Thermal and Mechanical Properties of Plasticized Poly(L-lactic acid)

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ABSTRACT: Acetyl tri-*n*-butyl citrate (ATBC) and poly-(ethyleneglycol)s (PEGs) with different molecular weights (from 400 to 10000) were used in this study to plasticize poly(L-lactic acid) (PLA). The thermal and mechanical properties of the plasticized polymer are reported. Both ATBC and PEG are effective in lowering the glass transition (T_g) of PLA up to a given concentration, where the plasticizer reaches its solubility limit in the polymer (50 wt % in the case of ATBC; 15–30 wt %, depending on molecular weight, in the case of PEG). The range of applicability of PEGs as PLA plasticizers is given in terms of PEG molecular weight and concentration. The mechanical properties of plasticized PLA change with increasing plasticizer concentration. In all PLA/plasticizer systems investigated, when the blend T_g approaches room temperature, a stepwise change in the mechanical properties of the system is observed. The elongation at break drastically increases, whereas tensile strength and modulus decrease. This behavior occurs at a plasticizer concentration that depends on the T_g-depressing efficiency of the plasticizer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1731–1738, 2003

Key words: thermal properties; mechanical properties; glass transition

INTRODUCTION

Aliphatic polyesters represent an important family of biodegradable polymers. Some of them can be produced from renewable resources[1,2] and poly(L-lactic acid) (PLA) is one of the most promising polymers of this family.[3] It is used in a great number of medical applications, such as sutures, orthopedic implants and drug delivery systems.[4] Currently, there is an increasing interest in utilizing PLA in applications that require disposable and biodegradable materials. Recent advances have been made in polymerization technology, so that the previously expensive PLA should become competitive with lower priced polymers.[5,6]

PLA possesses good mechanical properties, with elastic modulus and tensile strength in the range of 3.2-3.7 GPa and 55–60 MPa, respectively.[7] PLA is a partially crystalline polymer with a glass transition temperature (T_g) in the range of 65–70°C and a melting temperature (T_m) around 160–170°C. PLA has been blended with a number of different polymers. Poly-(hydroxy butyrate),[8,9] poly(vinyl acetate),[10] poly-(methyl methacrylate)[11] and poly(ethylene oxide)[12–16] have been reported to form miscible blends with PLA.

PLA is a rather brittle and rigid polymer. Plasticizers are widely used in the plastics industry to improve processability, flexibility and ductility of glassy polymers.[17,18] In the case of semicrystalline polymers like PLA, an efficient plasticizer is expected not only to reduce the glass transition of the amorphous domains, but also to depress the melting point of the crystalline phase.[11,19] It is common knowledge that the lactide monomer is an excellent plasticizer for PLA, but it tends to migrate at the material surface, causing the surface to turn sludgy. As a consequence of plasticizer loss, the polymer gradually stiffens. Labrecque et al.[20] have shown the good miscibility of PLA with different citrate esters up to 20–30 wt % plasticizer concentration, depending on the type of citrate employed. The mechanical properties of PLA plasticized with glucose monoesters and with poly(ethylene glycol) (PEG) (MW = 1.5×10^3) were studied over a narrow composition range by Jacobsen and Fritz.[21] In addition, Younes and Cohn[16] investigated the thermal properties and morphology of PLA blended with PEGs with molecular weights ranging from 3.5×10^3 to 3.5×10^4. Their results showed that, depending on PEG molecular weight, microphase separation occurred at given compositions. Recently Bechtold et al.[22] studied the thermal properties of PLA blended with poly(3-methyl-1,4-dioxan-2-one) (PDMO), a copolymer alternating lactic and ethylene oxide units. The blends were found to be miscible in all proportions, with a single composition-dependent glass transition.

In this study, two types of plasticizers were examined: the non-polymeric substance acetyl tri-*n*-butyl

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citrate (ATBC), and PEGs with various molecular weights (from 400 to 1×10^4) as polymeric plasticizers. ATBC is derived from naturally occurring citric acid, is non-toxic and is an approved additive for polymers used in medical, personal care and food contact applications.[20] Poly(ethylene glycol) is commercially available over a broad range of molecular weights (from 200 to 2×10^4). PEGs are used as lubricants, intermediates, binders, carriers and coatings in the cosmetic, pharmaceutical, textile and chemical specialty fields.[14,23]

This article studies the plasticization of PLA by both monomeric and polymeric substances, over the whole composition range. The range of miscibility of the binary polymer/plasticizer systems is evaluated by analyzing the composition-dependence of the glass transition of the melt-quenched blends. In addition, the influence of the different plasticizers on the mechanical properties of poly(lactic acid) is also investigated.

EXPERIMENTAL

Materials

PLA (Lacea H.100-E) was supplied by Mitsui Fine Chemicals (Dusseldorf, Germany). The average molecular weight was 8.4×10^4 with a polydispersity index (PDI) of 1.7, as determined by gel permeation chromatography using polystyrene standards. ATBC and PEG with molecular weights of 400 (PEG 400), 900 (PEG 900), 2×10^3 (PEG 2K) and 3.4×10^3 (PEG 3.4K) were purchased from Sigma-Aldrich (Milan, Italy). PEG with a molecular weight of 1.5×10^3 (PEG 1.5K) and 1×10^4 (PEG 10K) were obtained from Fluka (Milan, Italy). The reported PEG molecular weights were provided by the suppliers. All substances were used without further purification.

Blending procedure

Solution casting

PLA/ATBC and PLA/PEG mixtures spanning the whole composition range were solubilized in CH_2Cl_2. The solutions (5% w/v) were cast on glass Petri dishes, and the solvent was allowed to evaporate at room temperature. All obtained films were further dried overnight under vacuum at room temperature to eliminate residual solvent.

Melt blending

Before thermal processing, PLA was dried in an oven under vacuum at 45°C for 24 h. PLA was melt blended with various amounts (up to 20 wt %) of ATBC, PEG 400, PEG 1.5K and PEG 10K using a twin screw extruder with a 25 mm screw diameter and a L/D ratio

of 22 (Brabender DSK 25, Duisburg-Germany). The screw configuration had a zone with kneading elements after the polymer inlet in order to shear the polymer intensively during melting and to provide a homogeneous melt blend. PLA and the solid plasticizer granules (PEG 1.5K and PEG 10K) were introduced into the extruder at a controlled rate using an electrical hopper. The liquid plasticizers (ATBC and PEG 400) were fed through a drip dosing system. Extrusion of all compounds was performed at a temperature of 170°C and a screw speed of 20 rpm. All melt extruded samples showed a homogeneous distribution with no accumulation of plasticizer at the surface. The extruded strands were then air-cooled. The extrudates were granulated and dried under vacuum at 45°C for 24 h before injection molding. Injection molding was performed on a Ferromatik Milacron injection-molding machine (Type K40-80V/2F, Malterdingen, Germany) using a screw of 25 mm diameter and a L/D ratio of 22. The temperature in the barrel for all blends was 155°C at the feed and 170°C at the end of the barrel. The nozzle temperature was adapted to the requirements of the respective compound. The die temperature was set to 40°C. Tensile test bars with a cross section of 5×3 mm were injection molded.

Characterization methods

Mechanical properties were assessed with a universal testing machine (ZWICK 1456 Ulm, Germany) at room temperature. The crosshead speed was 5 mm/min, and the Young's modulus was measured between 0.05 and 0.25% linear elongation. Plastic elongation was calculated by subtracting the elastic elongation from the total elongation at break of the specimen.

The surfaces of the fractured test bars were analyzed using a Scanning Electron Microscope (SEM) (Hitachi S-2500C). The acceleration voltage at the cathode was 15 kV. The samples were sputter coated with platinum using a Balzers SCD 004 (600 s, 9–12 mA).

Differential scanning calorimetry (DSC) was performed using a TA-DSC2010. The temperature scale was calibrated with high purity standards. The sample (about 8 mg) was preliminarily heated to 200°C to erase previous thermal history, then quenched to −100°C, and finally heated at 20°C/min from −100°C to 200°C. Repeated DSC scans showed excellent reproducibility. The glass transition temperature was taken both at the midpoint of the specific heat increment (T_g) and at the onset of the step (T_g^{onset}), determined as the intercept between the baseline preceding the transition and the steepest tangent to the step. The melting temperature (T_m) was taken at the end of the melting endotherm, as the intercept between the baseline in the melt state and the steepest tangent to the final part of the melting peak. T_m is the temperature where the
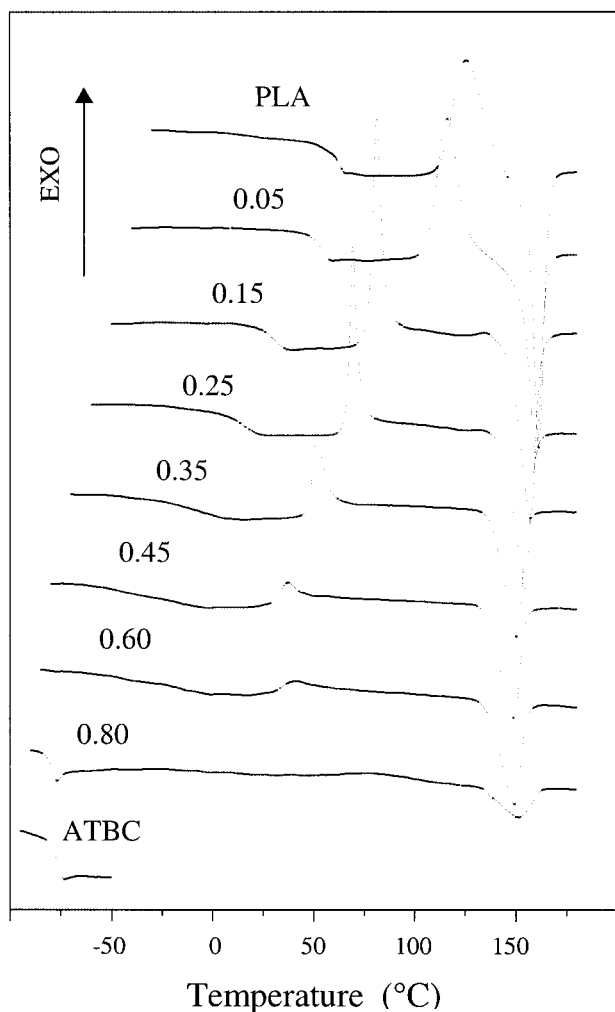
Figure 1 DSC curves after melt quenching of solution-cast PLA plasticized with different ATBC weight fractions.

RESULTS AND DISCUSSION

Thermal characterization

Monomeric plasticizer (ATBC)

The thermal behavior of PLA/ATBC blends was investigated over the whole composition range. Figure 1 shows the DSC curves after the melt quenching of solution-cast PLA/ATBC mixtures, pure polymer and plasticizer. The curve of quenched PLA shows the endothermal baseline shift associated with the glass transition followed sequentially by the exothermal cold crystallization peak and by the melting endotherm. The crystallization and melting enthalpies are identical, showing that PLA is totally amorphous after melt quenching. The degree of crystallinity developed

by PLA during the thermal scan can be calculated by comparison of the experimental melting enthalpy with literature data for totally crystalline PLA.[25] The obtained value is about 40% of the literature value.

The DSC curves of PLA/ATBC blends with plasticizer content ranging from 0 to 45 wt % show a single glass transition that decreases with increasing plasticizer concentration. This result agrees with earlier data by Labrecque et al.,[20] who analyzed PLA/ATBC blends over a more limited composition range (0–20% ATBC). A decreasing trend with increasing plasticizer content is also shown in Figure 1 by the cold crystallization and melting phenomena. Analysis of the melting enthalpy shows that, in the mixtures with ATBC, PLA crystallizes to the same extent as in the pure state. At ATBC concentrations higher than 45 wt %, the specific heat shows two endothermal baseline shifts (not easily identifiable in Fig. 1, but quite clear in magnified curves).

The glass transition temperatures of solution cast PLA/ATBC mixtures are plotted as a function of plasticizer weight fraction, w_1 in Figure 2. T_g is seen to regularly decrease in the range of 0–60% ATBC. When w_1 is greater than or equal to 0.6, the blends show two

last crystals melt. When binary systems are analyzed, this is the temperature where the melt in equilibrium with the crystals has the same composition as the nominal overall composition of the blend.[24]
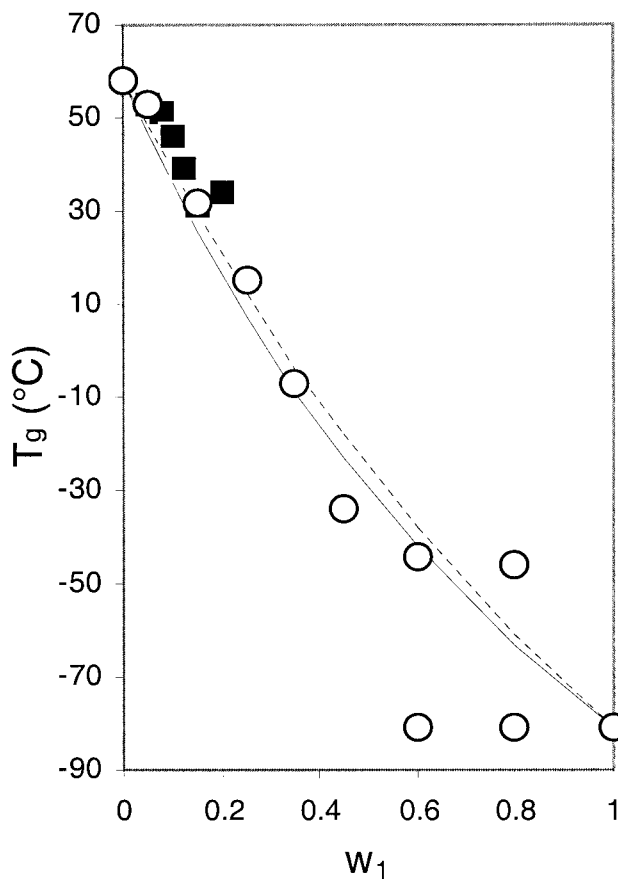

Figure 2 Glass transition temperatures as a function of ATBC weight fraction w_1 of: (○) solution cast and (■) melt blended and injection molded samples; (− −) Fox equation (1); (—) Couchman-Karasz eq. (2).

constant-temperature glass transitions. The constancy of temperature indicates constancy of composition of the phase undergoing the glass-to-rubber transition. The higher T_g is that of a PLA/ATBC mixture containing 50–60 wt % ATBC, a composition that represents the solubility limit of ATBC in PLA. All ATBC in excess of this limit phase-separates and gives rise to a pure ATBC phase, identified by the low-temperature glass transition in Figure 2.

The regular change of T_g with ATBC content up to the solubility limit is satisfactorily described by two well-known equations. Eq. (1) was proposed by Fox[26] for the T_g/composition dependence of polymer/diluent mixtures and miscible polymer blends:

$$1/T_g = w_2/T_{g2} + w_1/T_{g1} \qquad (1)$$

Eq. (2) was proposed by Couchman and Karasz[27] for miscible binary systems on the basis of thermodynamic considerations:

$$\ln(T_g/T_{g2}) = \lfloor w_1 \Delta c_{p1} \cdot \ln(T_{g1}/T_{g2}) \rfloor$$
$$\div (w_1 \Delta c_{p1} + w_2 \Delta c_{p2}) \qquad (2)$$

where subscripts 1 and 2 refer to plasticizer and polymer, respectively. The value Δc_p is the specific heat increment at the glass transition, T_g is the glass transition temperature and w is the weight fraction. Neither eq. (1) nor eq. (2) contain adjustable parameters, and the agreement of their predictions with the experimental T_g/w_1 behavior of the PLA/ATBC system strongly supports the conclusion that PLA and ATBC form a miscible blend over a broad range of compositions that comprise the normal range of commercial plasticized polymer formulations (0–50 wt %).[17] ATBC is therefore a promising candidate plasticizer for PLA, especially on account of its acceptance as a non-toxic additive for medical, personal care and food contact applications.

Figure 2 also shows the T_g values of the melt-blended and injection molded PLA/ATBC bars used in the tensile mechanical tests. Considering that the plasticizer content in the test bars after the various processing steps may be slightly different (i.e. lower) than that of the nominal blend composition, the agreement of the T_g data on test bars (represented in Fig. 2 by full squares) and solution cast films (represented by open circles) can be considered satisfactory.

As already observed, PLA/ATBC blends melt at temperatures that decrease with increasing plasticizer content (Fig. 1). An analysis of the dependence of the melting temperature on blend composition in the range where PLA and ATBC are miscible can give interesting indications on polymer-plasticizer interactions. According to Flory,[19] the following equation should hold for miscible polymer-diluent mixtures:
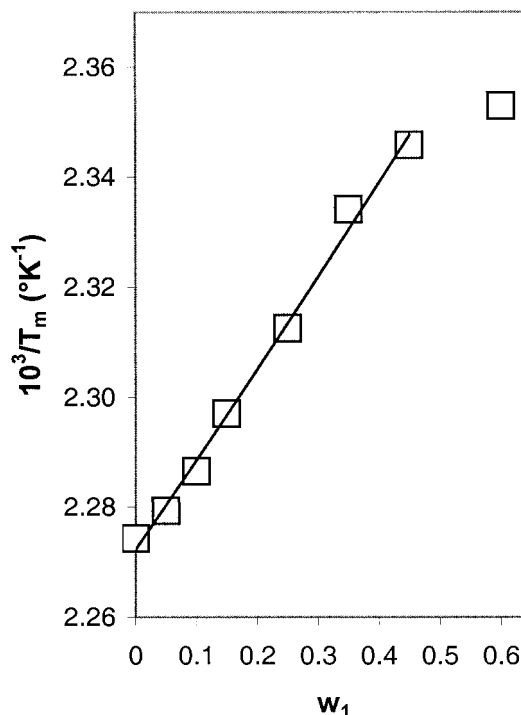

Figure 3 Reciprocal melting temperatures of PLA/ATBC mixtures as a function of ATBC weight fraction w_1: ($\square$) experimental data; (—) eq. (4) best fit.

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \cdot \frac{V_u}{V_1} \cdot (\phi_1 - \chi_1 \cdot \phi_1^2) \qquad (3)$$

where T_m^0 and T_m are the melting temperatures of the pure polymer and of the polymer in a mixture with diluent volume fraction ϕ_1, respectively. As mentioned in the Experimental, T_m and T_m^0 are taken as the temperatures where the last trace of crystallinity disappears. The values ΔH_u and V_u are the heat of fusion and the molar volume per polymer repeating unit, V_1 is the diluent molar volume and χ_1 is the polymer-diluent interaction parameter. The commonly used approximation of substituting weight fraction (w_1) for volume fraction (ϕ_1) can be introduced, and eq. (3) can be rearranged as follows:

$$\frac{1}{T_m} = \frac{1}{T_m^0} + \left(\frac{R}{\Delta H_u} \cdot \frac{V_u}{V_1} \right) \cdot w_1 - \left(\frac{R}{\Delta H_u} \cdot \frac{V_u}{V_1} \cdot \chi_1 \right) \cdot w_1^2 \qquad (4)$$

Figure 3 shows a plot of the reciprocal melting temperature of PLA/ATBC blends as a function of ATBC weight fraction, w_1. The line drawn is a polynomial second order equation, like eq. (4), that well fits the experimental data plotted in Figure 3 up to $w_1 = 0.45$. By introducing the best fit numerical constants into eq. (4), the melting enthalpy per PLA repeating unit (ΔH_u) and the interaction parameter (χ_1) can be estimated. Using the molar volume of crystalline PLA ($V_u = 55.86$ cm^3/mol) from the literature[25] and taking V_1 to be
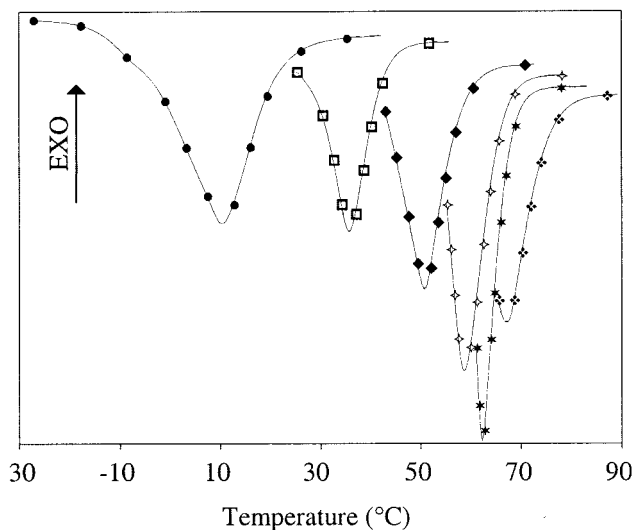
Figure 4 DSC melting curves of PEGs with different molecular weights: (●) PEG 400; (□) PEG 900; (◆) PEG 1.5K; (☆) PEG 2K; (★) PEG 3.4K; (◇) PEG 10K.

383.31 cm^3/mol, a ΔH_u for PLA of 7.5 kJ/mol is obtained, a value that agrees with earlier melting enthalpy estimates.[25] The obtained interaction parameter is negative ($\chi_1 = -0.1$) and indicates, according to Flory,[19] that good polymer-plasticizer interactions promote the mixing of ATBC with PLA in the range of compositions where eq. (4) fits the experimental data reported in Figure 3. It is worth noting that this is the same plasticizer concentration range where the experimental T_g data shown in Figure 2 follow the predictions of eqs. (1) and (2) for miscible binary systems.

Polymeric plasticizers

PEGs with different molecular weights are used in this work to plasticize PLA. The physical state at room temperature of the employed PEGs ranged from liquid (MW = 400) to waxy (MW = 900) to solid (MW $\geq 1.5 \times 10^3$) with increasing molecular weight. Such changes are clear in Figure 4, where the melting curves of the PEGs investigated are seen to fall below (PEG 400), around (PEG 900) or above room temperature.

Figure 5 shows selected DSC curves of PLA plasticized with PEG 400, PEG 1.5K and PEG 10K. Though the whole range of concentrations was explored, only blends with PEG content up to 20 wt % are shown in Figure 5. In this composition range, the three polymeric plasticizers cause a decrease in the glass transition temperature and a slight decrease in the melting temperature of PLA. The magnitude of the plasticization effect is not the same in the three systems illustrated in Figure 5, but depends on the molecular weight of the plasticizer. When blends with a given PEG content are compared, it is found that the de-

crease of T_g is the strongest for the lowest molecular weight PEG.

In Figure 5 the curve of the blend with 20 wt % of PEG 10K shows a small melting endotherm superimposed on the blend glass transition, which reveals the presence of phase-separated pure PEG 10K in this blend (compare with the melting curve of PEG 10K in Fig. 4). In the PLA/PEG blends investigated in this work, segregation of a pure PEG phase always occurs when the amount of PEG exceeds a critical value that depends on the molecular weight of the plasticizer employed. Segregation is observed at higher plasticizer contents, when low molecular weight PEGs are used to plasticize PLA, showing that the miscibility of
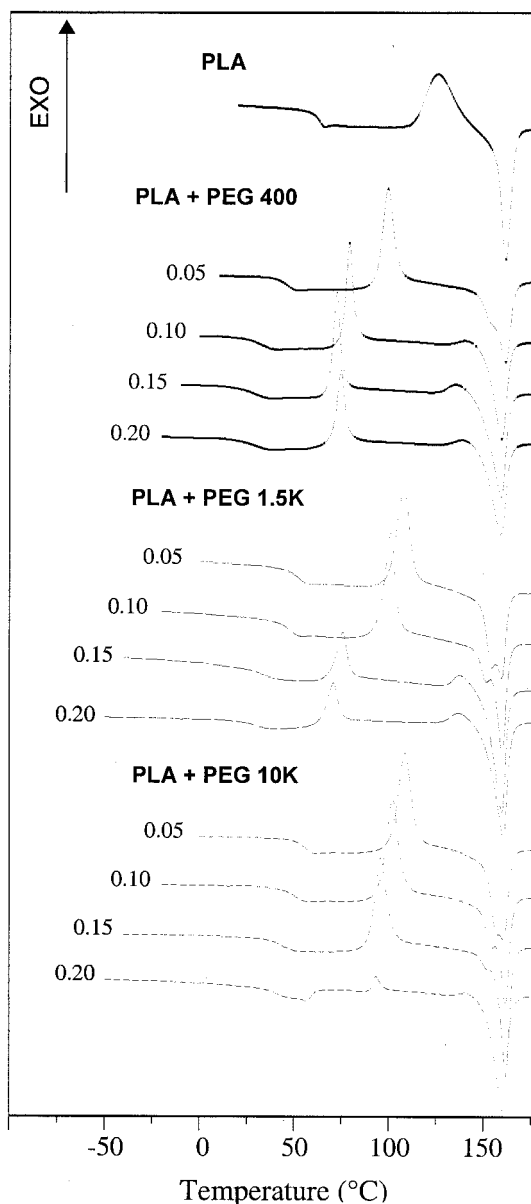

Figure 5 DSC curves after melt quenching of PLA blended with different PEGs (PEG 400, PEG 1.5K, PEG 10K). PEG weight fraction is shown on curves.
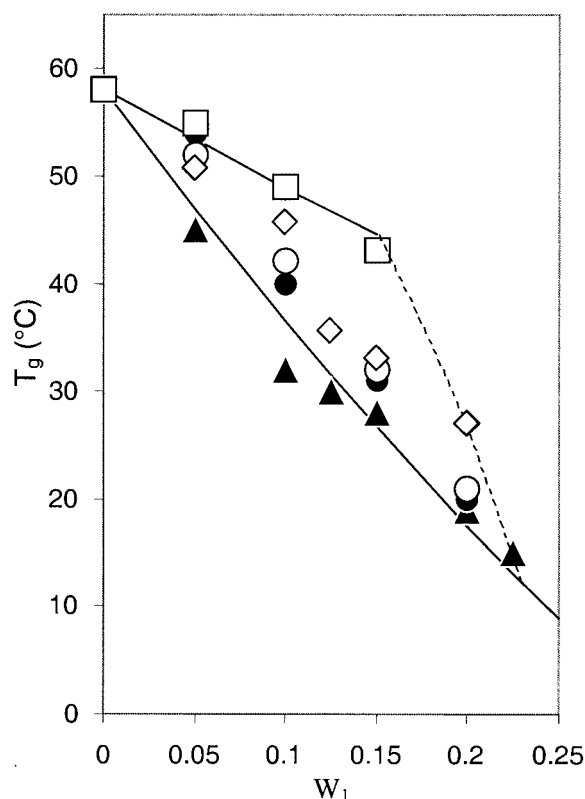
Figure 6 Glass transition temperature of miscible PLA/PEG blends as a function of plasticizer weight fraction w_1 and molecular weight: (▲) PEG 400; (◇) PEG 1.5K; (●) PEG 2K; (○) PEG 3.4K; (□) PEG 10K.

PLA with PEG increases with decreasing plasticizer molecular weight. This behavior is quite common in polymer blends.[28]

In each system, when the solubility limit of PEG in PLA is attained, the glass transition temperature of the PLA/PEG blend stops decreasing with increasing plasticizer content, as expected for a constant-composition mixture. Figure 6 summarizes the experimental T_g's of all PLA/PEG blends investigated as a function of PEG weight fraction, in the range of compositions where no PEG segregation occurs, i.e., the range of miscibility of PLA with the polymeric plasticizer. The T_g/composition dependencies of the blends with PEG 10K and with PEG 400 (solid lines in Fig. 6) are the upper and lower boundaries, respectively, that enclose the T_g's of the blends with intermediate molecular weight PEGs. The different plasticizing efficiency of the various PEGs investigated is quite clear. The dashed line in Figure 6 shows the miscibility limit in PLA of PEGs with different molecular weights. The miscibility limit clearly moves toward lower PEG contents with increasing PEG molecular weight. The composition-molecular weight range enclosed by the curves drawn in Figure 6 represents the applicability window of the investigated PEGs as PLA plasticizers.

Mechanical Properties

The goal of adding plasticizer to PLA is to enhance plastic elongation and to reduce brittleness while maintaining maximum polymer strength and stiffness. The mechanical properties of melt processed plasticized PLA are given in Table I. The glass transition onset temperature of each plasticized PLA sample is also reported.

As already mentioned, PLA shows high elastic modulus and tensile strength and is quite brittle. Plasticizer addition favorably changes the mechanical properties, as shown in Table I. With increasing plasticizer content, a common trend is shown by all systems investigated: the tensile modulus (E) and tensile strength (σ_b) decrease, while elongation at break (ϵ_b) increases. Inspection of the ϵ_b values in Table I shows that a very significant (two orders of magnitude) change of elongation occurs at a plasticizer content that depends on the type of plasticizer employed. When PEG 10K is used, 20 wt % is needed to induce a large increase of ϵ_b, whereas the same change is attained by 10 wt % of low molecular weight PEG 400. Analysis of the glass transition temperatures of the different plasticized PLA systems shows that the abrupt change of elongation occurs in all blends when T_g is around 35°C. Figure 7 shows a plot of ϵ_b as a

TABLE I
Mechanical Properties of Plasticized PLA

Material	σ_b (MPa)	E (GPa)	ϵ_b (%)	T_a^{onset} (°C)
Pure PLA	66	3.3	1.8	60
PEG 400 (wt %)				
5	41.6	2.5	1.6	40
10	32.5	1.2	140	23
12.5	18.7	0.5	115	22
15	19.1	0.6	88	20
20	15.6	0.5	71	19
PEG 1.5K (wt %)				
5	52.3	2.9	3.5	46
10	46.6	2.8	5	42
12.5	18.5	0.7	194	30
15	23.6	0.8	216	27
20	21.8	0.6	235	20
PEG 10K (wt %)				
5	53.9	2.8	2.4	49
10	48.5	2.8	2.8	42
15	42.3	2.5	3.5	36
20	22.1	0.7	130	34
ATBC (wt %)				
5	53.4	3.2	5.1	49
10	50.1	2.9	7	41
12.5	17.7	0.1	218	26
15	21.3	0.1	299	27
20	23.1	0.1	298	24

function of T_g^{onset}, illustrating that when the glass transition decreases down to 35°C the mechanical behavior of plasticized PLA changes from fragile (low ϵ_b) to ductile (high ϵ_b). Analogous elongation changes were earlier found in plasticized PLA.[12,20] Also the tensile modulus and the strength of the present PLA/plasticizer blends change stepwise when T_g approaches room temperature. The sigmoidal behaviors shown in Figure 7 are common to all systems investigated, independent of the type of plasticizer, and the glass transition acts as a normalizing factor.

It is well known that the mechanical properties of polymers depend on temperature, and in particular on the location of the test temperature with respect to the glass transition.[29] In high-T_g polymers, the same effect as increasing the test temperature towards T_g can be obtained by decreasing T_g through plasticizer addition. When the T_g of the plasticized polymer approaches the test temperature, or in the present case when the glass transition is around 35°C, a drastic change in mechanical properties is observed. Figure 7 shows that the magnitude of such a change is not the same for the three mechanical properties investigated, being two orders of magnitude for ϵ_b, and much smaller for E and σ_b.
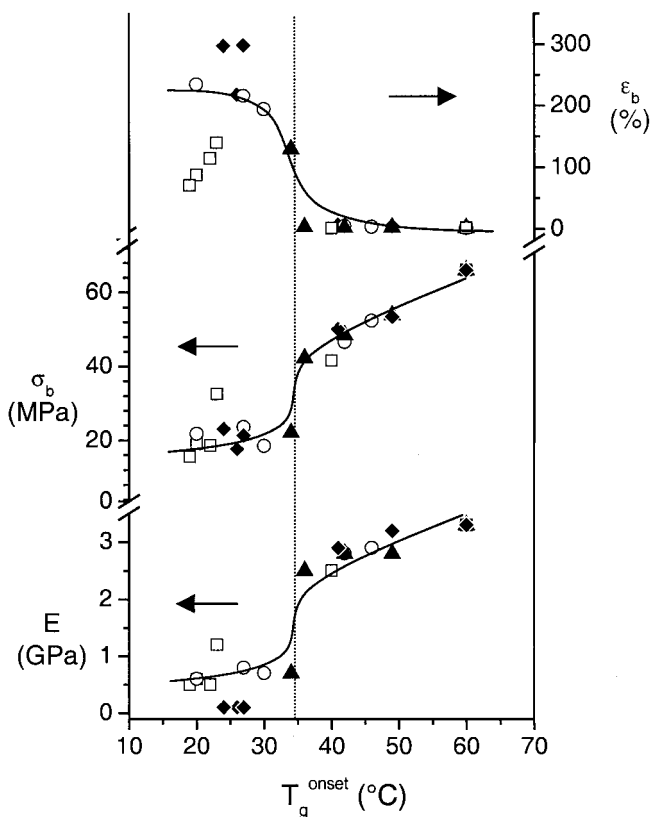

Figure 8 SEM micrographs of blends of PLA with 15 wt % PEG 10K (A) and PEG 1.5K (B). Bar: 90 μm

Scanning electron microscope analysis of the fracture surface of plasticized PLA test bars confirms the effect of the PEG molecular weight on the mechanical behavior of the polymer, as discussed above. Figure 8 compares the fracture surfaces of two PLA/PEG blends containing the same amount (15 wt %) of plasticizer (PEG 1.5K in one case, PEG 10K in the other). The fracture surfaces are quite different. Plastic deformation is evident when PEG 1.5K is used, whereas a typical brittle fracture, similar to that of pure PLA, is shown by PLA plasticized with high molecular weight PEG 10K. The change in the fracture mechanism is associated with different plasticizing efficiency (T_g depressing ability) of the two plasticizers (Fig. 6).

Figure 7 Elongation at break (ϵ_b), tensile strength (σ_b) and elastic modulus (E) as a function of the glass transition temperatures of plasticized PLA. Plasticizer: (□) PEG 400; (○) PEG 1.5K; (▲) PEG 10K; (◆) ATBC.
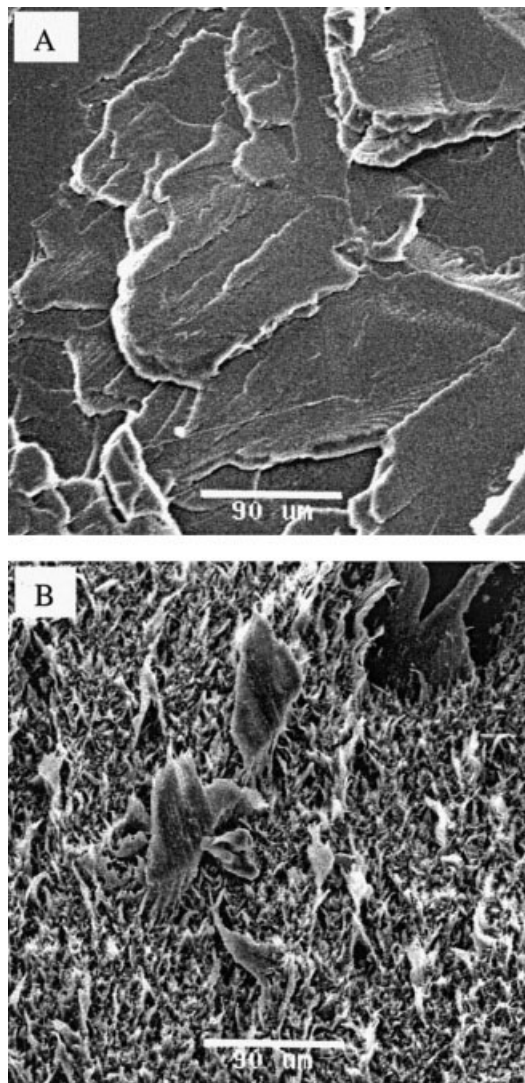
CONCLUSIONS

The results of this study show that both ATBC and PEGs with different molecular weights (from 400 to

10000) can act as plasticizers for PLA. The range of miscibility of the polymer with the plasticizer decreases with increasing molecular weight of PEG (30 wt % for PEG 400, 15 wt % for PEG 10 K). In the case of ATBC, the miscibility limit is 50 wt %. The plasticizing efficiency of PEG increases with decreasing molecular weight. A significant increase of the elongation at break of PLA is achieved by plasticization, at the expense of strength and tensile modulus. The chief parameter dictating the mechanical properties of plasticized PLA, independent of the identity of the plasticizer considered, is the glass transition of the polymer-plasticizer mixture.

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