MORPHOLOGY AND MECHANICAL BEHAVIOR OF POLY(ε-CAPROLACTONE)/NANOCLAY AND POLY(ε –CAPROLACTONE)/CARBON NANOFIBER COMPOSITES

*A. López-Arraiza, N. López-Rodríguez, E. Meaurio, J. R. Sarasua**
University of Basque Country (EHU-UPV), School of Engineering, Alameda Urquijo, s/n
48013 Bilbao, Spain.
* iipsaoij@bi.ehu.es

The demand for biodegradable polymers is growing at rapid rate for both biomedical and ecological applications. Poly (ε-caprolactone) (PCL) is a semicrystalline biopolymer showing at room temperature low tensile modulus (300 MPa) and high strain at break (>500 %). As revealed by the degree of stiffness, strength, heat resistance, and improved barrier properties attained in already reported polymer nanocomposites[1-5], nanoclays such as montmorillonite (MMT) and carbon-nanofibers (CNF) a priori seem good candidates to strengthen PCL.

In this work, two types of commercial nanoclay were used: a natural sodium-rich montmorillonite (MMT-Na), and a natural montmorillonite modified with a quaternary ammonium salt (MMT-10A). Carbon-nanofibers were also used as reinforcement. The composites were prepared in a Brabender PL2000 by addition of 1.5, 3.0 and 4.5 wt % reinforcement into the melted PCL, and conformed in sheets by compression molding.

Tensile tests were conducted according to ISO527 in a ZWICK Z010 universal testing machine at 23 ºC with a constant deformation rate of 50 mm/min. **Figure 1** shows the tensile stress-strain curves of PCL and its 1.5 wt.% nano-reinforced composites. A clear increase in the maximum stress and a slight reduction in break strain can be observed, particularly for the CNF-composite, with regard to the neat PCL. The values of Young's modulus, yield strength and break strain are summarized in **Table 1**.

The dynamic mechanical behavior was determined using a DMA/STDA861 METTLER TOLEDO in shear mode, at a heating rate of 3ºC/min and a frequency of 1 Hz. **Figure 2** shows the evolution of storage modulus of PCL and its 1.5 wt. % MMT and CNF-composites between -90ºC and 30ºC. The glass transition of PCL is inferred at about -60 ºC in which the modulus begins to rapidly decrease with temperature. The storage modulus values confirm that MMT-Na is, regarding the stiffness of the systems, the most efficient reinforcement, followed by CNF and finally MMT-10Na, in agreement with the quasi-static results of Table 1.

Differential scanning calorimetry (DSC) was conducted on a DSC 2920 from TA Instruments. The results show that the degree of crystallinity of the PCL in presence of carbon nanofibers and both MMTs is enhanced (**Figure 4**). However, the crystallinity degree hardly increases for MMT contents above 1.5 % while it goes on increasing for higher CNF contents. These results are attributed, in agreement with SEM observations (**Figure 3**), to a better dispersion of the CNFs and therefore to the interfacial contacts between PCL and CNFs, larger than those between PCL and MMTs where rough surfaces are observed.

Although we have not confirmed whether intercalated or exfoliated structures are obtained, the nanocomposites display interesting mechanical properties and expand the possibilities of PCL based systems to be used in biomedical or packaging applications.

References:

[1] S. Sinha-Ray, M. Bousmina. Progress in Materials Science **50** (2005) 962.
[2] S.A. Meguid, Y. Sun. Materials and Design **25** (2004) 289.
[3] S. Sinha-Ray, M. Okamoto. Prog. Polym. Sci. **28** (2003)1539.
[4] B. Lepittevin et al. Polymer **43** (2002) 4017.
[5] M. Alexandre, P. Dubois. Materials Science and Engineering **28** (2001) 1.

Figures:

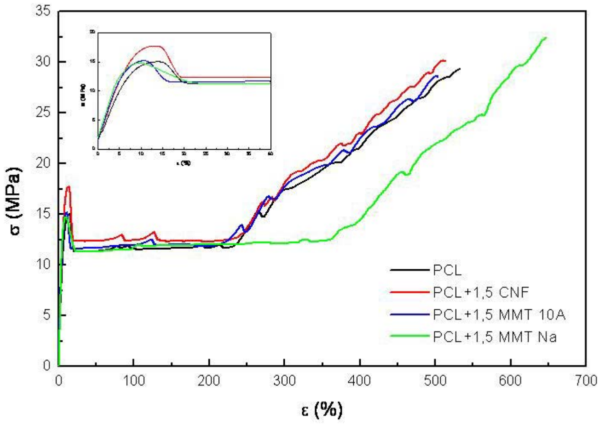

Figure 1: Stress-strain tensile curves of PCL nanocomposites

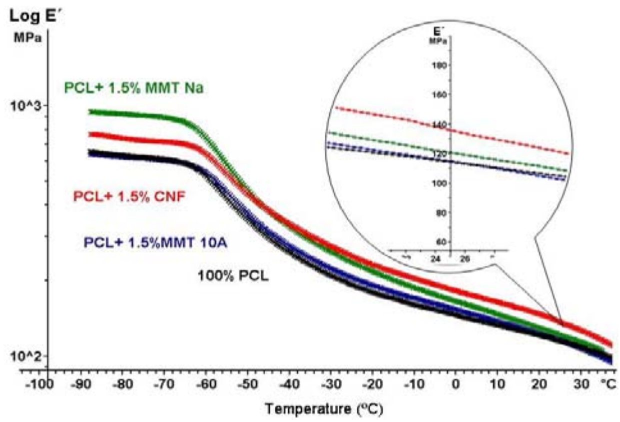

Figure 2: Dynamic storage modulus of PCL nanocomposites

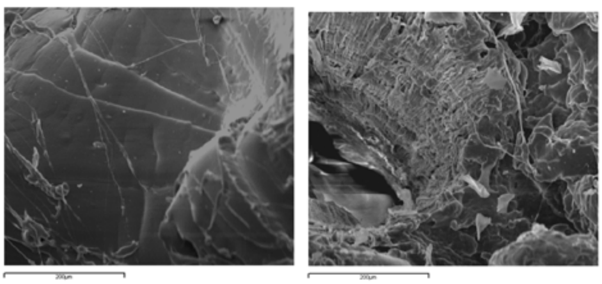

Figure 3: SEM images of PCL+1.5wt%CNF (left) and PCL+1.5wt%MMTNa (right)

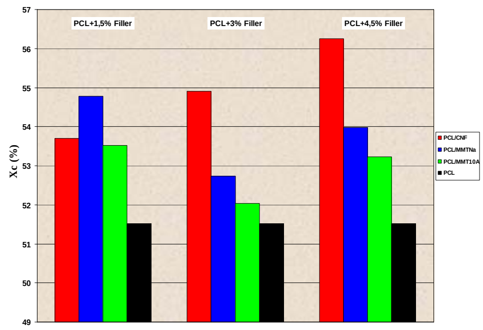

Figure 4: DSC cristallinity degree, X_c (%), of PCL and its nanoreinforced composites

Filler content	CNF			MMT Na			MMT 10A		
(wt%)	E (MPa)	σ (MPa)	ε (%)	E (MPa)	σ (MPa)	ε (%)	E (MPa)	σ (MPa)	ε (%)
0	268 ± 23	15.2 ± 0.7	608 ± 52	268 ± 23	15.2 ± 0.7	608 ± 52	268 ± 23	15.2 ± 0.7	608 ± 42
1.5	307 ± 18	17.1 ± 1.2	490 ± 32	453 ± 43	14.3 ± 0.7	707 ± 23	301 ± 27	14.6 ± 0.6	582 ± 30
3	303 ± 22	17.4 ± 0.3	513 ± 20	426 ± 32	13.8 ± 1.7	697 ± 13	308 ± 20	15.8 ± 0.2	543 ± 25
4.5	340 ± 27	17.2 ± 1.1	565 ± 44	466 ± 40	14.6 ± 1.0	716 ± 38	339 ± 12	15.5 ± 0.2	565 ± 35

Table 1. Tensile properties of PCL nanocomposites