

Ageing of poly(lactic acid) films plasticized with commercial polyadipates

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Abstract

BACKGROUND: Amorphous poly(lactic acid) (PLA) was plasticized with two polyadipates with different molar masses. Some physical properties were studied over time to evaluate the stability of these blends. The aim of this study was to improve PLA ductility and consider the feasibility of its use in flexible films for food packaging.

RESULTS: The addition of polyadipates caused a decrease of the glass transition temperature (T_g) and an increase of PLA chain mobility. Samples with T_g values above the storage temperature suffered physical ageing with a reduction in free volume. All the unaged blends were mainly amorphous, but samples with T_g below the storage temperature developed crystallinity during ageing leading to phase separation. Ductile properties of films improved with plasticizer content immediately after blending, but there was a deterioration in such properties upon ageing due to matrix densification and crystallization of PLA chains.

CONCLUSION: PLA can be efficiently plasticized by polyadipates and the results have shown that some of the prepared films remain flexible with no phase separation after 150 days.

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Keywords: poly(lactic acid); polyadipates; films; ageing; crystallinity

INTRODUCTION

Several biodegradable polymers have been investigated during the last few decades as alternatives to non-degradable polymers currently used in film production.^{1–4} Among them, poly(lactic acid) (PLA) has been broadly studied due to its interesting properties and the fact that it can be obtained from common agricultural products, such as corn.^{5,6} However, certain characteristics, such as its high brittleness, are undesirable for flexible film manufacturing. Therefore, it needs to be modified and/or additivated. Several substances have been studied as PLA plasticizers, such as citrate esters,^{7–9} glycerol and oligomeric lactic acid⁹ and poly(ethylene glycol) (PEG).^{9–11} In general, good ductile properties were only obtained after the addition of plasticizer concentrations higher than 10 wt%. Compatibility of blends and plasticizer efficiency are the main conditions for the development of flexible films for packaging, but it is also necessary to ensure the permanence of the plasticizer in the matrix and consequently the stability of films during their shelf life. Some ageing studies have been carried out on PLA blends with different substances. Effective plasticization of semicrystalline PLA with tributyl citrate (TbC) and triacetine was possible with 15 wt% of additive but resulted in unstable systems due to cold crystallization which caused partial phase separation. Consequently, migration of these monomeric compounds to the film surface occurred and the material became more brittle.¹² To overcome this problem, the molar mass of plasticizers was increased, maintaining the same chemical structure.¹³ But, to remain compatible with PLA, the molar mass of plasticizer should not go beyond a certain limit to avoid a decrease in solubility leading to the formation of a two-phase system. A trimer of TbC (TbC-3) was considered a good compromise between the monomer, which was too inclined to migrate, and the heptamer

of TbC, where phase separation was observed already at a concentration of 15 wt% in the unaged material.¹³ TbC-3 was compatible with PLA up to 20 wt%. However, some phase separation in the bulk upon ageing at ambient temperature for 4 months was observed even for 10 wt% TbC-3, but migration of the plasticizer to the film surface was only observed for 20 wt% TbC-3.

Oligomeric plasticizers based on diethylbishydroxymethyl malonate (DBM) with a better compatibility with PLA were also synthesized.¹⁴ Blends were compatible up to concentrations of 25 wt% of the DBM monomer. However, samples with 15 wt% showed phase separation and plasticizer migration after six weeks of storage at ambient temperature. A DBM oligomer with eight repeating units was miscible up to 15 wt% and the system remained stable upon ageing for six weeks. The introduction of polar amide groups in the oligoesteramides enhanced the plasticization by increasing their solubility in PLA as a result of polar interactions and hydrogen bonding. Thus, increased compatibility was achieved and morphological stability was enhanced even further with strain at break values above 200% as compared to that before ageing.¹⁵

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These oligomers were not commercially available and had to be synthesized.

PEG is one of the most studied polymeric plasticizers for PLA. It was found that blends with up to 30 wt% of PEG with molar mass of 8000 Da were miscible when they were quenched from the melt. However, blends were not stable and suffered significant changes in properties over time.¹⁶ It was found that when PLA had a low stereoregularity the ageing was caused by slow crystallization of PEG. Modification of tensile properties was associated with this process, which was arrested when the glass transition temperature (T_g) of the blend reached the ageing temperature. If the optical purity of PLA was high enough, it could also crystallize.¹⁷ Other studies also reported some phase separation upon ageing for 20 wt% of PEG with molar mass 1000 Da, increasing the stiffness of plasticized PLA.¹⁸ Other authors proposed the use of poly(propylene glycol) (PPG) as a PLA plasticizer,^{19,20} since it is not able to crystallize. It was found that PPG with molar mass of 500 Da was miscible with the matrix up to 12.5 wt% while PPG of 1000 Da was miscible only up to 10 wt%. Such formulations showed deformations at break as high as 700 and 500%, respectively. It was assumed that blends should be stable over time since their T_g was above ambient temperature, although ageing studies were not reported for such materials.

Our current work is focused on the study of the morphological stability of amorphous PLA films plasticized with two commercial polyadipates with different molar masses based on the condensation reaction of adipic acid and propan-1,3-diol. Blends were prepared in mass ratios of 10 and 20 wt% and processed into films by compression moulding. The compatibility of blends with up to 20 wt% of polyadipates was studied immediately after processing in our previous work.²¹ In order to evaluate whether the blends remained miscible during the foreseen shelf life of the material, films were stored for 5 months at $28 \pm 2^\circ\text{C}$. Structural, thermal, mechanical and thermomechanical properties were studied at different ageing times with the aim of finding PLA formulations with adequate properties for use in flexible food packaging. Concerning food contact materials, several additional requirements should be fulfilled. Besides good compatibility, low plasticizer migration and appropriate thermal and mechanical properties, barrier properties, essentially to oxygen, are also relevant.²² Therefore, the oxygen transmission rate (OTR) of films was also measured over time.

EXPERIMENTAL

Materials

PLA (CML PLA, $M_n = 63\,000 \pm 12\,000$ Da, $T_g = 58.2^\circ\text{C}$) was purchased from Hycail Finland Oy (Turku, Finland). Polymeric commercial plasticizers were kindly supplied by Condensia Química SA (Barcelona, Spain) and are described elsewhere.²¹ They were identified with commercial names as G206/2 ($M_n = 1532$ Da; $T_g = -72.9^\circ\text{C}$) and G206/7 ($M_n = 2565$ Da; $T_g = -53.8^\circ\text{C}$).

Methods

PLA pellets were dried at 60°C under vacuum for 4 h and milled with a RETSCH ZM200 Ultra Centrifugal Mill (Haan, Germany) to a final particle size of approximately 1 mm. Then, they were manually pre-mixed with plasticizers at 10 and 20 wt%. After standing for 2 h at ambient temperature, samples were charged into a Haake Rheomix 9000 internal mixer (Karlsruhe, Germany) equipped with a pair of high-shear roller-type rotors and were melt-blended at 50 rpm during 8 min. The processing temperature was set at

170°C but it increased to 190°C upon mixing. Blends were then processed into films by compression moulding at 180°C in a hot press (Collin GmbH, Ebersberg, Germany) using stainless steel frames to ensure a constant film thickness. Materials were kept between the plates at atmospheric pressure for 5 min until melting and then they were successively pressed at 3 MPa for 1 min, 5 MPa for 1 min and 10 MPa for 3 min. Samples were then cooled with water under pressure (10 MPa). The obtained films were stored at $28 \pm 2^\circ\text{C}$ for 5 months and periodically evaluated by means of DSC, wide-angle X-ray scattering (WAXS), tensile tests, dynamic mechanical analysis (DMA), OTR analysis and SEM.

DSC tests were conducted using a TA Instruments DSC Q-100 (New Castle, DE, USA) under nitrogen atmosphere. For the ageing study, thermograms were obtained at $10^\circ\text{C min}^{-1}$ heating from -90 to 180°C at different storage times. In order to obtain the thermal behaviour of unaged samples, the material was kept at 180°C for 5 min, followed by quenching to -90°C and further heating from -90 to 200°C at $10^\circ\text{C min}^{-1}$.

WAXS patterns of films were recorded with a Seifert diffractometer, model JSO-DEBYEFLEX 2002, equipped with a Cu $K\alpha$ radiation source ($\lambda = 0.1546$ nm), operating at an applied voltage and current of 40 kV and 40 mA, respectively. The incidence angle was varied between 2° and 90° at a scanning rate of 1°min^{-1} .

SEM was performed using a JEOL JSM-840 (Japan) in order to analyze the cross-sections of samples.

Tensile tests were carried out with a universal electronic dynamometer from LLOYD Instruments, model LR30K (Fareham, Hants, UK). Film thickness was measured using a Digimatic micrometer series 293 MDC-Lite (Mitutoyo Corporation, Japan) to ± 0.001 mm. Tensile tests were performed with rectangular probes (100×10 mm²) at a crosshead speed of 10 mm min^{-1} . Initial grip separation was 5 cm and a load gripping force of 500 N was applied. Average tensile strength, percentage deformation at break (% ϵ) and elastic modulus (E) were calculated from the resulting stress-strain curves according to the standard procedure (ASTM D882-91).²³ Results were the average of at least six measurements.

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

OTR was measured with an oxygen permeation analyser from Systech Instruments, model 8500 (Metrotec SA, Spain). Films with an average thickness of 160 ± 10 μm were selected and 14 cm diameter circle samples were cut for each formulation. Films were clamped in a diffusion chamber where pure oxygen (99.9%) was introduced into the upper half while nitrogen was injected into the lower half of the chamber where an oxygen sensor was placed.

RESULTS AND DISCUSSION

Quenched PLA/polyadipate blends were miscible at all the compositions tested since a single T_g was observed in every case with significant reductions in its value compared to neat polymer (Fig. 1, upper curve for each formulation). For equal concentration, the effect was more pronounced for the polyadipate with the lower molar mass due to its lower T_g . Although no crystallization peak was detected for plasticized quenched samples, a slight shift in the baseline of the DSC traces was noticed. For 10 wt% of both polyadipates a small melting peak was observed

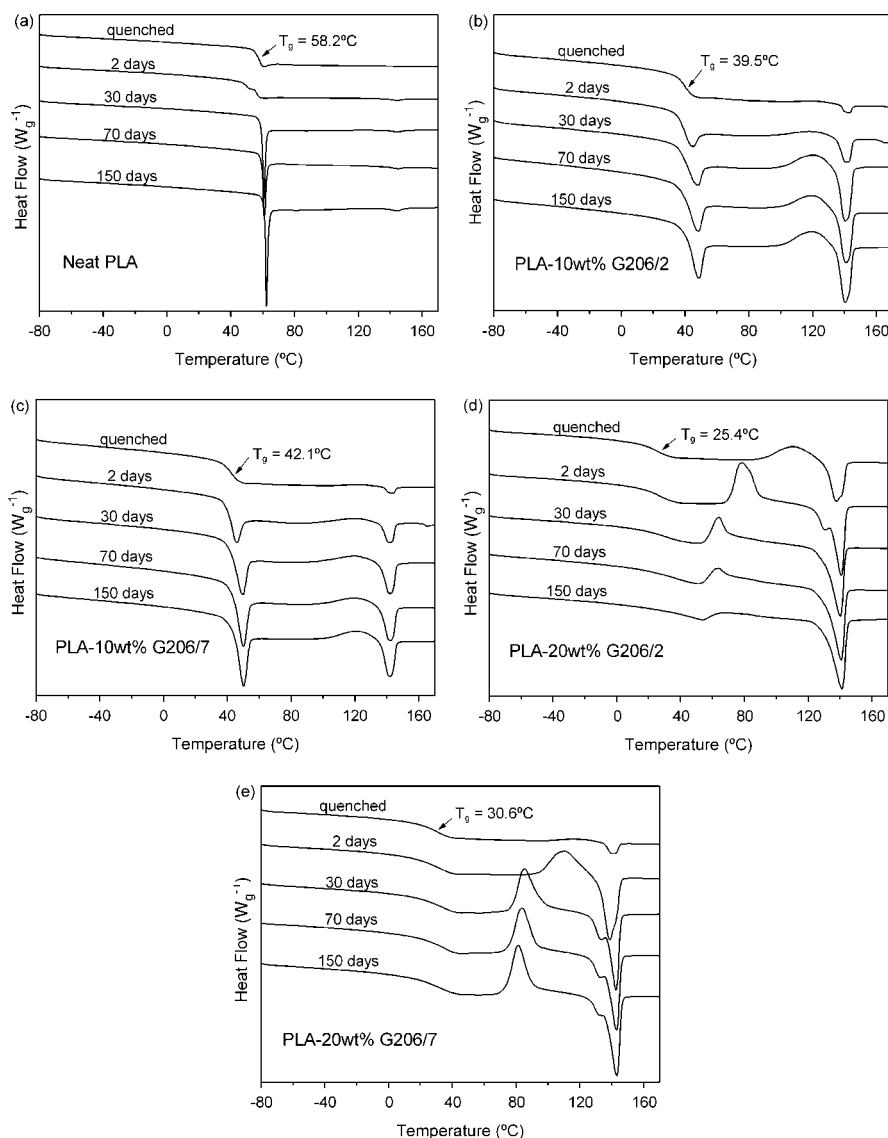


Figure 1. DSC thermograms of (a) neat PLA, (b, d) PLA films plasticized with G206/2 and (c, e) PLA films plasticized with G206/7 at various storage times.

at approximately 143 °C. As chain mobility increased due to a greater amount of plasticizer, melting temperatures were shifted to lower values, in particular for 20 wt% of G206/2 (Table 1). The increased chain mobility of PLA due to the plasticizing effect only induced crystallization and further melting during heating, since the original material had an amorphous nature at room temperature. This was revealed by the fact that the crystallization exotherm and the melting endotherm in the DSC curves at two days of storage had very similar heat content since differences between areas enclosed in the respective peaks are near zero (Table 1).

When amorphous PLA is quenched into the glassy state, it is in a non-equilibrium state and slow thermodynamic changes occur with time as the polymer structure spontaneously progresses to a lower free-energy state when it is stored at temperatures below T_g .^{24,25} Due to such physical ageing, the material undergoes changes in its physical properties that might be significant for food packaging applications since it affects mechanical and barrier properties.^{26,27}

Neat PLA films and those plasticized with 10 wt% of both polyadipates suffered physical ageing, as can be concluded from the endothermic peak at T_g (Fig. 1). The area of this peak increased considerably at short times as the result of a higher relaxation enthalpy, but after 70 days of storage the increments were not significant (Table 1). This means that the rate of physical ageing was very fast initially and decreased with time. Formulations with 20 wt% of plasticizer showed no relaxation enthalpy since their T_g values were below or near the storage temperature.

The amount of crystallizable material during heating increased upon ageing due to the reorganization of the PLA structure involving molecular rearrangements, as already stated by Pluta *et al.*²⁸ As can be observed in Fig. 1, the crystallization and melting peak areas increased with time but the peak positions for 10 wt% of polyadipates did not undergo significant changes. The difference between melting (ΔH_m) and crystallization (ΔH_c) enthalpies was approximately zero for such formulations during the whole storage period (Table 1). However, for 20 wt% of G206/2 the area for the crystallization peak after 2 days started to decrease and shifted to lower temperatures, whereas the area for the melting peak still

Table 1. Relaxation enthalpy (ΔH_r), crystallization temperature (T_c), melting temperature (T_m) and $\Delta H_{mc}(= \Delta H_{melting} - \Delta H_{crystallization})$ of plasticized PLA films at different storage times

Ageing time (days)	Thermal property	G206/2		G206/7	
		10 wt%	20 wt%	10 wt%	20 wt%
Quenched	T_c (°C)	122	112	123	119
	T_m (°C)	143	138	143	141
	ΔH_{mc} (J g ⁻¹)	0.05	0.19	0.23	0.03
2	ΔH_r (J g ⁻¹) ^a	3.45	–	4.41	–
	T_c (°C)	119	79	121	111
	T_m (°C)	141	130–141	142	139
30	ΔH_{mc} (J g ⁻¹)	0.64	0.08	0.27	0.05
	ΔH_r (J g ⁻¹) ^a	4.08	–	5.88	–
	T_c (°C)	121	64	121	85
70	T_m (°C)	141	140	142	133–143
	ΔH_{mc} (J g ⁻¹)	3.21	7.44	0.65	0.62
	ΔH_r (J g ⁻¹) ^a	5.48	–	6.55	–
150	T_c (°C)	120	63	121	84
	T_m (°C)	140	141	142	132–143
	ΔH_{mc} (J g ⁻¹)	0.67	10.60	0.84	0.30
150	ΔH_r (J g ⁻¹) ^a	5.51	–	6.95	–
	T_c (°C)	120	–	121	82
	T_m (°C)	140	141	142	131–143
	ΔH_{mc} (J g ⁻¹)	0.86	16.74	0.36	0.02

^a ΔH_r was measured by integration of the difference between the quenched and aged DSC curves. Values of ΔH_r for neat PLA film were 5.22 J g⁻¹ (30 days), 6.32 J g⁻¹ (70 days) and 6.80 J g⁻¹ (150 days).

increased. Therefore the material was able to crystallize at the storage temperature for this formulation. This behaviour was not observed in the case of 20 wt% G206/7 for which, despite the shift in the crystallization peak to lower temperatures, $\Delta H_m - \Delta H_c$ was also approximately zero up to 150 days of storage, meaning that this material remained mostly amorphous, as for those formulations with 10 wt% of plasticizer.

It should also be emphasized that a double melting peak was observed for materials plasticized with 20 wt% of both plasticizers. This is an indication of a simultaneous melting and recrystallization during the temperature scan of unstable crystals at temperatures between cold crystallization and melting.²⁹ This was not considered to be due to the presence of two distinct crystals in the initial sample since all the materials that showed such behaviour were mainly amorphous.

In accordance with the DSC results, WAXS analysis showed that all samples were mainly amorphous after processing (Fig. 2). However, the lower molar mass polyadipate at the higher concentration level developed crystallinity upon ageing (Fig. 2(b)), while the rest of the samples remained mostly amorphous during the whole storage period (Figs 2(a) and (c)). Crystallization of PLA chains led to partial phase separation between polymer and plasticizer due to the densification of the matrix structure. Consequently there could be easier diffusion of the polyadipate through the polymer structure and further migration to the film surface. This fact was also manifested by the sticky surface developed by such samples with time.

SEM observations also confirmed these results, since for unaged films with 20 wt% of both plasticizers homogenous morphologies were registered (Figs 3(a) and (b)). However, after 30 days of

Table 2. T_α values at different storage times for all samples

Sample	T_α (°C) (unaged)	T_α (°C) (30 days)	T_α (°C) (70 days)	T_α (°C) (150 days)
Neat PLA	58	60	61	59
PLA–10 wt%	G206/2	44	45	46
	G206/7	44	46	47
PLA–20 wt%	G206/2	27	33	33
	G206/7	32	34	34

storage, the micrograph of PLA–20 wt% G206/2 revealed some macroscopic phase separation in the system (Fig. 3(c)). In the case of G206/7, although development of crystallinity was not detected, and its morphology seemed to be homogenous (Fig. 3(d)), certain stickiness on its surface was observed with time.

Regarding the mechanical properties, the decrease in T_g due to the incorporation of plasticizers corresponded with a decrease in the elastic modulus (E) and an increase in the deformation at break (Fig. 4). This indicates the higher ductility of plasticized films compared to the neat polymer which showed brittle behaviour. It was found that all samples suffered progressive changes in elastic modulus and elongation at break upon ageing. After 70 days of storage there were clear increases in E (e.g. 325% increase for 20 wt% G206/2) and decreases in $\% \varepsilon$ (from 485 to 309% for the same sample) with the final result of a more fragile material. No significant changes were observed for times longer than 70 days, as in the case of the DSC tests.

The largest changes in mechanical properties were found for the formulations with 20 wt% of plasticizer (e.g. 367% increase in E for 20 wt% G206/2 and 7% for neat PLA after 150 days of storage). Nevertheless, it should be emphasized that the results for deformation at break of such formulations were still two orders of magnitude higher than those obtained for the neat polymer. This means that the improvement in ductile properties for plasticized PLA (at the highest concentration tested in this work) was still significant after storage at ambient temperature for 150 days. Although some of the changes in mechanical properties for neat PLA and films plasticized with 10 wt% are within the experimental error, such behaviour could be attributed to physical ageing since the relaxation enthalpy induced a reduction in free volume in the polymer structure.²⁶

The dynamic mechanical relaxation behaviour of the blends was represented by the temperature dependence of storage modulus (E') and loss modulus (E'') (Fig. 5). In accordance with the DSC and tensile experiments, it was observed that the incorporation of plasticizers increased the chain mobility of the PLA matrix and consequently its ductility. Parameter T_α , defined as the maximum of the loss modulus and related to T_g ,^{13,16} was shifted to lower temperatures with increasing plasticizer content. The obtained results correlated closely with T_g data from DSC (Fig. 1) as was also reported for polylactide/PEG blends.¹⁶ The elastic modulus also decreased at temperatures around ambient (20–25 °C). In the plastic region, an increase in E' was observed, which was attributed to the cold crystallization process promoted by the increased chain mobility. Similar results were reported for PLA plasticized with citrates.¹³ In addition, the plasticizer with the lowest molar mass was the most effective, as concluded from the highest depression in T_α for unaged materials (Table 2). For such samples, no plasticizer segregation was detected by DMA, since, as in DSC thermograms, only one T_g was observed for

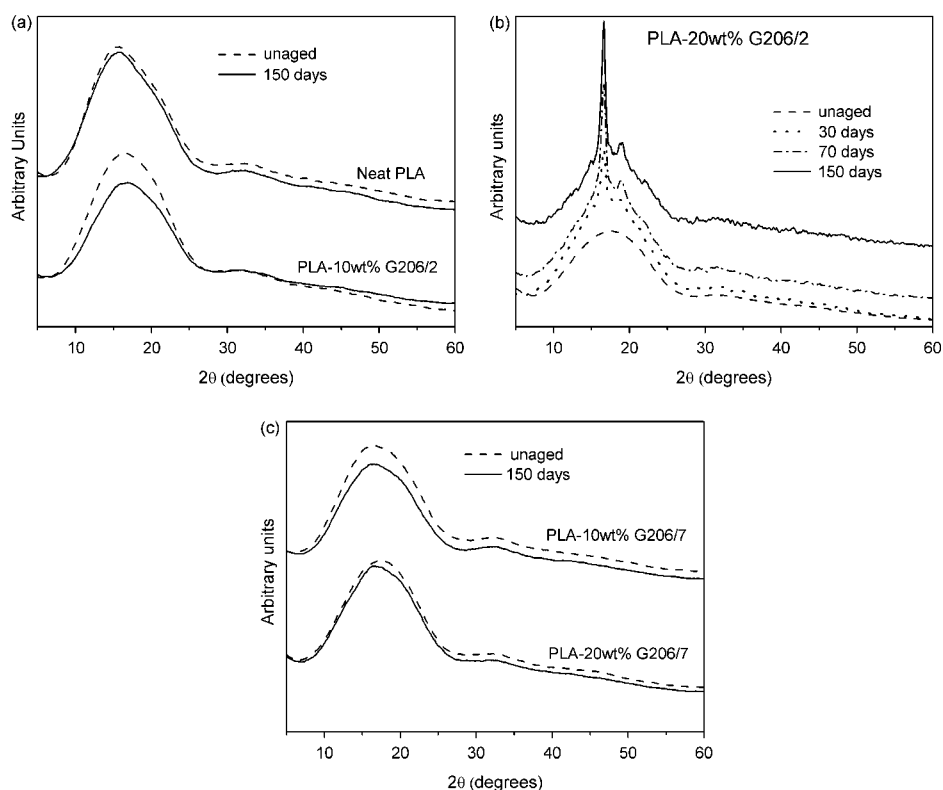


Figure 2. WAXD patterns of (a) neat and plasticized PLA with 10 wt% G206/2, (b) plasticized PLA with 20 wt% G206/2 and (c) plasticized PLA with G206/7 at various storage times.

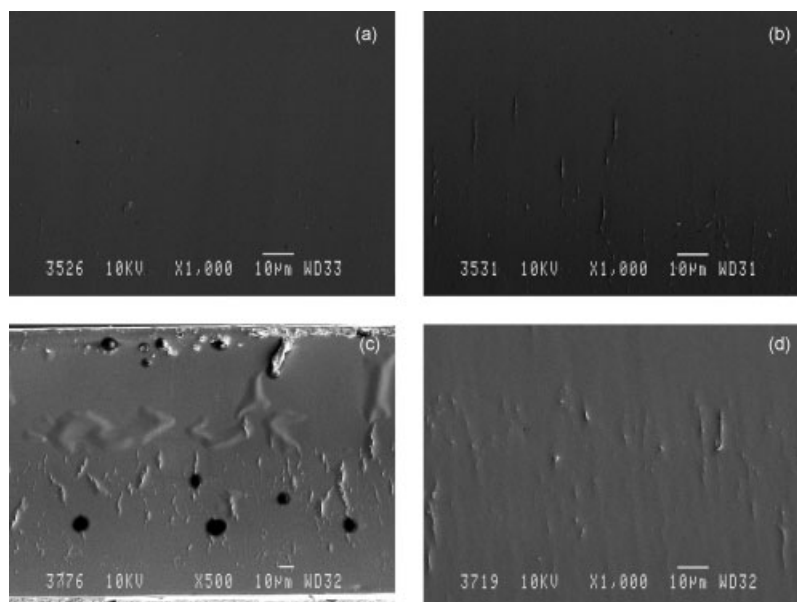


Figure 3. SEM micrographs of fracture surfaces: (a) unaged PLA–20 wt% G206/2 ($\times 1000$); (b) unaged PLA–20 wt% G206/7 ($\times 1000$); (c) PLA–20 wt% G206/2 after 30 days of storage ($\times 500$); (d) PLA–20 wt% G206/7 after 30 days of storage ($\times 1000$).

each formulation even at the highest plasticizer concentration. This confirmed that blends did not suffer any phase separation immediately after processing.¹³

In the case of neat PLA and blends containing 10 wt% of polyadipates, the aged samples showed no important differences from the unaged ones (Fig. 5), indicating that there was no apparent segregation of the plasticizer in such systems during

the five-month storage period. The changes in T_{α} for all samples during ageing are given in Table 2. The slight increase in T_g observed for most of the samples with ageing time could be another indication of the effect of the decrease of free volume in the polymer structure caused by chain packing.

An additional peak was observed in the E'' curve around -66°C for the formulation with 20 wt% G206/2 after 30 days

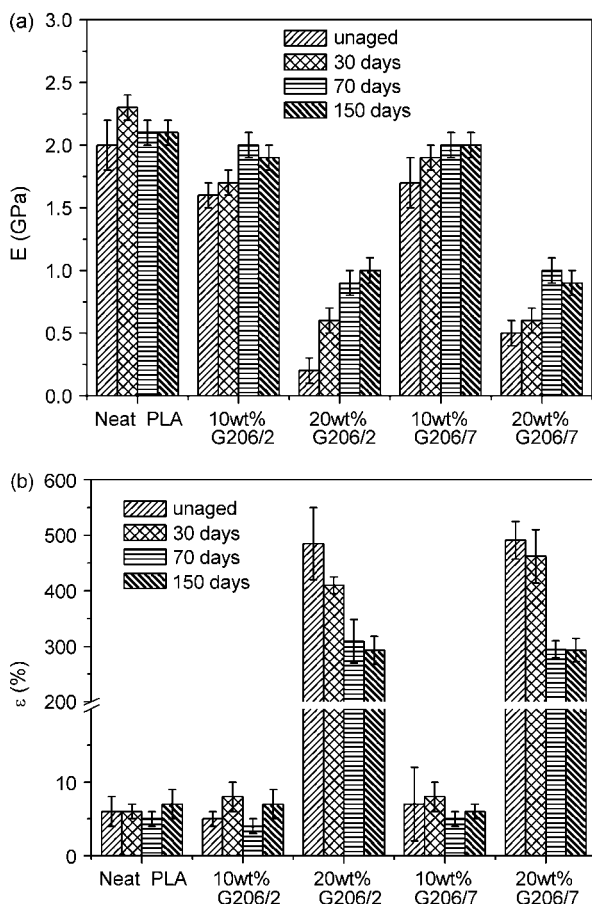


Figure 4. (a) Elastic modulus (E) and (b) percentage deformation at break (ϵ) for neat PLA and PLA plasticized with polyadipates at various storage times.

of storage, confirming the partial phase separation of this blend as a consequence of the ageing process. This additional peak appeared at higher temperature than T_g of the pure plasticizer (-73°C) determined by DSC. It must be considered that the experimental conditions were not the same for both techniques, and that in general T_g values obtained from E'' were a few degrees higher than those determined by DSC.

It is important to mention that aged material with 20 wt% of G206/2 presented small drops all over its surface after the experiment because of the exudation of plasticizer during heating and tensing. This fact could be responsible for the different behaviour of this formulation at temperatures above T_g . In the case of 20 wt% of G206/7, the exudation observed after heating

the tensile specimen up to 130°C was less, and consequently changes were smaller relative to the unaged material.

Peak temperatures calculated from $\tan \delta$ curves are shown in Table 3. They were always higher than those values obtained from E'' (Table 2). As expected from amorphous samples, peak values in the $\tan \delta$ curve ($\tan \delta_{\max}$) for all unaged samples were greater than unity (≥ 1). Neat PLA and samples plasticized with 10 wt% of polyadipate had $\tan \delta_{\max} > 2$, while those plasticized with 20 wt% of polyadipate had $1 < \tan \delta_{\max} < 2$. Upon 30 days of ageing the intensity of the $\tan \delta$ peak for 20 wt% of G206/2 became smaller than unity due to the crystallization process, with the consequence of a reduction in the number of polymer chains participating in the glass transition.³⁰ For the rest of the samples $\tan \delta_{\max}$ remained in the same range for 150 days as in the unaged state.

The physical ageing process of amorphous glassy polymer films also affects their gas-transport properties, due to the gradual decrease of the free volume available for gas molecules to move through the polymer matrix.²⁶ This process is dependent on the thermal history and thickness of samples. Since all films in this study were prepared under the same conditions, OTR of all samples per film thickness was compared at different storage times to evaluate the changes in this important property for the intended food packaging application. After processing it was observed that the addition of plasticizers increased the OTR with increasing amounts of additive (Fig. 6). This was due to the fact that the plasticizers act by reducing the polymer chain-to-chain interactions by distributing themselves homogeneously within the polymer, increasing the free volume.³¹ The effect was more important with the low molar mass polyadipate since the resistance of the film to oxygen transmission was reduced by the increase in mobility of the polymer chains.^{32,33} However, the molecular rearrangement during storage led to important OTR reductions for all samples compared to the initial values due to the gradual decrease of the free volume available to gas diffusion due to physical ageing (Fig. 6). In the case of formulations with 20 wt% of plasticizers which did not show relaxation enthalpy, the reduction in OTR was due to the crystallization process and consequent densification of the polymer structure. No significant differences in OTR were observed between 45 and 150 days of storage, which means that samples should be stored at least 45 days in order to obtain stable OTR performance.

CONCLUSIONS

The addition of polyadipates to amorphous PLA caused a decrease in its T_g due to enhanced mobility of polymer chains. This fact also resulted in structural rearrangements and reduction of free volume during ageing. In the case of 10 wt% of additive, this

Table 3. Temperature of $\tan \delta$ peak ($T_{\tan \delta}$) and peak value ($\tan \delta_{\max}$) for all samples at different storage times

Sample	Unaged		30 days		70 days		150 days	
	$T_{\tan \delta}$ ($^\circ\text{C}$)	$\tan \delta_{\max}$	$T_{\tan \delta}$ ($^\circ\text{C}$)	$\tan \delta_{\max}$	$T_{\tan \delta}$ ($^\circ\text{C}$)	$\tan \delta_{\max}$	$T_{\tan \delta}$ ($^\circ\text{C}$)	$\tan \delta_{\max}$
Neat PLA	66	2.4	67	2.5	66	2.8	65	2.7
10 wt% G206/2	52	2.5	52	2.5	53	2.2	53	2.4
20 wt% G206/2	43	1.7	44	0.6	44	0.5	55	0.4
10 wt% G206/7	53	2.3	53	2.6	55	2.2	55	2.2
20 wt% G206/7	47	1.8	47	1.6	46	1.5	47	1.3

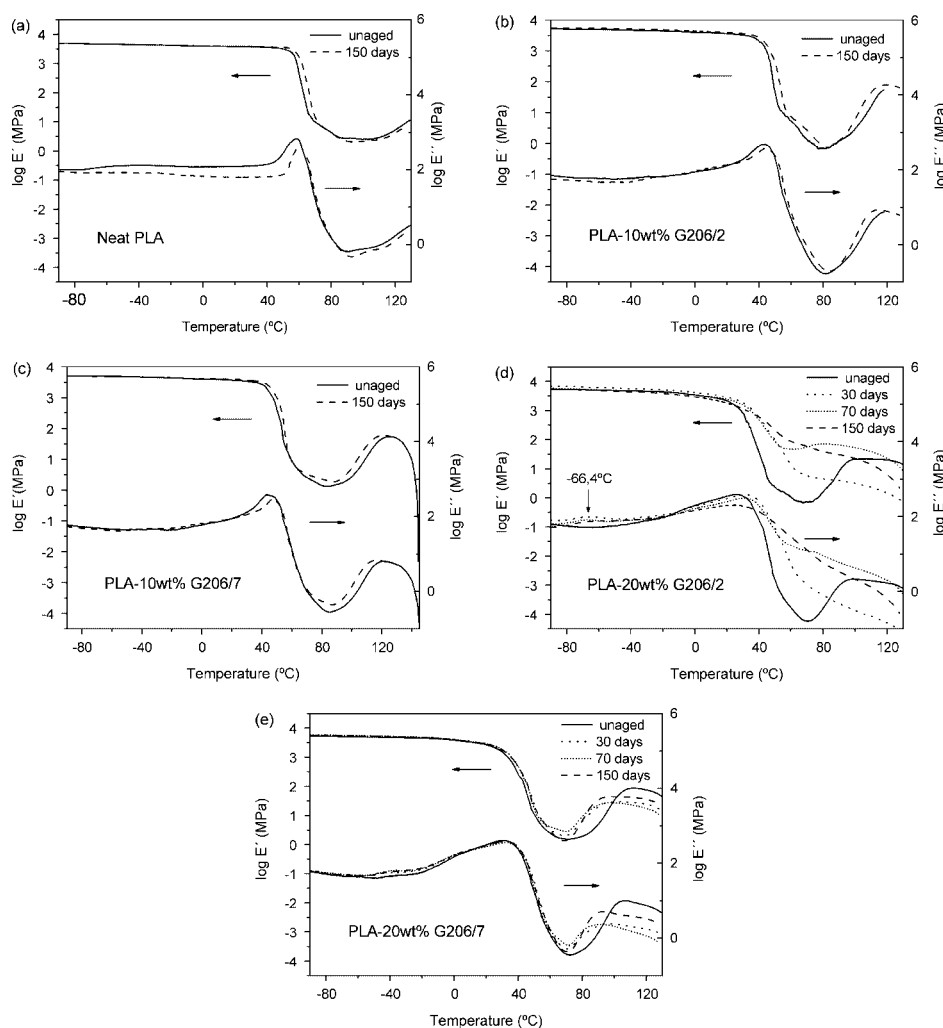


Figure 5. Temperature dependence of storage and loss modulus curves from DMA runs of (a) neat PLA, (b, d) plasticized PLA with G206/2 and (c, e) plasticized PLA with G206/7 at various storage times.

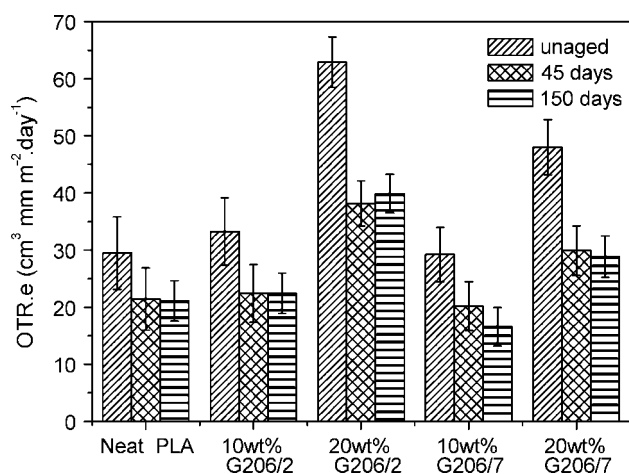


Figure 6. OTR values per film thickness of neat and plasticized PLA films at various storage times.

rearrangement only served to increase the crystallizable material upon heating, but samples remained essentially amorphous at the storage temperature. Blends seemed to be stable over time,

since no evidence of phase separation was found. However 10 wt% additive formulations did not show enough ductility for the intended application in flexible food packaging.

In the case of formulations with 20 wt%, the lower molar mass polyadipate yielded non-stable materials during storage, since T_g values were below the ageing temperature ($28 \pm 2^\circ\text{C}$). Although elastic modulus and deformation at break are more advantageous for flexible films, they are not suitable for food packaging due to plasticizer migration to the film surface. In the case of 20 wt% of G206/7, the T_g value was very close to ageing temperature. Although development of crystallinity was not detected, a certain stickiness was observed with time.

Further work is currently in progress to find an adequate formulation for which both good ductility and absence of phase separation during storage are required. Optimum formulations of plasticized PLA should show enough chain mobility to be flexible for the intended application, without significant cold crystallization and plasticizer migration during storage time.

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