

Structure and properties of clay nano-biocomposites based on poly(lactic acid) plasticized with polyadipates

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The use of nano-biocomposites based on plasticized poly(lactic acid) (PLA) has been proposed as a way to improve the polymer ductility and to expand PLA applications window. Novative nano-biocomposites were elaborated with PLA plasticized by polyadipates (15 wt%) with different molar masses (from 1500 to 2500 Da), with 2.1 wt% of an organo-modified montmorillonite (O-MMT). These materials showed enhanced ductility and barrier properties. The clay was swelled in liquid polyadipates prior to their blending with PLA to facilitate chains intercalation and nanofiller exfoliation during melt-blending. In certain processing conditions, quite homogenous and exfoliated structures were obtained, as shown by X-ray diffraction (XRD) and transmission electronic microscopy (TEM) results. Irrespective of the average molar mass of the polyadipate, the clay addition induced a reduction in around 25% in oxygen transmission rate (OTR) without an important detriment in tensile properties. Nano-biocomposites prepared with higher molar masses polyadipates showed the highest thermal stability as well as the lowest OTR, resulting in very promising and novative materials for different applications such as soft packaging. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: poly(lactic acid); polyadipates; montmorillonite; oxygen transmission; ductility

INTRODUCTION

Biopolymers are a growing research issue since they appear as a solution to the emerging environmental concerns that have risen in recent years. They represent an interesting alternative to synthetic polymers for a short-life range of applications (packaging, agriculture, etc) and for biomedical uses (implants, etc). At present, due to its availability in the market and low price, poly(lactic acid) (PLA) has high potential for being used as alternative material to some common polymers, such as poly(ethylene terephthalate), PET. With biomedical, packaging remains a major outlet in PLA applications because of some favorable properties, such as high transparency, excellent printability, and low-temperature sealability.^[1] PLA has been labeled as GRAS (Generally Recognized as Safe) material by the FDA (Food and Drug Administration) which ensure its application in food-contact items. Unfortunately, so far the use of PLA for food packaging is strongly limited because of somewhat poor mechanical, thermal, and barrier properties.^[1–4]

Different solutions have been proposed in the literature to improve PLA's performance. The lack of ductility can be overcome, for instance, with the addition of plasticizers,^[5–8] although this association increases the gases permeability of the matrix which could be detrimental for packaging use.^[9] Besides, great attention has recently been paid to the association between biopolymers with nano-sized fillers forming hybrid organic–inorganic systems and, in particular, to those in which layered silicates are dispersed at a nanometric level in a biopolymer matrix.^[10–11] Such nanocomposites called nano-biocomposites,

often show improved barrier properties, mechanical and oxidation stability, decreased solvent uptake, self-extinguishing behavior, and, eventually, tunable biodegradability.^[10–16]

Naturally occurring layered silicates and particularly montmorillonite (MMT) can be used to prepare polymer nanocomposites, since they are low cost and environment friendly materials.^[12] The stacking of layers or platelets leads to a regular gap which is negatively charged and counterbalanced by alkali and alkali-earth cations located inside the galleries. When the extent of the intercalation process due to polymer chains reptation between layers is large enough, delamination of the clay platelets

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Contract/grant sponsor: Spanish Ministry of Science and Innovation, Project Ref.; contract/grant number: MAT2008-06840-C02-01.

takes place. Consequently the structure presents no order anymore which is referred as an exfoliated nanocomposite. Complete exfoliation of all the individual platelets is very difficult to achieve and most nanocomposites contain regions of both intercalated and exfoliated structures. Attention should be paid to the compatibility between the polymer matrix and the silicate.^[11–12] In general, non-modified MMT is compatible with hydrophilic polymers or polyelectrolytes.^[17] Aliphatic polyesters, in particular PLA, are organophilic materials and consequently their compatibility with natural MMT is low. To improve the affinity, the natural clay must be organically modified by ion-exchange reactions with cationic surfactants, including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations, obtaining the so-called organo-modified layered montmorillonites (O-MMT).^[10–15] Such modifiers reduce the surface energy of the inorganic host, improve the wetting with the polymer matrix, and increase the distance between the inorganic platelets (d-spacing).

Many studies on nano-biocomposites based on the association of O-MMT with bio-based and/or biodegradable polymers such as starch,^[18–20] gelatin,^[17,21] polyhydroxycanoates,^[22–25] polybutylene adipate co-terephthalate,^[26,27] neat PLA,^[28,29] and plasticized PLA^[30–35] were recently published. Paul *et al.*^[30] indicated that intercalation in nano-biocomposites based on plasticized PLA with or without MMT organo-modification was essentially provoked by the interlayer migration of plasticizers, such as poly(ethyleneglycol) (PEG). The subsequent increase in d-spacing facilitates the polymer migration between platelets. However, a competition between polymer and plasticizer intercalation was observed. Paul *et al.*^[32] settled a protocol consisting in *in situ* polymerization of lactide from end-hydroxylated PEG with Cloisite[®]-30B and tin octoate (Sn(Oct)₂) as activator/initiator. The as-obtained plasticized PLA/O-MMT nanocomposites showed an exfoliated structure with enhanced thermal properties. Crystallinity was also affected since the mobility of the resulting grafted chains was restricted. Glass transition (T_g) and melting (T_m) temperatures were not influenced by the nanoclay.

In previous works the plasticization of amorphous PDLA with commercial polyadipates to prepare films for food packaging applications was reported.^[8,36] These polyadipates were selected since they were supposed to limit their migration to foodstuff and they were approved for food contact materials. Two different concentrations were tested (i.e. 10 and 20 wt%). Ageing studies demonstrated that the addition of 10 wt% of polyadipates to PDLA yielded materials that remained basically amorphous and seemed to be stable over time, but they did not show flexibility for films manufacturing. On the other hand, the incorporation of 20 wt% conducted to clear improvements in ductility, but oxygen transmission rate (OTR) was considerably increased and materials were not completely stable after 90-days storage.^[36] The addition of polyadipates at 15 wt% to PLA seems to be convenient to get the balance between all properties and to reduce OTR results by combination with organically modified layered silicates. It is anticipated that these nano-biocomposites would produce stable materials with good compromise between barrier and mechanical properties.

The aim of this paper is the preparation and characterization of novative nano-biocomposites based on PLA plasticized with 15 wt% of selected polyadipates and O-MMT. Their nanostructure and the structure/property relationships were analyzed. Since final properties are strongly dependent on the structure, this paper is first dedicated to the determination of clay organization

in the matrix, using advanced characterization techniques such as X-ray diffraction (XRD) and transmission electron microscopy (TEM). Further nanocomposite structural characterization was carried out by using XRD and testing OTR. The thermal and mechanical properties were also determined and correlated to the structure to establish structure/property relationships.

EXPERIMENTAL

Materials

PLA (CML PLA, $M_n = 63000 \pm 12000$ Da, $T_g = 58^\circ\text{C}$) was purchased from Tate&Lyle (Turku, Finland). Commercial polyadipates were kindly supplied by Condensia Química S.A (Barcelona, Spain) and were described elsewhere.^[8] They were identified as G206/2 ($M_n = 1532$ Da; $T_g = -73^\circ\text{C}$), G206/5 ($M_n = 2209$ Da; $T_g = -58^\circ\text{C}$), and G206/7 ($M_n = 2565$ Da; $T_g = -54^\circ\text{C}$). O-MMT Cloisite[®]-30B (C30B) with a CEC (cation exchange capacity) of 90 meq/100 g clay was provided by Southern Clay Products Inc (TX, USA). This O-MMT is based on a quaternary ammonium surfactant, $\text{N}^+(\text{Me})(\text{EtOH}_2)\text{T}$, where T is Tallow (~65% C18; ~30% C16; ~5% C14) with 30 wt% organics content.

Preparation of plasticized PLA and nanocomposites

PLA and clay were dried overnight at 80°C in a ventilated oven while plasticizers were dried at 55°C during 2 hr in desiccator with P_2O_5 . They were kept more than 24 hr in desiccator under vacuum before processing.

Plasticizer-clay mixtures were previously prepared to study the swelling ability of the polyadipates to the clay. The preparation of nano-biocomposites was performed by using polyadipates at 15 wt% on PLA basis and 3 wt% clay (2.1 wt% inorganic content) relative to the plasticized PLA matrix. Firstly, the addition order between the three components, liquid plasticizers and solids (PLA and clay), was explored. The effect of sonication (60°C for 2 hr) was also studied and it was verified that the polyadipate molar mass was not affected during this treatment. After homogenization of the corresponding mixture at ambient temperature, it was added into a Haake Rheomix 600 internal mixer (Karlsruhe, Germany) and was melt-blended at 100 rpm with the processing temperature set at 170°C . Torque and temperature were monitored all through the process. A slight increase in temperature up to 180 – 190°C was observed but no other relevant differences during processing could be reported. As a first approach, a mixing time of 8 min was used according to a previous study with plasticized PLA.^[8] After the optimization step, three component mixtures (PLA, polyadipates, and clay) were prepared under the same conditions but mixing time was varied from 8 to 20 min to study the clay organization in the matrix, i.e. the nanofiller dispersion and the exfoliation/intercalation state.

The nano-biocomposites were further moulded by compression at 180°C in a hot press (Collin GmbH, Ebersberg, Germany) using stainless steel frames ($16 \times 16 \text{ cm}^2$) to ensure constant thickness. Materials were kept between the plates at atmospheric pressure for 5 min until melting and then they were pressed in a multistep process (5 MPa for 1 min, 10 MPa for 1 min, and 20 MPa for 6 min) to remove air bubbles. Samples were then cooled under pressure (20 MPa). All blends were moulded into films (170–200 μm thick) and sheets (0.8–0.9 mm thick). The corresponding unfilled plasticized PLA were prepared with the same processing conditions.

Characterization

Differential scanning calorimetry (DSC) tests were carried out on a TA Instruments DSC Q-2000 (New Castle, DE, USA) under nitrogen atmosphere ($50 \text{ cm}^3 \text{ min}^{-1}$ flow rate). 5–10 mg of samples were placed in aluminium pans and main thermal parameters were determined during the second scan at $10^\circ\text{C min}^{-1}$ from -90°C to 180°C . Thermal history of samples was erased during a first scan from room temperature up to 180°C ($10^\circ\text{C min}^{-1}$), followed by 5 min at such temperature and quenching to -90°C .

Thermogravimetric analysis (TGA) was performed in a TGA/SDTA 851 Mettler Toledo thermal analyzer (Schwarzenbach, Switzerland). Samples were heated from room temperature up to 600°C at $10^\circ\text{C min}^{-1}$ under oxygen atmosphere ($50 \text{ cm}^3 \text{ min}^{-1}$).

XRD patterns of films were recorded with a Seifert diffractometer, model JSO-DEBYEFLEX 2002 equipped with $\text{CuK}\alpha$ radiation source ($\lambda = 0.1546 \text{ nm}$), 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^{-1} . The degree of intercalation/exfoliation of the nano-biocomposites was determined by using a powder diffractometer Siemens D-5000 (Munich, Germany) with $\text{CuK}\alpha$ radiation source ($\lambda = 0.1546 \text{ nm}$). The incidence angle was varied between 2° and 10° with step size of 0.015° and step time of 4 sec (scanning rate $0.225^\circ \text{ min}^{-1}$).

TEM images were recorded with a JEOL JEM-2010 (Tokyo, Japan) using an accelerating voltage of 100 kV. Samples were previously ultra-microtomed in order to obtain slices 100 nm thick (RMC, model MTXL). At least 3 different areas of each sample were examined for all materials.

Tensile tests were carried out by using a uniaxial tensile testing machine IBERTEST ELIB 30 (Ibertest, Madrid, Spain). Tensile tests were performed at a crosshead speed of 10 mm min^{-1} at ambient temperature (23°C) according to the standard procedure (ASTM D882-01).^[37] Average percentage deformation at break ($\epsilon\%$) and elastic modulus (E) were calculated from the resulting stress-strain curves as the average of five measurements.

OTR was measured with an Oxygen Permeation Analyser from Systech Instruments, model 8500 (Metrotec S.A, Spain). Films were previously equilibrated to $25 \pm 1^\circ\text{C}$ and relative humidity (RH) 50% in a Dycometal-CM81 climatic testing chamber (Barcelona, Spain). 14 cm diameter circle samples were prepared for each formulation. They were taken from the climatic chamber and immediately they were clamped in the diffusion chamber where pure oxygen (99.9% purity) was introduced into the upper half while nitrogen was injected into the lower half where an oxygen sensor was placed.

Size exclusion chromatography (SEC) measurements were performed using a Shimadzu apparatus (Kyoto, Japan) equipped with a RID-10A refractive index detector, a SPD-M10A UV detector, and PLGel Mixed-B 10 mm columns. Calibration was carried out with polystyrene standards from 580 to $1.6 \cdot 10^6 \text{ g mol}^{-1}$. Chloroform (Riedel-de Haden, p.a.) was the mobile phase and the analyses were performed at 25°C with a solvent flow rate of 0.8 ml min^{-1} .

RESULTS AND DISCUSSION

The influence of the addition order of the different components during the mixing stage as well as the effect of sonication were mainly investigated by analyzing the XRD patterns of the O-MMT. The interlayer distances (d-spacing) were calculated by using

Bragg's equation to evaluate the possible interactions between components. As can be observed in Fig. 1(a), the diffraction peak of pristine C30B appeared at $2\theta = 4.9^\circ$ corresponding to the basal d-spacing or interlayer spacing (d_{001}) of 18.0 \AA .

Binary mixtures of C30B with plasticizers were prepared in order to check their ability to swell the clay. A clear increment in d_{001} with respect to the value obtained for O-MMT was observed when mixing the clay with both plasticizers (Fig. 1(b)). This result suggested an effective intercalation of polyadipate chains into the C30B layers. Similar results were reported for different montmorillonites, based on their interactions with various solvents.^[38,39] For the lowest molar mass plasticizer the basal peak of C30B shifted to lower angles and its intensity diminished giving indication of a greater extent of intercalation and higher platelets dispersion than in the case of G206/7. These results could be attributed to the differences in plasticizers diffusivity due to their chain length. The polyadipate with the shortest chains intercalate more easily into the O-MMT interlayer spacing. In addition, in both mixtures a second diffraction peak at angles slightly lower than those obtained for the pristine clay could be observed, confirming the intercalated structure obtained under mild mixing conditions.

Table 1 shows the different mixing conditions and the corresponding d_{001} values for each nanocomposite. For comparison purposes, neat PLA was also melt-blended with C30B in the same

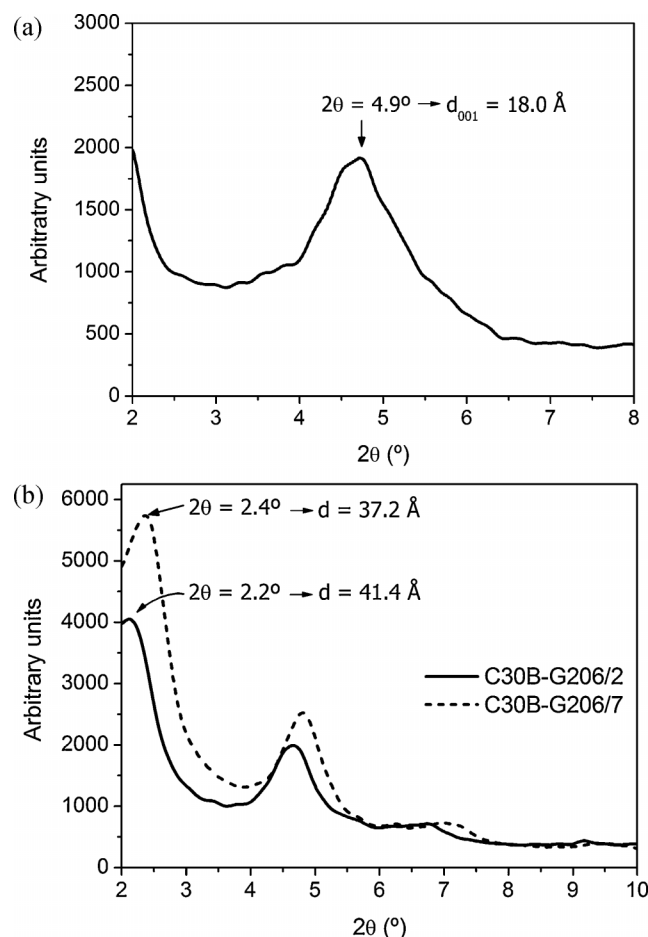


Figure 1. XRD patterns of pure Cloisite®-30B (a) and mixtures with plasticizers (30wt% C30B) after sonication at 60°C during 2 hr (b).

Table 1. Interlayer spacing of nano-biocomposites determined by XRD analysis after melt-blending during 8 min at 170°C.

Mixing order	Sample name	d_{001} (Å)
PLA-C30B	A	35.4
(PLA-G206/7) + C30B	B	38.7
(C30B-G206/7) + PLA	C	38.9
(C30B-G206/2) + PLA	D	shoulder
(C30B-G206/7) ^s + PLA	E	41.8
(C30B-G206/2) ^s + PLA	F	no peak

^s Submitted to sonication at 60°C during 2 hr, before melt blending.

processing conditions to show the clay-polymer interaction degree.

Neat PLA chains increased the interlayer distance from 18.0 Å for the pristine clay (Fig. 1(a)) to 35.4 Å in the nanocomposite. Table 1 shows that the addition of plasticizer increased even more the d_{001} —spacing due to some interactions, such as hydrogen bonding, between PLA, plasticizers, and the nanofiller. This behavior was previously observed in nano-biocomposites based on plasticized PLA with PEG.^[30]

No substantial differences were observed in d-spacing values when changing the mixing order for G206/7 without sonication (B-C blends, Table 1). In addition, nano-biocomposites obtained after sonication showed higher d_{001} values for the higher molar mass polyadipate (E compared to C, Table 1). These results suggested that the clay swelling after the plasticizers addition and sonication treatment influences the chains intercalation and then facilitates the nanofiller exfoliation during melt-blending. This fact was particularly significant in composites with the lower molar mass polyadipate, since no clear diffraction peaks could be observed at least at angles equal or higher than 2°. Similar results were published for nanocomposites based on starch and C30B plasticized with glycerol.^[40–41]

Optimization of mixing time is necessary to obtain homogeneous materials with good nanofiller dispersion and the

minimum matrix degradation. Nano-biocomposites were prepared with both polyadipates following the protocol used for E/F blends (Table 1) but varying the mixing time from 8 min up to 20 min. Figure 2 shows SAXS patterns for the corresponding materials after different processing times (8, 14, and 20 min). As it could be expected, no diffraction peaks at any time were observed when using G206/2 (Fig. 2(a)). However, for those formulations prepared with the highest molar mass plasticizer, one small diffraction peak was observed near $2\theta = 5^\circ$ after 8 and 14 min processing (Fig. 2(b)). This suggests that the clay was not fully exfoliated for PLA plasticized with G206/7 at short mixing times. But after 20 min, nano-biocomposites had no visible diffraction peaks from 1° to 8°. According to literature,^[10–16] the absence of diffraction peaks is due to the clay exfoliation (random diffraction of MMT platelets). This result is in agreement with TEM analysis (see below).

According to SAXS results, an increase in mixing time could be suitable to obtain a higher degree of clay dispersion.^[10] But it is well known that long melting times can lead to significant polymer thermomechanical degradation.^[42] SEC measurements were carried out at each mixing time with the lower molar mass plasticizer, to assess the eventual PLA degradation (Table 2). It was observed that the number-average molar mass (M_n) and weight-average molar mass (M_w) of PLA did not considerably change after 8 min. Further increases in mixing time lead to a clear decrease in the average molar masses (M_n and M_w). But, even after 20 min this decrease was only 15% (M_n) or 16% (M_w) and the polydispersity index (PDI) remained practically constant, so a reasonable stability of PLA after 20 min mixing time could be concluded. Therefore, a balance between high clay dispersion

Table 2. SEC: Average molar masses of PLA plasticized with G206/2 relative to PS standard at different mixing times.

t_M (min)	M_n (kDa)	$PDI = M_w/M_n$
0	116	2.02
8	118	2.16
14	103	1.94
20	99	2.00

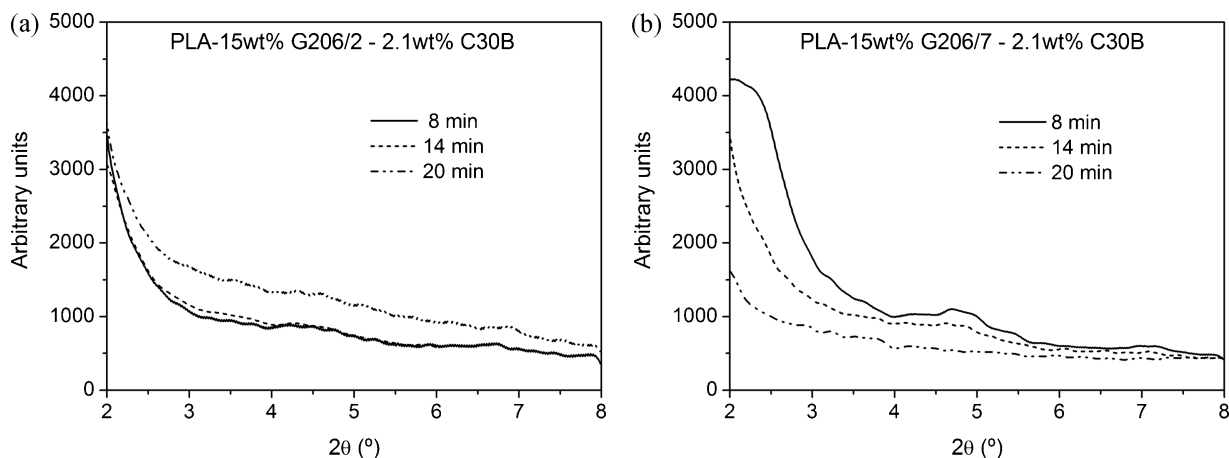


Figure 2. XRD diffractograms obtained for plasticized nano-biocomposites containing 2.1 wt% of C30B at different mixing times.

and low degree thermo-mechanical degradation of PLA could be achieved by setting the mixing time at 20 min. Materials with all the above-referred polyadipates were prepared under the selected processing conditions and they were further fully characterized.

Figure 3 shows some representative TEM images of neat PLA-C30B and PLA-G206/7-C30B nano-biocomposites at different magnifications. The darkest lines correspond to silicate layers while bright field belongs to PLA matrix. Some intercalated and even agglomerated structures were observed in un-plasticized nanocomposites although the dispersion was still good (Fig. 3(a)-(b)). The incorporation of plasticizers resulted in a more homogenous distribution improving the dispersion of the clay in the polymer (Fig. 3(c)), since a good dispersion of the clay platelets was observed throughout the matrix. Despite the presence of some small tactoids, no agglomerates were observed resulting in a mostly homogeneous distribution. At higher magnifications (Fig. 3(d)) individual platelets could be observed showing a mostly exfoliated structure with some small clusters randomly distributed through the matrix. Besides, similar results were obtained for nano-biocomposites with G206/2 and G206/5. These results are in agreement with previous XRD observations.

The main thermal results for these materials are shown in Table 3. It was observed in DSC curves that the addition of plasticizers to PLA made the material more crystallizable due to the increased chain mobility, but crystallization and melting enthalpy values were almost invariable suggesting that no net crystallinity was developed after processing (Fig. 4). On the other hand, the addition of C30B did not affect the T_g value of the neat PLA matrix, since it was 58°C before and after blending, but a small melting peak could be observed at 146°C (Table 3). In the case of plasticized PLA-C30B based nanocomposites, the incorporation of clay did not affect significantly the melting temperature of the un-filled plasticized PLA matrix. As expected, a

Table 3. Glass transition (T_g) and melting (T_m) temperatures determined by DSC during the second heating scan and thermo-oxidative stability determined by TGA for various formulations.

Sample	T_g (°C)	T_m (°C)	$T_{-95\%}^a$ (°C)	T_{max}^b (°C)
PLA pellets	59	—	337	368
Processed PLA	58	—	336	366
PLA-2.1 wt% C30B	58	146	333	364
PLA-15 wt% G206/2	33	140	309	363
PLA-15 wt% G206/2 -2.1 wt% C30B	33	140	320	364
PLA-15 wt% G206/5	34	141	319	361
PLA-15 wt% G206/5 -2.1 wt% C30B	35	141	327	364
PLA-15 wt% G206/7	36	141	319	364
PLA-15 wt% G206/7 -2.1 wt% C30B	35	142	326	363

^a Determined from 5% mass loss by TGA.
^b Determined from the maximum of DTG curves.

clear reduction in T_g values for all plasticized samples was observed. This is caused by the plasticizing effect of polyadipates and was also reported and discussed in a previous study.^[8] Besides, T_g values of nano-biocomposites remained close to those of the corresponding unfilled systems (Table 3) indicating that the nano-scale reinforcements did not restrict the polymer segment motions. Polyadipates kept their plasticizing effect probably because their affinity with the silicate layers surface was not enough to force the majority of the plasticizer to interact with the nanoclay.^[33]

The eventual crystallization of PLA chains during processing was monitored by using XRD (Fig. 5). It could be concluded that samples did not develop any crystallinity during cooling and remained mostly amorphous since no diffraction peaks at angles between 10° and 30° were observed. Despite the increase in

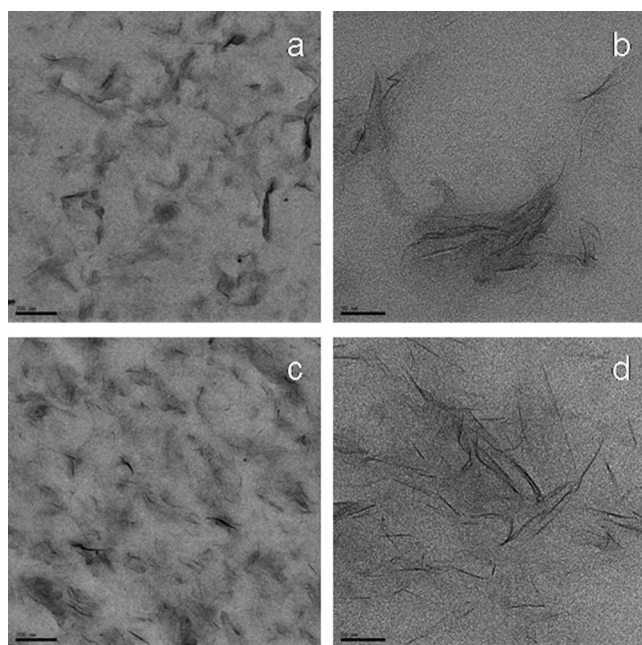


Figure 3. TEM images of neat PLA nano-biocomposite (a,b) and plasticized with 15 wt% of G206/7 (c,d) (reference bars: 200 nm (a,c) and 50 nm (b,d)).

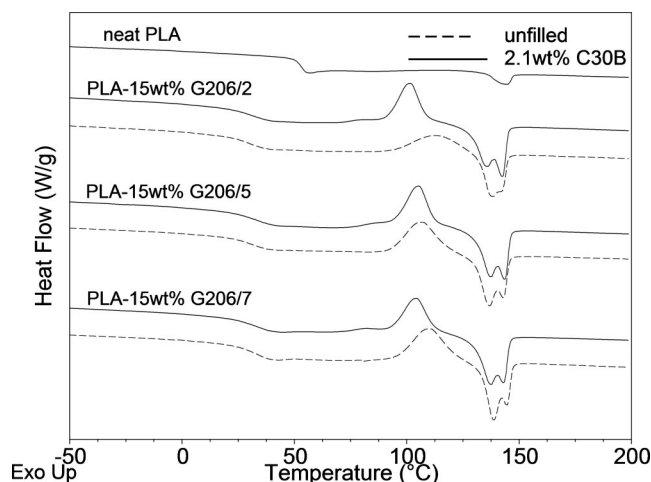


Figure 4. DSC curves of plasticized PLA and nano-biocomposites with 2.1 wt% C30B.

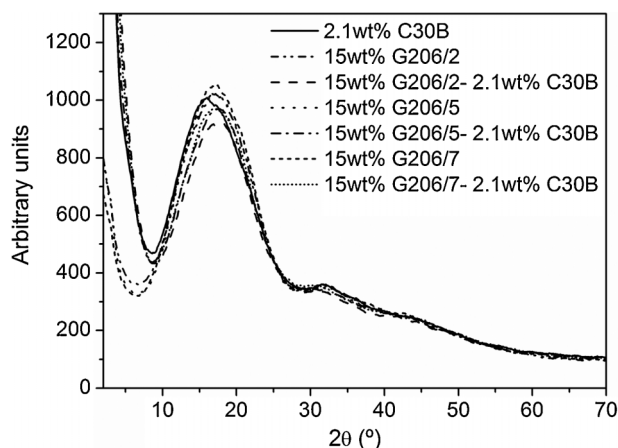


Figure 5. XRD patterns obtained for plasticized PLA films and filled systems.

chain mobility due to the plasticizing action and the presence of clay which could act as a nucleating agent,^[43] the cooling rate during processing was too fast compared to the PLA crystallization kinetics.

The resistance to thermo-oxidative degradation of plasticized PLA nano-biocomposites is an important issue in some applications. Thermo-oxidative stability was determined by TGA under oxygen. A one-step process was observed for all formulations. The addition of C30B slightly shifted the onset of the thermo-oxidative degradation process towards higher temperatures, but no important changes in temperature at the maximum degradation rate (T_{max}) were observed (Table 3). The poor enhancement in thermo-oxidative stability given by C30B to nano-biocomposites could be linked to the fact that clay may act as heat barrier only at the beginning of the thermal decomposition giving rise to the slight improvement in $T_{95\%}$.^[12,26] At higher temperatures the silicate layers could accumulate heat and then promote the degradation process.

Figure 6 shows uniaxial tensile test results. The materials based on PLA plasticized with 15 wt% polyadipates showed high deformation at break values, around 250–300% compared to 5% for the neat PLA. The incorporation of O-MMT at low content (2.1 wt%) induced some increase in the elastic modulus values and decrease in the elongation at break, as usual for composite materials. These results could be partially counterbalanced by the slight degradation of PLA in plasticized materials during processing (Table 2). This fact was particularly noticeable for the elastic modulus values (Fig. 6(a)) where a higher increase could be expected by the addition of C30B. But the overall result of slight increase in modulus and decrease in elongation at break is consistent with the expected tendency in tensile properties for the addition of nanoclay to plasticized PLA, as shown in Fig. 7 for the system plasticized with G206/2 and the corresponding nano-biocomposite. Nevertheless, despite the loss in ductility due to the addition of clay, elongation at break was kept above 200% in all cases (Fig. 6(b)).

In previous studies it was observed that the rate of oxygen permeation through PLA films increased with the addition of polyadipates, depending on their average molar mass and the plasticizer concentration.^[8,36] The potential for enhanced barrier properties of nanocomposites was reported as the consequence of a more tortuous path for the gas molecules to pass through the material when the reinforcement is sufficiently dispersed

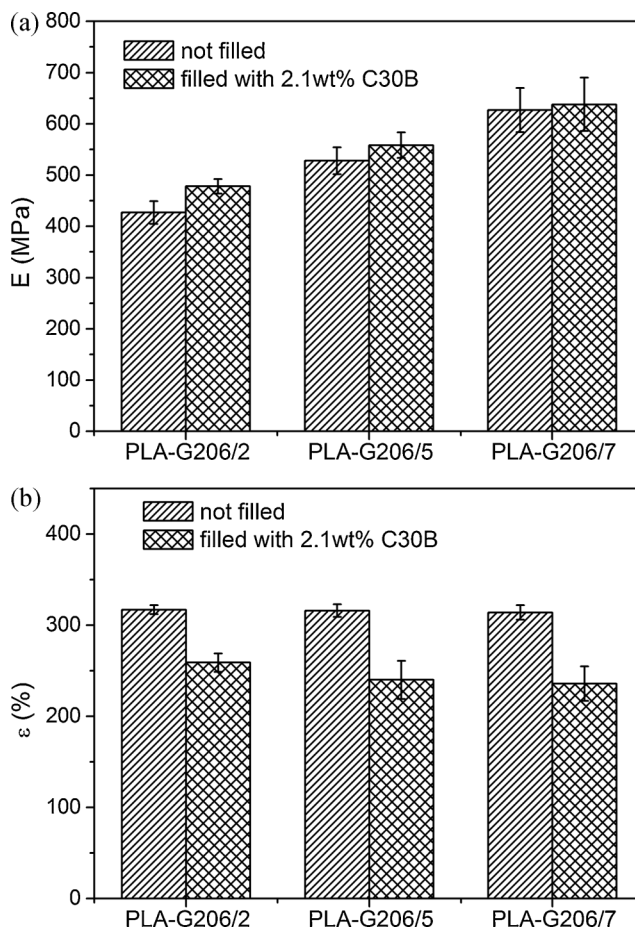


Figure 6. Elastic modulus, E (a) and percentage deformation at break, ϵ (b) for unfilled 15 wt% plasticized PLA and filled with 2.1 wt% C30B.

throughout the matrix.^[12] Results of OTR per film thickness (OTR.e) of each material are shown in Fig. 8. The plasticization process with 15 wt% G206/2, G206/5, and G206/7 resulted in OTR.e values 70, 29, and 17% (respectively) higher than those for neat PLA. However, the addition of 2.1 wt% O-MMT resulted in

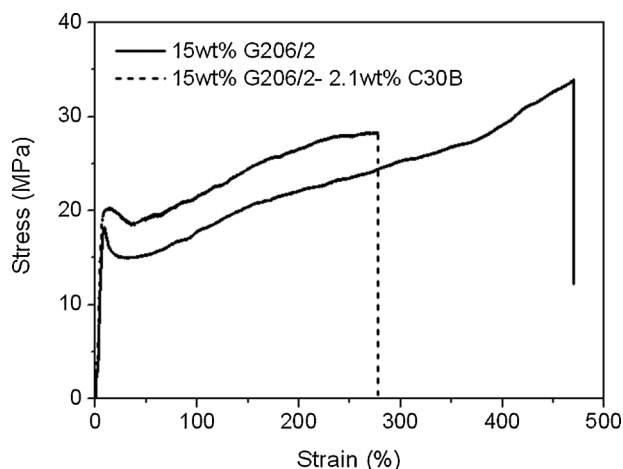


Figure 7. Stress–strain curves for PLA plasticized with G206/2 (15 wt%) and the corresponding nano-biocomposite.

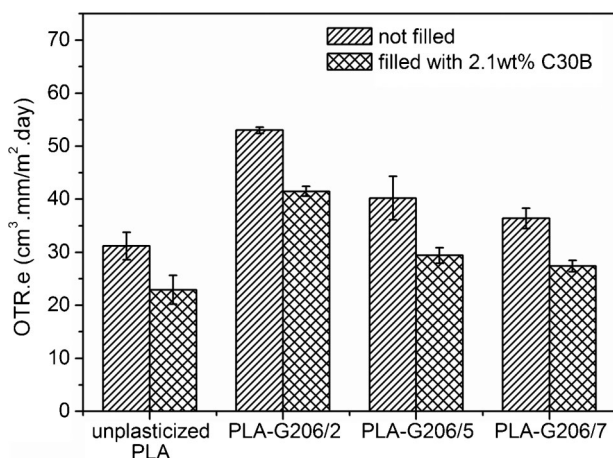


Figure 8. OTR values per film thickness (OTR.e) of neat and plasticized PLA films and nanocomposites.

significant improvement in oxygen barrier properties (around 25%) in plasticized nanocomposite films when compared to the corresponding unfilled matrices. Thellen *et al.*^[31] reported a higher improvement (around 48%) in oxygen barrier for a PLA-based nanocomposite with 5 wt% of organically modified MMT (Cloisite[®] 25A) and 10 wt% acetyltriethyl citrate. But it should be considered that nano-biocomposites prepared in that study showed some significant differences in formulation, considering the nanofiller and plasticizer nature as well as their content, with those used in this work. Finally, OTR.e results for the filled systems compared to neat PLA showed that only some nano-biocomposites (those with the higher molar mass plasticizers) improved the oxygen barrier property (6% for G206/5 and 12% for G206/7). In the case of unplasticized PLA, the incorporation of 2.1 wt% C30B reduced the OTR in about 27%.

As it was above discussed, all samples were amorphous after processing. Therefore, changes in barrier properties of nano-biocomposites should not be associated to matrix densification due to the increased crystallinity, but to a geometric factor which increased the tortuousness for gas molecules pathway to go through the film thickness as a consequence of the nanofiller addition.^[44]

CONCLUSIONS

Novative nano-biocomposites based on PLA plasticized with polyadipates were obtained by the addition of low amounts of organo-modified montmorillonite and the structure/properties relationships of these materials prepared by a melt-intercalation method were analyzed.

Processing of nano-biocomposites depending on the polyadipate is an important issue. The highest improvement in the oxygen barrier property for 15 wt% plasticized PLA with 2.1 wt% clay (inorganic content) was reached by the formulation with the highest molar mass polyadipate (G206/7). In addition, the use of this plasticizer in these nano-biocomposites would be preferred to those lower molar mass polyadipates which, in turn, also show good dispersion of the clay into the polymer matrix, but could lead to some loss of plasticizer during processing and/or exudation caused by ageing. Nano-biocomposites with G206/7 showed OTR.e values even lower than those for the neat polymer

film, while the decrease in ductile properties by the addition of C30B was very low compared to the unfilled counterpart. In general, the degree of intercalation-exfoliation strongly depends not only on the matrix nature and the organo-clay structure but also on the processing steps and the eventual plasticizer loss, which is particularly critical with lower molar mass polyadipates. Structural characterization showed that the nanofiller was quite homogeneously dispersed after 20 min of melt-blending, reaching exfoliated structures whatever the average molar mass of polyadipates. The improvement in barrier properties preserving the materials ductility as well as limiting the eventual exudation with time made these nanocomposites, in particular those with the highest molar mass polyadipate, able to be used in soft materials for e.g. flexible films.

Further studies to evaluate the effect on the final properties, such as the biodegradability and ecotoxicity of nano-biocomposites, by varying the clay and plasticizer amounts as well as ageing studies are currently on-going.

Acknowledgements

Authors would like to express their gratitude to Condensia Química S.A (Barcelona, Spain) for kindly supply of plasticizers. Thanks are also extended to Dr Frederic Chivrac and Dr Eric Pollet (LIPHT-ECPM-Strasbourg) for their insight.

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