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Synthesis of Biodegradable Polycaprolactone/Montmorillonite Nanocomposites by Direct In-situ Polymerization Catalysed by Exchanged Clay

A. Harrane, M. Belbachir*

Summary: Poly (e-caprolactone) (PCL) layered silicate nanocomposites have the advantage adding biocompatibility and biodegradability to the traditional properties of nanocomposites. They can be prepared by in situ ring-opening polymerization of e-caprolactone using conventional initiator to induce polymerization in the presence of an organophilic clay, such as organomodified montmorillonite. In this work, we have used an alternative method to prepare poly(e-caproilactone)/montmorillonite nanocomposites. The cationic polymerization of e -caprolactone was initiated directly by Maghnite-TOA, organomodified montmorillonite clay, to produce nanocomposites. Resulted nanocomposites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), force atomic microscopy (AFM) and thermogravimetry. The evolution of mechanical properties was also studied.

Keywords: biodegradable; montmorillonite; nanocomposites; polycaprolactone

Introduction

During the last decade, polymer/montmorillonite nanocomposites have received increasing attention from scientists and industrial researchers because they generally exhibit greatly improved mechanical, thermal, barrier, and flame-retardant properties at low clay content in comparison with unfilled polymers or more conventional microcomposites.[1–10]

Poly(e-caprolactone) (PCL) layered silicate nanocomposites have the advantage adding biocompatibility and biodegradability to the traditional properties of nanocomposites.[11,12] They can be prepared by in situ ring-opening polymerization of e-caprolactone using conventional initiator to induce polymerization in the presence of an organophilic clay, such as organometallic initiators.[13,14] In this work, we have used an alternative method to prepare poly(e-caprolactone)/montmorillonite nanocomposites. The cationic polymerization of e-caprolactone was initiated directly by Maghnite-TOA, organomodified montmorillonite clay, to produce nanocomposites.

Nanocomposites Synthesis

Because of its ability to disperse in the Matrix of polymer, the use of organomodified clay is meaningful in the process of forming polymer – clay nanocomposites. For this purpose, sodium montmorillonite Maghnite-Na has been co-intercalated by mixtures of tetraoctylammonium cations and protons to produce the organoclay Maghnite-TOA. The presence of protons on maghnite-TOA surface may induce ring-opening polymerization of e-caprolactone (Scheme 1). ^{1}H NMR analyses were used to determine the polymer structure (Figure 1).

Morphology

XRD analyses (Figure 2) show that, for low clay content (1 and 3 wt%), XRD gives evidence for an exfoliated structure (absence of diffraction peak in the small angle region). For high clay content (5 and

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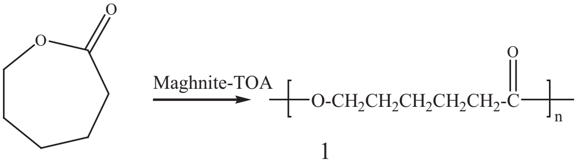

Scheme 1.

10 wt%), a broad peak in the small angle region indicates the formation of a partially exfoliated/partially intercalated structure. The exfoliated structure of nanocomposites PCL/Maghnite-TOA of low clay content is fully confirmed by TEM analyses. Figure 3 shows that, With 3 wt% Maghnite-TOA , individual clay platelets are randomly distributed in the poly(e-caprolactone) matrix and confirm the exfoliated structure of the resulted nanocomposite.

Atomic force microscopy (AFM) observations of the resulting nanocomposites (Figure 4) have clearly highlighted the effectiveness of the polymer grafting onto the clay surface. The polymer grafting may be occurred by the combination of polymer growing chain with a negative charge on the clay surface.

Isothermal crystallization of the resulted nanocomposites and neat polycaprolactone (PCL) were carried out under a nitrogen atmosphere with a Perkin–Elmer DSC-7 apparatus.

The neat PCL and the polycaprolactone/ Magfhnite-TOA nanocomposites (5.3 ± 0.3 mg), encapsulated in aluminium pans, were heated to 100 °C at a rate of 20 °C/min, held 5 min at this temperature to destroy all crystallites, and cooled to an appropriate

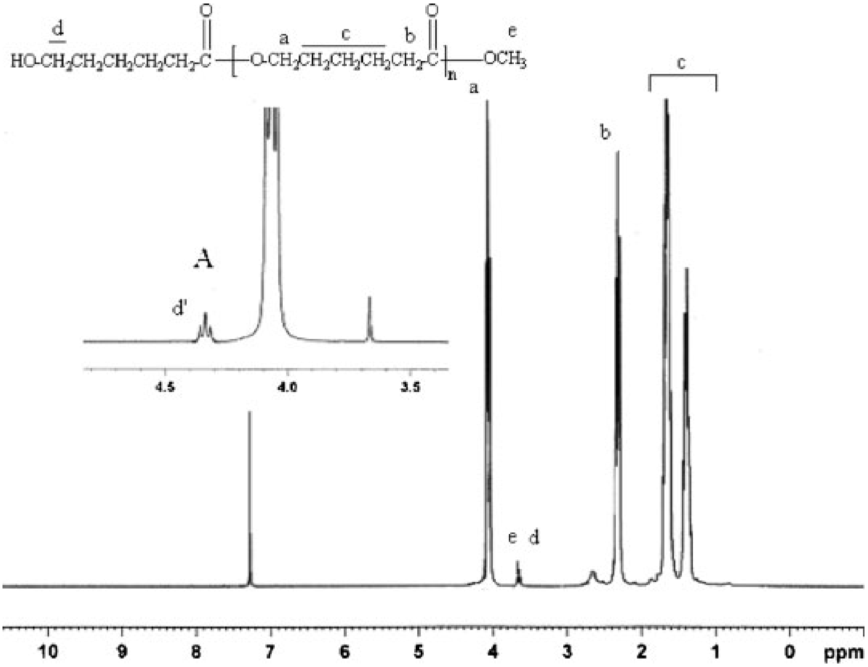

Figure 1.
^{1}H NMR spectra of poly (e-caprolactone) before and after reacting the polymer with an excess of trifluoroacetic anhydride (A).

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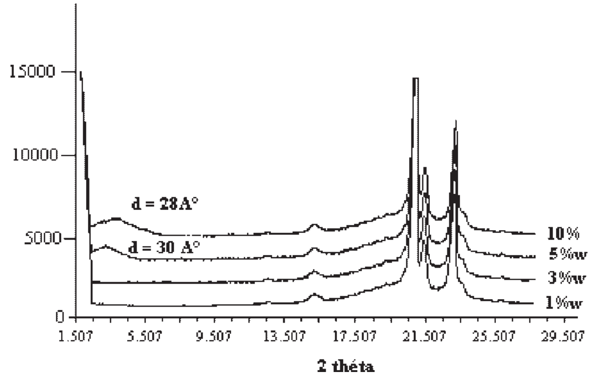

Figure 2.
XRD patterns of PCL/Maghnite-TOA nanocomposites of different w% Maghnite-TOA.

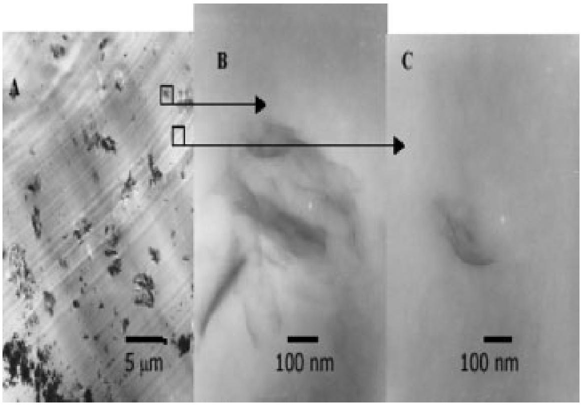

Figure 3.
TEM images for PCL/Maghnite-TOA (3w%) nanocomposite at low (left) and high (right) magnification.

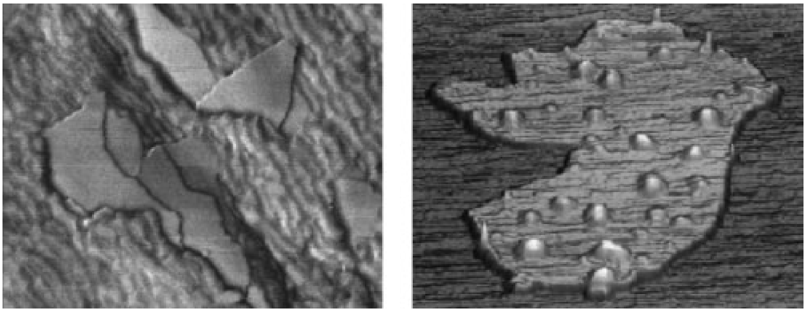

Figure 4.
On the left: phase picture TMAFM (500 × 500 nm^2), showing the dispersion of individual clay platelets in poly(ε-caprolactone)/Maghnite-TOA (3%$_w$) nanocomposite. On the right: topography picture TMAFM (500 × 500 nm^2) showing grafted PCL chains onto montmorillonite clay surface.

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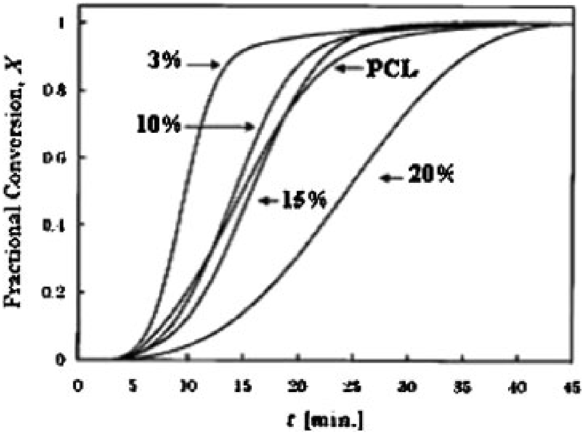

Figure 5.

Isothermal crystallization for Polycaprolactone/maghnite-TOA nanocomposites and pure polycaprolactone PCL crystallized at 40 °C.

crystallization temperature ($Tc = 40\,^{\circ}C$), at 200 °C/min cooling rate.

From isothermal crystallization experiments, the fractional crystallinity conversion (X) was calculated as the ratio of the area under the exotherm at time $t$to the total area. Figure 5 shows the relationship between X and t. As can be seen, the X value of nanocomposite with 3 w% of Maghnite-TOA is larger than that of pure polycaprolactone (PCL) at a given t. However, when Maghnite-TOA ratio is larger than 3%, X at a given t is noted to decrease with increasing Maghnite-TOA amount. Thus it can be said that a small amount of clay in the polymeric matrix accelerates the crystallization of PCL, while large clay content delays it. The overall isothermal crystallization rate is thought to be governed by two terms, namely, diffusion and nucleation.[15] The diffusion term is related to the activation free energy for transporting a polymer segment to a growing crystal face, and the nucleation term is related to the thermodynamic driving force for nucleation of new layers on the crystal. Considering these two terms, a small amount of clay seemed to serve as a nucleating agent whereas a large amount of it seemed to hinder the transportation of polymer segments. Accordingly, we found that the clay has two opposing effects on the

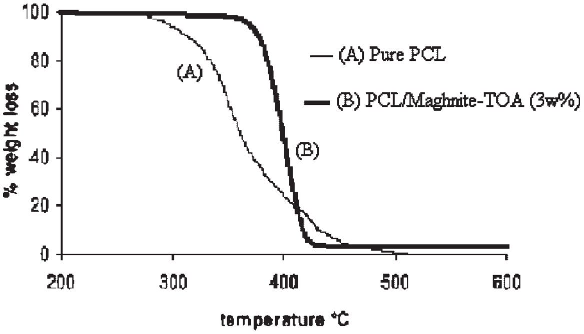

Figure 6.

Temperature dependence of weight loss (TGA) for pure poly(e-caprolactone) (A) and Poly(e-caprolactone)/ Maghnite-TOA (3 w%) nanocomposite (B).

Table 1.
Mechanical properties of PCL/clay nanocomposites.

%w de Maghnite-TOA	Ultimate tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
0	48.1	750	222
1	36.8	612	269
3	35.1	578	282
5	32.5	570	331
7	18.3	204	365
10	15.3	25	403

crystallization of PCL and, further, that these effects are dependent on the clay content.

Thermal Properties

The thermal stability of the PCL-based nanocomposites prepared by in situ polymerisation process has been studied by TGA with a heating rate of 20 °C/min under airflow. Figure 6 shows the thermograms for the nanocomposite that contain 3 wt% of Maghnite-TOA and that of pure poly (e-caprolactone). The nanocomposite has a degradation temperature higher than neat PCL. It has been recently reported that the thermal degradation of PCL fits a two-step mechanism.[16] There is first a statistical rupture of the polyester chains by pyrolysis of ester groups with release of CO_2, H_2O and hexenoic acid. In the second step, e-caprolactone is formed as result of an unzipping depolymerization process. Whereas the temperature dependent weight loss curve recorded for neat PCL displays two consecutive steps, the nanocomposite of 3 w% Maghnite-TOA is characterized by a single weight loss with the beginning of the degradation shifted to much higher temperature. The temperature at which 50 wt% is lost, is shifted by 50 °C towards higher temperature. This effect is explained by the fine dispersion of the clay layers, which decreases the polymer permeability to both oxygen and the volatile decomposition products.

Mechanical Properties

The evolution of mechanical properties of PCL/Maghnite-TOA nanocomposites, as a function of the clay content, is reported in Table 1. The nanocomposites display good rigidity, it can be noted that increasing in the Maghnite-TOA weight ratio in the nanocomposites increases Young 's modulus and decreases both elongation at break and ultimate tensile strength.

Conclusion

Poly(e-caprolactone)/Montmorillonite nanocomposites have been prepared by in situ ring opening polymerisation of e-caprolactone catalysed by a montmorillonite clay. For this purpose, Maghnite-Na has been modified by exchange of the constitutive Na cations by tetraoctylammonium cations and protons. Results from ^{1}H NMR indicate that the polymerization occurs by monomer insertion into the growing chains by the acyl-oxygen bond scission. X-ray diffraction and transmission electron microscopy show the complete exfoliation of the silicate sheets in the polyester layered silicate nanocomposites containing low w% of Maghnite-TOA (1 and 3%). Effectiveness of the polymer grafting onto the clay surface was demonstrated by AFM measurements. The thermal stability of the resulted nanocomposites is much higher than pure poly(e-caprolactone). The resulted nanocomposites display good mechanical properties.

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Correction

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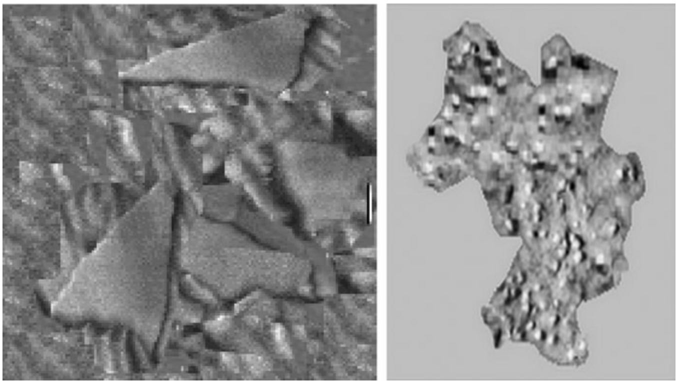
The authors would like to announce that they have used AFM figures of Prof. R. Lazzaroni (published in *Langmuir* **2003**, *19*, 9425 and in *JACS* **2004**, *126*, 9007) as an internal reference, but by mistake Figure 4 in their paper was not updated with their own experimental data before publication.

The authors apologize to all parties involved for this error that unfortunately was detected only now. The corrected version of Figure 4 in enclosed below.



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