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Organo-modified montmorillonite/poly(ϵ -caprolactone) nanocomposites prepared by melt intercalation in a twin-screw extruder

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A B S T R A C T

Nanocomposites based on biodegradable poly(ϵ -caprolactone) organo-modified clay have been prepared by melt intercalation using a twin-screw extruder. The screw configuration developed allowed us to obtain an intercalated/exfoliated nanocomposite structure using a modified montmorillonite containing no polar groups, in contrast to previous work using mainly alkyl ammonium containing hydroxyl polar groups in poly(ϵ -caprolactone). Montmorillonite nanocomposites were prepared using a specific extrusion profile from a 30 wt% masterbatch of organo-modified clay, which was then diluted at 1, 3 and 5%. Intercalated and/or exfoliated nanocomposites structures were assessed using rheological procedures and confirmed by transmission electron microscopy analysis. Mechanical and thermal properties were found to be strongly dependent on morphology and clay percentage. Crystallinity was only slightly affected by the clay addition. Effect of exfoliation on Young's modulus and thermal stability was investigated. Young's modulus increased significantly and onset degradation temperature measured by TGA was significantly reduced for an exfoliated nanocomposite composition containing 5 wt% organoclay.

Keywords:

Nanocomposites

ϵ -PCL

Montmorillonite

Thermal stability

Young's modulus

Exfoliation

1. Introduction

Polymer/layered silicate nanocomposites are a new class of materials with enhanced properties compared to filled composites containing mineral particles in the micron range.

It is well known that a few amount of nanofillers, particularly layered silicates, typically 1–5 wt%, depending on the morphologies obtained for the composite, are able to improve several functional properties, such as Young's modulus and tensile stress, permeability to gases and solvents, thermal stability and flame retardancy [1].

The most commonly used clay for polymer/clay nanocomposites is organo-modified montmorillonite (OMMT). When OMMT is dispersed within the matrix, several specific morphologies, intercalation, exfoliation or combinations of both, are possible. In contrast to morphologies corresponding to microcomposites, only these morphologies allow mechanical, thermal properties and fire behaviour to be notably improved.

Three main methods are used to prepare polymer/clay nanocomposites: melt intercalation, exfoliation–adsorption and *in situ* polymerization [2]. Melt intercalation is becoming a widely used process for the preparation of nanocomposites. The process is

usually carried out using an internal mixer or an extruder. The ability to disperse OMMT, to obtain intercalation and/or exfoliation by delamination of the layered silicates strongly depends on the extruder nature (single or twin-screw) and especially its screw configuration (shear rate).

Nowadays, for environmental concerns, a growing attention has been focused on biodegradable and biocompatible synthetic polymers, such as PCL (poly(ϵ -caprolactone)). PCL is biodegradable aliphatic polyester known for its use in medical devices, pharmaceutical controlled release systems and biodegradable packaging [3]. It is a crystallisable polymer with a crystallinity around 45%, a glass-transition temperature around -60 °C and a melting point near 60 °C.

Performances of this polymer can be greatly enhanced by dispersion of a small amount of layered silicates. Nanocomposites based on PCL have been widely reported [4–15].

Many works have investigated the influence of the methods of silicate modification and processing conditions on the morphology of nanocomposites and so, on their final properties. Overall, their goal was to increase the performance of mechanical and thermal properties of PCL.

Luduena and co-workers have studied the influence of exfoliation–adsorption and melt intercalation methods on the mechanical performance of a methyl tallow bis-2-hydroxyethyl, quaternary ammonium modified montmorillonite [14]. For exfoliation–adsorption, the nature of the solvent used and the operating

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conditions were found to have an influence on morphology and consequently on final properties. In the case of melt intercalation by intensive mixing, a higher clay dispersion degree was achieved up to 5 wt% due to the shear forces and the resultant mechanical properties were found higher to those obtained by solvent casting.

Melt intercalation using a two roll mixer was presented as a relevant method by Lepoittevin and co-workers [9], leading to a good dispersion of montmorillonites modified using hydrogenated tallow alkyl based quaternary ammonium cations. Stiffness and thermal stability improved with the filler loading up to a content of 5 wt%.

In situ polymerization and melt intercalation appeared to be more convenient to achieve intercalated/exfoliated structures. Several authors obtained intercalated/exfoliated nanocomposites using *in situ* polymerization [5–7,12,13,16]. The extent of exfoliation was controlled by the polarity of the organo-modified clay. Only intercalated structures could be obtained using OMMT with non-polar groups in the ammonium ion modifier [5].

A similar behaviour was found by Zheng et al. [13] using Cloisite 15A[®]. However, they obtained exfoliated structure, also using Cloisite 30B[®].

Melt intercalation methods were carried out, using a roller mixer [8–10,13,14] or an extruder. For PCL nanocomposites, no previous works were made using an extruder at a pilot-scale. A DSM micro-extruder was used by Homminga et al. [3,15], leading to intercalated/exfoliated morphologies. Once again, exfoliation depended on the polarity of the organophilic groups of the ammonium ion used as modifier [9]. Better mechanical performances of PCL were found using melt intercalation compared to adsorption–exfoliation method [14]. Thermal stability was also improved by using this method compared to *in situ* polymerization [13].

As a matter of fact, compatibilisation between PCL and montmorillonite seems to be the key issue, allowing nanocomposite morphologies to be achieved. It can be supposed that montmorillonite should be sufficiently polar (due to the nature of the groups of organo-modifier) to be well dispersed.

Nevertheless, the influence of the mixing process on the resulting morphologies has also to be taken into account for melt intercalation methods, particularly by twin-screw extrusion. Some previous studies have shown that the screw profile could play an important role on the composite morphology. Investigations made by the Southern Clay Company have shown that a high shearing profile could lead to an exfoliated nanocomposite [18]. It was also noticed that the location of the shearing zones also had an influence on the final morphology. As a matter of fact, shearing zones should be located at the first zone of the profile to ensure exfoliation. In consequence, the screw configuration given by Fig. 1 was developed.

The main objective of this study is to achieve nanocomposite morphologies (intercalated or exfoliated) for montmorillonites, modified using ammonium ions without any polar group. Melt intercalation technique carried out using a pilot-scale twin-screw extruder with a selected screw profile was used. The influence on

the mechanical properties and thermal stability of the PCL composite resulting to the incorporation of various organo-modified montmorillonites was also investigated.

2. Experimental part

2.1. Materials

Commercial grade poly(ϵ -caprolactone) (CAPA 6800[®]) was purchased from Solvay Chemicals ($M_w = 80\ 000$, $T_m = 60\ ^\circ\text{C}$);

Commercial organo-modified montmorillonites (noted OMMT: Nanofil5[®], Nanofil2[®]) were supplied by Süd-Chemie (Moosburg, Germany). Cloisite 30B[®] (C30B[®]) was supplied by Southern Clay Products. Nanofil5[®] was modified with a dimethyl-distearyl ammonium, Nanofil2[®] with dimethyl-stearyl-benzyl ammonium. C30B[®] was modified with methyl tallow bis-2-hydroxyethyl ammonium.

2.2. Preparation of masterbatches

A Haake RHEOMIX[®] 300 internal mixer with two counter-rotating rollers was used for the preparation of PCL/organoclay masterbatches at a clay percentage of 30 wt%. The processing temperature was set at 140 °C. The rotating speed of the rotor and the mixing time were respectively, 40 rpm and 10 min.

2.3. Extrusion and injection moulding procedures

PCL/organoclay nanocomposites were prepared using a Cleextral BC21 co-rotating twin-screw extruder ($L = 1200\ \text{mm}$, $L/D = 48$).

The processing temperature was set at 140 °C, the screw speed at 250 rpm and the polymer flow at 3 kg/h. Clay percentages were 1, 3 and 5 wt%. The samples will be referred, respectively, as PCL1, PCL3 and PCL5. Dumbbell specimens were produced at 140 °C using a Sandretto Otto 95 t injection moulding device.

2.4. Characterization of composite morphology

Morphologies were analyzed using a Bruker D8 diffractometer using $\text{CuK}\alpha$ radiation. Data were collected between 1 and 13° by step of 0.02° using an X-ray generator with $\lambda = 0.15406\ \text{nm}$. Transmission electron microphotographs were obtained using a JEOL 1200EX2 apparatus with an acceleration voltage of 120 kV. Samples were 70 nm thick and prepared with a Leica Ultracut UCT ultra-microtome. One millimetre-thick samples were analyzed using a Rheometric Scientific (ARES[®]) equipped with parallel plates. Each sample was analyzed at 140 °C in a frequency range from 10^{-1} to $10^2\ \text{Hz}$.

A Perkin–Elmer Diamond DSC differential scanning calorimeter was used to study crystallization processes. Samples were heated from 20 °C to 100 °C at 10 °C/min under nitrogen atmosphere and kept at 100 °C for 1 min. The cooling ramp was similar. The samples were then heated to 100 °C at 10 °C/min. The crystallization heat

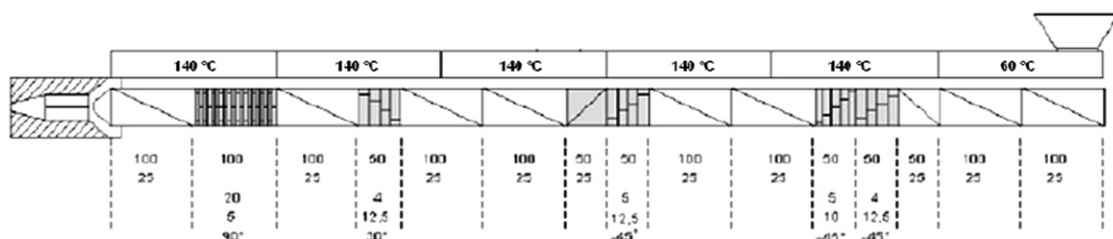


Fig. 1. Screw Configuration.

was, after normalization to the samples mass, converted to PCL crystallinity according to equation (1):

$$X_c(\%) = \frac{\Delta H_m}{W_{PCL} \times \Delta H_{100}} \quad (1)$$

where ΔH_m is the measured value of melting enthalpy, W_{PCL} is the weight fraction of PCL in nanocomposite and ΔH_{100} is the enthalpy of melting 100% crystalline PCL (136.1 J/g) [16].

The values were recorded during the first heating scan. The crystallinity rate value is the average of three measurements.

2.5. Thermal stability of composites

TGA (Perkin–Elmer Pyris 1) was used to evaluate the thermal stability of nanocomposites. Samples were heated from 50 °C to 700 °C at a scan rate of 10 °C/min under nitrogen at 20 ml/min. Curves presented were the average of three measurements.

TGA coupled with FTIR was used to investigate the mechanisms of thermal degradation. IR spectra were measured using a Bruker IFS66-IR Spectrometer at room temperature, where 32 scans at a resolution of 4 cm⁻¹ were signal averaged.

2.6. Mechanical properties of composites

Mechanical testing was performed using a ZWICK Z010 tensile test apparatus, at 20 °C at a constant rate of 1 mm/min for Young's modulus determinations, according to the ISO 527-1 standard.

3. Results and discussion

3.1. Analysis of clay dispersion by XRD

Nanocomposites were analyzed by XRD in order to estimate the extent of clay dispersion in the PCL matrix.

XRD patterns for PCL nanocomposite filled with 3 wt% of Nanofil2® are showed Fig. 2. The interlayer distance for the organoclay is 18.5 Å. After melt blending with PCL, a peak was observed at 37 Å, showing that intercalated nanocomposites were obtained. A second peak was also observed at 4.2° which indicates some ordering of the intercalated structure.

Fig. 3 shows XRD patterns for PCL nanocomposite filled with 3 wt% of Nanofil5®. The interlayer spacing for this organoclay is

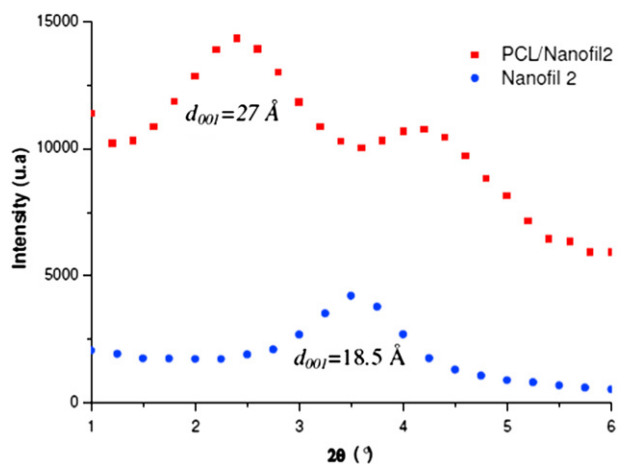


Fig. 2. X-ray scattering patterns of Nanofil2® and PCL filled with 3 wt% of Nanofil2®.

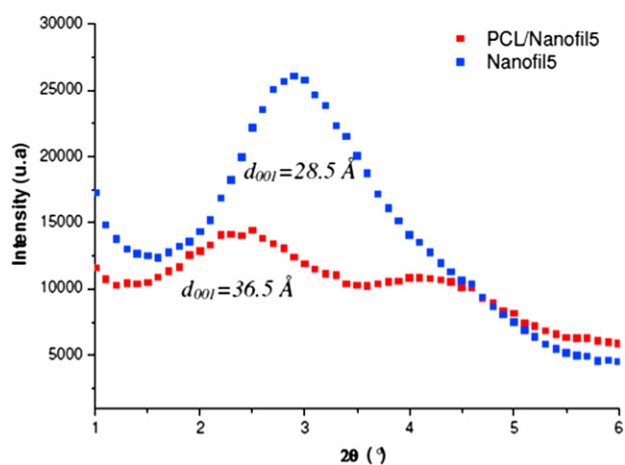


Fig. 3. X-ray scattering patterns of Nanofil5® and PCL filled with 3 wt% of Nanofil5®.

28.5 Å. For the nanocomposite, it is about 36.5 Å proving that PCL chains were intercalated between layers.

For PCL nanocomposites filled with C30B®, an intercalated/exfoliated nanocomposite was obtained from XRD patterns, with an interlayer distance of 18 Å in the organo-modified clay and 32 Å in the composite (Fig. 4).

3.2. Analysis of clay dispersion by TEM

Nanocomposites were analyzed by TEM. Fig. 5 shows the filler dispersion and subsequent morphologies. For each one, nanocomposites with 3 wt% of clay were chosen to estimate the extent of filler dispersion.

Intercalated/exfoliated nanocomposites were obtained using for each composite containing the organo-modified clays. The dispersion seems not to differ slightly for the different organo-modified montmorillonites.

3.3. Rheological properties

Dynamic Mechanical analysis is a relevant tool to investigate the dispersion of modified clays. Dynamic strain sweep tests were applied to materials samples (Fig. 6). Dynamic viscosity (η^*) of nanocomposites exhibited a Newtonian plateau at low strain

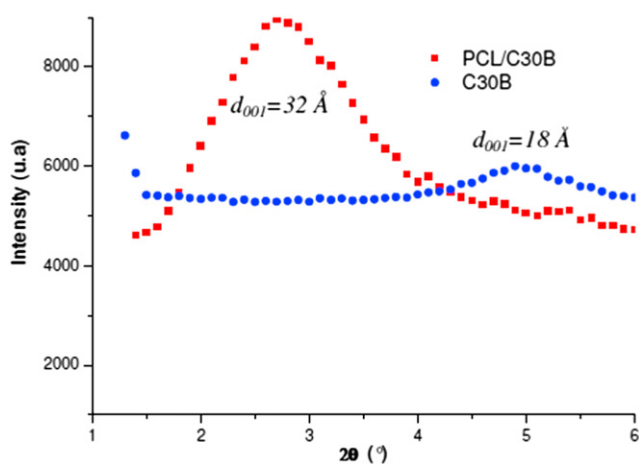


Fig. 4. X-ray scattering patterns of C30B® and PCL filled with 3 wt% of C30B®.

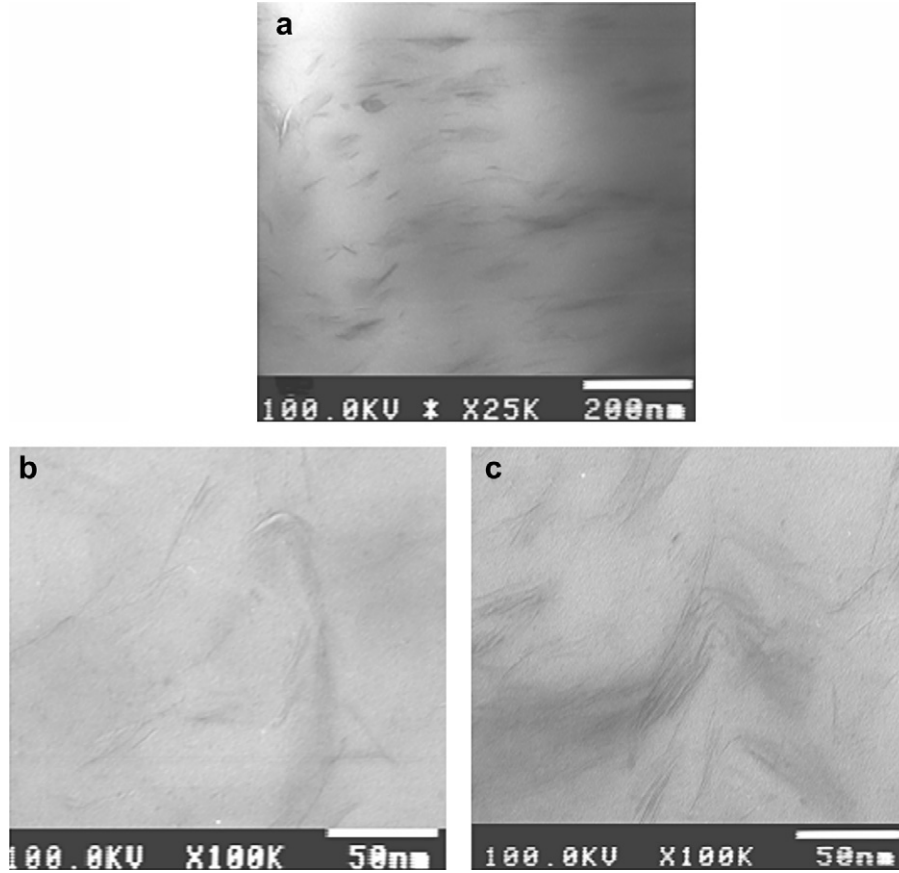


Fig. 5. Transmission electron microphotographs of PCL nanocomposites filled with 3 wt% of: (a) Nanofil5® (b) C30B® (c) Nanofil2®.

(less than 10%) and non-linear region at high strain amplitudes. For this study, we have chosen a strain (γ) of 1%.

Dynamic viscosity curves can be fitted by a power law model at low frequency zone. Several authors used dynamic viscosity to determine power law parameters at low frequencies [17]. Power law expression is written as follows equation (2):

$$\eta^* = k\omega^n \quad (2)$$

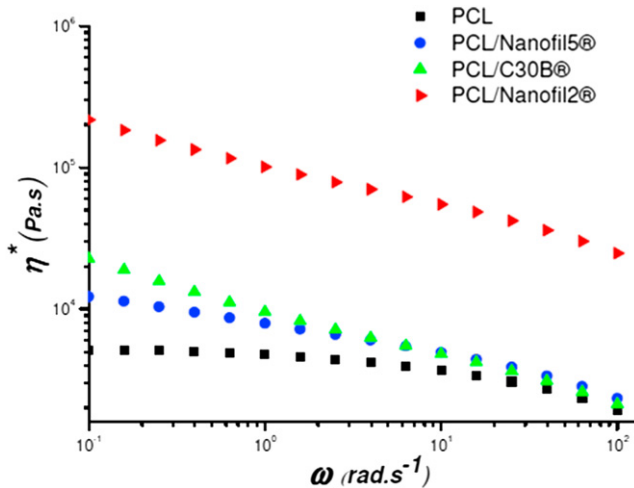


Fig. 6. Dynamic viscosity of PCL filled with 3 wt% of clay.

where η^* is the dynamic viscosity, k is the sample specific exponential factor, ω is the oscillation frequency in the frequency sweep test and n is the shear thinning exponent.

From equation (2), n and k could be determined from the logarithmic plot of dynamic viscosity vs. frequency (ω) equation (3):

$$\text{Log}(\eta^*) = \text{log } k + n \text{ log}(\omega) \quad (3)$$

An increase of the dynamic viscosity at low frequencies gives us information about strong interfacial interactions between the polymer phase and the filler but no information is given about the dispersion state. However, the power law exponent, n , is expected to assess the extent of clay dispersion.

Shear thinning exponents, n , for different nanocomposites, are listed in Table 1. The more exfoliated samples would display a higher shear thinning exponent. Conversely, a limited exfoliation would lead only to a moderate shear thinning exponent.

It can be seen that n values of C30B® and Nanofil2® are higher than that of Nanofil5®. It could be considered that Nanofil5® is less dispersed than C30B® and Nanofil2® in the PCL matrix.

Table 1
Power law exponents.

Samples	-n	R ²
PCL	0.025	0.886
PCL/Nanofil5®	0.412	0.993
PCL/C30B®	0.767	0.998
PCL/Nanofil2®	0.848	0.999

Table 2
Crystallinity rate of PCL/Nanofil2® nanocomposites.

Samples	Filler content (wt%)	ΔH_m (J/g)	X_c (%)
Neat PCL	0	71	52.1
PCL ₁	1	69.2	51.4
PCL ₃	3	68.1	51.6
PCL ₅	5	67	51.8

Since the viscosity of PCL/Nanofil2® appears significantly higher at low frequencies than that of PCL/C30B®, it seems indicate that a better dispersion has been achieved using a kind of organo-modified MMT without any polar modifier, despite the polar character of PCL. This proved the efficiency of the screw configuration.

3.4. Crystallinity and thermal stability

DSC measurements (Table 2) indicate that the melting enthalpy, ΔH_m , seems not affected by the clay addition. The crystallinity rate decreases slightly from 52% for virgin PCL to 51.4% for PCL filled with 1 wt% of Nanofil2®. Clay has consequently no significant nucleating effect.

The study of thermal degradation of organo-modified clays has shown that Nanofil2® and Nanofil5® present two similar weight losses respectively, at 200 °C and 360 °C for the first one (which is the less stable of the three clays) and at 230 °C and 340 °C for the second one (Figs. 7 and 8). Mass loss features indicated by TGA are confirmed by the number of peaks on Gram Schmidt patterns given by coupled FTIR analysis (not presented here).

Thanks to FTIR-TGA analysis, the first mass loss was identified and referred to CH₂ elimination (2853 and 2928 cm⁻¹), while the second degradation step was attributed to CH and CH₃ elimination.

The second peak for Nanofil2® (at 280 °C) was attributed to the benzyl group elimination (at 1497 and 1475 cm⁻¹).

Fig. 8 shows that the Cloisite 30B® also exhibits two degradation steps. The first one, which correspond to the maximum degradation temperature, at 250 °C, is similar to the first elimination for Nanofil2® and Nanofil5® (i.e. CH₂ elimination). The second mass loss, at 380 °C, is attributed to OH elimination (strong band at 3220 cm⁻¹). The absorption around 2300–2400 cm⁻¹ is ascribed to carbon dioxide (Fig. 9).

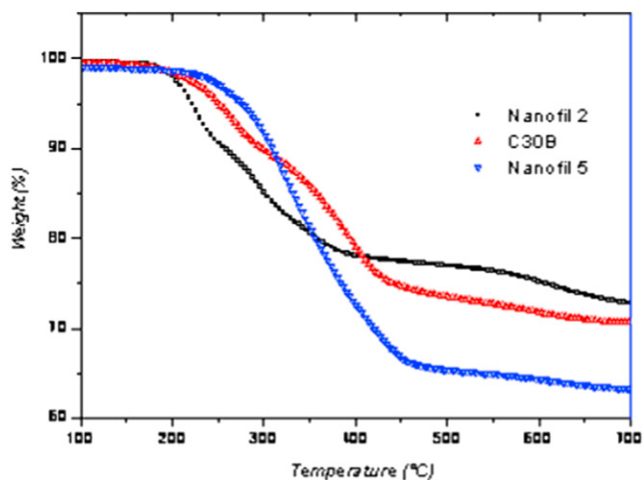


Fig. 7. TGA different nanofillers under nitrogen atmosphere at 10 °C/min temperature rate.

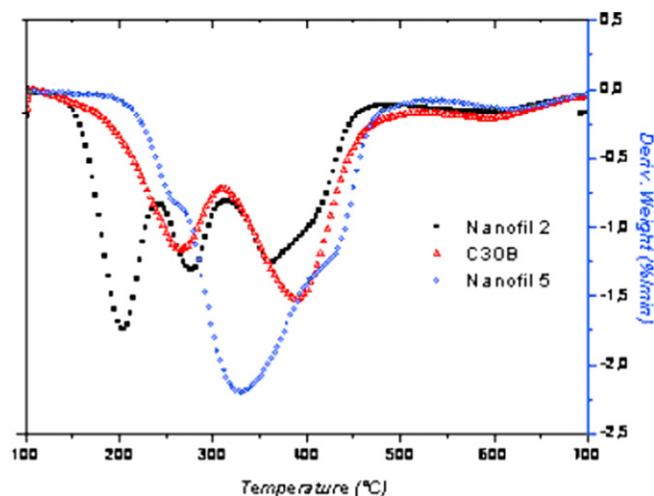


Fig. 8. DTG of different nanofillers under nitrogen atmosphere at 10 °C/min temperature rate.

These data allows us to propose degradation reactions for each alkyl ammonium modifier (Figs. 10, 11 and 12).

Investigations about thermal degradation of virgin PCL have shown that two degradation steps occurs [19]. The first step (near 380 °C) is characterized by the departure of the hex-5-enoic acid (random chain cleavage via cis-elimination) followed by unzipping (up 400 °C). From our TGA experiments under nitrogen, only one mass loss step for can be noticed for the PCL and the nanocomposites (Fig. 15). Moreover, for all materials, no significant residue can be observed at 500 °C. Despite the low percentage of clay introduced in PCL, strong differences can be noticed for the thermal degradation behaviour of nanocomposites in comparison with the virgin polymer. PCL/C30B® nanocomposite is less stable than PCL. As mentioned before, the decomposition of C30B® leave hydroxyl groups which could give water molecules (Fig. 12), able to hydrolyze the ϵ -caprolactone to produce hex-5-enoic acid, which can then accelerate PCL decomposition [19].

The nanocomposites containing the clays without polar modifier exhibit the highest thermal stability, but only up to 375 °C for Nanofil5®. It can be suggested that the very high interfacial area between montmorillonite and polymer for intercalated/exfoliated morphologies could produce a physical barrier effect, able to strongly decrease the diffusion of volatile products released by the

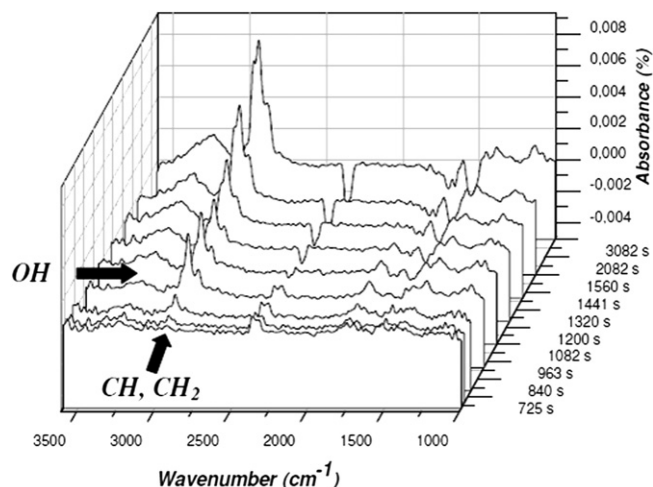


Fig. 9. Dynamic FTIR spectra of C30B® in function of time.

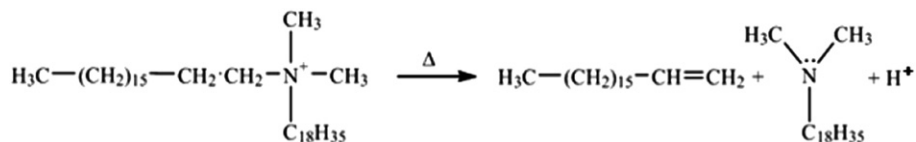


Fig. 10. Possible decomposition reaction of Nanofil5®.

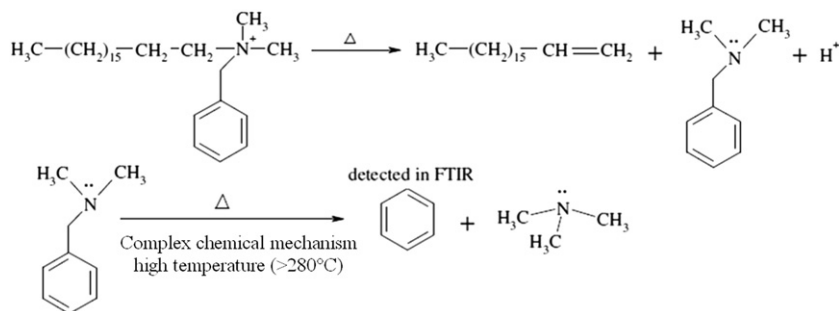


Fig. 11. Possible decomposition reaction of Nanofil2®.

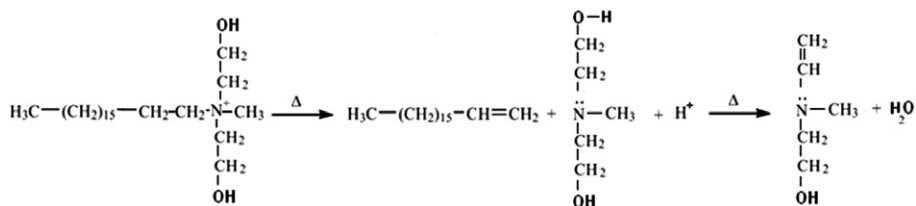


Fig. 12. Possible decomposition reaction of C30B®.

materials. At higher temperatures than 375 °C, differences can be noticed between PCL/Nanofil2 and PCL/Nanofil5. Paradoxically, the degradation of the first one occurs at higher temperatures, whereas the corresponding organo-modified clay is less stable.

This could be explained by the catalytic activity of clays after their thermal degradation involving the mechanisms proposed above (Figs. 10–12). The formation of acidic clays is able to generate a strong catalytic activity, which can be higher for Nanofil2®, due to its lower degradation temperature, its better initial dispersion in

the matrix, and also due to the higher clay content in the remaining material.

FTIR spectra of PCL nanocomposites display four broad absorptions (Figs. 13 and 14). The first strong band at 1771 cm⁻¹ is due to the carbonyl function of the carboxylic acid in the gas phase, produced by pyrolysis of the PCL ester functions. Moreover, the additional intense absorption centered on 1736 cm⁻¹ is ascribed to the ε-caprolactone. The peak at 1200 cm⁻¹ is attributed to C–O stretch vibration of acid group. Finally, the adsorption band from 2850 to 3020 cm⁻¹ is assigned to CH and CH₂.

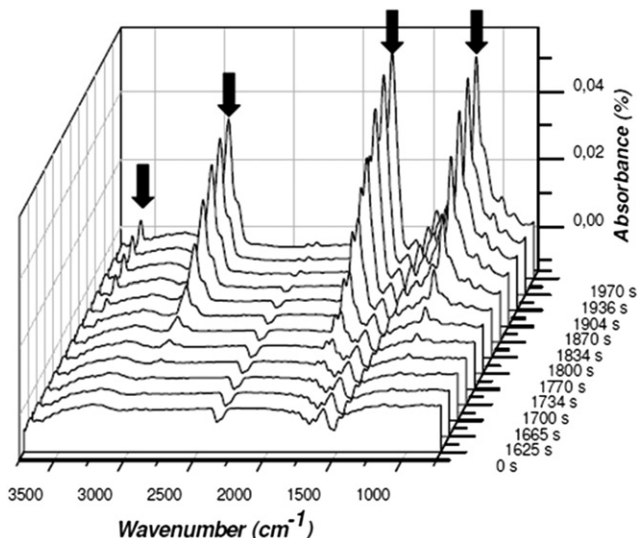


Fig. 13. Dynamic FTIR spectra of PCL/C30B® nanocomposites in function of time.

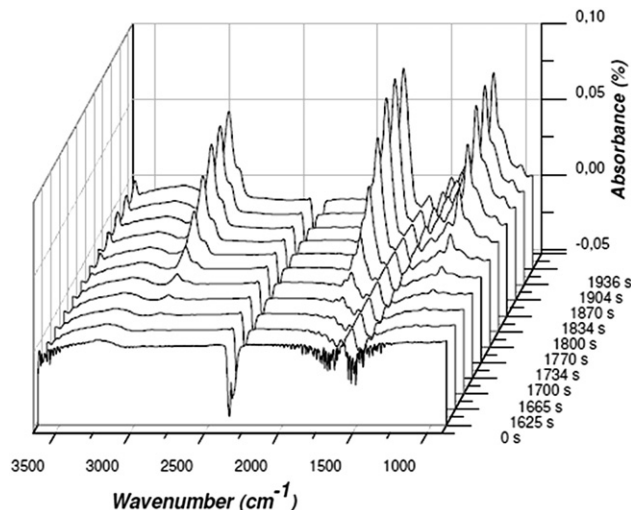


Fig. 14. Dynamic FTIR spectra of PCL/Nanofil2® nanocomposites in function of time.

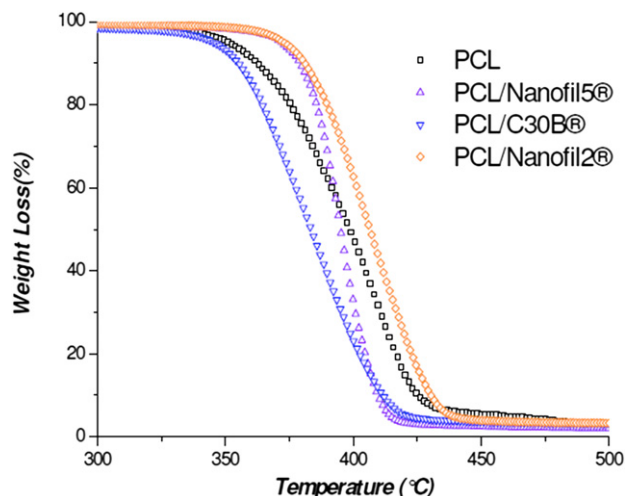


Fig. 15. TGA of PCL filled with 3 wt% of clay under nitrogen atmosphere at 10 °C/min temperature rate.

Decarboxylation of hex-5-enoic acid or other carboxylic acid can lead to carbon dioxide (band around 2300–2400 cm^{-1}). Water band is also detected at 3620 cm^{-1} and may result from the condensation of hydroxyl groups for PCL/C30B.

Whatever the nature of composite, all the peaks appear at the same time in Figs. 13 and 14 (except that of water). Nevertheless, their magnitudes are lower for PCL/Nanofil2 in comparison with PCL/C30B.

3.5. Mechanical properties

Mechanical properties of nanocomposites depend on many factors, including, the amount of the filler, clay dispersion and adhesion between filler and matrix.

Fig. 16 shows Young's modulus for the different nanocomposites. It increases with clay incorporation in comparison to the virgin PCL and strongly depends on the clay amount and its nature. The highest value for a percentage of 1 wt% is obtained for Nanofil2® and this can also be ascribed to a better dispersion. At this very low percentage of organo-modified clays in the matrix, one can notice that the highest modulus values correspond to the clays containing only modifiers with non-polar chains.

Regardless the nature of modified clay, the tensile modulus is increased twice at a percentage of only 5 wt%, in comparison to the virgin matrix.

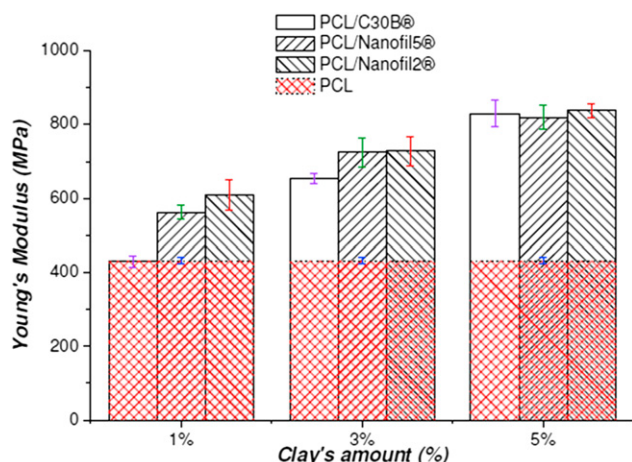


Fig. 16. Young's modulus of different nanocomposites.

4. Conclusions

Three commercial montmorillonites, Nanofil5®, Nanofil2® and Cloisite 30B® were used to prepare organo-modified montmorillonite/poly(ϵ -caprolactone) composites by melt intercalation. A twin-screw extruder with a specific screw profile was designed in order to promote the formation of nanocomposites. Clay dispersion was investigated by XRD, TEM and rheological behaviour of samples. All techniques showed exfoliated/intercalated morphologies and rheological tests and highlighted a better dispersion degree for Nanofil2®.

Owing to the selection of the screw profile, nanocomposite morphology was achieved in this study, regardless of the polar (Cloisite 30B®) or non-polar nature of the alkyl chains of the clay modifier.

The incorporation of organo-modified clays allowed the thermal stability to be improved in comparison with the virgin PCL. However, due to PCL hydrolysis caused by the presence of hydroxyl groups in the modifier, a lower thermal stability was noticed for Cloisite 30B® composition in comparison with that of Nanofil2®, which modifier contains only non-polar groups, and which seems to create a better barrier effect and promotes catalytic activity due to its acidic surface after its own thermal degradation.

Young's modulus was also significantly increased by the incorporation of the organo-modified clays. The marked increase of Young's modulus is ascribed to the high degree of dispersion and the relatively low value of residence time using twin-screw extrusion, in comparison with the processing techniques used in previous studies, which could entail PCL thermal degradation during the processing stage.

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