

Dissimilar Tendencies of Innovative Green Clay Organo-Modifier on the Final Properties of Poly(ϵ -caprolactone) Based Nanocomposites

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Abstract Composites based on poly(ϵ -caprolactone) (PCL) were prepared by melt blending the polymer with natural and modified bentonite. Soy lecithin (SL), a natural and nontoxic biosurfactant, was used as modifier agent. Three organoclays with different SL contents were employed as fillers and composites containing 1 and 2 wt% of each clay, were prepared. Thermal (by thermogravimetric analysis, and differential scanning calorimetry), morphological (by X-ray diffraction (XRD) and melt rheology), mechanical (by tensile tests) and barrier properties (by means of water vapor permeability tests) of matrix and composites were studied as a function of clay type and content. Morphological analysis by XRD showed nanocomposites with intercalated-exfoliated structures while melt rheology suggests thermal degradation of PCL matrix catalyzed by SL bentonite modifier. Thermal and mechanical properties were consistent with this assumption, due to the slight increment in crystallinity percentage and detriment in the Young's modulus of the nanocomposites in comparison with the neat matrix. On the other hand, water vapor permeability of PCL significantly decreased in composites, as is expected for polymer/clay nanocomposites, favoring its potential application as food packaging. Thus, dissimilar tendencies were found in the final properties of the nanocomposites that were attributed to the matrix molecular weight degradation catalyzed by the novel green clay organo-modifier.

Keywords Biodegradable polymer · Composite · Polyester degradation · Bentonite · Soy lecithin

Introduction

The problem of litter requires an immediate solution. It not only results in visual pollution but also presents a threat to animals and results in a reduction of agricultural productivity [1]. Among the different options to deal with the problem of disposal of the used polymeric materials (biodegradation, incineration and recycling), biodegradation appears as the best solution to overcome this drawback [2].

Nowadays the packaging industry is by far the major user of plastics while food packaging is the largest growing sector within this market [1, 3]. In addition, more than 60% of plastic waste produced in households comes from single-use packaging [4].

The goal of food packaging is to maintain food safety and minimize environmental impact [3]. Biodegradable plastic materials are considered as a viable alternative for conventional plastics [5]. However, to replace them, mechanical, thermal, optical and barrier properties of biodegradable plastics must be improved in order to cover full range of properties provided by the traditional ones [5, 6].

Poly(ϵ -caprolactone) (PCL) is a linear semicrystalline biopolyester synthesized from fossil resources and produced by the ring opening polymerization of ϵ -caprolactone [7, 8]. It is a polymer with a strong hydrophobic nature, a degree of crystallinity around 45%, a glass-transition temperature around -60°C and a melting point near 60°C [8, 9]. It seems to be an important matrix for design of biodegradable nanocomposites because of its biocompatible and biodegradable properties [8]. Its potential uses are currently being examined in biodegradable packaging

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materials [6, 10–12], in pharmaceutical controlled release systems [13–16] and other medical applications [16–19]. Moreover, PCL-based antimicrobial composites were developed for active packaging use [20–22]. However, it has poor mechanical, barrier and thermal properties compared with conventional polymers [7, 8]. One way to improve these properties is to incorporate nano-sized fillers to the matrix. Nanocomposites based on PCL have been widely reported [23–27]. The most reported nano-fillers in poly(ϵ -caprolactone)-based materials are represented by organo-modified clays [3, 7, 9]. The main advantages of nanoclay particulates are easy availability, low cost, easy processability and good performance [3].

In order to improve polymer intercalation, clay minerals must be previously modified by the exchange of the native alkaline counterions by organic cations. The previous modification reduces their hydrophilic character, increasing the compatibility with the matrix [3, 7]. Primary, secondary, tertiary and quarternary alkylammonium cations [28, 29] or phosphonium cations [30, 31] having various substituents, have been widely employed as surface modifiers regardless of the toxicity they introduce in the final product, especially when the material is designed for its use in food contact applications, cosmetic and biomedical industries [3, 7, 32, 33]. Among the employed modifiers found in bibliography, some natural compounds were used to modify bentonite, i.e. amino acids, proteins, nucleic acids, DNA and RNA. Most of these compounds were utilized as catalyst for biological reactions, drug delivery systems, enzyme immobilization, biosensing and biofunctional materials among others [34–36].

The aim of this work was to obtain a nontoxic and biodegradable material based on PCL and to analyze its use as a potential material for food packaging. For that, the effect of a novel green clay organo-modifier on the thermal, barrier, mechanical and morphological properties of PCL nanocomposites were studied. We focused on the effect that the Bentonite modifier has on the final properties of PCL nanocomposites.

Experimental Section

Materials

Commercial grade PCL (CAPA FB 100) was supplied by Perstorp, with $M_w = 100,000$ g/mol. The bentonite (Bent) was supplied by Minarmco S.A. (Argentina) and its cation exchange capacity (CEC) was 105 mequiv/100 g, measured by the methylene blue method. It consisted predominantly of montmorillonite and contained quartz and feldspar as major impurities, as well as traces of gypsum and sepiolite as evidenced by X-ray diffraction (XRD) analysis [37]. Soy

lecithin (SL) was provided by Melar S.A. (Argentina) and it was used as received.

Preparation of Soy Lecithin-Modified Clays

Soy lecithin-modified clays with different organic content were prepared by ionic exchange as reported in our previous work [38]. Briefly, 4 g of Bent were mixed with 1, 2 and 4 g of soy lecithin aqueous and acid solution and stirred at 75 °C for 2 h. Then, they were washed (with an equimolar mixture of ethanol—distilled water) and lyophilized for 72 h. Samples were labeled A, B and C for the nanoclays prepared with 1, 2 and 4 g of soy lecithin, respectively.

Composites Preparation

PCL matrix nanocomposites sheets with 1 and 2 wt% of each clay were prepared by melt-intercalation followed by compression-molding. An intensive Brabender type mixer with two counter-rotating roller rotors was used. Mixing temperature was 100 °C; screws speed was 100 r.p.m. and mixing time was 10 min. Compression molding was carried out in a hydraulic press under 75 kg/cm² for 10 min at 100 °C. The thickness of the sheets was 1 mm. Nanocomposites sheets were identified by the following code: PCL-“clay content”% “clay type”. For example, “PCL-1% Bent” is the nanocomposite sheet based on PCL matrix with 1 wt% of natural bentonite.

Characterization Methods

Diffraction patterns of organoclays and nanocomposites were obtained using a PANalytical X-Pert Pro diffractometer, operating at 40 kV and 40 mA, with Cu K α radiation ($\lambda = 1.5406$ Å), at room temperature. Organoclays were analyzed in the 2–10° range at scanning speed of 2 °/min and step size of 0.02°. The basal spacing distances (d_{001}) were calculated from the 2θ values using the Bragg's equation:

$$n\lambda = 2d \sin \theta \quad (1)$$

where λ is the source wavelength, θ is the diffraction angle and d is the interlamellar distance. Nanocomposites were examined in the 2–40° using the same conditions of organoclays.

Rheological tests were conducted in a Rheometric Scientific Ares rheometer under nitrogen atmosphere. Plate–plate geometry with a plate diameter of 25 mm was used. Samples were inserted and heated up to 80 °C. Low shear amplitude (2%) was used in order to avoid the destruction of any stabilized clay structure and work in the linear viscoelastic regime. Data were taken for shear rates ($\dot{\gamma}$) in the range of 0.002–12.5 s⁻¹. The melt rheology curves were fitted to the

power law expression in the range of 0.002–0.02 s⁻¹ by the following equation:

$$\eta_{Rh} = A_{Rh} \dot{\gamma}^{(n_{Rh})} \tag{2}$$

where the *Rh* subscript represents a rheology parameter, η_{Rh} is the complex viscosity, A_{Rh} is the pre-exponential factor, $\dot{\gamma}$ is the shear rate and n_{Rh} is the shear thinning exponent. In the double logarithmic plot, a linear zone at low shear rates (in our case up to 0.02 s⁻¹) can be seen. The n_{Rh} parameter was calculated from the slope of this region [39].

Thermogravimetric analysis (TG) was carried out in a TA Auto-MTG Q500 HI-Res™ (TA Instruments). Clay samples were heated from room temperature to 900 °C, at a rate of 10 °C/min in air flow. SL-modified clays were analyzed in order to quantify the organic content present. Also, nanocomposites samples were analyzed from room temperature to 600 °C in air flow and at 10 °C/min, with the aim to obtain their characteristic degradation temperatures. Temperature at which the mass loss is 10%, $T_{-10\%}$, and temperature of maximum degradation rate, T_{max} , were obtained from the derivative of TG curves (DTG). In addition, nanocomposite clay content (NCC) was determined by subtracting the residual mass of PCL at 600 °C to the residual mass of nanocomposites at the same temperature, correcting for the weight loss of the organo-modifiers at the same temperature.

Measurements of nanocomposites and PCL crystallinity percentage were conducted in a differential scanning calorimeter (DSC) TA instruments model Q2000, operating from 20 to 120 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The degree of crystallinity of each sample, X_C (%), was calculated according to the following equation:

$$X_C(\%) = \frac{\Delta H_m}{w_{PCL} \times \Delta H_{100}} \times 100 \tag{3}$$

where ΔH_m is the experimental melting enthalpy, w_{PCL} is the PCL weight fraction and ΔH_{100} is the melting enthalpy of 100% crystalline PCL (142 J/g [40]). Crystallization temperature of each sample was obtained from cooling curves conducted from 120 to 0 °C at 10 °/min.

Tensile tests were performed in a universal testing machine INSTRON 3396 at a constant crosshead speed

of 20 mm/min. Samples were prepared according to the ASTM D638 and tests were performed at room temperature; at least four specimens of each sample were analyzed.

Water vapor permeability (WVP) of each film was determined following the method of the desiccant proposed on ASTM E 96-00. Circular test vials with 5 cm internal diameter were filled with CaCl₂ (desiccant) to produce a 0% RH. Films were sealed to the vial mouth and stored in a moisture-controlled chamber at 65 ± 1% RH and 20 °C. Vials were weighted with an analytical balance (±0.0001 g) every day. A plot of weight (g) versus time (h) was used to determine the water vapor transmission rate (WVTR). Then, WVTR (g/h m²) was calculated by dividing the plot slope by the exposed film area (m²). The WVP of films was then calculated as follows:

$$WVP = WVTR \times l/S(R_1 - R_2) \tag{4}$$

where *l* is the film thickness (m), *S* is the saturation vapor pressure at test temperature (mmHg) and R_1 and R_2 are the relative humidity at the test chamber and at the vial interior, respectively. Measurements were taken after an initial equilibration period to ensure steady state diffusion and at least six measurements of each sample were realized.

Results and discussion

Soy-Lecithin Modified Bentonite Characterization

The results of the characterization of soy-lecithin modified Bent were presented in our previous work [38]. Briefly, their main characteristics are shown in Table 1.

It can be observed from the previous table that the organic content in the organoclays significantly increased with the initial amount of SL. However, the basal spacing shows a slow raising tendency as a function of SL content, probably because the additional amount of SL may be adsorbed on the platelet edges, the platelet faces on top of stacks or modifier adsorbed on modifier instead of the interlayer region [30, 41]. As it is known, thermal stability of organoclays is significantly influenced by the surfactant adsorbed on the external surfaces of the silicate layers, such as platelet edges and platelet faces on top of stacks. This phenomena can be observed from the thermal

Table 1 Results of TG, XRD and moisture adsorption for bent and its organoclays

Sample	g SL/g Bent ratio	Organic content (%)	d_{001} (Å)	Moisture absorption (%)	$T_{-10\%}$ (°C)
Bent	–	0	13.2	18.3 ± 0.1	>900
A	0.25	16.2 ± 0.2	15.1	8.6 ± 0.4	318
B	0.50	22.8 ± 0.2	16.5	6.4 ± 0.3	267
C	1.00	41.9 ± 0.4	24.5 and 16.0	6.3 ± 0.5	197

degradation temperatures ($T_{-10\%}$) that show a decrease in the thermal stability of organoclays as a function of the absorbed SL content [30]. Even so, $T_{-10\%}$ is above 190 °C in all cases, which is well above the processing temperature of PCL (100 °C). So, even in the presence of shear forces during melt mixing at 100 °C, thermal degradation of the SL organo-modifier during processing is not expected for these nanocomposite systems. Higher values of d_{001} are mostly desired due to the possibility of easier intercalation of polymer chains between the silicate layers [25]. In this regard, there is a compromise between thermal stability and the interlayer spacing of the clays when using them as reinforcement of a polymer matrix. On the other hand, moisture absorption is another interesting parameter that can be related with the compatibility between the reinforcement and the polymer matrix. Lower moisture adsorption is desired for nanoclays used as reinforcement of PCL, which has a strong hydrophobic nature. Moisture adsorption tests (Table 1) showed a huge reduction of this parameter for the organoclays when they are compared with raw bentonite. Also, it was found that the moisture adsorption slightly decrease as a function of the organic content increase. That can be attributed to the presence of residual cations in the interlayer region of ionically-exchanged clays that are solvated by water molecules which interact most strongly with the compensation cations [41].

PCL-SL-Bent Nanocomposites

XRD tests constitute an important technique to analyze the dispersion of the clay into the matrix. Bent can be intercalated or exfoliated depending on the increment in their basal spacement caused by interactions of polymer chains between the silicate layers [5, 7]. If an intercalated structure is found, the XRD pattern shows a shift on the 001 diffraction peak towards lower angle values, but if no more diffraction peaks are visible, we may be in the presence of an exfoliated or mixed intercalated-exfoliated structure [7, 42]. XRD curves of PCL, clays (Bent, A, B and C) and their nanocomposites are shown in Fig. 1. Figure 1a compares the position of the unmodified Bent diffraction peak ($2\theta=6.69^\circ$, $d_{001}=13.2 \text{ \AA}$) with those for PCL-1% Bent ($2\theta=6.01^\circ$, $d_{001}=14.7 \text{ \AA}$) and PCL-2% Bent ($2\theta=5.87^\circ$, $d_{001}=15.03 \text{ \AA}$). As can be seen, there is a shift of the Bent diffraction peak towards lower angles, indicating an increase in the interlaminar spacing of Bent in nanocomposites. Furthermore, this effect increases as a function of Bent content. This result suggests that intercalated nanocomposites were obtained [43]. Figure 1b again shows the appearance of an intercalated compound, due to the displacement of A diffraction peak ($2\theta=5.88^\circ$, $d_{001}=15.1 \text{ \AA}$) to lower diffraction angles in the nanocomposites PCL-1% A ($2\theta=5.19^\circ$, $d_{001}=17.00 \text{ \AA}$) and PCL-2% A ($2\theta=5.11^\circ$,

$d_{001}=17.27^\circ$). In the case of nanocomposites obtained with B, no significant changes were observed in the peak positions of B and B in PCL-1% B and PCL-2% B (Fig. 1c). This suggests that non-intercalated particles of B are randomly oriented in the PCL matrix [44]. Finally, Fig. 1d shows C diffraction peaks ($2\theta=3.6^\circ$ and 5.52° , $d_{001}=24.5$ and 16.0 \AA) and C in PCL-1% C and PCL-2% C nanocomposites, in which peaks decrease in intensity and almost disappear suggesting that possibly a predominantly exfoliated structure is formed (although TEM would be required to confirm this) [45].

Melt rheology can also be useful to compare the clay dispersion degree of polymer/clay nanocomposites. Several authors [39, 46–48] have found that the n_{Rh} parameter (see Eq. (2)) is higher as a function of the clay dispersion degree. Zhao et al. [46] have proposed n_{Rh} as a semi-quantitative measure of the clay dispersion degree of the sample. It must be noted that the average number of nanoplatelets per tactoid for a given nanocomposite cannot be calculated from n_{Rh} . Therefore, the measured rheology needs to be ‘calibrated/correlated’ with known nanocomposite morphology, previously characterized by the traditional techniques (XRD, TEM). It must be also taken into account that XRD and TEM analysis are performed in the solid phase while rheology in the molten one. Even so, good correlation between n_{Rh} studied by melt rheology and clay dispersion degree analyzed by XRD/TEM for different polymer/clay nanocomposites was found by several authors [39, 46, 48, 49]. Figure 2 shows the log–log complex viscosity as a function of shear rate curves and Table 2 resumes the n_{Rh} values in descending order.

Lower n_{Rh} values for the nanocomposites with organo-modified clays were observed while the interlayer distance was higher for these materials. Therefore, the expected correlation between XRD and melt rheology was not observed. In addition, significant detriment of the viscosity of these nanocomposites is observed in comparison with the neat matrix (Fig. 2) even when the incorporation of a rigid filler such as clays in a polymer matrix should increase the viscosity of the system. Moreover, n_{Rh} parameter decreases as the amount of SL and the SL-modified Bent increases in PCL composites. These unexpected results may be a consequence of polymer matrix degradation catalyzed by clay organo-modifiers. Lin et al. [50] studied the effect of molecular weight catalytic degradation of PCL in solid state by the presence of a methanolic solution of alkylamines. They found that the primary amines possessed the ability to degrade the matrix by 50% after 8 days depending on the type of amine and the test conditions. Additionally, they found that the degradation rate increased with the length of the alkyl chain of the amine and that drugs with secondary and tertiary amino groups do not react directly with the PCL but catalytically accelerate its degradation.

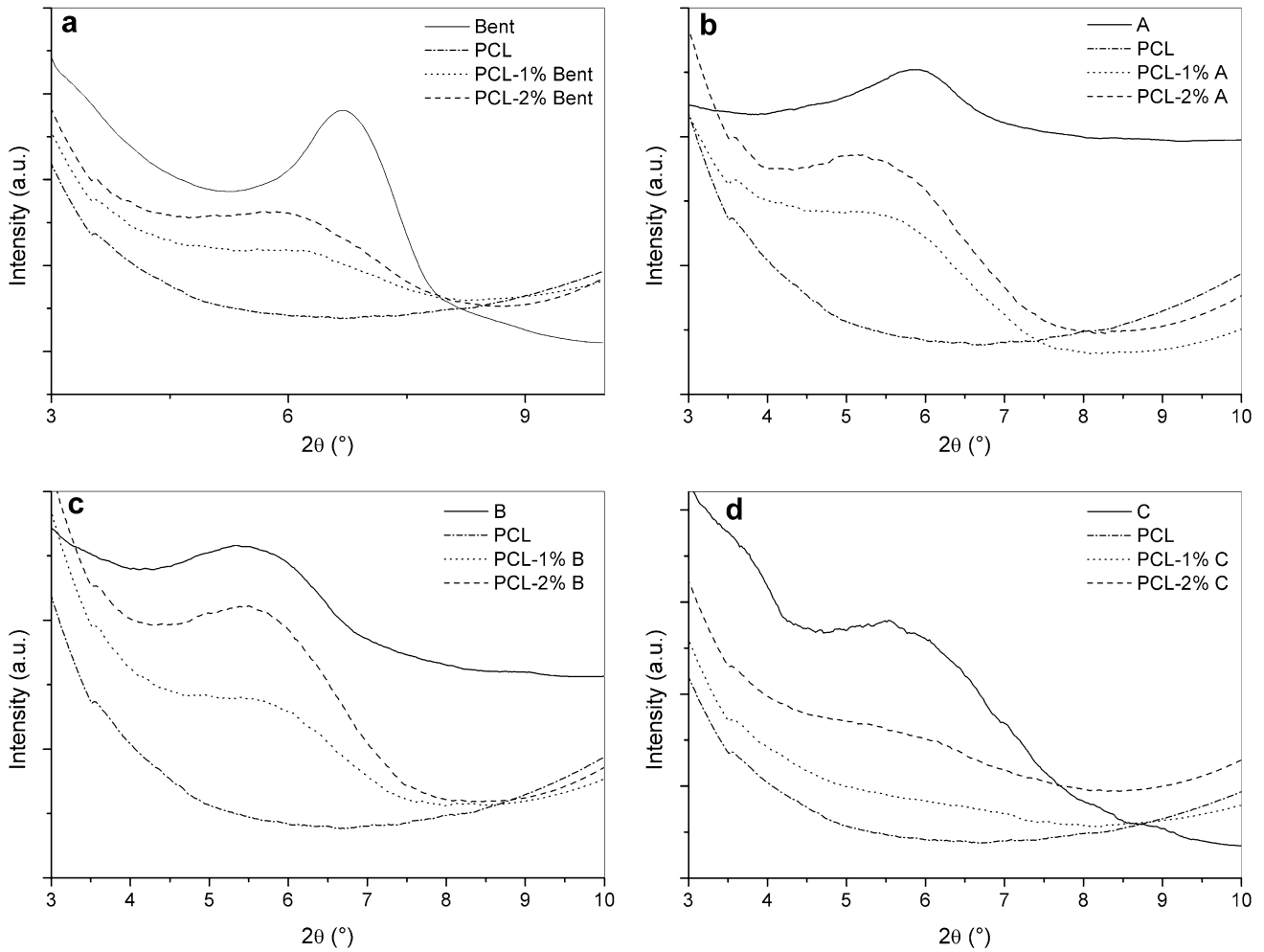


Fig. 1 XRD patterns of clays, PCL and their nanocomposites with 1 and 2% of: **a** raw Bent, **b** organoclay A, **c** organoclay B and **d** organoclay C

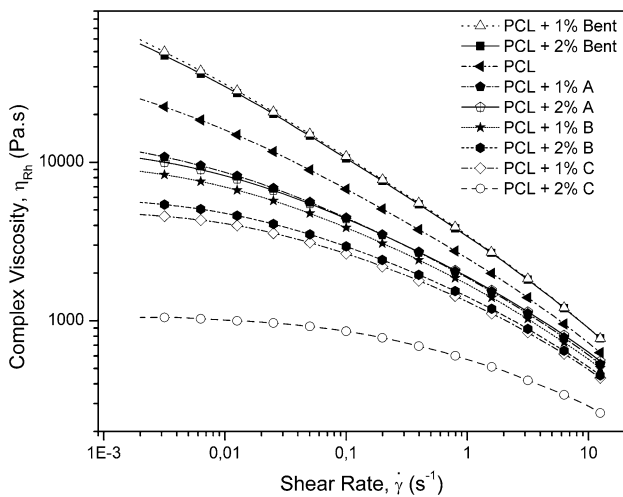


Fig. 2 Double logarithmic plot of complex viscosity as a function of shear rate for the neat PCL and nanocomposite

Table 2 Parameters representing nanocomposite morphology: shear thinning exponent ($-n_{Rh}$) from rheologic tests and interlaminal distance of the nanocomposites $d_{001}^{nanocomposites}$ from XRD analysis

Sample	$-n_{Rh}$	$d_{001}^{nanocomposites}$ (nm)
PCL + 1% Bent	0.41	14.7
PCL + 2% Bent	0.40	15.03
PCL	0.30	—
PCL + 1% A	0.20	17.0
PCL + 2% A	0.18	17.3
PCL + 1% B	0.16	15.9
PCL + 2% B	0.12	16.2
PCL + 1% C	0.10	—
PCL + 2% C	0.03	—

Similar results were reported by Cha Y. et al. and Shah S. et al. [51, 52], who studied the decrease of the molecular weight of PCL, PGLA (glycolic acid-co-DL-lactic acid) and

PLLA (poly L-lactic acid) microspheres that housed drugs with amino functional groups.

According to Pitt et al. [53], the first step in the degradation of aliphatic polyesters is the scission of the ester bond. This reaction is self-catalyzed by the carboxylic groups at the end of the chain and its effect can be increased by adding substances with acidic or basic groups, such as amines. Furthermore, other possible reactions should be considered such as transesterification of the ester group present in the polymer with OH groups [54]. Soy lecithin is rich in phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol and phosphatidic acid. It has to a lesser degree phosphatidylserine and sphingomyelin [38]. Among these, phosphatidylethanolamine has a primary amino group and phosphatidylinositol a saccharide ring with OH groups. These components present in SL could be responsible for the observed effects.

Although there are not many publications that consider the effect of catalytic degradation of polyesters, this could be of practical importance for controlled drug release, because depending on the drug, the molecular weight and

type of polyester could be regulated to control the time to release it. In the case of food packaging, the catalytic degradation of PCL can be a problem during processing and can lead to undesirable final mechanical and barrier properties of the final nanocomposite product. In addition, the balance between polymer matrix degradation, clay dispersion degree and clay platelet content will define the final mechanical and barrier performance of the nanocomposites [53].

Thermal stability of nanocomposites was investigated by TG. Temperatures at mass loss of 10%, $T_{-10\%}$, and temperatures at maximum thermal degradation rate, T_{max} , were obtained from the TG and DTG curves (Fig. 3a–d) and are presented in Table 3.

In general, degradation temperatures of all samples are above 320 °C, which is enough thermal stability for the potential application as food packaging. Not only does the application not deal with such high temperatures, but also the temperatures developed in the processing techniques will not exceed these values. Particularly, it was found that $T_{-10\%}$ for PCL was 349 °C and that value had

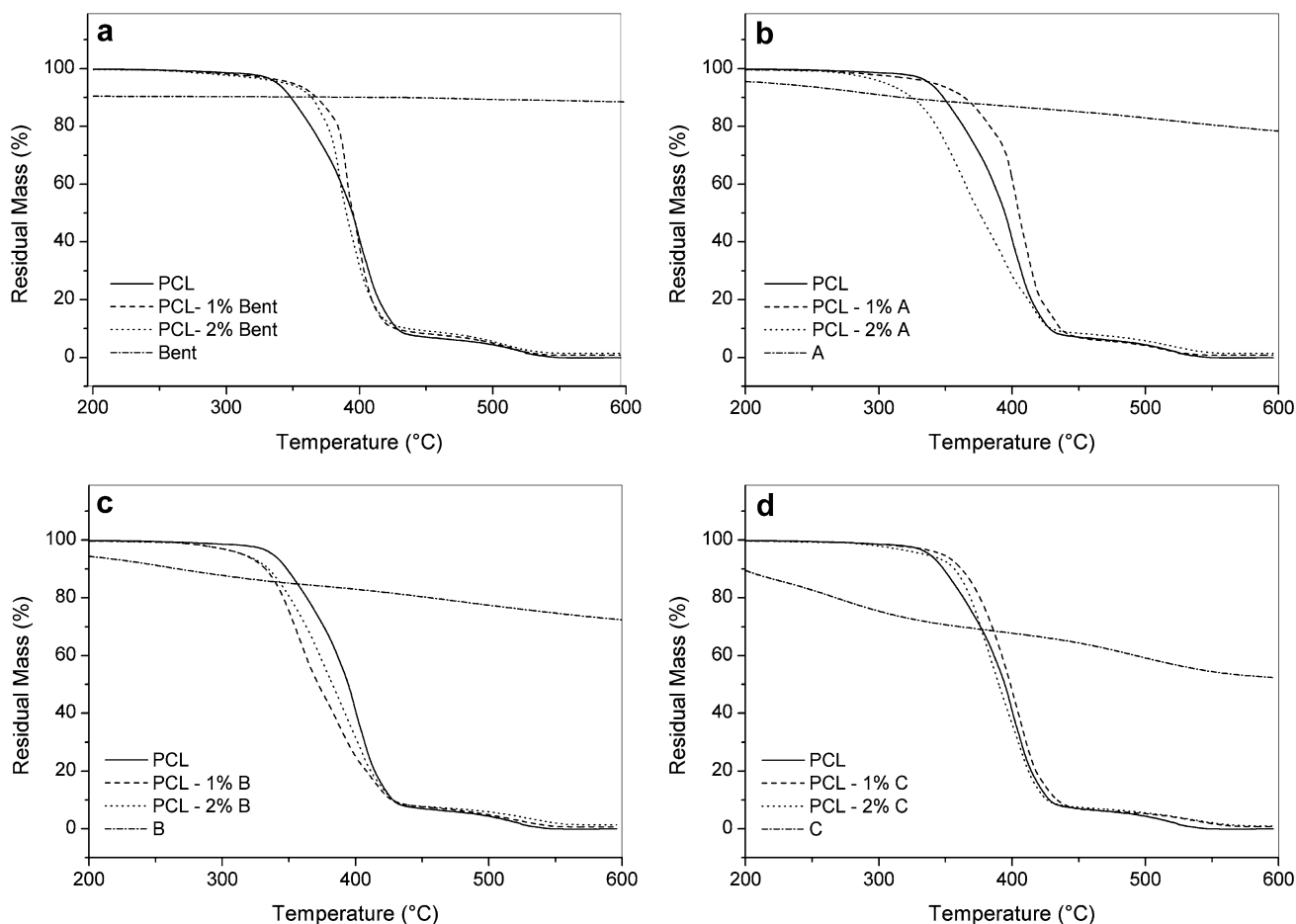


Fig. 3 TG thermograms of PCL and their nanocomposites with 1 and 2% of: **a** raw Bent, **b** organoclay A, **c** organoclay B and **d** organoclay C

Table 3 TG, DTG and DSC test results for PCL matrix and nanocomposites

Sample	T _{-10%} (°C)	T _{max} (°C)	NCC (%)	T _m (°C)	X _c (%)	T _c (°C)
PCL	349	400	0	59.2	52.6	40.7
PCL-1% Bent	368	390	0.80	59.5	54.1	40.2
PCL-2% Bent	364	386	1.35	60.0	52.0	40.6
PCL-1% A	364	402	0.80	59.0	59.8	40.1
PCL-2% A	325	365	1.38	58.5	52.0	40.1
PCL-1% B	332	357	0.69	58.5	52.2	40.3
PCL-2% B	335	393	1.34	58.7	51.2	40.2
PCL-1% C	362	403	0.77	59.3	56.7	40.0
PCL-2% C	357	385	0.95	58.3	57.5	40.1

an improvement in samples with 1 and 2% of raw bentonite and for the one with 1% of A (Table 2), although, T_{max} was only higher than PCL for the latter. The remaining nanocomposites showed a slight decrease in thermal stability (the largest decrease was 24 °C for PCL-2%A). Similar results were reported by Chrissafis et al. [55] for PCL/Cloisite 20A samples which showed a decrease in thermal stability of nanocomposites in opposition to the commonly observed results attributed to the decomposition of the ammonium salt used as modifier of the bentonite [55].

In the case of soy lecithin-modified Bent it was found that only PCL-1%A enhances both thermal parameters (T_{-10%} and T_{max}) with respect to neat PCL. In addition, it was found that an increase in clay content produces a decrease in thermal stability. An additional comparison can be observed taking into account the amount of soy lecithin present in the organoclay and its influence on the thermal stability of nanocomposites. Thus, if we compare T_{-10%} and T_{max} for samples with Bent, A, and C, it is possible to realize that there is a slight decrease in thermal stability when soy lecithin content increases.

Figure 4a–d shows DSC thermograms. PCL nanocomposites presented similar glass transition temperatures (around –59 °C), which is in accordance with that informed by Lepoittevin et al. [44]. Percentages of crystallinity, X_c (%), and melting temperatures, T_m (°C), are introduced in Table 3. Pitt et al. [53] has reported that polymer chain degradation of PCL can be associated with an increase in their crystallinity. They claim that the degree of crystallinity of the PCL can increase by up to 40% by changing their molecular weight from 50,000 to 5000. It was observed that only PCL-1% A, PCL-1% C and PCL-2% C had a slight increment in their percentage of crystallinity while the other samples analyzed showed similar results to neat PCL. This small change in crystallinity could be related to the change in molecular weight of PCL in these nanocomposites, as suggested by rheology analysis. Regarding melting temperatures all values were similar to that for PCL and no significant changes were observed.

Figure 5 presents the DSC cooling curves of PCL and its nanocomposites. Crystallization temperatures of each are included in Table 3. As can be appreciated no significant differences were observed, which suggests that the silicate layers do not act as nucleating agents [45, 56]. The other observed change, i.e., the increase on crystallinity was related with the polymer chain degradation of PCL and reduction of Mw [56]. However, could also be affected by the organo-modifier or the clay itself. It should also be noted that nucleating agents may not affect the onset temperature of crystallinity, but can affect the extent of X_c and also crystallite (spherulite) size or polymorph.

Mechanical characterization of samples was performed in order to analyze potential applications of PCL nanocomposites. So, Young's modulus, tensile stress and elongation at break were calculated from the stress–strain curves obtained in tensile tests (Fig. 6a–d). Results are summarized in Table 4.

Mechanical properties of nanocomposites depend on the amount of the filler employed, clay dispersion, compatibility degree between filler and matrix and polymer molecular weight, among others [9, 57]. It was found that stiffness of nanocomposites in all cases was lower than the pure PCL while tensile strength and elongation at break increases in all samples compared to raw PCL. This is an unexpected result since in most cases for nanocomposites, Young's modulus increases and elongation at break decrease compared to those for PCL when an intercalated/exfoliated structure is achieved [44]. However, if we consider that there is a reduction in the molecular weight of PCL, as suggested by rheology analysis, it is right to expect a reduction in the rigidity of the nanocomposites given that clay modifier and the smaller polymer chains can act as slippage zones between the long polymer chains [57].

For PCL reinforced Bent it is observed that Young's modulus increases as a function of the clay content incorporated into the matrix as was expected due to more rigid filler being present. However, in both cases the Young's modulus is lower than that of the neat PCL, which cannot be attributed to degradation of the matrix. It may be due to

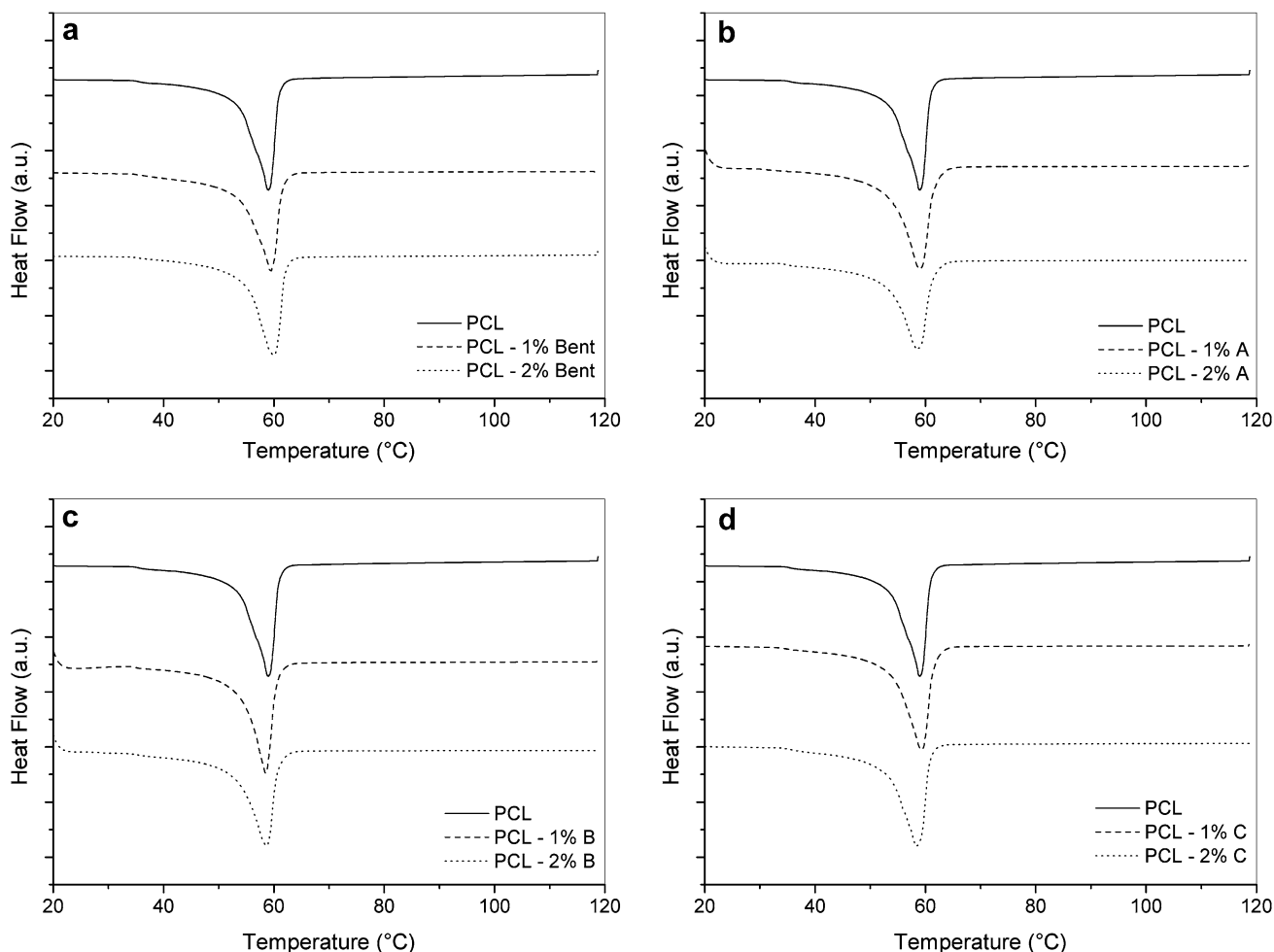


Fig. 4 DSC curves of PCL and their nanocomposites with 1 and 2% of **a** raw Bent, **b** organoclay A, **c** organoclay B and **d** organoclay C

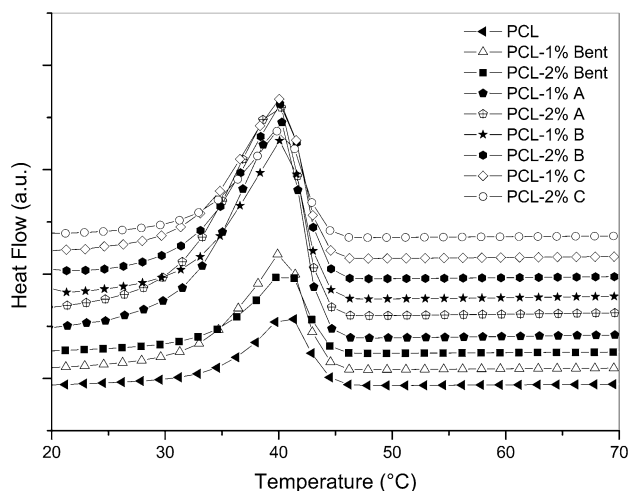


Fig. 5 DSC cooling curves of PCL and its composites with Bent, A, B and C

poor dispersion by low compatibility between the clay and the matrix.

As it was stated before, we suggest that nanocomposites with A, B and C produced a decrease in molecular weight of PCL and this could be responsible for the detriment in Young's modulus. However, Young's modulus is also affected by the relative amounts of modifier present in each case, the clay content and degree of dispersion in the matrix. Taking into account these factors it may justify that the PCL-2% C nanocomposite has the highest Young's modulus, since it is the only one that showed no diffraction peak in the diffraction pattern of Fig. 1d, indicating that it had at least a mixed intercalated-exfoliated structure.

Barrier properties of films were also studied by measuring the water vapor transmission rate. Results are introduced in Table 4. It can be noticed that WVP of PCL decrease in all nanocomposites due to the presence of clay, which provides a hindered path to water molecules to diffuse, and thus, increasing the diffusion path length [58, 59]. Several authors have reported that when the

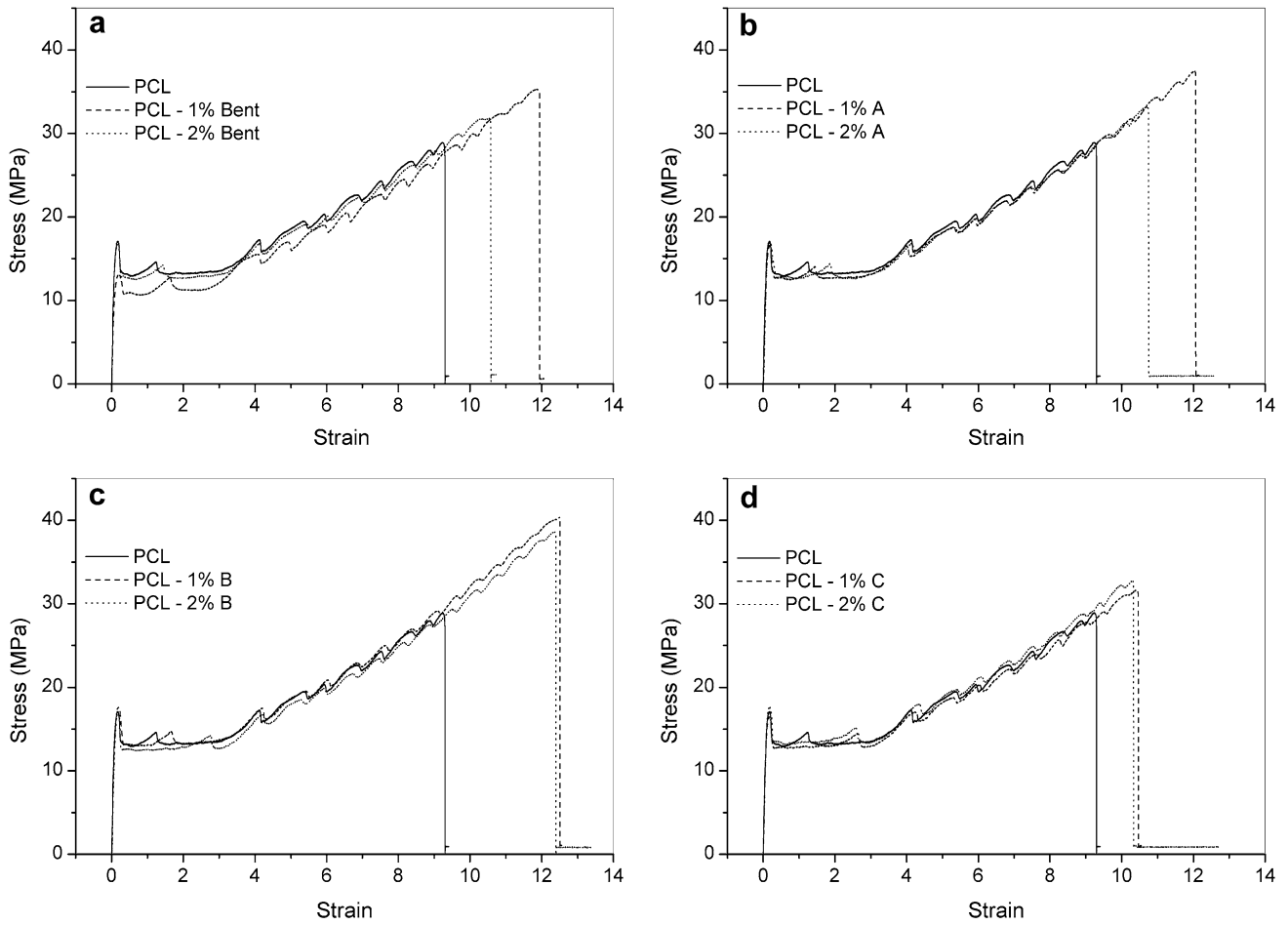


Fig. 6 Tensile stress–strain diagram of PCL and its nanocomposites with 1 and 2% of: **a** Bent; **b** Organoclay A; **c** Organoclay B and **d** Organoclay C

Table 4 Mechanical properties of PCL and its nanocomposites

Sample	Young’s modulus (MPa)	Tensile strength (MPa)	Elongation at break (mm/mm)	WVP (g/hmPa*10 ⁻¹⁰)
PCL	199.2±4.5	27.7±1.9	9.0±0.5	23±0.0
PCL-1% Bent	146.2±7.3	33.6±2.9	12.4±1.1	6.1±1.6
PCL-2% Bent	190.2±9.7	30.8±5.0	10.3±1.5	3.8±0.1
PCL-1% A	144.4±4.9	36.5±2.9	11.9±0.8	4.3±0.8
PCL-2% A	140.8±12.0	31.4±2.3	10.4±0.8	7.1±0.6
PCL-1% B	157.4±11.5	38.9±1.5	12.5±0.2	3.4±1.6
PCL-2% B	153.3±6.3	38.5±0.6	12.8±0.4	4.7±0.0
PCL-1% C	173.0±15.7	29.5±1.8	9.7±0.6	3.3±0.0
PCL-2% C	190.5±10.8	31.4±1.8	10.2±0.2	1.9±0.0

clay is well dispersed in the matrix, the WVP decreases with increasing clay content [6, 59]. This occurs for PCL reinforced with Bent and with C, in the range of studied clay concentrations. However, for PCL nanocomposite with A and B opposite trend is observed: when the clay content increases, the WVP also increases. This has been

previously observed by Rihm et al. who suggest that this may be due to the formation of clay tactoids [59].

The large decrease in water vapor permeability has practical importance for the use of PCL as a matrix for obtaining nanocomposites with potential use for food

packaging applications, since they could extend food shelf-life by maintaining its moisture content [10, 58].

Best candidate for food packaging applications is PCL-2%C which, comparing to the neat PCL, showed a slight detriment on Young's modulus (4%), an increment of 13% in the tensile strength and elongation at break and 90% lower water vapor absorption.

Conclusions

This paper describes the preparation by melt blending of environmentally friendly compounds of PCL reinforced with natural and soy lecithin modified bentonite. X-ray characterization of the compounds suggested that PCL with Bent, A and B possessed an intercalated structure, while those obtained with C, intercalated-exfoliated. However, these results could not be directly confirmed by melt rheology. This characterization showed unexpected results that led to the belief that thermal degradation of the matrix occurs by catalytic action of the clay modifier (soy lecithin) due to the presence of amino groups that have the ability to break the ester bond present in the polymeric polyesters. The thermal analysis indicated that the thermal stability of clays with higher organic content decreases and the compounds obtained with C had higher percentages of crystallinity than the pure PCL, which is in accordance with the alleged decrease in molecular weight. The mechanical properties also showed unexpected values that can be explained by considering a decrease of the molecular weight of the matrix. This analysis is complex because many factors are involved such as the degree of dispersion, amount and type of filler and the change in the molecular weight of PCL. Again it could be seen that the compounds of PCL with C had the best performance, because although they indicated producing the highest degree of degradation of the matrix, they also exhibited a better dispersion of the reinforcement which gives them the best properties. The permeability test showed a significant reduction in WVP of clay compounds compared to pure matrix. A special reduction in permeability was obtained with the compounds obtained with C, which result attractive for its potential application in food packaging. Finally, it can be concluded that clay organo-modifiers should be designed not only based on improvements in the clay/matrix compatibility and clay interlayer distance but also by assessing the chemistry of the modifiers that may induce catalytic matrix molecular weight degradation and thus leading to unexpected tendencies on the final properties of the nanocomposites.

Acknowledgements Authors acknowledge the financial support of the National Research Council (CONICET) (PIP 00617), the National

Agency for the Promotion of Science and Technology (ANPCyT) (FS Nano 004), and the University of Mar del Plata (UNMDP), Argentina.

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