

Processing and Characterization of Poly(lactic acid) Films Plasticized with Commercial Adipates

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ABSTRACT: The high brittleness of Poly(lactic acid) is a major drawback for flexible food packaging applications. The aim of this work is to evaluate the potential use of commercial adipates as PLA plasticizers to obtain transparent films with enhanced mechanical properties. Processing conditions were optimized. The effect of plasticizers was characterized by a decrease on the glass transition temperature and an increase in PLA chains mobility, which induced crystallization on heating. Thermal stability was not significantly affected, and mechanical properties showed an increase in ductility with the plasticizer content. Oxygen transmission rate was also measured to eval-

uate the effect of the microstructures generated by the presence of these additives in PLA-based films. The monomeric adipate presented lack of homogeneity that makes films plasticized with this additive not useful for the intended application. Good compatibility was observed between polyadipates (up to 20 wt %) and the matrix, making them promising materials for biodegradable films manufacturing. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2010–2018, 2009

Key words: poly(lactic acid); adipates; mechanical properties; glass transition; gas permeation

INTRODUCTION

Poly(lactic acid) (PLA) belongs to the family of aliphatic polyesters commonly made from lactic acid, which can be produced from renewable resources such as starch via fermentation processes.¹ This thermoplastic aliphatic polyester has been extensively investigated during the last decades. It has been studied not only for medical purposes but also for food packaging applications, that is, it is classified as GRAS (Generally Recognized As Safe, GRAS).^{2–5} It shows some physical characteristics that make it suitable for the manufacture of rigid containers and bottles. However, its high brittleness limits PLA uses in flexible films and sheets.^{6–8} This drawback can be overcome by mixing the polymer with environmentally friendly plasticizers to get higher ductility with no changes in the biodegradable characteristics of the material. Concerning food contact materials, there are several requirements they should meet. Besides good compatibility and appropriate mechanical and thermal properties, plasticizer migration is a highly relevant topic in this field.⁹

Several substances have been studied as PLA plasticizers, showing compatibility at low concentrations but with not enough improvement in tensile properties as required for such applications.^{9,10} In general, films prepared by compression molding showed good flexibility for plasticizer concentrations over 10 wt %. However, in most cases, migration was observed with time due to the low molar mass of the additives tested.^{10–12} One way to overcome this drawback is by increasing the molar mass of the plasticizer up to an upper limit to ensure the miscibility with the matrix. Home-made plasticizers were also synthesized for this purpose, and they showed good performance for concentrations lower than a critical value beyond which phase separation was observed.¹³ The use of commercially available plasticizers, currently used with other polymers, with good compatibility with PLA and relatively high molar mass could be an acceptable solution to prepare plasticized PLA films.

In this work, amorphous PLA was melt-blended with three commercial adipates, one of them monomeric and other two with polymeric structure, based on adipic acid and 1-3 propanediol with different molar masses. Blends were prepared in mass ratio 10 and 20 wt % and processed into films by compression molding. Compatibility of blends after processing was studied and structural, thermal, mechanical, thermomechanical, and oxygen barrier properties were determined with the aim to find

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TABLE I
Number-Average Molar Mass (M_n), Polydispersion Index (PDI), Density (ρ), Global Solubility Parameters (δ), and Glass Transition Temperature (T_g) of Raw Materials

Material	M_n (g/mol)	PDI	ρ (g/cm ³)	δ^* (J/cm ³) ^{1/2}	T_g (°C)
PLA	63,000	2.38	1.25	19.93	58.2
DOA	371	–	0.93	16.67	–79.0
G206/2	1532	1.16	1.06	21.91	–72.9
G206/7	2565	1.44	1.10	22.87	–53.8

* Calculated by group contribution by using Hoy series.¹⁴

PLA formulations with adequate properties for flexible food packaging applications.

EXPERIMENTAL

Materials

Poly(lactic acid) (CML PLA) was purchased from Hycail Finland Oy (Turku, Finland). Monomeric and polymeric commercial plasticizers were kindly supplied by Condensia Química S.A. (Barcelona, Spain). They were di-2-ethylhexyladipate (DOA) and two polymeric adipates, which were identified with commercial names according to their increasing molar mass as G206/2 and G206/7. Properties of materials are summarized in Table I.

Preparation of the films

PLA pellets were dried in a vacuum oven at 60°C for 4 h and then milled with a RETSCH Ultra Centrifugal Mill ZM200 (Haan, Germany) to increase the surface area and favor the intimate contact with the plasticizer. In a previous work, the final particle size was ~ 2 mm and important losses of plasticizer were detected.¹⁵ For that reason, pellets were reduced to a particle size of ~ 1 mm. Polymer pellets were chilled with liquid nitrogen to avoid melting and thermal degradation of PLA on the sieve due to the increment in temperature during grinding. The milled pellets and plasticizers were manually premixed at 10 and 20 wt % and were then allowed to sit for 2 h at room temperature. Samples were charged into a Haake Rheomix 9000 internal mixer (Karlsruhe, Germany) equipped with a pair of high shear roller-type rotors and melt-blended at 50 rpm during 8 min. The processing temperature was set at 170°C but it was increased to 180–190°C on mixing. Blends were then processed into films by compression molding at 180°C in a hot press (Collin GMBH, Ebersberg, Germany) using a frame to ensure a constant film thickness. The material was kept between the plates at atmospheric pressure for 5 min until melting and then it was successively pressed under 3 MPa for 1 min, 5 MPa for 1 min, and 10 MPa for 3 min to liberate the trapped air

bubbles.¹⁶ Samples were then quenched with cold water at 10 MPa of pressure.

Methods

Cross sections of the films were sputtered with gold and analyzed by scanning electronic microscopy (SEM) on a JEOL JSM-840 (Japan). The acceleration voltage was 10 KV and images were registered at 500× and 1000× of magnification.

Thermogravimetric analysis (TGA) was performed in a TGA/SDTA 851 Mettler Toledo thermal analyzer (Schwarzenbach, Switzerland). Samples were heated from room temperature up to 700°C at 10°C/min under nitrogen atmosphere (200 cm³/min).

Differential scanning calorimetry (DSC) was conducted on a TA Instruments DSC Q-100 (New Castle, USA) under nitrogen atmosphere. The materials were exposed to the following thermal cycle; heating from –90 to 180°C at 10°C/min, followed by quenching to –90°C and further heating from –90 to 200°C at 10°C/min. The glass transition temperatures (T_g 's) were determined from the second scan. DSC thermograms of the pure plasticizers were also recorded from –90 to 80°C at 10°C/min, to determine their glass transition temperature.

Wide angle X-ray scattering (WAXS) was performed on a Seifert diffractometer; model JSO-DEBYEFLEX 2002 equipped with Cu K α radiation source ($\lambda = 0.1546$ nm), operating at 40 KV and 40 mA as the applied voltage and current, respectively. The incidence angle was varied between 2° and 90° at a scanning rate of 1°/min.

Dynamic mechanical analysis (DMA) was performed on a DMA Q800 from TA Instruments (New Castle, USA) operating in the tensile mode. Storage modulus (E') and loss modulus (E'') were determined from relaxation spectra obtained at a heating rate of 3°C/min between –90°C and 140°C with a frequency of 1 Hz. The α -relaxation process associated with the glass transition was determined from the maximum loss modulus curve.

Tensile tests were carried out on a Universal Electronic Dinamometer from LLOYD Instruments, model LR30K (Fareham Hants, UK). Film thickness was measured using a Digimatic Micrometer Series

293 MDC-Lite (Mitutoyo, Japan) to ± 0.001 mm. Tensile tests were performed on rectangular probes (dimensions: 100×10 mm²) and at a crosshead speed of 10 mm/min. Initial grip separation was 5 cm, and a load gripping force of 500N was applied. Average tensile strength (TS), percentage deformation at break ($\epsilon\%$), and elastic modulus (E) were calculated from the resulting stress–strain curves according to the standard procedure (ASTM D882-91). Results were the average of six measurements.

Oxygen transmission rate (OTR) was measured with an oxygen permeation analyzer from Systech instruments, model 8500 (Metrotec S.A, Spain). Films with an average thickness of 160 ± 10 μm were selected and 14 cm diameter circle samples were cut for each formulation. Samples were clamped in a diffusion chamber at 25°C. Pure oxygen (99.9%) was introduced into the upper half of the sample chamber while nitrogen was injected into the lower half of the chamber where an oxygen sensor was placed.

RESULTS AND DISCUSSION

Processing conditions

Mixing temperature was selected to minimize the loss of plasticizer due to volatilization. According to the supplier,¹⁷ the boiling temperature of the monomeric plasticizer (DOA) used in this work is 216°C. It was assumed that a mixing temperature of 170–180°C was low enough to restrict plasticizer volatilization during processing. Mixing time was adjusted to prevent thermomechanical degradation during this process.¹⁸ This was accomplished by measuring the torque on the mixer's rotors as a function of time. The torque increased sharply as the material was added to the mixing chamber, after which it eventually decreased and leveled off after 7 min mixing. It was also verified by Gel Permeation Chromatography (GPC) that the mixing conditions did not induce any significant thermal degradation to the matrix. At a mixing time of 8 min, the average molar mass did not vary from the value determined for the milled pellets, whereas for higher mixing times, such as 15 min, it was decreased around 14%. Therefore, blends were considered homogeneous without any significant degradation after 8 min processing.

Although blending was performed at 170°C, some plasticizer loss was detected during mixing, particularly for 20 wt % DOA. Evolution of vapors was observed during heat pressing, indicating that a significant amount of plasticizer was lost during processing. This result agreed well with TGA results for pure DOA, which started to decompose at temperatures as low as 140°C. It was observed that pure DOA was lost at processing temperatures (between

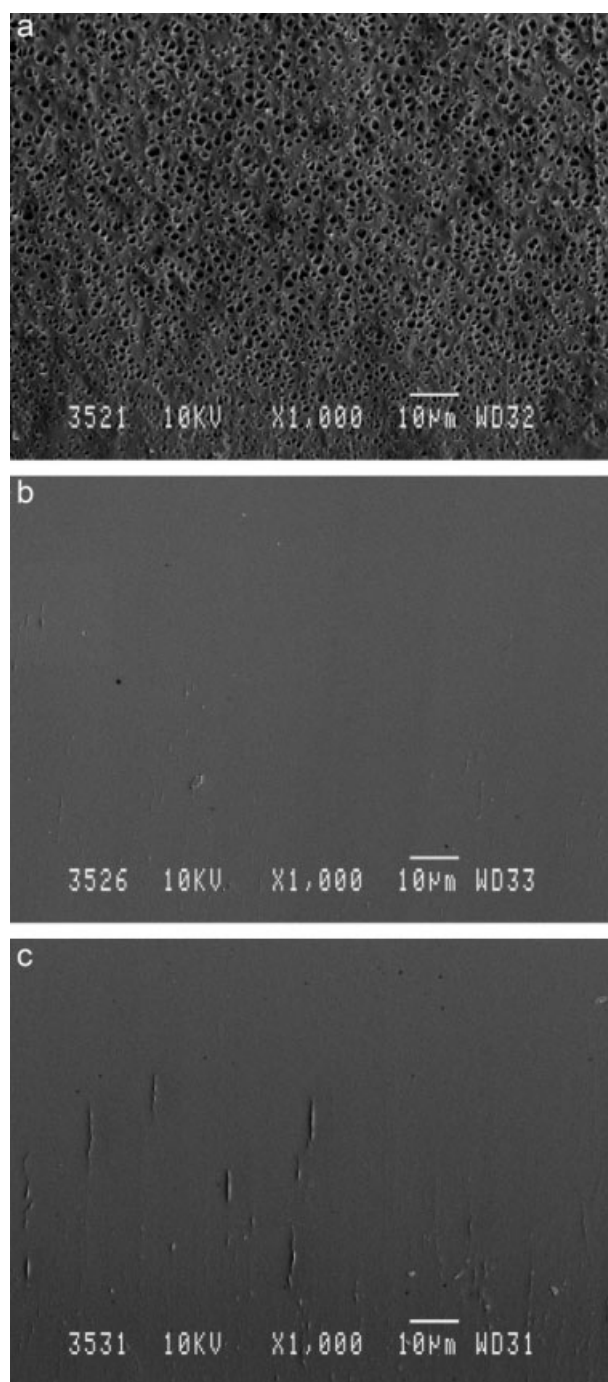


Figure 1 SEM micrographs ($\times 1000$) of fracture surfaces: PLA-20 wt % DOA (a), PLA-20 wt % G206/2 (b) and PLA-20 wt % G206/7 (c).

170°C and 190°C), with plasticizer release of 4 and 13 wt %, respectively, as determined from TGA curve. As expected, the plasticizer evaporation generated a porous morphology as can be observed in Figure 1(a). Moreover, PLA-20 wt % DOA presented certain whitening on its surface as a consequence of the heterogeneity in the material structure due to the plasticizer release. In the case of polymeric plasticizers, the films obtained were completely transparent

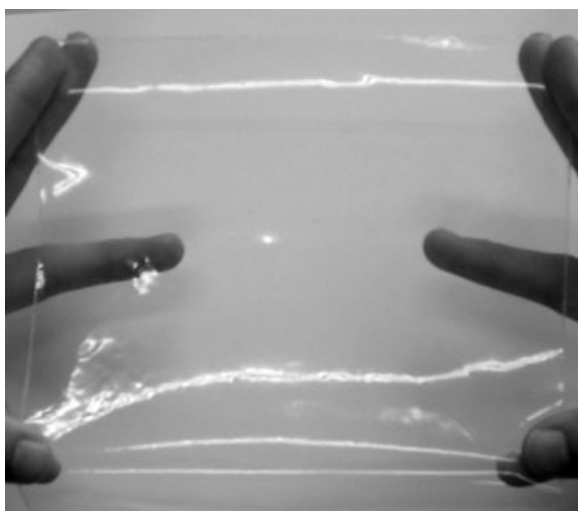


Figure 2 Example of transparent films based on PLA and polyadipates.

(Fig. 2) and homogenous morphologies were obtained as confirmed by SEM observations [Fig. 1(b,c)]. This fact implies that high molar mass plasticizers remained in the bulk of the film.

Thermal properties of the obtained blends

The process of previous milling and further thermal processing did not affect the thermal stability of the polymer, as neat PLA film showed the same thermal degradation pattern than that of the original pellets. This finding agrees well with GPC results above discussed. Neat PLA was stable up to 314°C, where thermal decomposition began, reached the maximum degradation rate at about 366°C and completed degradation at 388°C. For plasticized films, the thermal decomposition started at lower temperatures (Table II), but clearly higher than those of pure plasticizers which were 212°C for G206/2 and 240°C for G206/7 as determined by TGA. This was particularly noticeable for 20 wt % content of plasticizers

where a shoulder was observed in curves at temperatures some degrees lower than the beginning of the polymer degradation. This could be due to the evolution of low molar mass components in commercial polyadipates, such as polymerization residues. All blends showed a maximum weight loss at temperatures between 364 and 369°C, similar to those of the neat polymer. Therefore, the addition of plasticizers did not affect thermal stability of PLA produced films.

As expected from the comparison of solubility parameters (Table I), polyadipates showed good compatibility with PLA and only one T_g was detected by DSC in plasticized PLA films at each concentration (Table II). The loss of DOA due to evaporation during processing in the formulation with 20 wt % was confirmed, as no significant reduction in T_g was detected when compared with the formulation with 10 wt % DOA. The incorporation of polymeric plasticizers significantly reduced the T_g of the material in all cases, but this effect was more pronounced for the polyadipate with lower molar mass (G206/2), as expected from T_g values of pure polymeric plasticizers (Table I). No apparent phase separation was noted in any case. Table II shows the theoretical T_g values expected for binary miscible blends calculated by using Fox equation.¹⁹

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

where w is the weight fraction and the subscripts 1 and 2 refer to the blends components. Because no apparent plasticizer segregation was observed, it was assumed that differences between predicted and experimental data were due to plasticizer losses mainly on the walls of the mixer, due to the relative low viscosity of the mixture at the blending temperature. It is noteworthy that theoretical and experimental values approached as plasticized molar mass increased, confirming the above-mentioned assumption. The experimental T_g values obtained for samples plasticized with G206/7 are those in better

TABLE II
Thermal Parameters of Samples Obtained from TGA, DSC, and DMA Experiments and Theoretical T_g Value for Each Formulation According to Fox Equation (1)

Sample	T_0^a (°C)	T_m (°C)	T_g^b (°C)	$T_{g,theor}$ (°C)	T_α^c (°C)
Neat PLA	314	–	58.2	–	58.0
PLA-10 wt % DOA	228	138.4	40.8	36.3	43.3
PLA-20 wt % DOA	226	135.2–140.2	40.1	17.1	–
PLA-10 wt % G206/2	284	142.7	39.5	37.8	43.9
PLA-20 wt % G206/2	290	138.0	25.4	19.8	26.9
PLA-10 wt % G206/7	291	143.4	42.1	42.1	44.0
PLA-20 wt % G206/7	291	140.9	30.6	27.5	31.9

^a Initial degradation temperature determined by TGA at $\alpha = 0.01\%$ (10°C/min).

^b Measured by DSC at 10°C/min during the second heating stage.

^c From E'' curve.

agreement with the values predicted by Fox equation (Table II). This may be ascribed to the higher plasticizer viscosity that reduced mass losses during blending. However, results for G206/7 at 20 wt % did not correlate with those found by preparing similar films by casting from chloroform solutions.²⁰ To explain such difference, the processing conditions must be considered. Casting is a three-component system and the solubility parameter of chloroform is $19.0 \text{ (J/cm}^3)^{1/2}$, clearly smaller than that for G206/7 (Table I). The lack of compatibility reported in our previous work could have been caused by the mixture of chloroform and the plasticizer. Another discrepancy with such former results was that neither phase separation nor exudation was observed for 20 wt % DOA because it was not possible to incorporate more than 10 wt % of plasticizer due to evaporation during processing.

On the other hand, deviations between theoretical and experimental values for blends with G206/2 were quite smaller than those observed in our previous results,¹⁵ in particular for 20 wt % of polyadipate. This may be attributed to the difference in particle size of the premix. For 2 mm-particle size and 20 wt % of G206/2, a T_g value of 33°C was obtained.¹⁴ However, in this work T_g decreased to 25°C for the same plasticizer concentration using a final particle size of 1 mm.

The increase in chains mobility due to the plasticizing effect induced crystallization and further melting during heating, in particular at high concentration and low molar mass of the plasticizer (Fig. 3). For 10 wt % G206/7 a very small melting peak was observed at $T_m = 143^\circ\text{C}$. No crystallization peak was detected, but a slight shift in the baseline of DSC trace was noticed before melting. As chain mobility increased due to the higher amount of plasticizer and/or its lower molar mass, the blends crys-

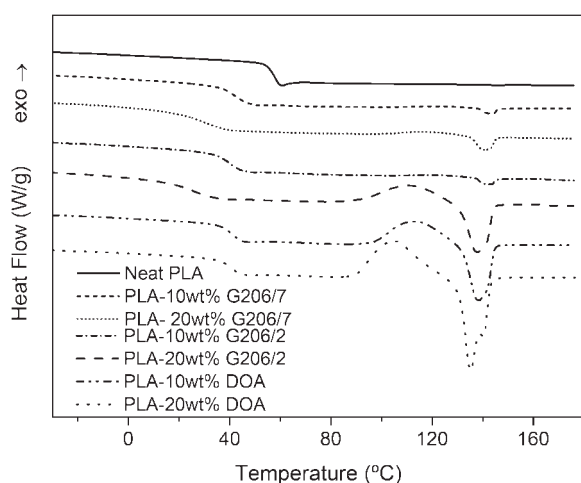


Figure 3 DSC thermograms obtained during the second heating of samples after quenching.

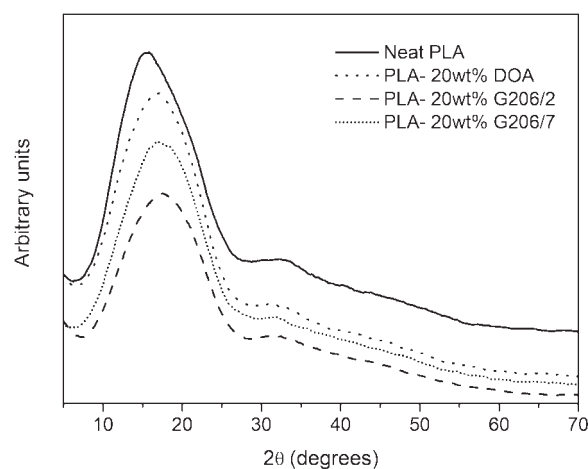


Figure 4 WAXS patterns obtained for neat and plasticized PLA films with 20 wt % of plasticizer.

tallized and melted upon heating and melting temperatures were shifted to lower temperatures (Table II). For 20 wt % DOA two melting peaks were observed, as the result of annealing during the temperature scan. Less perfect crystals melted (first peak) and further had time to recrystallize few degrees above and finally remelted (second peak).^{21,22} This behavior was not considered to be due to the presence of two distinct crystals in the initial sample as it was verified by WAXS patterns (Fig. 4), the cooling rate used during processing was enough to get samples mainly amorphous. The amorphous nature of the original material was also revealed by the fact that the crystallization exotherm and the melting endotherm in DSC curves had identical heat contents (same area).

Dynamical-mechanical properties

DMA provides information on mechanical behavior, molecular relaxations as well as interactions taking place in the obtained materials as the temperature is varied.²³ The storage modulus (E') and loss modulus (E'') are shown in Figure 5. In the glassy region, the storage modulus remained almost constant and decreased near room temperature, being this reduction more significant as plasticizer content increased or their molar mass decreased (Fig. 5). In the plastic region, an increment in E' was observed, which was attributed to a cold crystallization process. This crystallization was promoted by the increased chain mobility in this region. Similar results were reported for PLA plasticized with citrates²⁴ and for nanocomposites with cellulose whiskers.²⁵

The $T_{\alpha'}$, defined as the maximum of the loss modulus, E'' was related with T_g .^{16,24} The T_{α} values were shifted to lower temperatures with increasing plasticizer content, indicating an increased chain mobility

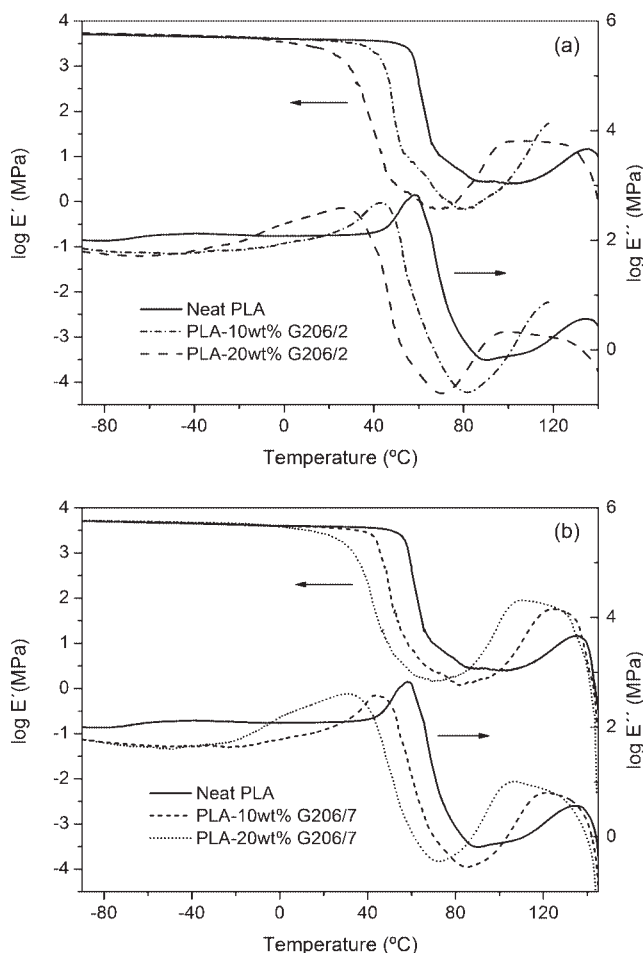


Figure 5 Storage (E') and loss (E'') modulus as a function of the temperature for neat PLA and plasticized with G206/2 (a) and G206/7 (b).

of the PLA matrix. In addition the plasticizer with the lowest molar mass was the most effective, as concluded from the highest depression in T_g (Table II). The T_g values obtained from the peak temperature in E'' correlated closely with T_g data from DSC (Table II). Similar results were reported for polylactide/polyethyleneglycol blends.¹⁶ It is important to remark that no additional peaks different than those assigned to T_g were observed in E''

curves, confirming that quenched blends did not suffer phase separation after processing.²⁴

Tensile properties

Tensile properties were measured to assess the differences in ductile behavior between neat and plasticized PLA. A decrease in the elastic modulus (E) and tensile strength (TS) values and an increase in the percentage deformation at break ($\epsilon\%$) with the addition of plasticizers were observed, showing an enhancement in ductility of blends (Table III). Amorphous PLA behaved as a brittle material with a high modulus (around 2.0 GPa) and a small deformation at break (about 6%), while in plasticized PLA, the deformation at break increased up to almost 500% for 20 wt % of both polyadipates. Such increase in material ductility was directly correlated to the decreases in T_g observed for each formulation (Table II).

DSC and SEM analyses were also performed on samples after tensile tests to verify the structural changes caused by the stress applied. It was found that the difference between melting (ΔH_f) and crystallization (ΔH_c) enthalpies, which was around zero before mechanical tests increased for samples plasticized with DOA and 20 wt % of polyadipates after testing (Table III). As can be observed in Figure 6(a,b), only neat PLA and films with 10 wt % of polymeric plasticizers did not suffer crystallization due to the alignment of polymer chains during elongation. According to SEM images the fracture surface of samples with 10 wt % plasticizer showed their fragile behavior [Fig. 7(a)]. Formulations with 20 wt % of polyadipates that were initially homogeneous and transparent [Fig. 1(b,c)] kept mostly transparent although they crystallized during testing. In this case the fracture surface showed the ductile nature of such materials [Fig. 7(b)]. Samples plasticized with 20 wt % DOA that were not completely transparent after processing, became white after tensile tests. This may be ascribed to the heterogeneity in such samples [Fig. 7(c)] together with the increased crystallinity degree induced during tensile testing.

TABLE III
Elastic Modulus (E), Tensile Strength (TS), and Percentage Deformation at Break ($\epsilon\%$) of Samples Obtained from Tensile Testing According to ASTM D882-91 and $\Delta H_{fc} = \Delta H_{\text{fusion}} - \Delta H_{\text{crystallization}}$ Before and After Tensile Tests

Sample	E (GPa)	TS (MPa)	ϵ (%)	ΔH_{fc} (J/g) before stress	ΔH_{fc} (J/g) after stress
Neat PLA	2.0 (± 0.2)	47 (± 5)	6 (± 2)	0.11	0.54
PLA-10 wt % DOA	1.6 (± 0.1)	27 (± 4)	259 (± 64)	0.76	5.07
PLA-20 wt % DOA	1.4 (± 0.1)	17 (± 1)	295 (± 89)	1.56	12.15
PLA-10 wt % G206/2	1.6 (± 0.1)	34 (± 2)	5 (± 1)	0.11	0.46
PLA-20 wt % G206/2	0.2 (± 0.1)	25 (± 4)	485 (± 65)	0.19	6.71
PLA-10 wt % G206/7	1.7 (± 0.2)	36 (± 2)	7 (± 5)	0.23	–
PLA-20 wt % G206/7	0.5 (± 0.1)	28 (± 2)	491 (± 34)	0.59	5.37

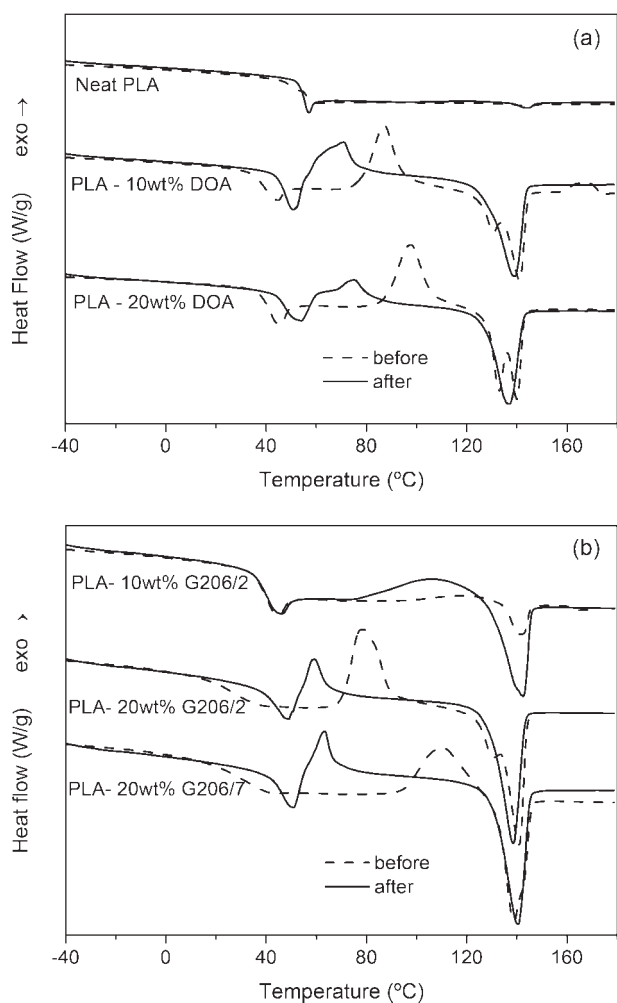


Figure 6 DSC thermograms obtained during the first heating of samples before and after tensile testing for neat PLA, plasticized with DOA (a) and plasticized with polyadipates (b).

Oxygen transmission rate

Concerning to barrier properties, the oxygen permeation process was clearly slower in the case of the pure polymer and significant increases in OTR were observed after the plasticizer addition. It was observed that the steady-state of oxygen flux was reached more rapidly with increasing amounts of additive. The final results of OTR in the steady-state per film thickness (e) are summarized in Table IV. It can be observed that the addition of plasticizer increased the oxygen transmission rate through films, being the higher values for 20 wt % formulations. This could be due to the increase in mobility caused by the addition of polyadipates as it reduced the resistance of the film to oxygen transmission, as reported by other authors.^{26,27} The monomeric plasticizer produced the greater increases in OTR due to the presence of holes and microstructures generated by the release of additive during processing, as it was previously stated.

When comparing both polyadipates as plasticizers for PLA, significant differences were observed. The addition of the polyadipate with higher molar mass resulted in lower OTR values compared to the other plasticized materials at the same plasticizer concentration. Materials with 20 wt % of G206/2 (lower molar mass) behaved similarly to those with DOA in the same concentration. The interpretation of the plasticizer release during processing was not valid

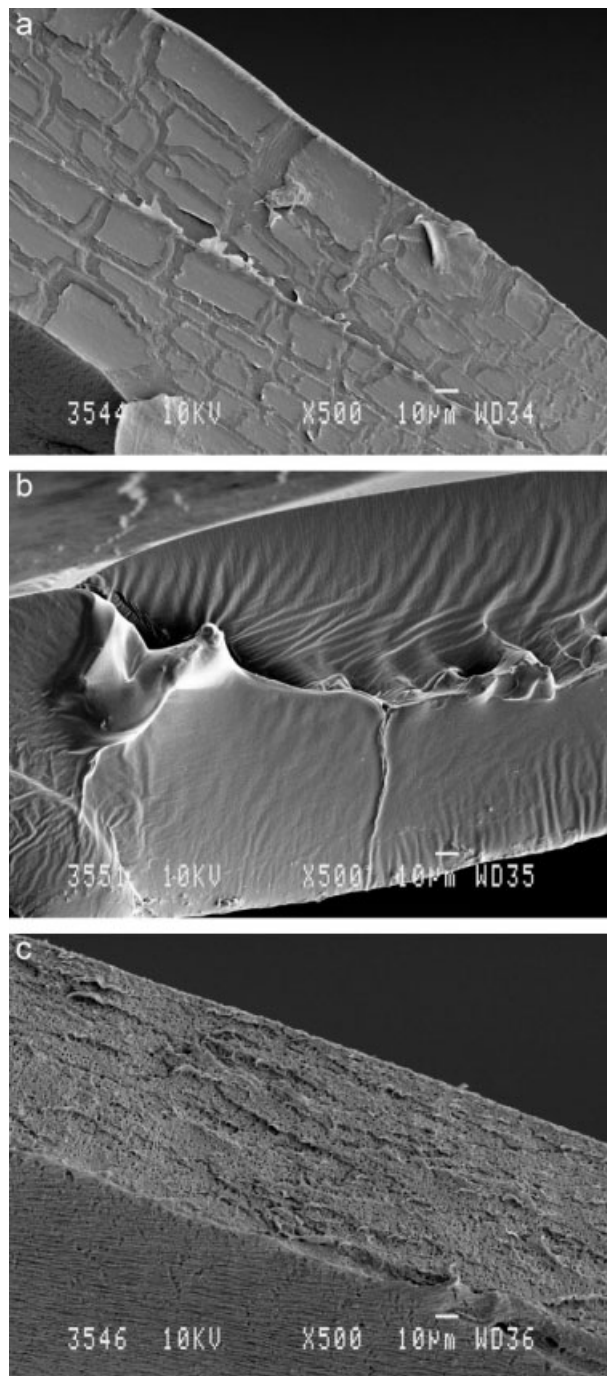


Figure 7 SEM micrographs ($\times 500$) of fracture surfaces after tensile testing: PLA-10 wt % G206/2 (a), PLA-20 wt % G206/2 (b) and PLA-20 wt % DOA (c).

TABLE IV
Oxygen Transmission Rate per Film Thickness (OTR.e)
of Neat and Plasticized PLA Films

Sample	OTR. e (cm ³ .mm/m ² day)
Neat PLA	29.5
PLA-10 wt % DOA	45.6
PLA-20 wt % DOA	66.4
PLA-10 wt % G206/2	33.3
PLA-20 wt % G206/2	62.9
PLA-10 wt % G206/7	29.2
PLA-20 wt % G206/7	48.0

in this case as no further evidence by other techniques (i.e., by electronic microscopy) was obtained. Several factors could be responsible of this behavior: molar mass of the plasticizer, chemical interactions between plasticizer and oxygen, and the ability of small molecules to place in the free volume between polymer chains.²⁶ Among them the only significant difference between both polyadipates is their molar mass. This parameter conditions the mobility of polymer chains, being higher for G206/2. This behavior was already described for other plasticized polymers.²⁶

For comparison purposes, tests with similar samples of low density polyethylene (LDPE) and polyethylene terephthalate (PET) were also carried out. OTR results for plasticized PLA were still lower than those obtained for LDPE in similar conditions (OTR.e = 160 cm³.mm/m².day). As this material is currently used in films manufacturing, the use of plasticized PLA could be acceptable for food packaging with reduced oxygen permeation. On the other hand, PET film showed OTR.e values as low as 3 cm³.mm/m².day, which is a very small compared to these materials. This was expectable because oxygen barrier properties of PET are well known and were reported as better than those of pure PLA.⁸

CONCLUSIONS

Pretreatment of PLA pellets was a key factor in the melt blending of PLA with liquid plasticizers to avoid additive losses during processing. The incorporation of plasticizer to the polymeric matrix was improved by reducing the final particle size after milling. The effect of the plasticizers addition to PLA was characterized by a reduction on the glass transition temperature due to the enhanced mobility of polymer chains, increasing with the plasticizer content. This resulted in a decrease in elastic modulus and tensile strength and a clear increase in elongation at break. Results showed that polyadipates had good compatibility with PLA, as only one T_g was observed for each formulation and no apparent phase separation was detected immediately after processing. DOA is not appropriate for the prepara-

tion of films by melt blending because significant release of plasticizer was observed during processing.

It can be concluded that G206/2 is the most efficient plasticizer, as it produced the higher decrease in T_g of PLA at 20 wt % and improved considerably the ductile properties. However, there is a limit to the plasticizer incorporation to assure that T_g do not reach values near ambient temperature to avoid losses in physical stability. Besides compatibility and efficiency, plasticizer selection should be also based on its permanence in the polymer structure. For that reason, a final decision on which additive is the ideal for the intended application in flexible food packaging, should take into account aging studies in blends to assure compatibility and appropriate properties during the shelf-life of films. In addition, the biodegradability of the resulting formulations should be evaluated to verify if these materials remain biodegradable as the neat polymer. At the present, test for polyadipate-plasticized PLA films are on-going. Preliminary results allow us to anticipate that plasticized films are more bio-susceptible to microbial attack. Final results will be reported in a forthcoming article.

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