

NANOCOMPOSITES BASED ON POLY (P-DIOXANONE) AND ORGANICALLY MODIFIED CLAYS

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Poly(p-dioxanone)¹ (PDS) is an aliphatic poly (ether ester) with numerous medical applications as it can be metabolized or bioabsorbed by the human body. Moreover, the PDS is a crystallisable polymer suitable for melt extrusion which confers it great potential for general applications other than biomedical uses. In order to prepare materials with tailor made mechanical properties the addition of nanometric dimension fillers² to the polymeric matrix can be interesting, as a way to improve the polymer matrix properties with low filler content.

Clays are suitable material for preparation of polymer nanocomposites³ due to their ability to be exfoliated by polymer molecules originating a material with excellent properties, as consequence of the high polymer/ filler surface area.

In this study the ability of cationic (1:2 phyllosilicates) and anionic (hydrotalcite) clays to obtain exfoliated nanocomposites using poly(p-dioxanone) as matrix polymer has been analyzed. Fluorohectorite (FH) and vermiculite (VMT) were employed as 1:2 phyllosilicate type clays and hydrotalcite (HT) as layered double hydroxide (LDH) type clay.

In order to obtain nanometer size dispersions, the hydrophilic clays have been organically modified (OM) to improve the compatibility with the more hydrophobic PDS. In this way, the interlayer ion of the cationic clays has been replaced by oleyl bis(2-hydroxyethyl) methyl ammonium chloride (Ethoquad). In the case of the anionic clays the organic modification involved sodium 4-hydroxy benzene sulphonate and sodium 12-hydroxy dodecanoate.

Nanocomposites of PDS and organically modified clays (5 wt%) were melt-mixed using a Mini-Max molder at 160° C. The intercalation of the organic modifier in the clays and the dispersion degree of the organically modified clays in the PDS composites have been analyzed by wide-angle X-ray scattering (WAXS) and Atomic Force Microscopy (AFM) in a complementary manner.

WAXS patterns of unmodified and modified clays were interpreted taking into account the position of the basal peak which depends on the distance between two adjacent clay layers. In Fig. 1 (a) WAXS patterns of the organically modified clays show that the position of the (001) peak shift to lower 2θ value for phyllosilicates treated with Ethoquad, resulting in an enlargement of interlayer distance from 1.43 to 2.88 nm for fluorohectorite (OMFH) and from 1.39 to 4.17 nm for vermiculite (OMVMT). Therefore, the observed d-spacing suggests a parallel monolayer of the organic modifier in case of fluorohectorite and a perpendicular monolayer structure in case of vermiculite.

Referring to hydrotalcite (Figure 1 (b)), the position of the (003) diffraction peak also shift to a lower 2θ value when it was treated with sodium 4-hydroxy benzene sulphonate (OMHTA), resulting in an increase of basal space of 0.74 nm that corresponds to a horizontal orientation of interlayer organic anion. In the case of hydrotalcite modified

with sodium 12-hydroxy dodecanoate (OMHTB) the interlayer dodecanoate anions are vertically arranged leading to an expansion of the basal spacing of 1.54 nm.

PDS nanocomposites of organomodified hydrotalcites (PDS-OMHTA and PDS-OMHTB) did not show the characteristic peak of basal spacing (Fig. 1 (c)) indicating that the clay layers could be completely exfoliated and dispersed in the PDS matrix, being nanometer-scale composites. Contrarily, for the composites based on fluorohectorite and vermiculite modified with Ethoquad (PDS-OMFH and PDS-OMVMT, respectively) the peaks of modified clay are shown clearly, giving evidence that the exfoliation of these clays had not taken place.

AFM was used to investigate the dispersion of the clay in the PDS matrix. In PDS-OMFH sample AFM image reveals tactoids and sometimes agglomerates of organo-fluorohectorite, suggesting that a good dispersion has not been achieved. However, in nanocomposites of PDS and organo-LDHs (PDS-OMHTA and PDS-OMHTB) AFM reveals that the clay is well dispersed throughout the polymer with no significant aggregation consequence of a completely mixed nanocomposite systems. These results can be explained on the basis of the different lengths and flexibility of the clay platelets. HT clay platelets, being smaller in size (70-100 nm) and more flexible than FH (500-600 nm) and VMT (200-300 nm), are easily distorted and dispersed by means of mechanical forces allowing the penetration of the polymer.

In summary, novel composites based on poly(p-dioxanone) and organically modified cationic and anionic clays have been prepared using the environmentally benign technique of melt-extrusion. The dispersion morphologies were observed by X-ray diffraction and AFM, indicating that exfoliation has been achieved for nanocomposites of organically modified anionic clays.

Acknowledgements:

Financial support is acknowledged from the Spanish Ministerio de Educación y Ciencia (MEC) (project MAT 2005-03358) and also from the University of the Basque Country (Subvention to Grupo Consolidado Ref 97UPV00203.215-1359/2001).

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Figures:

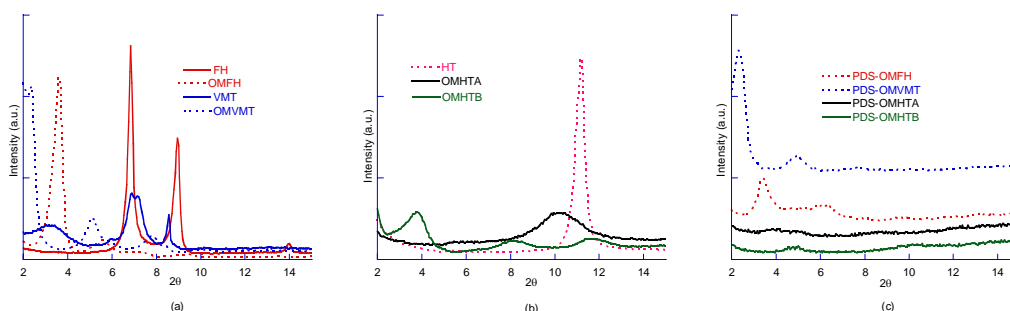


Figure 1. XRD profiles of: (a) cationic clays and its organic modifications, (b) anionic clays its organic modifications (c) nanocomposites of PDS with anionic and cationic clays.