*Macromol. Symp.* **2006**, 233, 191–197 DOI: 10.1002/masy.200650124

# Optimization of Biodegradable Nanocomposites Based on aPLA/PCL Blends for Food Packaging Applications

*Lluís Cabedo,*[1,3] *José Luis Feijoo,*[2] *María Pilar Villanueva,*[1] *José María Lagarón,*[3] *Enrique Giménez**[1]

**Summary:** Biodegradable blends of amorphous poly(lactic acid) (aPLA) and polycaprolactone (PCL) and nanocomposites of these blends were developed by melt blending. A morphological study of the bioblends was carried out by means of WAXS and SEM showing immiscible behavior. The nanocomposites were also characterized morphologically by WAXS, TEM and SEM, revealing high degree of interaction of the nanoclays with the aPLA. Mechanical, thermal and gas barrier properties of the different blends and nanocomposites were studied and the effect of blending and clay addition on the above-mentioned properties was evaluated.

**Keywords:** amorphous poly(lactic acid); biodegradable blends; polymer layered nanocomposites

## 1. Introduction

The utilization of oil based materials in packaging applications imposes a number of well reported issues mainly related to the waste management of the plastic residues[1]. The main problem is the lack of biodegradation of these materials. In this context, plastic materials obtained basically from renewable sources are a new generation of materials capable of reducing significantly the environmental impact in terms of satisfying certain technical requirements and being fully biodegradable. Therefore, these materials offer a feasible alternative to the traditional polymeric materials when recycling is not cost-effective or technically impossible[2].

Biopolymers are usually divided in three groups, depending on the production process and sources[3]. The first class are the polymers directly extracted from biomass (e.g. polysaccharides, proteins, lipids...). The second type is the polymeric materials produced by classical synthesis using either renewable biobased monomers (such as poly(lactic acid)) or oil based monomers (such as polycaprolactones). Finally, the third kind consists of the polymeric materials produced by microorganisms and genetically-modified bacteria (for instance the polyhydroxyalkanoates).

One of the most promising candidates of the above biopolymers is poly(lactic acid) (PLA), produced from renewable resources and readily biodegradable. PLA is a linear thermoplastic polyester produced by the polymerization of lactide. Lactide is a cyclic dimer prepared by the controlled depolymerization of lactic acid, which is obtained from the fermentation of sugar feedstock, corn, etc.[4]. In general commercial PLA grades are copolymers of poly(L-lactic acid) and poly(D-lactic acid), which are produced from L-lactide and D-lactide respectively. The ratio of L-enantiomer to D-enantiomer

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[1] Department of Industrial Systems Engineering and Design, Area of Materials Science, ESTCE, University Jaume I, 12071 Castelló, Spain
Fax: (+34) 964 72 81 70
E-mail: gimenezt@esid.uji.es

[2] Departament of Materials Science. University Simón Bolívar, 89000 Caracas, Venezuela

[3] Packaging Group, IATA, CSIC, Aptdo. Correos 73, 46100 Burjassot, Spain

is known to affect the properties of PLA[5], i.e. if the materials are semicrystalline or amorphous; until now all the efforts reported in order to improve the properties of PLA are focused on the semicrystalline material, e.g. D-content less than 6%. Nevertheless, in this work the poly(lactic acid) chosen is a fully amorphous grade containing 12% D-lactide, because amorphous polymers are easier to transform into actual packages by thermoforming, which is a common technology in the food packaging sector.

There is increasing interest in using PLA for disposable compostable plastic articles; however, there are properties such as flexural properties, gas permeability, impact strength, processability, etc. that are often not good enough for some end use applications [6]. The most important limitations in the application of aPLA in the food packaging industry are: medium gas barrier properties and brittleness. A feasible strategy to decrease the brittleness of aPLA is by blending it with polycaprolactone (PCL). Polycaprolactone (PCL) is also a biodegradable polyester obtained by ring-opening polymerization from the ε-caprolactone. The PCL is a semicrystalline polymer with low tensile strength, high elongation at break (above 400%) and processing temperatures similar to the aPLA, therefore it is expected to act as a plasticing agent when blending it with the amorphous aPLA polymer. A potential drawback of these blends is the increase in gas permeability undergone by aPLA as a consequence of the poor gas barrier properties of PCL.

The nanocomposites technology is a relatively new approach used to enhance the properties of a matrix by addition of low loadings of highly dispersed nanoparticles of a suitable filler[7]. Modified layered clays are very often used for this purpose. The clay used in this work was a commercially available modified kaolinite. Kaolinite ($Al_2Si_2O_5(OH)_4$) is a 1:1 phyllosilicate containing a gibbsite octahedral layer and a silicon oxide tetrahedral sheet. This asymmetric structure allows the formation of hydrogen bonds between consecutive layers, providing a large cohesive energy[8]. As a consequence of the high layer-to-layer interactions, the intercalation of the polymer chains in between the kaolinite platelets is greatly impeded, being thus necessary a layer surfaces chemical treatment to both facilitate the intercalation and further exfoliation of the clay and to enhance compatibility between the biopolymer and filler.

The blends and nanocomposites have been obtained by melt-mixing. The melt intercalation process is a very convenient approach to make polymer layered silicate nanocomposites by using a conventional polymer extrusion process widely spread in the polymer processing industry [9]. In this process, the clay is intercalated and dispersed in the polymer melt by application of shear forces during compounding.

In this study, it is reported about the morphology and properties of nanobiocomposite blends of aPLA, PCL and kaolinite.

## 2. Experimental

### 2.1. Materials

The amorphous poly(lactic acid) (aPLA) used in this work was a commercial grade (Galastic®), containing 12 mol % of D-Lactide, with a mean molecular weight of ca. 190000 g/mol, supplied by Galactic (Belgium). The polycaprolactone (PCL) used was also a commercial grade produced and kindly supplied by Solvay (CAPA® FB100), having a mean molecular weight below 100000 g/mol.

The clay used in this work was a chemically modified kaolinite kindly supplied by NanoBioMatters S.L. (Paterna, Spain). The chemical modification treatment of the clay was specifically designed to be melt blended with poly(lactic acid). No further details about its composition or modification were disclosed by the manufacturer.

### 2.2. Blends and Nanocomposites Preparation

Prior to the mixing step, aPLA and PCL were dried at 50 °C under vacuum for 24 hours to remove the remaining moisture.

Polymer blends as well as nanocomposites were obtained by melt blending in an internal mixer (Haake Polylab) during a mixing time of 8 minutes at a temperature of 150 °C. The mixing was performed at a rotor speed of 60 rpm. The batch was extracted from the mixing chamber manually and allowed to cool to room temperature in air. The so-obtained materials were grinded in a rotatory mill. The resulting material was dried again at the above-mentioned conditions. The polymer powder was finally transformed into sheets (0.8 mm thick) by compression moulding in a hot-plate hydraulic press at 125 °C and 2MPa of pressure during 4 minutes. The polymer sheets were eventually allowed to cool to room temperature under pressure. All the measurements and experiments were carried out on the polymer sheets.

The composition of the bioblends obtained in this work was (aPLA/PCL) 80/20, 70/30, 64/34 and 20/80. The clay loading of the nanocomposite samples was 4% w/w. The neat polymer was also processed under the same conditions to ensure that all samples were processed under similar conditions.

### 2.3. Characterization Techniques

Wide angle X-ray experiments (WAXS) were performed using a Siemens D5000D equipment. Radial scans of intensity versus scattering angle ($2\theta$) were recorded at room temperature in the range 2 to 28°($2\theta$) (step size = 0.03°($2\theta$), scanning rate = 8s/step) with identical settings of the instrument by using filtered Cu $K_\alpha$ radiation ($\lambda = 1.54$Å), an operating voltage of 40kV, and a filament current of 30mA. To calculate the clay basal spacing Bragg's law ($\lambda = 2d\sin\theta$) was applied.

Transmission electron microscopy (TEM) was performed using a JEOL 1010 equipped with a digital Bioscan (Gatan) image acquisition system. TEM observations were performed on ultra-thin sections of crymicrotomed thin nanocomposite sheets.

Thermo-gravimetric analysis (TGA) was carried out using a Setaram TGA92 thermogravimeter at a heating scan of 10 °C/min from room temperature to 900 °C under nitrogen flow. The thermal degradation temperature was taken as the minimum of the first derivative of the weight loss with respect to time (this point corresponds to the maximum weight loss rate).

Dynamic-mechanical experiments were performed in a Perkin Elmer DMA 7e equipment in three-point bending setup. The temperature range registered was −130 °C to 55 °C at a heating rate of 2 °C/min, at 1Hz frequency.

The scanning electron microscopy (SEM) experiments were developed using a JEOL JSM-6300. The polymeric samples were previously coated by sputtering with Au-Pd and finally a conductive wire of colloidal Ag.

The oxygen transmission rate through vacuum dried compression molded films specimens was measured at 25 °C under dry conditions using an Oxtran 100 instrument (Modern Control Inc., Minneapolis, MN, USA). The sensitivity of the instrument was 0.05 $cm^3/m^2$ day.

## 3. Results and Discussion

### Blends aPLA/PCL

A morphological study of the blends was obtained by means of scanning electron microscopy (SEM). Figure 1 shows a SEM photomicrograph taken from a fractured surface of the sample aPLA/PCL(70/30). Numerous PCL particles, with diameters above 5 μm, can be seen dispersed all over the aPLA matrix, revealing a clear immiscible behaviour. In spite of the fact that the polymers are clearly inmiscible, the lack of extensive voiding and debonding at the interphase suggests some sort of compatibility for the two polymers. This type of morphology was also observed in all samples studied, being thus these polymers immiscible across the compositional range studied.

Dynamic-mechanical analysis experiments were also carried on the blends.

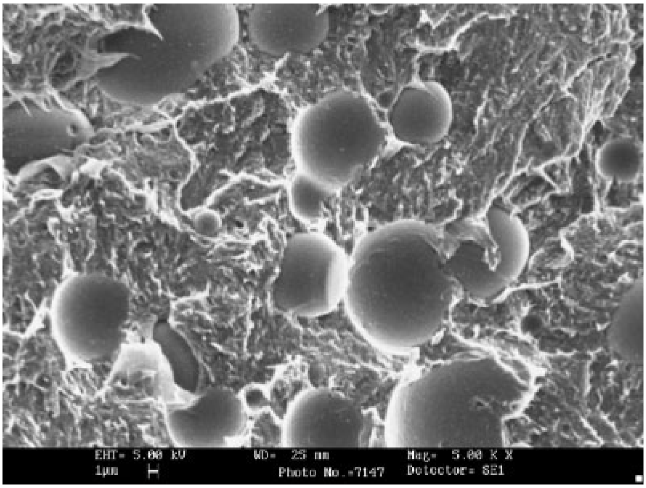

*Figure 1.*
SEM photomicrograph from a cryofractured surface of the sample aPLA/PCL(70/30).

Figure 2 depicts the storage modulus (E′) vs. temperature curves for the pristine polymers as well as for the blends. The aPLA shows a gentle decrease in E′ with no relevant changes in slope along the temperature range registered until the mechanical collapse due to glass transition at ca. 43 °C. PCL presents the mechanical relaxation associated to the glass transition at ca. −48 °C and the eventual melting of the crystalline phase at around 50 °C. The addition of PCL to the aPLA has a double effect on the mechanical behaviour of the composite material: the first effect is a plasticization of the blend compared to the aPLA matrix; the second is a slight increase in its thermal stability. These effects are more relevant as the PCL fraction is increased in the blend. The plasticization effect is more significant at temperatures above the mechanical relaxation associated to the glass transition of the PCL. However, the observed increase in the temperature at which the mechanical collapse of the polymer takes place is not significantly affected, for instance on the sample aPLA/PCL(70/30) it is approximately of 7 °C.

Figure 3 depicts the TGA mass loss curves for the neat polymers and the corresponding blends. From this figure, it

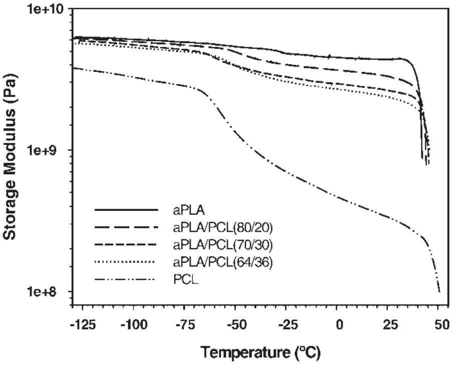

*Figure 2.*
Storage modulus as determined by DMA of the neat polymers and blends.

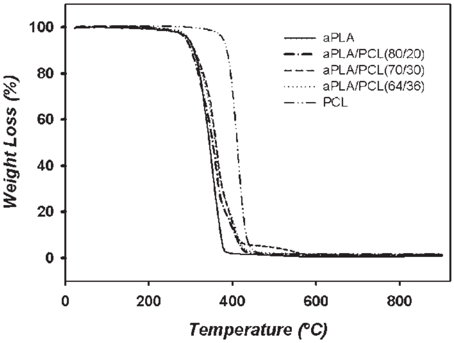

*Figure 3.*
TGA curves of the neat polymers and blends.

is observed that the blending of aPLA with PCL results in improved thermal stability, as derived from the increase in the temperature of the maximum weight loss rate. This enhancement in stability performance is, however, not very large. In the Figure 3, thermal degradation takes place in two different steps associated to the contribution of the two neat polymers, suggesting further a lack of miscibility between the blend constituents. Figure 3 also shows that even when the $T_d$ increase is small but clearly discernible, the temperature for the onset of degradation remains, however, unaffected.

### Nanocomposites of the Blends aPLA/PCL

The combination of WAXS and TEM results has extensively been used with success to characterize the morphology of polymer layered-clay nanocomposites [10]. Figure 4 plots the WAXS patterns of aPLA/K, aPLA/PCL(80/20)/K, aPLA/PCL(70/30)/K, aPLA/PCL(64/36)/K and PCL/K. The aPLA/K does not present any peak in the basal range of the kaolinite, suggesting thus a high level of interaction between the nanoclays and the polymer matrix has been achieved. The absence of the clay basal reflection indicates that the stacking of the clay platelets has been broken down during the melt processing event. As a result of this only two possible morphologies can be derived: exfoliation or/and intercalation (with basal distances larger than 3 nm). WAXS experiments in the blends yield similar patterns in the basal region, i.e. the absence of any noticeable basal peak.

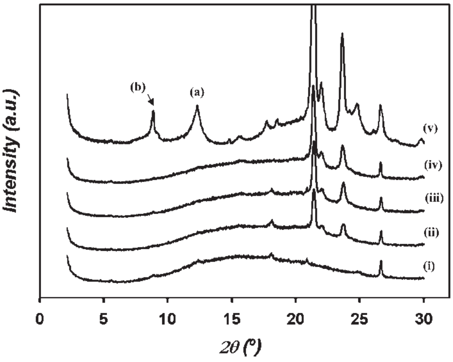

*Figure 4.*
WAXS patterns of the nanocomposites of the pristine polymers and their blends: (i) aPLA/K, (ii) aPLA/PCL(80/20)/K, (iii) aPLA/PCL(70/30)/K, (iv) aPLA/PCL(64/36)/K and (v) PCL/K.

In the PCL/K WAXS pattern the natural basal peak of the kaolinite (a) can be observed 12.4° 2theta angle. This peak is associated to the natural basal plane of the clay fraction that has lost the modification during the blending, due to processing at high temperature[8]. Therefore, in this sample, some of the clay remains stacked in relatively large tactoids dispersed throughout the polymer matrix. The peak (b) belongs to the (001) reflection of the illite, another phyllosilicate that is present as impurity in the natural kaolinite.

TEM offers a more visual and direct description of the existing morphology. Figure 5 is a TEM bright field image of the nanocomposite aPLA/PCL(64/36)/K, in which the dark entities are the cross section of stacked intercalated nanoclay layers while the bright areas correspond to the polymer matrix. In the TEM image, it is possible to observe exfoliated layers which are randomly distributed in the blend matrix. It is also noticeable the presence of small intercalated structures. Thus, Figure 5 confirms what was inferred by observation of the WAXS results, i.e. the predominant morphology of the nanocomposite blend is exfoliation and intercalation.

Figure 6 plots the storage modulus versus temperature for the pristine polymers and their nanocomposites. An anomalous trend in the mechanical performance is observed for the case of aPLA, were the nanoclay is seen to promote a plasticizating effect, i.e. the values of storage modulus are persistently lower for the nanocomposite than for the raw polymer across the whole temperature range registered. However, the temperature at which the mechanical collapse takes place is not seen to be modified by the presence of the nanofillers. On the other hand, this trend is not observed for the nanocomposites of the

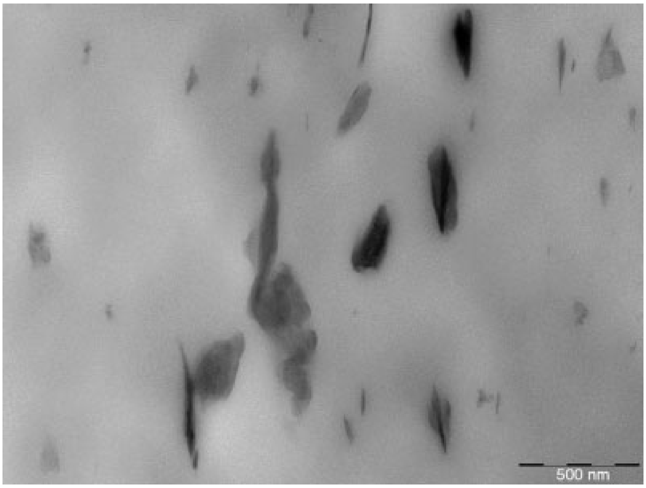

***Figure 5.***
TEM bright field image of the nanocomposite aPLA/PCL(64/36)/K.

semicrystalline PCL. The nanocomposites of the blends exhibit similar behaviour to the aPLA, since the poly(lactic acid) is the predominant component of the blend. A possible explanation for this plasticizating effect observed could be a catalytic effect of the hydroxyl groups of the clay in the hydrolytic degradation of the polymer matrix[11]. However, we think that this model can not be applied to our system since a decrease in the molecular weight of the polymer would imply a decrease in glass transition temperature and degradation onset, and such effect is not observed. An understanding for this counterintuitive plasticization phenomenon is currently under study. In spite of the origins of this effect, it is relevant to note that nanocomposites could actually be a very valid route to decrease the inherent rigidity of some biopolymers and, therefore, to enhance their application.

Oxygen permeability of the neat polymers, the aPLA/PCL(64/36) and the nanocomposites of these samples are shown in Figure 7. Raw aPLA presents an oxygen permeability value of $1.125 \cdot 10^{-18}$ ($m^3$ m)/($m^2$ s Pa) and pristine PCL of $5.8 \cdot 10^{-18}$ ($m^3$ m)/($m^2$ s Pa). As expected the addition of PCL to the aPLA results in a significant decrease of the gas barrier properties, in the

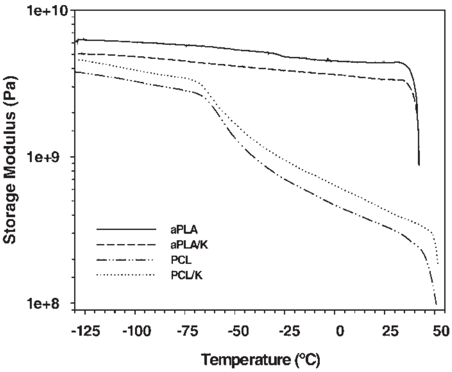

***Figure 6.***
Storage modulus versus temperature for the aPLA, aPLA/K, PCL and PCL/K samples.

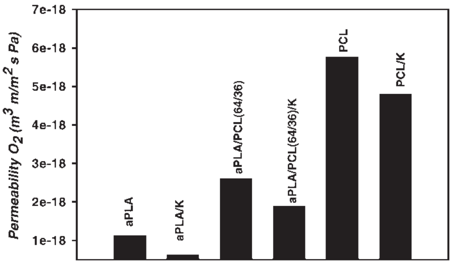

***Figure 7.***
Oxygen permeability of the neat polymers, the aPLA/PCL(64/36) and the nanocomposites of these samples.

case of the blend containing 36% PCL, the oxygen permeability has increased a 136% with respect to the pure aPLA. The decrease in the barrier properties is proportional to the amount of PCL added.

On the other hand, the nanocomposites showed enhanced gas barrier properties, due to the effect of the nanoplatelets on increasing the tortuosity factor across the film thickness. The increase in the diffusion path length is highly dependent on the morphology of the nanocomposite; the higher the degree of exfoliation of the clay platelets in the polymer matrix, the better the gas barrier properties. The oxygen permeability value of the aPLA/K is $6.25 \cdot 10^{-19}$ ($m^3$ m)/($m^2$ s Pa), while for the PCL/K is $4.8 \cdot 10^{-18}$ ($m^3$ m)/($m^2$ s Pa), these values represent an increase in oxygen barrier of 43% and 17% respectively. In the nanocomposite of the blend, the addition of the kaolinite nanofillers represent an increase of 27%, being the actual value of $1.9 \cdot 10^{-18}$ ($m^3$ m)/($m^2$ s Pa). From the observed results it can be seen than the addition of nanoclays to the blends partially compensate the decay in gas barrier properties undergone by aPLA when it is blended with PCL.

## 4. Conclusions

Blending amorphous PLA with PCL leads to an improvement in mechanical properties and thermal stability without significant decrease in barrier properties. This is expected to result in better processability of the material.

Highly exfoliated nanocomposites of the aPLA and aPLA/PCL blends can be successfully obtained by melt-mixing with a properly modified kaolinite. All nanocomposites showed an improvement in the mechanical properties with regard to the polymers and blends without clay; but the main advantage of adding nanoclays to the polymers is the increase in gas barrier properties. Hence a blend of low content of PCL and 4% kaolinite results in better processability, thermal stability and similar gas barrier properties than the neat aPLA.

*Acknowledgements:* This work has been supported by the Ministerio de Ciencia y Tecnología (project MAT 2003-08480). Authors would like to acknowledge Mr. José Ortega and Ms. Raquel Oliver for experimental support. The authors would also express their gratitude to Nanobiomatters S.L. and Solvay for kindly supply the materials. L. Cabedo and J.M. Lagaron would also like to acknowledge the I3P scholarship program of CSIC and the Integrated Project SUSTAINPACK (FP6-500311-1) for funding.

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