PCL nanocomoposites prepared byconventional "in situ" polymerization.

L. López*[,1], N. Navascués[1], S. Irusta[1], J. Santamaría[1]

[1] *Institute of Nanoscience of Aragon, University of Zaragoza, C/Mariano Esquillor s/n 50018 Zaragoza, Spain.*
lauralopezfigueras@gmail.com

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Abstract

PCL/MCM-41, Closite 15A and Cloisite 30B nanocomposites (1wt%) were prepared by "in-situ" polymerization. Monomer conversion and molecular weight development with reaction time were studied using $SnCl_2.2H_2O$ as catalyst. The composites obtained were characterized by TEM, TGA, NMR, and *GPC*. The "in situ" polymerization method produces composites with good dispersion of the fillers in the polymeric matrix as showed by TEM micrographs. TGA results showed that the degradation temperature of the composites was up to 65ºC higher than the polymeric matrix decomposition temperature. PCL nanocomposites prepared by "in situ" polymerization" present good thermal properties due to the high degree of dispersion of the fillers achieved.

1 Introduction

One of the problems of plastics that do not degrade spontaneously is the tremendous amounts and varieties that are consumed and discarded into the environment promoting the appearance of large amounts of carbon dioxide and toxic gases that contributes to global warming. The use of "green polymers" would not involve the use of toxic or noxious components in their manufacture and could allow degradation via a natural composting process. Poly(ε-caprolactone) (PCL) is a synthetic semicrystalline aliphatic polyester that is one of the most promising biodegradable polymers currently available on the market [1]. The use of this material for biomedical or packaging applications is due to the good biodegradable and mechanical properties. Besides, the relatively low melting point allows the processing of PCL by conventional plastic machinery. For improving further the mechanical properties, PCL is usually modified by blending with other resins or filling with inorganic particles. Recently, a number of inorganic particle-filled PCL composites have been prepared and characterized. PCL/Closite 30B films were found to have higher thermal properties compared to the neat polymer matrix [2]. The addition of carbon nanotubes and Ag nanoparticles increase the Young modulus of PCL besides providing improved electrical conductivity to the prepared films [3]. Carbon nanotubes and carbon nanofiber increase barrier properties, water and oxygen transmission and conductivity and mechanical properties of PCL [4]. A lot of research has been focused on the melt intercalation method to obtain PCL nanocomposites since it the preferred method in industry due to the flexibility of the process and cost reasons. However, a good dispersion is only achieved by this way in a few cases, such as in polyamide6/clay systems [5]. *In situ* polymerization is other technique to prepare composites where the filler is dispersed in the monomer and, after addition of the catalysts, the polymerization take place around the filler particles leading to a good dispersion. MCM-41 has been extensively used as an effective reinforcement filler to enhance the mechanical, thermal properties of polymer materials, due to its unusual characters, such as exceptional long-range ordering, highly tunable textural and large surface area properties, controlled pore size and shape [6]. The tensile modulus, tensile strength and elongation at break of composites were improved by the co-incorporation of MCM-41/OMMT to polypropylene. The filler also acts as nucleation agent leading to superior toughness [7]. MCM-41 with polystyrene or polymethyl methacrylate inside the pores improves the strength and toughness of commercial PP [8]. In the present study the use of a novel

catalyst and the addition of nanoclays and MCM-41 have produced nanocomposites which improved their properties in comparison with the polymer without filler content.

2. Experimental

2.1 Materials

The monomer, ε-caprolactone 99% and the novel catalyst, Tin(II) chloride have been supplied by Sigma Aldrich.

The clays used as fillers; Cloisite 15A of cationic exchange capacity 125 mequiv/100 g clay has 2M2HT as modifier (dimethyl dehydrogenated tallow). Distance between layers: 31.5 Å and Cloisite 30B of cationic exchange capacity 90 mequiv/100 g clay has MT2EtOH as modifier (bis-2-hydroxiethyl methyl tallow) and the distance between layers: 18.5 Å have been supplied by Southern Clay products.

2.2. Preparation of the MCM-41 filler

In a typical synthesis 0.5 g of CTABr were added to 500 mL of deionized water, 3.5 mL of NaOH 2M solution were mixed with the surfactant solution. The mixture was stirred for 30 minutes and then 2.5 mL of TEOS were added to form the oxo silicate structure. The resulting gel was stirred at 353 K for 3 hours and the precipitate filtered and washed with deionized water. The final step to obtain the mesoporous material was the calcinated at 823K for 5 hours to remove the surfactant.

2.3. Preparation of the polycaprolactone nanocomposites

The bulk polymerizations were carried out in 500 cm^3 round-bottomed flasks equipped with a stirrer. The formation of the PCL-nanofiller systems was accomplished through the in situ polymerization technique. The mixture of monomer and catalyst was previouly sonicated for 5 min and then 1 wt % of filler was added to this mixture, sonicated again for 10 min and introduced to the reactor. The polymerization mixture was purged with dry argon.

Thereupon, the reaction was carried out at 170ºC for 8 h. Polymerization was stopped by fast cooling to room temperature and washed with ethanol to remove unreacted monomer. The fillers used are: MCM-41, Cloisite 15A and Closite 30B.

2.4. Measurements

2.4.1. WAXD

Low angle XRD patterns were obtained using a diffractometer Philips X'Pert Plus with CuKα radiation (λ = 1.5406 Å, 40 kV) in the range of 0.6º to 10.0º (2θ) with a step of 0.02º (2θ) and time Analysis of 5 s. All measurements were performed on DC power. (Facultad de farmacia,Universidad Complutense de Madrid).

2.4.2. Thermogravimetric analysis, TGA

Thermogravimetric analysis of samples was performed in a controlled atmosphere to observe the change in mass. The samples were placed in a ceramic crucible and at 5°C/min. Under a nitrogen flow of 30 mL/min. The analysis were carried out in the thermogravimetric analyzer METTLER TOLEDO SDTA851, Departamento de Ingeniería Química y tecnologías del medioambiente (Universidad de Zaragoza).

2.4.3. SEM

The beam is focused onto the surface of the sample, performing a sweep of it. By analyzing the signal produced by secondary electrons yields the three-dimensional appearance of the sample, whereas the signal of the scattered electrons can reveal differences in the chemical composition of the sample. The samples were prepared onto a metal surface, polished and coated by sputtering with gold (metallic). The images of the topography were taken in a FEI InspectF equipment (INA).

2.4.4. TEM

For TEM images of powder, a suspension of the solid in ethanol was sonicated in order to get a better dispersion. A drop of this dispersion was deposited on a grid and then it was air dried. Images of nanocomposites were prepared embedding polymer in an epoxy resin and cutting them with a diamond

blade in an ultra-microtome. TEM consists of irradiating a thin sample with an electron beam of uniform current density, whose energy is within the range of 100 to 200 kV. Part of those electrons is transmitted, scattered elsewhere and some results in interactions. These signals provide information on the nature of the sample morphology, composition, crystal structure, electronic structure.

2.4.5.-NMR

The NMR spectra of ^{1}H have been studied in a spectrophotometer Broker ARX 400 to 400 MHz for 1H. Chemical shift values were expressed in δ (ppm) using tetramethylsilane as the external reference (^{1}H), 85%. The deuterated solvent used was $CDCl_3$. The coupling constants are expressed in hertz (Hz). ICMA (Universidad de Zaragoza).

2.4.6-GPC

Molecular weight and polydispersity index were measured by size exclusion chromatography (SEC) using a Waters 2695 liquid chromatography system equipped with a Waters 2420 evaporation light scattering detector using a combination of two Ultrastyragel columns with pore size of 500 and 104 Å, calibrated using (poly(methyl methacrylate) standard and THF as solvent. Departamento de Química Orgánica y Química Física (Universidad de Zaragoza).

3. Results and discussion

3.1. Synthesis of polycaprolactones

The ring-opening polymerization of ε-CL has been studied in the literature by using a variety of catalyst such as lanthanides [9] and the common Stannous 2-ethylhexanoate $Sn(Oct)_2$ [10]. In this work, another catalyst has been successfully applied to the polymerization reaction, Tin(II) chloride. This material presents a high solubility into the monomer that provides a very homogenous reactive solution.

The polymerization reaction has been studied to fix the optimal conditions to obtain a polymer with the lower content of monomer (~ 0.5 wt%), and the higher molecular weight. As can be seen in Table 1, the content of remaining monomer decrease with time and after 2 hours is lower than 0.5. Figure 1 shows that the molecular weight continuously increases with reaction time. The conditions adopted for the composites preparations were: 170ºC reaction time during 8 hours.

TIME (MIN)	P/P+M	M/P+M
5	4.7	95.3
15	18	82
30	50	50
60	91.3	8.7
120	99.5	0.5
240	99.5	0.5
360	99.5	05
480	99.5	0.5

Table 1. Percentage of monomer and polymer content on the final material
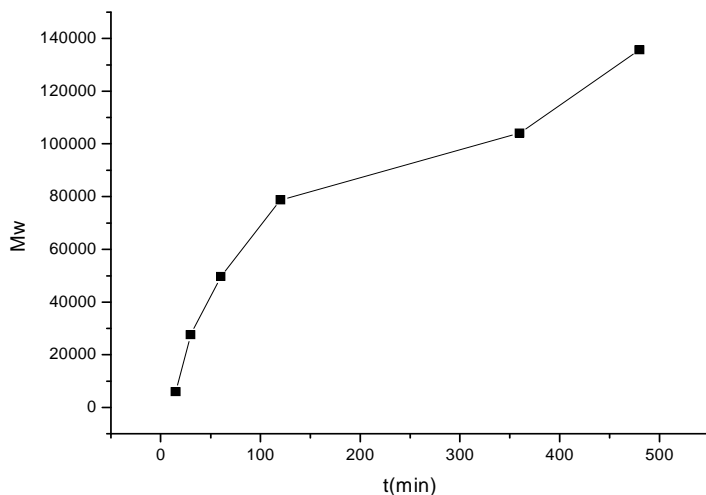
Figure 1. Molecular Weight evolution as a function of time reaction

3.2. Synthesis of nanocomposites

The decomposition process of the prepared composites was study by TGA, as is shown in Figure 2 the degradation temperature of the nanocomposites (table 2.) prepared is dramatically increased compare to the polymeric matrix. The highest degradation temperature was obtained for the MCM-41 composite.
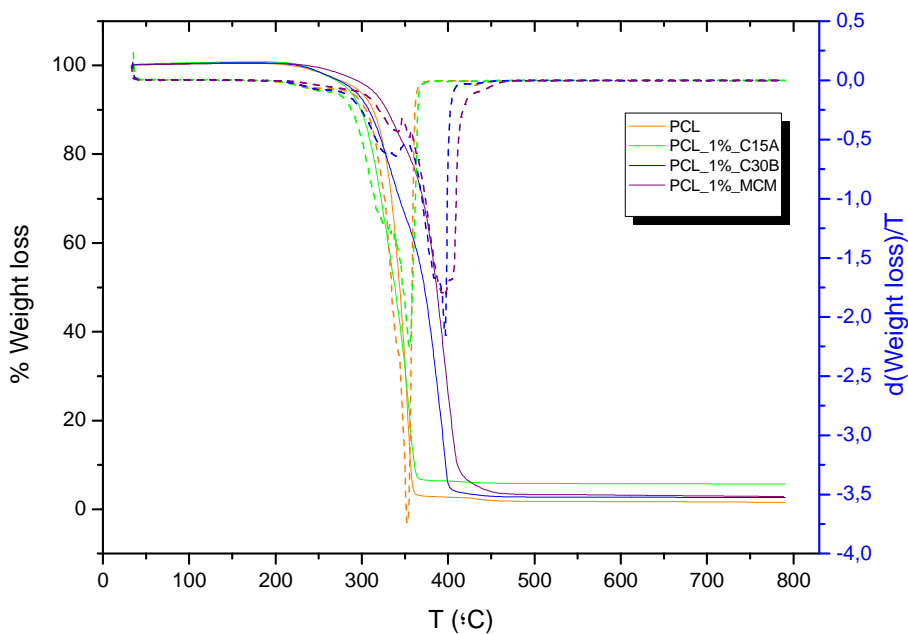

Figure 2. TGA and dTGA of neat PCL and nanocomposites

MATERIAL	$T_{degradation 50\%}$(°C)	$T_{degradation}$(°C)
PCL	344	353
PCL_1%_C15A	338	356
PCL_1%_C30B	389	372
PCL_1%_MCM	400	386

Table 2. Degradation temperature at 50% and 100%.

In Figure 3, the molecular weight of the prepared composites is compared with PCL. It can be seen that the presence of fillers promotes the appearance of shorter polymer chains decreasing the MW in comparison with the polymer without filler. The presence of inorganic material hinder the grow of the polymeric chains.
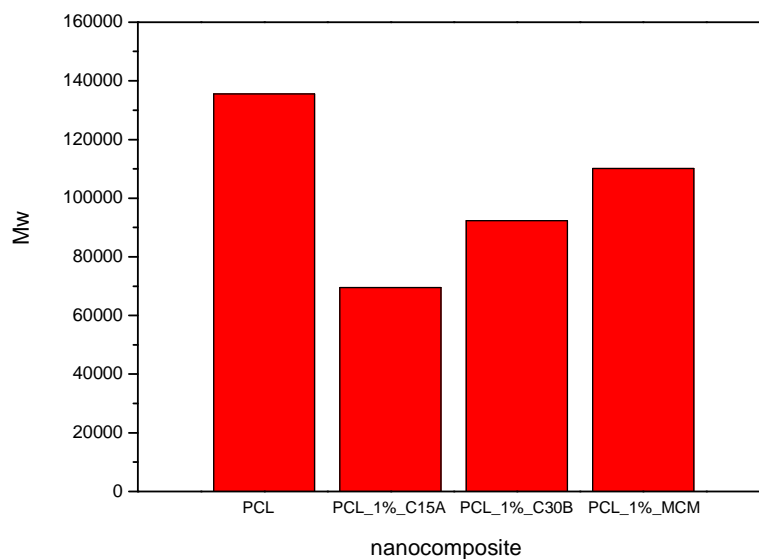

Figure 3. Molecular weight of PCL and nanocomposites

In order to study the degree of exfoliation of the nanoclays in the composites, low angle XRD were performed. From the diffractograms the distances between layer were calculated using the Bragg equation, results are shown in table 3. The exfoliation of the clays increased the distance between the (100) plane of the layers. It can be seen that the nanocomposite with Cloisite 30B presents a higher exfoliation degree and this can explain the higher degradation temperature and higher molecular weight of this nanocomposite compare with Cloisite 15A composite.

MATERIAL	2Θ (100)	DISTANCE (Å)
CLOISITE 15A	2.8	31.5
PCL_1%_C15A	2.42	36.77
CLOISITE 30B	4.6	19.2
PCL_1%_C30B	1.79	49.29

Table 3. Distance between layers of Cloisite 15A and 30B

TEM images of composites showed the distribution of filler in the polymeric matrix (Figure 4). The comparison of composites images showed better filler dispersion for MCM-41 nanocomposites. These results suggest that the improvement of the thermal resistance would be related to the filler dispersion.
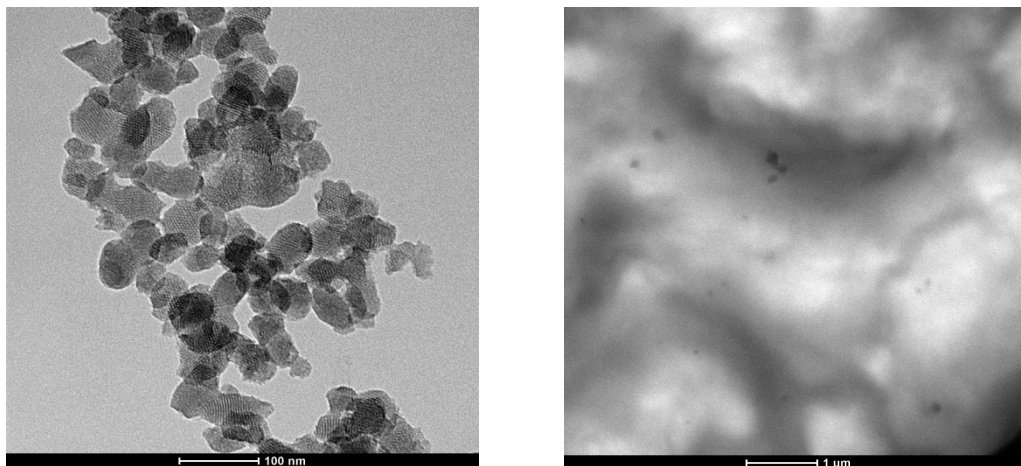
Figure 4. Images of MCM-41 and nanocomposite including it as a filler**.**

4. Conclussions

In this work the synthesis of PCL has been made by using a novel catalyst: Tin(II) chloride. The polymerization process has been studied to approach the best conditions to form nanocomposite materials. The nanocomposites obtained present higher degradation temperatures that the started material due to the good filler dispersion achieved.

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