^{-1})[b]	n	T_g (°C)[c]
PLA	20.1	—	—	—	52
DBM	20.2	220	—	1	−50
DBM-A-8	18.7	2500	4200	8	−52
DBM-A-18	18.7	5300	8900	18	−42
DBM-S-4	18.4	1300	1800	4	−26
DBM-S-7	18.4	2100	3500	7	−29

[a] As calculated with group molar attraction constants from the Hoy series.[43]
[b] Measured at the inflection point of the DSC trace.
[c] Measured by DSC at the inflection point of the change in the ΔC_p baseline.

RESULTS AND DISCUSSION

Synthesis and characterization of malonate oligomers

The aim of the syntheses was to prepare oligoesters of DBM and acid dichlorides of two chain lengths, that is, DBM-A and DBM-S oligomers. Each type of oligomer was synthesized in two sizes, and this produced a total of four oligomers. The solubility parameter of any chemical substance can be calculated as follows:

$$\delta = \frac{\Sigma F \rho}{M_0}$$

where δ is the solubility parameter, ρ is the density, M_0 is the molar mass, and F is the group molar attraction constants according to the Hoy series.[43] DBM was chosen as the monomeric unit for the synthesis because its calculated solubility parameter, being close to that of PLA, suggested that it would be an efficient plasticizer for PLA. The solubility parameters for the malonate oligomers were also in the vicinity of that of PLA, though slightly lower, as shown in Table I. Varying the hydrophobic chain length of the acid dichloride altered the value of the solubility parameter for the corresponding ester: a shorter chain resulted in a slightly lower solubility parameter.

The syntheses of the DBM-A oligomers were run until the inert carrier gas leading from the reaction vessel no longer contained HCl. This took 7 h for both the short and long oligomers. In the DBM-S syntheses, the reaction time was much longer. After 7 h the gas still contained HCl, and there was also a distinct smell of SuCl from the reaction vessel. The reactions were allowed to continue for a total of 14 and 15 h for the short and long DBM-S oligomers, respectively. After this time, the amount of HCl in the N$_2$ gas stream was considered negligible. To characterize the obtained oligomers, we performed SEC, FTIR, ^{1}H-NMR, and DSC analyses.

SEC traces of the four oligomers are shown in Figure 2, and their main physical characteristics, such as their molar masses and T_g values, as well as those of DBM and PLA, are reported in Table I. The SEC traces (Fig. 2) clearly show that all the oligomers had a broad molecular mass distribution. According to polystyrene standards, the apparent number-average molecular masses (M_n's) of the oligomers could be estimated. Thus, in the DBM-A series, the short oligomer had a molar mass of 2500 g/mol (Table I), which corresponded to an octamer. It is therefore called DBM-A-8. Similarly, the long oligomer with an M_n value of 5300 g/mol, corresponding to 18 repeating units, is denoted DBM-A-18. In the DBM-S series, the molar masses were 1300 and 2100 g/mol, respectively, and this led to the denotations DBM-S-4 and DBM-S-7, respectively. The reactions of DBM with SuCl took longer and resulted in oligomers with lower molar masses than those of DBM-A; this suggested that there existed kinetic limitations. These limitations were likely a result of shorter SuCl chains having less mobility than AdCl chains.

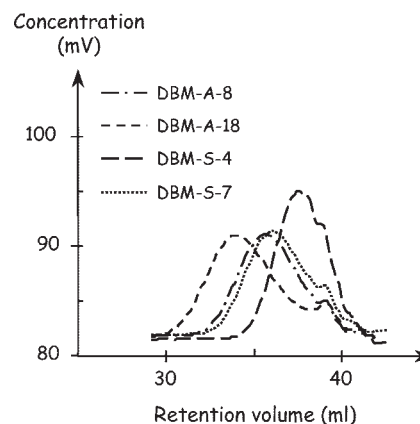FTIR and ^{1}H-NMR analyses were carried out to further characterize the oligomers. Figure 3 displays

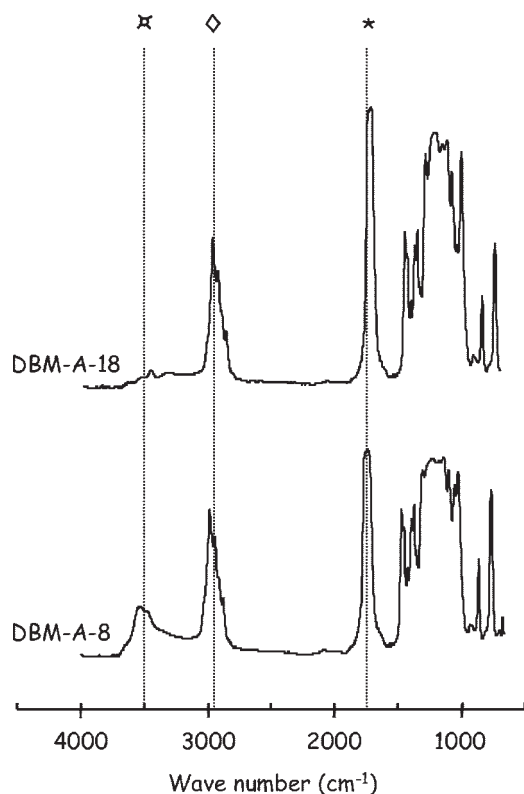**Figure 2** SEC traces for DBM-A-8, DBM-A-18, DBM-S-4, and DBM-S-7.

Figure 3   FTIR spectra of DBM-A-8 and DBM-A-18.

the FTIR spectra of DBM-A-8 and DBM-A-18. The spectra for DBM-S-4 and DBM-S-7 were very similar to those for the DBM-A series and are, therefore, not shown. The large peak at the wave number 3500 cm^{-1} represented the O—H stretching, and the peak decreased when the molar mass of the oligomers within each series increased. The bands at 3000 and 1750 cm^{-1}, reflecting the C=O groups, remained unchanged during the course of the reaction, as expected according to the reaction path in Figure 1.

Figure 4 displays the ^{1}H-NMR spectrum of DBM-A-18, which is representative of all the oligomers. The assignment of the chemical shifts was made according to the formula in the figure. The protons assigned to the methylene groups in the acid dichloride chains had chemical shifts of 1.3 and 0.6 ppm for the DBM-A oligomers, whereas the DBM-S ones only portrayed the peak at 1.3 ppm as a result of the shorter hydrophobic chain.

Thermomechanical film properties

DMA measurements

Figure 5 shows the temperature dependence of the viscoelastic loss [Fig. 5(a)] and storage [Fig. 5(b)] mod-
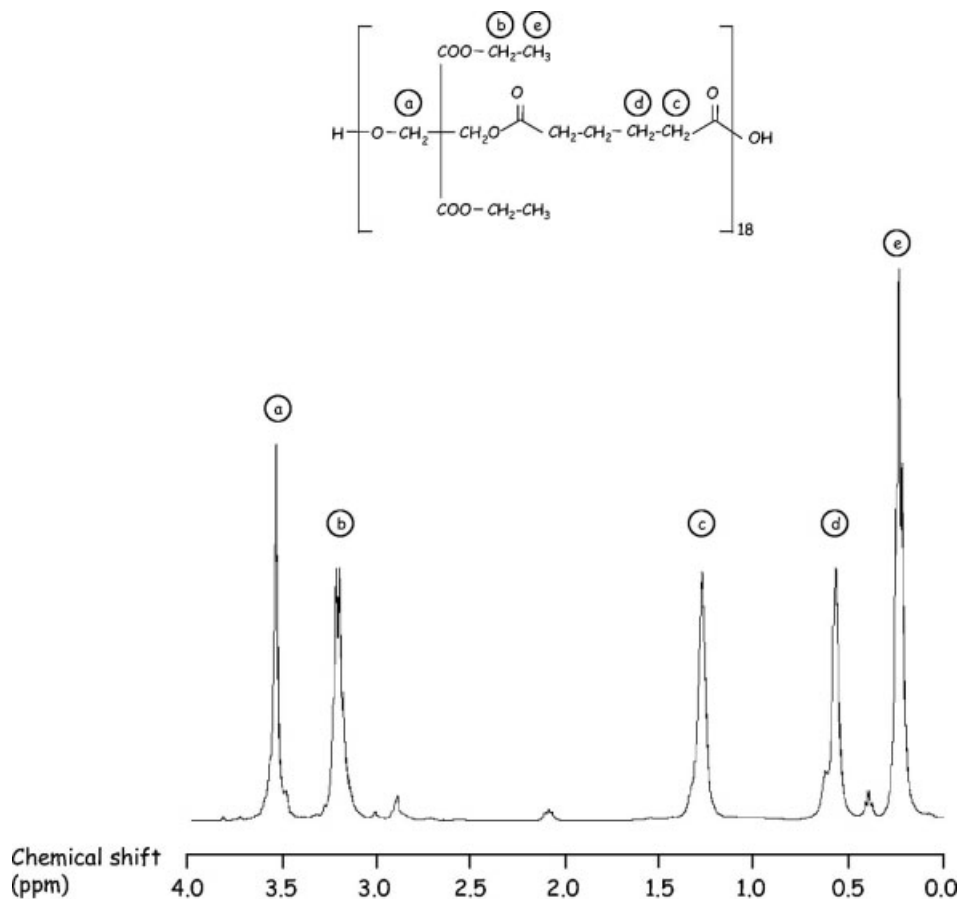

Figure 4 ^{1}H-NMR spectrum of DBM-A-18 recorded in chloroform-d_6.
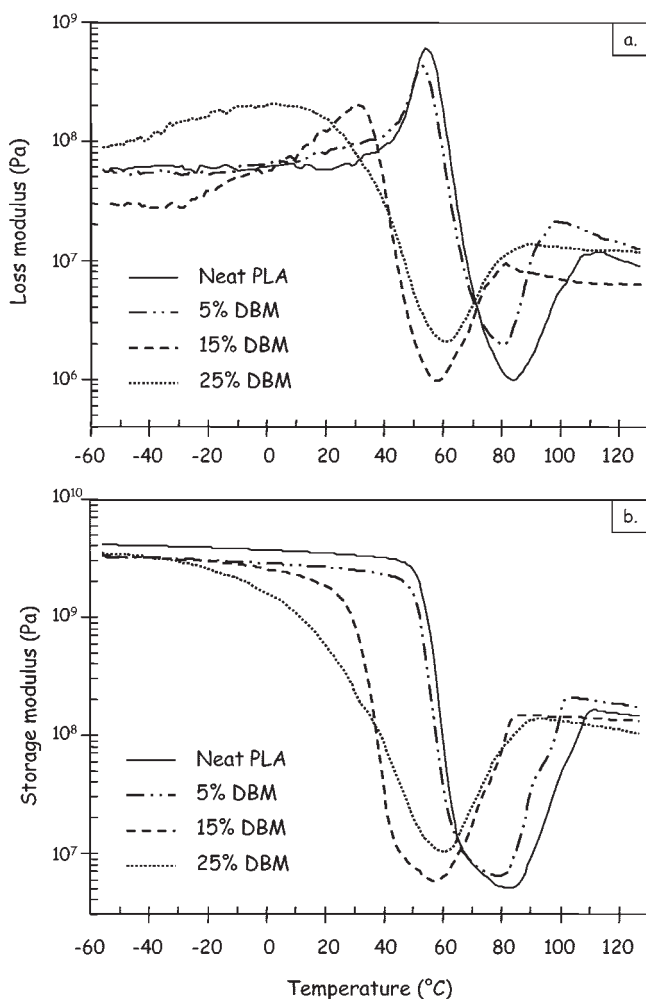
Figure 5 Temperature dependence of (a) the loss moduli and (b) storage moduli of neat PLA and blends containing 5, 15, or 25 wt % DBM.

uli recorded for films of neat PLA and blends containing various concentrations of the low-molar-mass plasticizer DBM. As the temperature increased, the curves of the loss modulus [Fig. 5(a)] displayed two maxima corresponding to the α relaxation (associated with the glass transition) of the amorphous phase and to its cold crystallization, respectively. The T_α values of the films, defined as the temperature location of the maximum of the loss modulus obtained for the α relaxation at 1 Hz, are reported in Table II. The T_α values for the plasticized materials [Fig. 5(a) and Table II] were significantly reduced in comparison with that of neat PLA. In addition, increasing the amount of the plasticizer resulted in a larger reduction of T_α. The reduction with respect to the plasticizer concentration was comparable to those obtained by plasticization with other substances, such as TbC[37,39] and low-molecular-weight poly(ethylene glycol).[14] DBM was seemingly compatible with PLA at concentrations of 5 and 15 wt %, whereas the blend containing 25 wt % displayed a much broadened loss-modulus peak at low temperatures, indicating phase separation and saturation in the system. It seems as if the amorphous domains of semicrystalline PLA were only capable of accommodating a certain amount of the plasticizer through swelling. Above this critical swollen state, the excess plasticizer exhibited phase separation. These observations were in good agreement with those on PLA/TbC blends previously reported,[37] in which the system became saturated and started to phase-separate when containing approximately 20 wt % plasticizer. In addition, the thermograms of the storage modulus [Fig. 5(b)] showed that the cold crystallization appeared at lower temperatures with an increasing amount of plasticizer. Also, the drop in the storage modulus for the 25 wt % DBM blend occurred over a much wider temperature span than for the other materials, and this supported the suggestion of phase separation in the system.

Dynamic mechanical experiments were also performed on the blends with the synthesized DBM-A and DBM-S oligomers. Figure 6 displays the loss modulus as a function of temperature for blends containing 15 wt % of the four oligoesters. As shown in the figure and in Table II, all the blends had reduced T_α values in comparison with T_α of neat PLA. Accord-

TABLE II
T_α Measured by DMA and Thermal Data Obtained by DSC Measurements for Films of Neat and Plasticized PLA

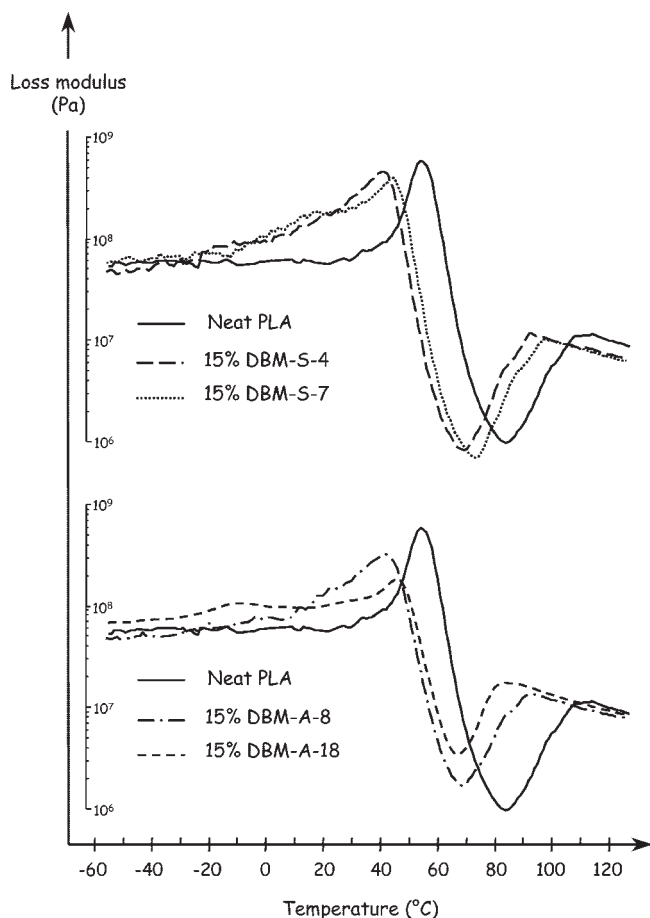|	Content (wt %)	T_a (°C)	T_g (°C)	Cold-crystallization temperature (°C)	T_m (°C)	Crystallization temperature (°C)	ΔH_f (J/g)
PLA	100	54	52	91	173	95	17*
DBM	5	52	43	84	170	97	20
	15	30	29	72	165	93	25
	15	30	29	72	165	93	25
	25	5	4	67	160	92	39
DBM-A-8	15	41	39	74	170	95	24
DBM-A-18	15	47	42	76	170	94	24
DBM-S-4	15	41	36	75	167	88	24
DBM-S-7	15	44	40	80	169	89	24

Figure 6 Temperature dependence of the loss moduli of blends containing 15 wt % DBM-A-8, DBM-A-18, DBM-S-4, or DBM-S-7. The viscoelastic properties of neat PLA are shown for comparison.

ingly, the drop in the storage modulus (not displayed in the figure) occurred at a lower temperature for the blends: the lower the molar mass was of the plasticizer, the larger the reduction was in T_{α}.

The DBM-A and DBM-S oligoesters could also be compared in terms of their efficiency as plasticizing agents for PLA. DBM-A-8 had a molar mass almost twice that of DBM-S-4, but they had the same T_{α} value (see Table II). The molar mass of DBM-S-7 was only slightly lower than that of DBM-A-8, but it had a T_{α} value 3°C higher. Thus, it can be reasonably concluded that the DBM-A oligoesters were more efficient as plasticizers for PLA than the DBM-S ones. This would suggest that increasing the hydrophobicity of the chains linking the DBM monomers together positively affected the compatibility of the resulting oligomer with PLA for the given blend composition. In addition, DBM-A-8 and the two DBM-S esters seemed to provide reasonably homogeneous blends with PLA, whereas PLA/DBM-A-18 displayed a second loss-modulus peak at a low temperature (-10°C) that was much weaker than the other one. The presence of such

a peak indicated the early stages of phase separation in the plasticized system. Because DBM-A-18 had a higher molar mass than the other plasticizers, the swelling equilibrium of the amorphous phase in PLA was logically reached at a lower concentration.

DSC measurements

The thermal properties of the blended materials were also investigated by means of DSC. Figure 7(a) shows a typical DSC trace for neat PLA displaying a shift in the signal baseline related to the glass transition, two exothermic peaks of crystallization, and an endothermic melting peak. In addition, the thermogram for the blend containing 15 wt % DBM-A-8 is shown in Figure 7(b). This thermogram is very similar to those of the other blends. The thermal characteristics from all the DSC runs are summarized in Table II. As already noted for the T_{α} values, the T_g values identified in the DSC traces were lower in the blended materials than in neat PLA. For the blends containing various concentrations of DBM, the reduction in T_g was larger with an increasing amount of plasticizer in the system. However, the sensitivity of the DSC measurements was too low for an additional T_g value to be detected at low temperatures in the DSC trace recorded for the blend containing 25 wt % DBM. This may also be related to the separate DBM phase being too small. In
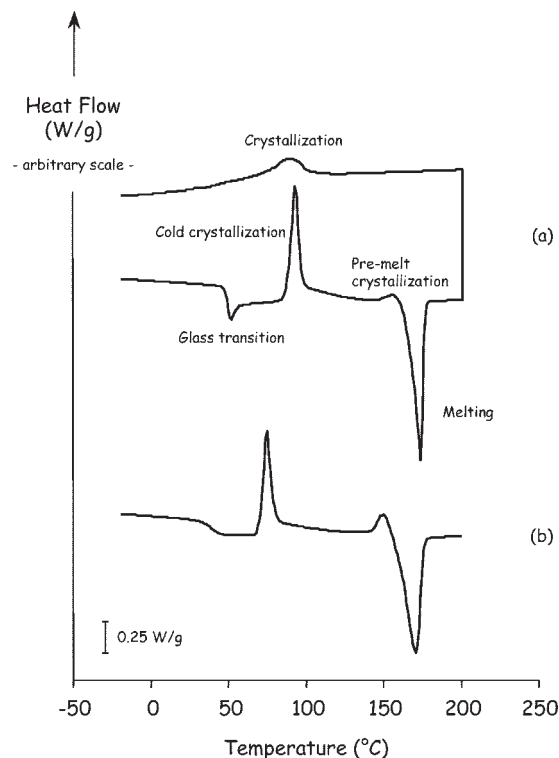

Figure 7 DSC traces recorded for (a) neat PLA and (b) PLA blended with 15 wt % DBM-A-8.

terms of the efficiency of the four malonate oligoesters as plasticizers for PLA, blends containing the plasticizer with the lowest molar mass (Table I) showed the lowest T_g values (Table II). These results correlate well with those obtained in the DMA measurements.

Increasing the concentration of DBM in the blends caused a shift toward a lower temperature in both the cold-crystallization and melting peaks. The higher the DBM concentration was, the larger the shifts were to lower temperatures. Similarly, the blends containing the oligomers also displayed this shift to lower temperatures: the oligomers with the lowest molar mass led to the largest shift in T_g.

The heat of fusion (ΔH_f) of the materials after blending and film pressing (Table II) was determined by the subtraction of the enthalpies for the premelt crystallization and cold crystallization from the melting enthalpy. This value was then divided by the weight fraction of PLA in the sample because the plasticizer did not contribute to ΔH_f. The materials containing a plasticizing agent had higher ΔH_f values than neat PLA, and ΔH_f increased with an increasing plasticizer concentration. These results were directly related to the higher mobility in the plasticized PLA chains, in comparison with that of neat PLA. As a result, a larger portion of the amorphous phase had time to crystallize during the cooling of the plasticized films. Moreover, a slight shift was noticed in the baseline of the DSC traces, and this suggested that crystallization occurred continuously between the cold crystallization and the premelt crystallization, that is, from 80 to 150°C. However, this could not be taken into account when ΔH_f was calculated because it was very difficult to assess the baseline.

Aging

It was interesting to investigate the morphological stability of PLA/oligoester blends because of its great importance for most applications. Previous studies have focused on the progressive phase separation and migration of TbC[38] and TbC oligomers,[40] and it has been shown that increasing the molar mass of the plasticizer leaves it less inclined to migrate.

Samples of blended materials containing 15 wt % DBM or DBM-A-8 were allowed to age naturally under the ambient conditions (ca. 22°C) in sealed plastic bags for 4 months. Figure 8 displays DMA curves of the loss [Fig. 8(a)] and storage moduli [Fig. 8(b)] as a function of temperature for aged and unaged samples of PLA/DBM (15 wt %) blends in comparison with neat PLA. The neat PLA showed[38] no changes in the dynamic mechanical or thermal properties after aging within this timeframe.

The loss-modulus curve for the aged blend containing 15 wt % DBM [Fig. 8(a)] displayed two separate peaks. The first peak at a low temperature (−30°C)
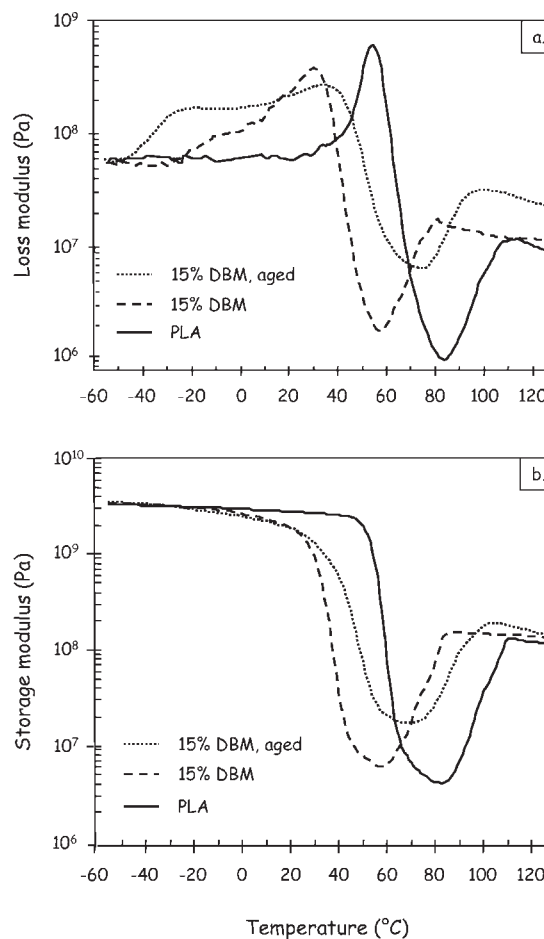

Figure 8 Temperature dependence of (a) the loss moduli and (b) storage moduli of aged and unaged PLA blends containing 15 wt % DBM. The viscoelastic properties of neat PLA are shown for comparison.

was assigned to the α relaxation of DBM because its location was in good agreement with the glass transition of neat DBM from DSC runs (Table I). In addition, the second peak portraying the α transition of the blended material shifted to a higher temperature. The presence of two separate peaks strongly indicated that the plasticizer had created a separate phase and that the low molar mass of DBM (Table I), in combination with the low T_g of the blend (Table II), significantly facilitated the migration of the plasticizer from the bulk of the material to the film surface. The character of the material that remained after DBM had migrated to the surface resembled that of neat PLA, and this led to the unfortunate conclusion that the aged material regained the brittle properties of the unplasticized polymer. This can also be noticed in Figure 8(b): the increase in the storage modulus corresponding to the cold crystallization was shifted from 80°C in the unaged sample to 100°C in the aged one, thus coming very close to that of neat PLA.

The viscoelastic properties of aged and unaged samples of the blend containing 15 wt % DBM-A-8 are
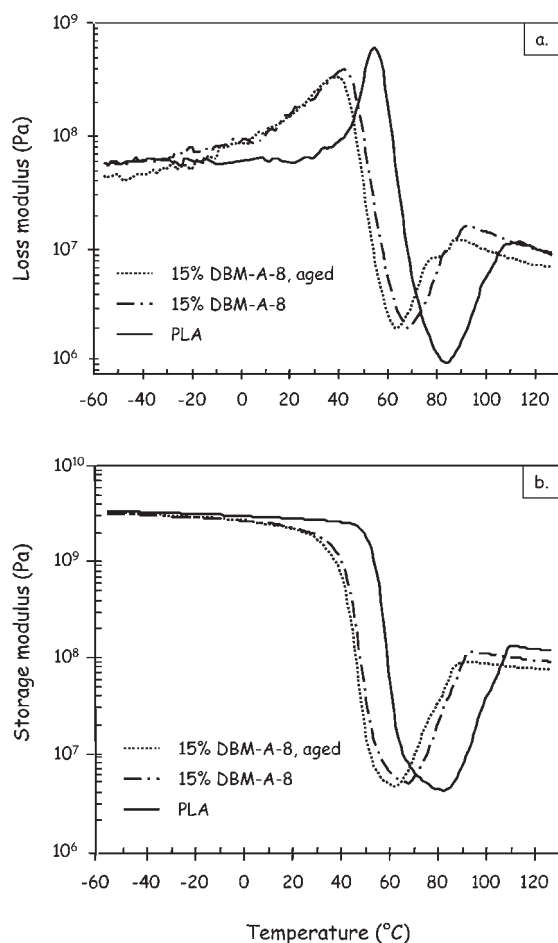
Figure 9 Temperature dependence of (a) the loss moduli and (b) storage moduli of aged and unaged PLA blends containing 15 wt % DBM-A-8. The viscoelastic properties of neat PLA are shown for comparison.

presented in Figure 9. The loss-modulus curve of the aged sample [Fig. 9(a)] showed no major difference from that of the unaged one, indicating that phase separation did not occur in this system during the aging period of 4 months. Subsequently, the jump in the modulus, related to the cold crystallization of the aged sample, was also unchanged [Fig. 9(b)] in comparison with that of the unaged one. Thus, increasing the molar mass of the plasticizer (i.e., going from DBM to DBM-A-8) resulted in a system with increased flexibility, in comparison with neat PLA, that also displayed stability within the given timeframe.

CONCLUSIONS

Oligomeric malonate esters were synthesized through the reaction of DBM with either AdCl or SuCl, which produced DBM-A and DBM-S oligomers, respectively. Because of kinetic limitations, the reaction of DBM with SuCl resulted in oligomers with lower molar masses than those of the DBM-A ones.

Blending PLA with the monomeric unit from the synthesis, DBM, reduced T_g of the polymer, but at a concentration of 20–25 wt %, phase separation occurred because of saturation of the amorphous phases of PLA. Aging a blend containing 15 wt % DBM for 4 months at the ambient temperature also led to phase separation and the migration of the plasticizer to the film surface. Thus, blends of PLA and DBM were not stable, and aging of the material caused them to regain some of the brittle properties of unplasticized PLA.

Blending PLA with the malonate oligomers resulted in decreased T_g's, with the T_g reduction being larger for the material within each series containing the plasticizer with the lower molar mass. The DBM-A oligomers were more efficient as plasticizers than the DBM-S ones, and this suggested that increasing the hydrophobicity of the chains linking the DBM monomers together increased the compatibility of the resulting oligomer with PLA. Aging the PLA/DBM-A-8 blend for 4 months under the ambient conditions left the material unchanged. This indicated that increasing the molecular weight of the plasticizer (i.e., going from DBM to DBM-A-8) resulted in a system with increased flexibility, in comparison with neat PLA, that also displayed morphological stability within the storage period.

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