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SCIENCE DIRECT

Polymer 46 (2005) 1601–1608

polymer

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Incorporation of Mg–Al hydrotalcite into a biodegradable Poly(ε-caprolactone) by high energy ball milling

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Received 22 April 2004; received in revised form 21 October 2004; accepted 7 December 2004

Abstract

The technique of high energy ball milling (HEBM) was used to prepare nanocomposites of poly(ε-caprolactone) (PCL) and an organically modified Mg–Al layered double hydroxide. The amount of inorganic material was varied from 0 to 6 wt%, and the samples were melted and quenched in ice–water after milling. The molecular weight of PCL decreased and its distribution increased as a consequence of milling. The structural analysis of the milled samples, conducted by X-ray diffraction and infrared absorption techniques, showed that the 12 hydroxydodecanoates organic modifier was still attached to the inorganic lamellae even if a partial delamination of the layered compounds occurred. The mechanical parameters (modulus, stress at yield point, strain at break point and stress at break values) derived from the stress–strain curves, improved in the composite samples containing up to 2.8 wt% of inorganic filler, with respect to the pure polymer, in spite of the molecular weight decrease. The thermodynamic diffusion coefficient of water vapor in composite samples was lower than in pure PCL, indicating an improvement of the barrier effect.

Keywords: High energy ball milling; Nanocomposites; Hydrotalcites

1. Introduction

Polymeric nanocomposites are a new class of materials having an inorganic dispersed phase with at least one dimension in the 1–100 nm range. They show better physical and chemical properties than conventional composites, partly thanks to the much stronger interfacial forces between the nanometer-sized domains [1–9]. In the last years the exfoliated smectite clays have received considerable attention as filling nano-particles because their structure exhibits stiffness, strength and dimensional stability [2,3]. Very recently, interest is being devoted to layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, as versatile inorganic filler materials. These materials, in which the M^{2+} of the $Mg(OH)_2$ brucite structure cations are partially substituted by M^{3+} cations, are currently used in intercalation chemistry [10–15]. The possibility to replace the counter-balancing anions, located in the interlamellar region, with other anions by an ion-exchange process, makes LDHs a unique class of layered solids to be used as filler of polymers bearing a negative charge [17,18]. Further, LDHs can be rendered miscible with polymer matrices, converting the normally hydrophilic surface to an hydrophobic by ion-exchange reactions with anionic surfactants.

Generally, in order to obtain nanocomposites, intercalation of polymer chains into silicate galleries is done by using one of the following two approaches: (1) insertion of suitable monomers in the silicate galleries and subsequent polymerization or (2) direct insertion of polymer chains into the silicate galleries from either solution or the melt [2,3]. The melt blending process is a suitable method as it is a versatile and an environmentally benign approach from the

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doi:10.1016/j.polymer.2004.12.018

technological point of view. However, the interaction between the inorganic component and the organic guest molecule could not be thermally stable enough to withstand high melt processing temperatures. This is a serious obstacle in the developing of polymer/inorganic layers nanocomposites as engineering plastics.

A new alternative method for the preparation of nanomaterials relies on solid-state mixing at room temperature, which ought to involve an efficient mixing of two or more species by mechanical milling. High energy ball milling (HEBM) is an effective unconventional technique currently used in inorganic material synthesis and processing [18–21]. It consists of repeated events of energy transfer, promoted by the milling device, from the milling tools (generally balls) to the milled powder. During the milling the powder particles crack, clean surfaces are produced, atom diffusion and 'intimate mixing' are promoted [21]. As a consequence of the prolonged milling action, when the energy transferred during the hit is enough to overcome the activation barrier, chemical reactions may occur.

Recently it has been proved that HEBM on polymeric materials can help obtaining materials with new characteristics, that can difficultly be obtained with other conventional processes [22,23]. Although mechanical action can have deleterious effects on solid polymers by breaking chains and oxidizing the sample, the HEBM can be successfully used to obtain polymeric blends with improved mechanical properties as a consequence of its ability in production of cross linked chains [22–24].

With the aim to investigate if HEBM can be utilized as an alternative route to obtain polymeric composite materials with improved mechanical and transport properties, the preparation of nanocomposites by using HEBM on a modified hydrotalcite and Poly(ε-polycaprolactone) has been attempted. Actually, to overcome the incompatibility between the polymer and the inorganic sample, we modified the hydrotalcite with organic 12-hydroxydodecanoate anions, able to enhance the physical bonds of the inorganic lamellae with the polymer.

The structural characterization and physical properties of polymeric composites obtained by HEBM technique were studied.

2. Experimental

2.1. Materials

All the LDH materials utilized in this study were synthesized from C. Erba RP-ACS grade reagents. The $Mg_{0.66}Al_{0.34}(OH)_2(CO_3)_{0.17}$ precursor material was obtained using a procedure based on the in situ formation of ammoniun carbonate from urea [17]. The precursor has been converted in nitrate form, of formula $Mg_{0.66}Al_{0.34}(OH)_2\ (NO_3)_{0.34}.0.62H_2O$, by titrating the carbonate form, previously suspended in 1 M $NaNO_3$ aqueous solution, with a 0.100 M HNO_3 solution operating at pH-stat mode and pH = 4.5. 12-Hydroxydodecanoic acid (97% Aldrich), hexane (Lab Scan), tetrahydrofuran (THF, Lab Scan) were used as received. Poly(ε-caprolactone) in pellets was purchased from Aldrich. The as received material was added to chloroform and then stirred at ambient temperature for 10 min. After that, the mixture was precipitated in acetone, the resulting fine powders were filtered and dried in air.

2.2. Intercalation of 12-hydroxydodecanoate anion (HDA) in LDH (LDH–HDA)

A solution of deprotonated 12-hydroxydodecanoic acid was prepared by adding 28.3 ml of a 1 M KOH water solution to 100 ml of a 0.283 M of 12-hydroxydodecanoic acid solution in tetrahydrofuran. 55.2 mmol (5.05 g) of LDH in nitrate form were added to the HDA solution. The mixture reaction was then stirred at reflux for 12 h. The pale yellow solid obtained was isolated by centrifugation, suspended in THF and centrifugated for two times. The product was finally filtered and dried at 80 °C.

2.3. HEBM experiments

In every single milling experiment the LDH-HDA and the Poly(ε-caprolactone) powders were mixed in the proper weight ratio in a stainless steel vial designed to avoid excessive heating of the milling system. The vial was equipped with an external jacket, where a cooling liquid circulation maintained the mean temperature value not greater than 0 °C. In the vial 20 g of tungsten carbide balls (8–15 mm diameter) were added. In this way we contemporaneously realized a relevant value of energy transfer ($\sim 10^{-2}$ J/hit due to 15 mm balls [24]) and minimized the possibility of 'dead zone' in the vial, were the powder remain unmilled (8 mm balls). The vial was then hermetically closed and placed in a Spex 8000 apparatus, where the powder was milled for a time of 30 min. To avoid excessive heating of the apparatus as well as of the milled powders, every 10 min of active milling action was followed by an equivalent period of rest.

2.4. Film preparation

The powders obtained by the milling processes containing different percentages of inorganic phase, were molded in a Carver laboratory press, at the temperature of 100 °C, followed by a quick quenching in an ice–water bath. Films 100 μm thick were obtained and analyzed. In the following, samples will be coded as PCLn, where *n* is the amount of the inorganic component, evaluated as the oxide residue present at 800 °C.

Table 1
Molecular weight and molecular weight distribution of PCL before milling and PCL6 nanocomposite

Sample	M_w (KDa)	M_w/M_n
PCL	195	2.54
PCL6	96.3	3.50

2.5. Methods

Ion Chromotography (Dionex 500 instrument) was used for the determination of Mg, Al and nitrate content of the LDH samples. A weighed amount of the sample was dissolved in HCl 1.0 M solution and eluted with methylsulfonic acid to determine the Mg^{2+} with suppressed conductivity detection, and with HCl 0.75 M to obtain Al^{3+} with spectrophotometric detection after post column reaction with Tiron. The nitrate has been obtained after having equilibrated a given amount of sample with 1 M Na_2CO_3 solution.

Thermo Gravimetric Analysis (TGA) was carried out with a Mettler TC-10 thermobalance from 50 to 800 °C at a heating rate of 20 °C/min under an air flow.

X-ray Diffraction measurements (XRD) were performed with a Philips diffractometer (equipped with a continuous scan attachment and a proportional counter) with Ni-filtered Cu Kα radiation (1.5405 Å).

FT-IR Analysis was performed on the films with a Perkin–Elmer 1600 spectrophotometer with 0.2 cm^{-1} (20 scans collected) resolution.

Dynamic-mechanical properties were performed using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer. The spectra were recorded in the tensile mode, obtaining the logarithm of the modulus E_0, and the loss factor, tan δ, at a frequency of 1 Hz, as a function of temperature. The heating rate was 5 °C/min in the range from -100 to 150 °C.

Gel Permeation Chromatography (GPC) was carried out using a Waters 150-C ALC/GPC instrument, equipped with four 300×7.5 mm^2 columns type PL Gel MIXED A 20 µm and a Jasco 875 UV detector set at 254 nm. Polystyrene as standard and trichlorobenzene as solvent were used. The temperature of the experiment was 135 °C with a flow rate of 1 ml/min.

Diffusion coefficients were evaluated, using the microgravimetric method, at different vapor activities ($a = P/P_o$), where P is the actual pressure to which the sample was exposed, and P_o the saturation pressure at the test temperature. The penetrant was water vapor and the experiments were conducted at 30 °C.

The transport properties were measured with water vapor in a range of activities from 0.2 to 0.6. Measuring the increase of weight with time for the samples exposed to the vapor at a given partial pressure, p, both the equilibrium value of the sorbed vapor, C_{eq}, and the diffusion coefficient, D, were obtained.

3. Results and discussion

3.1. Characterization of the LDH–HDA/poly(ε-caprolactone) composites

3.1.1. Organically modified LDH filler

The organically modified hydrotalcite has been obtained by exchanging the nitrate anions of $Mg_{0.66}Al_{0.34}(OH)_2(NO_3)_{0.34}.0.62H_2O$ with 12-hydroxydodecanoate anions, as described in the experimental section. About 75% of the nitrate have been exchanged and a single phase $Mg_{0.66}Al_{0.34}(OH)_2(NO_3)_{0.08}(HDA)_{0.26}.0.4\ H_2O$, has been obtained. The remaining NO_3^- anions are solubilized into the interlayer of LDH–HDA structure. Upon the insertion of HDA anions, the interlayer distance of LDH increases from 9.02 to 22.7 Å, as shown later. On the basis of composition data and interlayer distance value and by assuming that the structure of the brucite layers remains practically inaltered as a consequence of intercalation, the arrangement of HDA anions in the interlayer region may be predicted. Very likely, the $-COO^-$ groups are placed alternatively near both the sides of the layer to balance the layer positive charges. The pendant hydroxy-alkyl groups are directed towards the interlayer region and form a monofilm of partially interdigitated HDA alkyl chains in trans planar conformation. The compound is stable up to about 250 °C (see later), temperature at which the thermal decomposition starts.

3.1.2. Molecular weight of composites

High energy mechanical milling can have a profound effect on the chemical structure of a polymeric material by breaking chains and creating free radicals that can promote inter-chain reactions. Therefore, we first investigated the change of molecular weight and molecular weight distribution of PCL, following the milling process. In Table 1 these parameters are reported for the pure polymer and the polymer recovered from sample PCL6. The polymer was quantitatively extracted with chloroform from the composite containing the highest fraction of inorganic component; then the molecular weight and molecular weight distribution were determined by GPC measurements. The molecular weight, both M_w and M_n, decreased and the molecular weight distribution increased as a consequence of chain scission during the process of milling. However, the molecular weight is still high, the distribution is in a good range and no detriment in the mechanical properties is expected. Moreover, the polymer can be quantitatively extracted by the solvent, in agreement with the hypothesis that, in the present case, cross-linking did not occur in the mechanical process.

Films were obtained by molding the powders above the melting point and quickly quenching in an ice–water bath. The films appeared homogeneous, white and opaque, without visible cluster of inorganic material under an optical microscope.

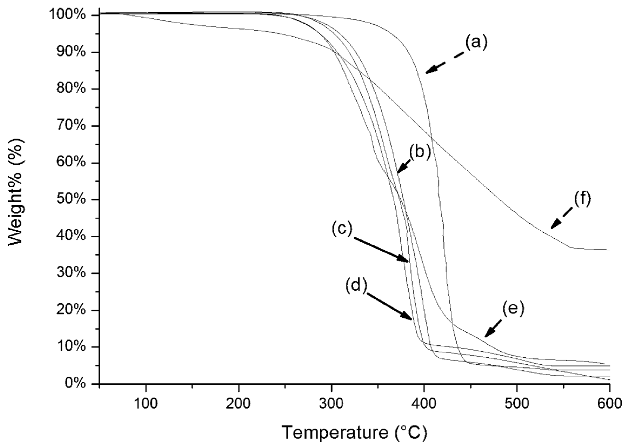

Fig. 1. The TGA curves for pure PCL (a), PCL1.4 (b), PCL2.8 (c), PCL4 (d), PCL6 (e), LDH-HDA (f).

3.1.3. Thermogravimetric analysis

All the composites were analyzed by thermogravimetric analysis to determine either the content of the inorganic component after the thermal decomposition of the organic part in air up to 800 °C, or the degradation temperatures (Fig. 1). In the analysis conditions it was shown that LDH material is transformed in Mg–Al oxides [16]. The curve of the LDH–HDA intercalate (see curve f) shows a first weight loss step starting around 100 °C (5%), attributable to the loss of hydration water, and a second loss starting at about 200 °C attributable to the thermal decomposition of the organic anion and to the loss of nitrate and constitution water. The shape of the curves for the composites (curves b,c,d,e) is very similar to that of the parent polymer (curve a), although the temperature of the decomposition step is slightly lower. This is due either to the presence of LDH–HDA, which starts to decompose at a lower temperature, or to the decrease of molecular weight of poly(ε-caprolactone) during the milling. However, the first effect seems predominant. In fact, by decreasing the inorganic content, we observed an increase of the decomposition temperature towards the value of the pure PCL polymer.

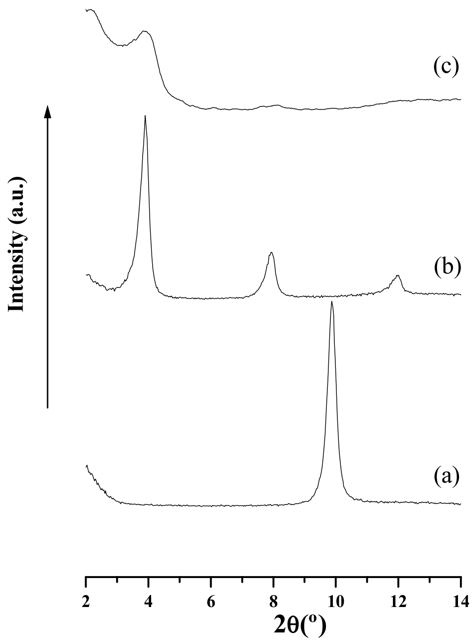

Fig. 2. X-ray diffraction spectra of LDH (a), LDH-HDA (b), PCL6 (c) in the interval 2–15° of 2θ.

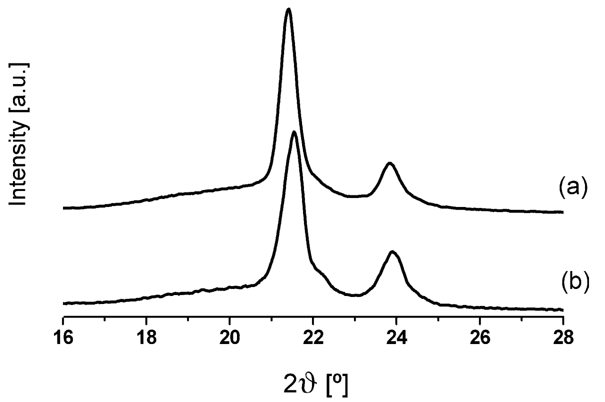

Fig. 3. X-ray diffraction spectra of neat PCL (a) and PCL6 (b) in the interval 16–28° of 2θ.

3.1.4. X-ray analysis

X-ray analysis was used to confirm the intercalation of HDA into the lamellae of LDH and study the dispersion degree of hydrotalcite in the composites, too. Fig. 2 shows, in the interval 2–15° of 2ϑ, the X-ray diffractograms of the starting hydrotalcite LDH (a), of the hydrotalcite modified with HDA (b), and of the composite of PCL6 obtained by ball milling and melt processing. The XRD pattern of the pristine LDH-NO_3 shows an intense peak at $2\vartheta = 9.8°$ which corresponds to 003 basal plane of 9.02 Å.

The exchange of nitrate with the organic anion OH–$(CH_2)_{11}$–COO^- gives rise to the expansion of the *d* spacing. We observe that the first peak of LDH–HDA (Fig. 2(b)) is located at $2\vartheta = 3.9°$ corresponding to a basal spacing of 22.7 Å. This reflection and the other reflections corresponding to the 2nd and 3rd harmonic, respectively, are sharp, indicating an ordered arrangement of intercalated organic anions into the hydrotalcite interlayer space. The diffractogram of the milled PCL6 (c) shows broad and very weak peaks. The low intensity of the peaks was expected, because of the low content of LDH–HDA in the composite. However, the broading of the peaks as well as the beginning of a peak at an angle lower than that of the intercalate indicate that the organic anion, after the mechanical milling, is still inside the inorganic lamellae and in a more disordered way.

Altough X-ray diffraction offers a convenient method to determine the interlayer spacing of the lamellae in the intercalated nanocomposites, very little can be said on the not well-defined peaks. Thus, peak broadening and intensity decrease are very difficult to study systematically, above all when the inorganic percentages are too much low.

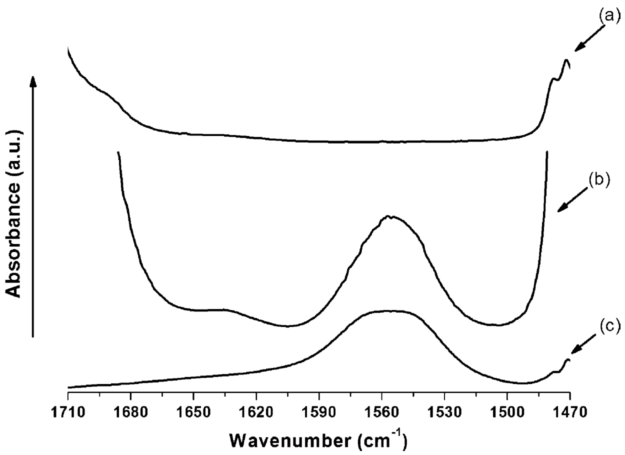

Fig. 4. The infrared spectrum of PCL (a), PCL6 (b) and LDH-HDA (c).

In this case, a serious analysis of the degree of exfoliation of the lamellae requires the employment of a direct method (TEM). However, the evaluation of the improvement of mechanical or barrier properties can be an indication of a good dispersion.

X-ray measurements on nanocomposites and PCL were performed in the range of 2ϑ values between 16 and 28° (Fig. 3). We observe that after milling with LDH-HDA and melting, poly(ε-caprolactone) crystallizes in the usual, already reported crystalline form, showing the main peaks at 21° and 23° of 2ϑ [25]. The polymeric part of the composite appears well crystallized and not oriented. The crystallinity degree of PCL and PCL composites was calculated and it was found very similar, ranging between 45–50%.

3.1.5. Infrared analysis

In Fig. 4 we report the infrared spectrum of the milled composite PCL6 (b) compared to the spectrum of the intercalated LDH–HDA sample (c) and of pure PCL (a), in the absorbance interval 1470–1710 cm^{-1}. The infrared analysis led to relevant information on the association of the organic anions into the host LDH before and after milling the sample. The spectrum of LDH–HDA shows the band at 1570 cm^{-1} corresponding to the anti-symmetric $\nu_{C=O}$ mode of the COO^{-} group, in a very clear way. This indicates that the organic HD is intercalated in the anionic form inside the hydrotalcite layers. In this interval of absorbance the pure PCL does not show any absorption band. The milled sample PCL6 shows the same band as the intercalated LDH–HDA, that testifies the presence of the COO^{-} in the milled blend. The original HDA is still attached to the inorganic layers in the anionic form. This result confirms and integrates the X-ray analysis.

3.2. Physical Properties of the LDH–HDA/PCL composites

3.2.1. Drawing behavior

In Fig. 5 we show the engineering stress–strain curves for samples PCL (a), PCL1.4 (b), PCL2.8 (c), PCL4 (d), and PCL6 (e). The drawing curve of sample PCL (a) is conventional with upper and lower yield points describing the neck formation and the subsequent transformation into an oriented structure. The neck propagation, after the yield drop, ends before 300% of elongation; afterwards a steeper increase of the stress and the breaking point at about 800% are observable. The composite samples show a much more pronounced and sharper yield and post yield drop than the neat sample. The behavior of sample PCL1.4 (b) is very similar to PCL, indicating an improvement of all the mechanical parameters. The value of the stress at the yield point increases as well as the elastic modulus. However, when the concentration of the inorganic component is higher than 1.4%, the drawing behavior shows some relevant differences. As a matter of fact sample PCL2.8 (c) shows a much longer interval in which the stress, after

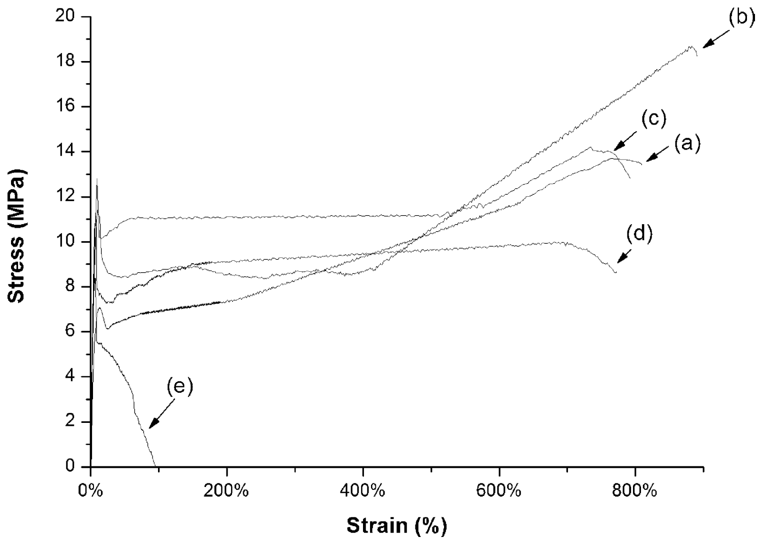

Fig. 5. The engineering load versus elongation curves for samples PCL (a), PCL1.4 (b), PCL2.8 (c), PCL4 (d), and PCL6 (e).

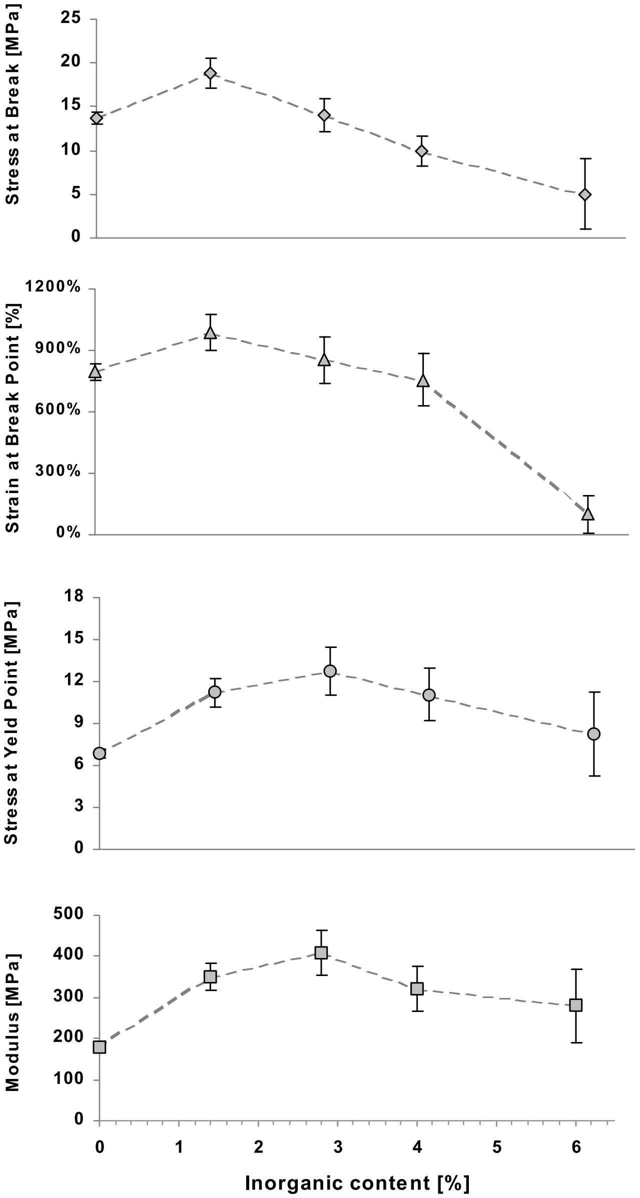

Fig. 6. The mechanical parameters, derived from the stress–strain curves, as a function of the inorganic content.

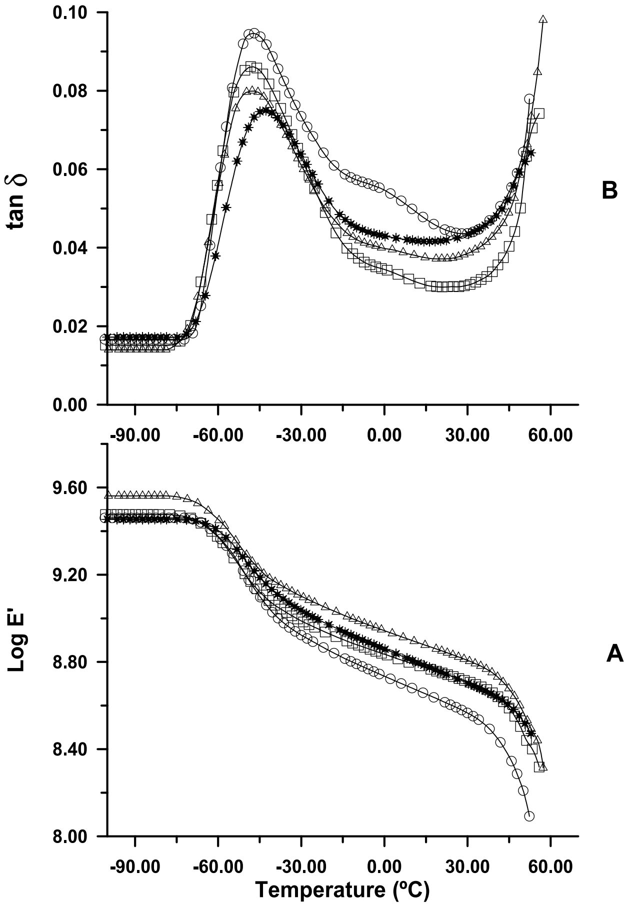

Fig. 7. (A) Log E′ (E′ in Pa) as function of temperature T(°C), and (B) tan δ as function of temperature T(°C) for: PCL (○), PCL1.4 (□), PCL2.8 (△) PCL4 (✱).

the yield drop, remains constant. This interval extends up to 500% and is followed by strain-hardening that produces the fracture of the sample at 750% of elongation. Sample PCL4 (d) does not show the strain-hardening, and breaks at about 800% at an almost constant stress. Sample PCL6 (e) breaks very rapidly after the yield drop, and the mechanical parameters are lower than in the other milled samples. In Fig. 6 all the mechanical parameters, derived from the stress–strain curves are reported as a function of the inorganic content. It is evident that the presence of even small amount of inorganic component largely improves the mechanical properties of the blends. Interestingly all the parameters go through a maximum for samples with low content of hydrotalcite (PCL1.4, PCL2.8 wt%) and then decrease, although some of them remain still higher than the initial parameters of PCL. We can deduce that the lower is the inorganic percentage, the better is the dispersion of the inorganic filler into the organic phase, with consequently improved mechanical parameters at low inorganic concentration. Increasing the percentage of LDH–HDA in the composites, the formation of inorganic clusters occurs, thus determining a deterioration of the mechanical parameters. Particularly the break elongation that becomes as low as 100% for sample PCL6. It is worth noting that 1.4% of inorganic component is enough to duplicate the modulus without detriment of the elongation at breaking.

3.2.2. *Dynamic mechanical analysis*

To investigate the stiffening effect in a broader temperature range we performed a dynamic mechanical analysis of all the samples. In Fig. 7 (A) we show the dynamic storage modulus and in (B) the loss factor tan δ as a function of temperature between $-100°$ up to 70 °C. The curves of the elastic modulus demonstrate that the addition of the hydrotalcite into PCL increases the stiffness in all the temperature range, and even just before the crystalline melting. Also with this technique we observed that the best sample, showing the highest modulus is the sample with

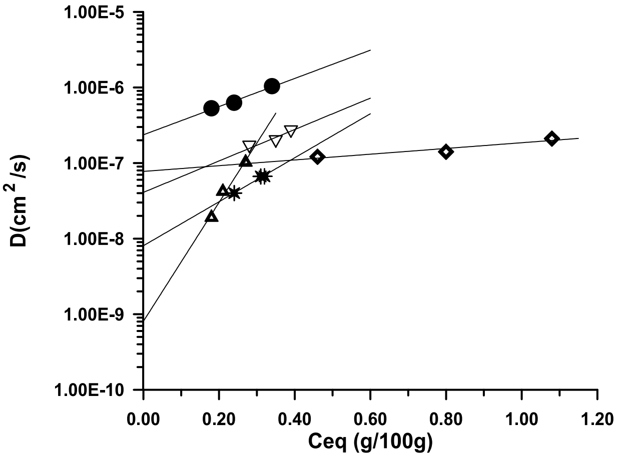

Fig. 8. The diffusion coefficient, D(cm^2/s), as function equilibrium concentration of water vapor sorbed, Ceq(g/100 g), for: PCL (●), PCL1.4 (✱), PCL2.8 (△), PCL4 (▽), PCL6 (◇).

2.8% of inorganic component. Correspondingly to the increase of the modulus the intensity of the tan δ values decrease. Form and location of the peak at about −40 °C, corresponding to the glass transition temperature, are almost unchanged for the composite samples, except sample PCL4 which shows a slightly higher temperature.

3.2.3. Transport properties

The transport properties of a liquid or a vapor in a semi-crystalline polymer are defined as the sorption and the diffusion of a solvent molecule across the amorphous phase: the crystalline regions are considered to be impermeable [26–30]. In the case of the composite materials, the system becomes more complicated due to the presence of domains of inorganic phase. Morphology and microstructure of this multi-phase system are expected to play a very important role in determining the transport phenomena [30].

In Fig. 8 the diffusion coefficients in the PCL composites samples as a function of the concentration of water vapor are reported. We observe a linear dependence of diffusion on concentration for all the samples, that allowed us to extrapolate to zero vapor concentration and obtain the thermodynamic diffusion coefficient, D_0. The numerical values of D_0 are reported in Fig. 9, as a function of the inorganic content. The improvement of the barrier properties, in terms of decrease of diffusion, is maximum for sample PCL2.8, whereas at higher inorganic content the diffusion parameters increase, even though they remain lower than the pure PCL.

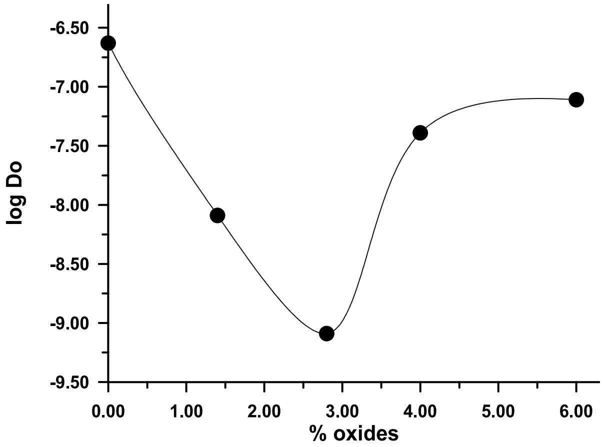

Fig. 9. The thermodynamic diffusion coefficient, D_0, as a function of the inorganic content.

In the X-ray measurements discussion, it has been evidenced that the crystalline degree of the PCL in the composites and in the pure polymer is about the same. As a consequence of an unchanged crystallinity degree for the composites samples, compared to pure PCL, the decrease of D_0 values must be ascribed to the presence of the inorganic filler. On the other hand, the presence of the filler increases to a large extent the tortuosity of the system, leading to an expected large decrease in the value of the diffusion coefficient. Indeed for composites of polycaprolactone with clays, as well as in the case of many other polymers, it was consistently found that the improvement of barrier properties is largely dominated by both the percentage and the shape of the inorganic filler dispersed in the polymeric matrix [5,7]. Exfoliation of the layered solid into individual lamellae leads to a remarkable increase of the surface of the filler with a consequent increase in the barrier improvement, also in the presence of very low inorganic content. In the present case, an increase of the filler content leads to a lower dispersion and exfoliation of the layered filler, with a decrease in the organic/inorganic interfaces.

4. Concluding remarks

High energy ball milling (HEBM) of powders constituted by organic polymers and inorganic fillers has been proved to be an alternative and efficient technique to produce novel composites. This technique may support the more conventional and utilized techniques based on in situ polymerization and melt extrusion, especially when the melting point of the polymer is so high that degradation of the organically modified filler may occur. Furthermore, it has been shown that composites of poly(ε-caprolactone) and modified Mg–Al layered double hydroxide, at different inorganic content, have a number of mechanical and physical properties enhanced in comparison to those of the pure PCL polymer. In particular, modulus and stress at yield point resulted improved for all the composites, in spite of the molecular weight reduction of PCL. Strain at break point and stress at break values improved in the composite sample containing 1.4 wt% of inorganic filler. The extension and the stress at breaking of the composite samples were similar to those of pure polymer. Finally the barrier effect of the composite containing 2.8% of inorganic filler results noticeably better than that of pure PCL.

The application of HEBM techique to the preparation of composites with different polymers is under investigation.

Acknowledgements

We thank the FISR Project 480 Ric, from the Italian Ministry of Education, University and Research, for the financial support.

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