THE EXTENT OF FILLER'S ORGANO-MODIFICATION AND THE RESULTING MORPHOLOGY AND THERMO-MECHANICAL PROPERTIES OF POLY(E-CAPROLACTONE)/CLAY NANOCOMPOSITES

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Introduction

The development of polymer/clay nanocomposites has attracted significant attention in recent years due to the exceptional physical property improvements that these materials often exhibit, at relatively low filler loadings [1]. In order to achieve these benefits, efficient dispersion levels of the reinforcing agent is a prerequisite, so that the high aspect ratio and surface area of the clay particles are fully utilized and the resulting nanocomposite properties are isotropic. In general, the inorganic filler neither has good interaction with the organic polymer to achieve good dispersion, nor adequate adhesion, and, as a result, surface organic treatments are common [2]. Organic modifier's packing density within the silicate galleries is a very important factor regarding the dispersibility of the clay into the matrix and the properties of the final hybrid material.

The present study was undertaken to elucidate the effect of the surfactant concentration on the thermo-mechanical behavior of poly(ε-caprolactone) nanocomposites. Hybrids were prepared by the addition of montmorillonite modified by various concentrations of hexadecylammonium cation. Dispersion of the organomodified clay into the polymer matrix was achieved by the melt intercalation technique. The structural characteristics of the as-prepared composites were investigated by X-ray diffraction and their thermal properties were studied by thermogravimetric analysis. The influence of the amphiphilic cation concentration on the material's mechanical properties was explored in tensile loading conditions.

Experimental part

Materials

Poly(ε-caprolactone) (PCL) (Mn=80000) was obtained from Aldrich. Organically modified montmorillonite (C_{16}MMT) was prepared through an ion-exchange reaction between sodium montmorillonite and hexadecylammonium salt (HDA) loadings ranging from 30 to 300% the cation exchange capacity (CEC) of the inorganic material. The structural, thermal and colloidal characteristics of the organophilic clay were studied in a previous work [3].

Preparation of nanocomposites

Nanocomposites were fabricated by the melt intercalation method, at 150°C and 120 rpm, under constant nitrogen flow, using a ThermoHaake Minilab microcompounder. The compounding time was 10 min. The inorganic content in every composite prepared was 3 wt%.

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Characterization

The effect of the hexadecylammonium salt loading of C_{16}MMT on the structure of the hybrids was investigated by X-ray diffraction (XRD) using a Rich. Seifert 3003 TT diffractometer with Ni-filtered CuKα radiation (λ=0.154 nm). The 2θ scanning range was varied from 1.5^o to 10^o with a step of 0.01 and a measuring time of 15 s per step.

Thermogravimetric analyses (TGA) of the hybrids were performed on a Shimadzu TGA-50 Analyzer with a heating ramp of 10 ^{o}C/min up to 750 ^{o}C both under flowing nitrogen (20 cm^3/min) and static air.

The mechanical properties of the produced composites were studied in tensile loading conditions using an Instron 3345 tensile tester according to ASTM D1708 method. The crosshead speed was 5 mm/min. At least five measurements were taken for each sample and the results were averaged to obtain a mean value.

Results and discussion

Morphology

Figure 1 depicts how the modified clay at various degrees affects the structure of the hybrid material. At low clay modification level (less than 50% of the CEC) mixing of polymer with organo-MMT did not result in the formation of a nanocomposite material. The hybrid displays two 001 reflections indicating an inhomogeneous dispersion of the clay particles into the matrix. Increase of the amphiphilic cation concentration facilitates PCL penetration into the modified mineral interlayer space shifting the clay's characteristic peak towards lower 2θ values.

However, at surfactant loadings higher than twice the clay CEC polymer insertion into the clay basal spacing tends to decrease. Lan et al. [4] reported that large population density of alkylammonium cations restricts intra-gallery penetration of polymer and there is a tendency to form intercalated nanocomposites rather than exfoliated ones. On the contrary, low population density provides more interlayer space to accommodate polymer chains. Mandalia et al. [5] suggested that lower concentration of surfactant aids the penetration of polymer probably due to a higher mobility of alkylammonium chains. Moreover, they concluded that the higher degree of organoclay dispersion can be achieved when the surfactant loading is equivalent to 1.2 to 1.5 times the clay CEC. Vaia et al. [6] reported that hybrid formation via polymer melt intercalation is entropically most favorable when the incorporated organoclay displays intermediate gallery heights and surfactant packing densities.

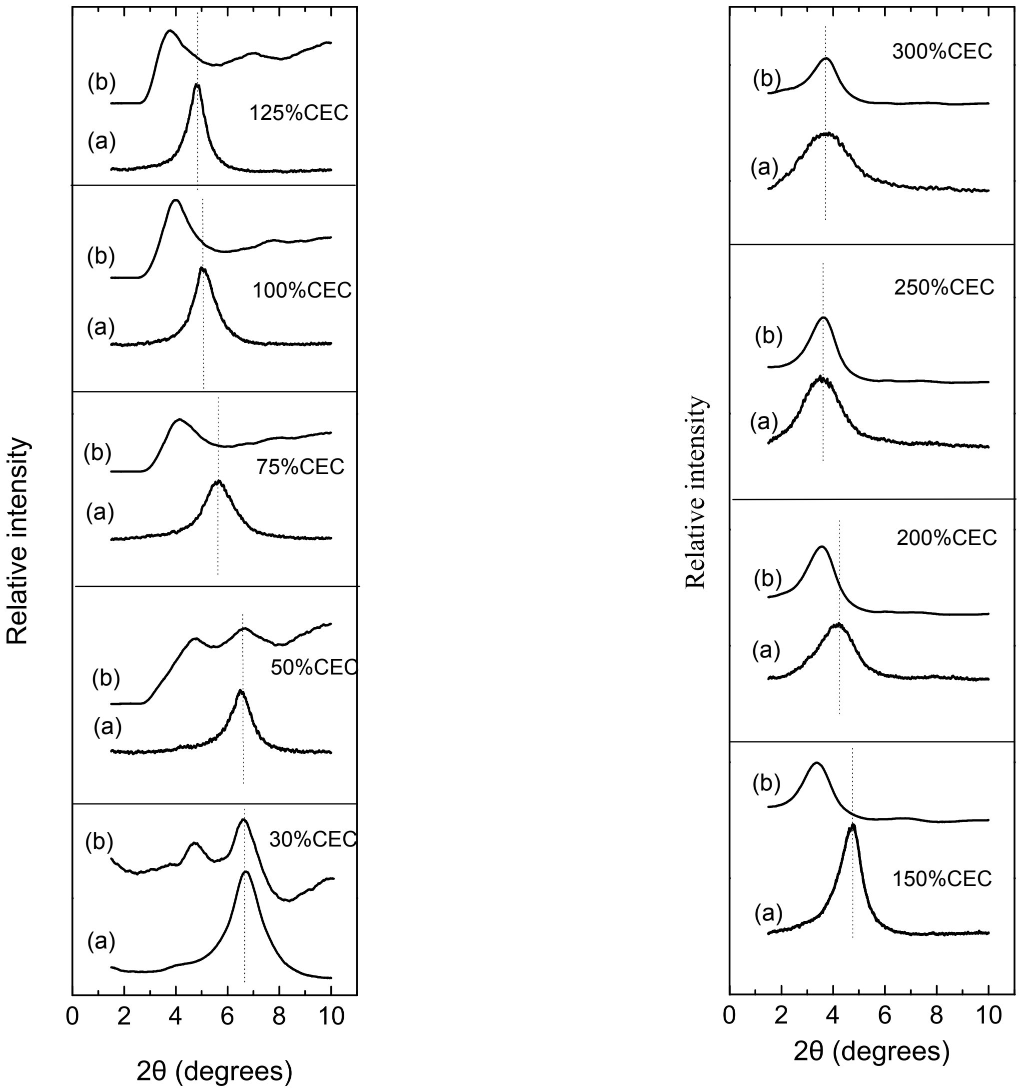
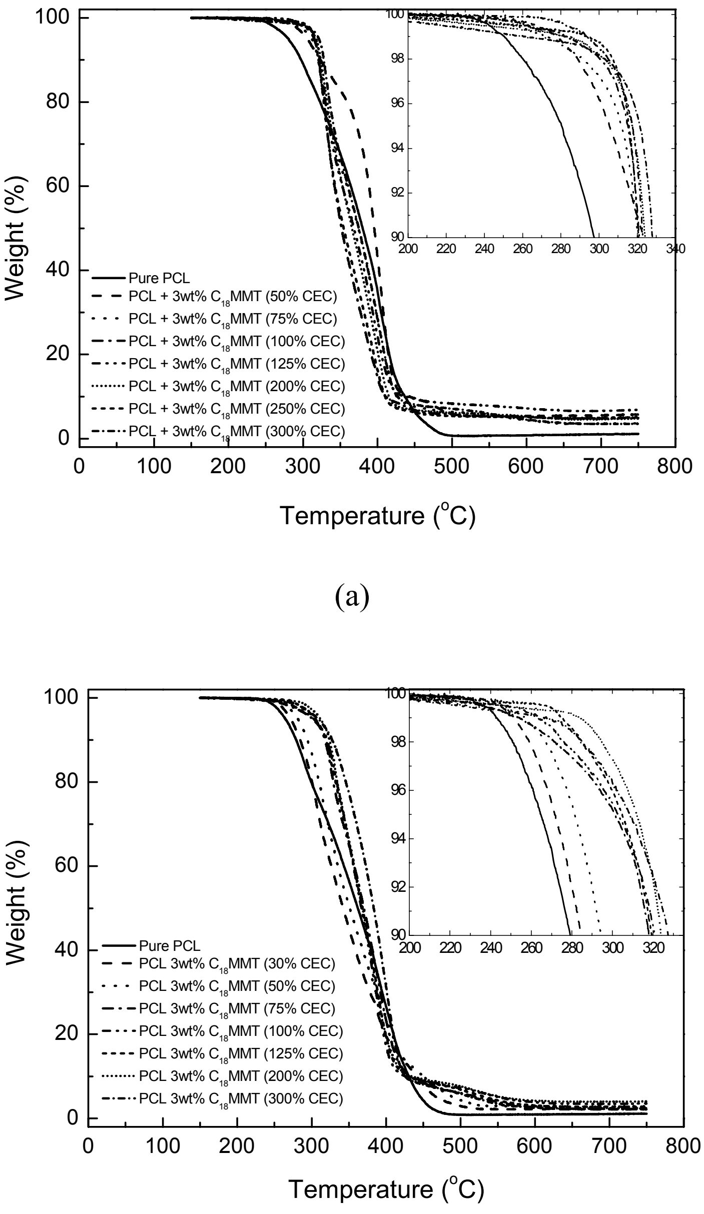


Figure 1. X-ray diffraction patterns of (a) the modified clay and (b) the resultant hybrid.

Thermal characteristics

Figure 2a shows the TGA weight loss curves of the prepared hybrids, which were obtained in a nitrogen atmosphere and for the temperature range between 150^{o}C (where the major part of humidity has been removed) and 750 ^{o}C. At low surfactant loadings (30% CEC) thermal decomposition initiation occurs at about 285 ^{o}C. Increase of the mineral modification degree reinforces its compatibility with PCL facilitating the dispersion of MMT into the matrix. This results in a significant enhancement of the hybrid thermal stability increasing the onset decomposition temperature. Due to the high aspect ratio, the dispersed clay platelets impede the escape of the volatile degradation products within the nanocomposites. However, at surfactant concentrations higher than 200% the clay CEC, the hybrid displays a reduced thermal stability.

The effect of the amphiphilic cation concentration on the thermal properties of the hybrids in oxidative conditions is shown in Figure 2b. Increase of the surfactant loading up to 200% CEC enhances the thermal stability of the hybrid shifting the onset temperature of the hybrid's degradation toward higher values. The layered silicate incorporation triggers char formation on the surface of the composite which hinders the flow of the volatile decomposition products within the material [7] and limits the access of oxygen to the remaining material. This charring process may be catalyzed by the decomposition of the alkylammonium cation [8].

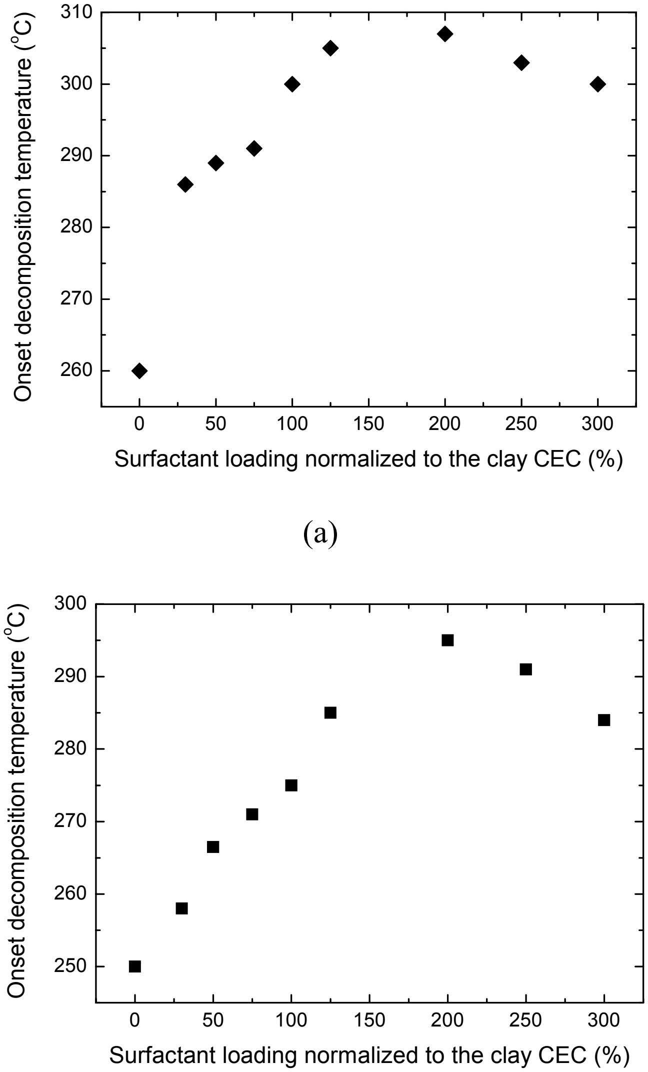


(a)

(b)

Figure 2. TGA curves for PCL hybrids prepared by the incorporation of MMT modified to a different extent, in (a) inert and (b) oxidant atmosphere.

The relation between the MMT modification level and the temperature required for 2% of hybrid decomposition in inert and oxidative atmosphere is presented in Figure 3. It is evident that the effect of the surfactant loading is similar in both cases. Moreover, oxygen causes decomposition of PCL/clay hybrids at a lower temperature than nitrogen.



(a)

(b)

Figure 3. Effect of clay modification degree on the onset decomposition temperature (estimated at 2% of weight loss) of PCL hybrids, in (a) inert and (b) oxidant atmosphere.

Mechanical properties

Table 1 presents the influence of the clay modification degree on the mechanical properties of the PCL hybrids. It appears that increase of the alkylammonium loading enhances the strength and the elongation at break of the hybrid. Low surfactant loadings cause incomplete dispersion of MMT particles and inadequate polymer chain linkage to the mineral surface. Consequently, large clay agglomerates formed can act as load-concentrated defects which promote crack initiation leading to a decreased strength and material ductility. The nanoscale dispersion achieved at intermediate HDA concentrations provides a substantial rise to the composite's plastic deformation. However, when the alkylammonium coverage exceeds the clay CEC, a drop of the tensile strength along with a material embrittlement is observed.

The trend in Young's modulus values is consistent with the trend of the aforementioned mechanical properties, when the clay modification level is varied. Silicate layers, due to their unique structure which includes a high aspect ratio and a large surface area, significantly improve the modulus of elasticity of the material. This improvement is expected to be larger by decreasing the scale of reinforcement, which is associated with the increase of the ammonium cation concentration. Additionally, an increase of HDA content reinforces polymer affinity and interfacial adhesion to the mineral surfaces and enhances their interaction. Therefore, the stresses are much more effectively transferred to the inorganic filler. Nevertheless, very large excess of the surface modifier triggers a substantial decrease of the material's modulus of elasticity. Ratinac et al. [9] mentioned that at high degrees of clay modification some of the excess modifier may leach or migrate to the matrix and cause plasticization effects reducing the material mechanical properties.

Table 1. Mechanical characteristics of PCL/organomodified MMT hybrids

Modification level of the added MMT (normalized to the % CEC)	Yield Strength (MPa)	Strength at break (MPa)	Elongation at break (%)	Young's Modulus (GPa)
0 (pure PHB)	16.5	33	850	352
30	16	25	603	390
50	16	26	632	417
75	16.2	27	720	438
100	17.2	31	815	498
125	17.4	29	750	494
150	17	27	745	490
200	16.5	26	730	480
250	16	26	712	469

Conclusions

The effect of the modification level of montmorillonite on the structural, thermal and mechanical characteristics of PCL composites prepared by the melt intercalation method is presented in this work. The clay was modified by hexadecylammonium cation with concentrations ranging from 0.3 to 3.0 times the cation exchange capacity of the mineral.

Investigation of the prepared composites' morphology by X-ray diffraction showed that proper swelling of the clay layers can be achieved provided that the alkylammonium concentration is higher than 50% the clay CEC. However, high levels of clay modification restrict intra-gallery penetration.

The influence of the surfactant concentration on the material's mechanical properties was studied in tensile loading conditions. It was found that, initially, an increase of the clay modification degree enhances the compatibility between the mineral and the matrix leading to a significant improvement of the composite's stiffness without sacrificing polymer ductility. However, higher hexadecylammonium concentrations have a negative impact to hybrid's mechanical properties causing their significant deterioration.

Thermogravimetric analysis (TGA) revealed that intermediate clay modification levels enhance the composites thermal stability by increasing the onset decomposition temperature.

Acknowledgements

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