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Nanometric Dispersion of a Mg/Al Layered Double Hydroxide into a Chemically Modified Polycaprolactone

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Polycaprolactone (PCL) was chemically modified by grafting maleic anhydride on it, through a radical reaction induced by benzoyl peroxide as initiator. To improve the grafting degree, a second unsaturated comonomer such as glycidyl methacrylate (GMA) has been added, demonstrating a good reactivity in melt grafting without leading to long grafted chains. The quantitative determination of grafted maleic anhydride, performed by FTIR analysis, revealed a grafting weight percentage of 9.5 ± 0.9, and the NMR characterization made it possible to propose a structure for the grafted polymer (PCLgMA). The modified polymer was analyzed by DSC and X-ray diffraction, showing a structural organization even better than that of the pristine polymer. An exchange reaction with a layered double hydroxide (LDH), hydrotalcite-like solid in the nitrate form, led to the disappearance of the crystalline basal peak of LDH in the X-ray diffractograms, suggesting a possible exfoliation of the inorganic sample. An oxidative etching on the composite surface followed by atomic force microscopy analysis made it possible to enlighten the lamellar structure in the pristine sample. In the composite sample, the well identifiable narrow fissures homogeneously distributed on the surface demonstrate that nanometer stacks of LDH sheets, embedded in a highly textured PCLgMA matrix, are present in the composite sample. The comparison of X-ray diffractograms and AFM analysis suggests either a partial exfoliation or an intercalation of the polymer in a lamellar texture with a basal spacing higher than 5 nm. In any case, the process of ionic exchange between nitrate LDH and PCLgMA led to the formation of nanocomposites, in which no large hydrotalcite aggregates are present. This is an interesting method to obtain a direct intercalation of the modified polymer into the inorganic solid with a simple ionic exchange reaction.

Introduction

Synthetic polymer nanocomposites have emerged as an area of research in recent years.[1−6] Their development represents a very attractive way to improve and diversify physical and chemical properties of polymers. The nanocomposites are two-phase materials in which the inorganic particles have at least one dimension in the nanometer (from 0.1 to 100 nm) range. If the nanometer-sized fillers are homogeneously distributed in the polymeric matrix, the very high specific surface areas result in a very effective influence on the matrix, and few percent nanofillers can significantly improve polymer properties.[7−10] In an ideal nanocomposite structure, all of the inorganic particles must be completely separated into individual layers, forming an exfoliated structure. As a consequence, most of the polymer is therefore located at the nanofiller−polymer interface, and the conversion of bulk polymer into interfacial polymer represents the key to new and diversified polymer properties. To increase the compatibility between the polymer and the filler, thus favoring the exfoliation, the inorganic compound has to be modified with an organic molecule, able to create physical bonds with the polymeric chains. The most common nanocomposites, investigated so far, are composed of polymers and organically modified silicates. Layered double hydroxides (LDHs) represent a different and interesting class of nanofillers for polymers.[11−15] LDHs particles are constituted of metal (II and III) hydroxide layers, but, in contrast to layered silicates, the hydroxide layers display a positive surface charge, which is counterbalanced by anions located in the domains between adjacent layers. Organophilic hydrotalcites can be synthesized by precipitation of aqueous solutions of aluminum and magnesium salts in the presence of organic acid anions.[16]

So far, many methods are used to obtain a good dispersion of the inorganic compound into the polymer.[17−20] In the melt-compounding method, polymer nanocomposites can be prepared by conventional compounding techniques (twin-screw extruder or melt compounder). If the compatibility between the polymer chains and the organic modification of the nanoparticles is sufficiently high, polymer chains penetrate into the galleries of the layered minerals, and intercalation or exfoliation of the layered clay can occur. The solution-blending method consists of dissolving polymer and organically modified clay in a mutual solvent and subsequently removing the solvent.

Another interesting possibility is to directly intercalate or exfoliate the clay with a charged polymer that can constitute the counterbalancing ion in the clay galleries. In this case, the organic modification of the clay is not necessary, because the polymer in the charged form can penetrate into the clay galleries by a simple exchange reaction, and intercalate or exfoliate the inorganic solid.

Poly (ϵ-caprolactone) (PCL) is a biodegradable polymer with excellent biocompatibility. It can be used as the matrix for bone

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substitutes, scaffolds, and drug carriers for controlled release.[21−25] Moreover, biodegradable and natural polymers are of interest in disposable packaging applications on environmental grounds. However, the applications for such polymers are limited because of their poor physical properties, and indeed reinforcement by clays is currently being investigated for these polymers.[26−28]

In the present study, we report a method to graft rather high amounts of maleic anhydride onto high molecular weight PCL, by using a bulk approach in a melt mixer apparatus, and the application of the modified PCL to obtain innovative nanocomposites by a direct ion exchange methodology. Although, in literature, grafting reactions in bulk to obtain maleic anhydride-modified PCL are described,[29] nevertheless the use of only maleic anhydride led to very low grafting efficiency and rather severe degradation. In our approach, a second unsaturated monomer, glycidyl methacrylate, is used in combination with maleic anhydride to increase the efficiency of grafting and reduce the time of melt processing. The maleic anhydride can be hydrolyzed in the presence of the anionic clay, allowing the polymer to intercalate or exfoliate the inorganic. The dispersion of the inorganic phase was investigated by a comparison between X-ray and atomic force microscopy.

Experimental Section

Materials. Polycaprolactone (CAPA 650, molar mass 50−80 kDa) was purchased from Solvay; maleic anhydride (MA) and benzoyl peroxide (BPO) were obtained from Fluka and used as received. Glycidyl methacrylate (GMA) was supplied by Aldrich Chemicals and was purified by passing through an aluminum oxide column before use. All solvents were of analytical grade and anhydrified following standard procedures.

A Mg/Al hydrotalcite-like compound with the formula $[Mg_{0.65}Al_{0.35}(OH)_2](CO_3)_{0.176}\cdot 0.4H_2O$ was a Sigma-Aldrich product. The nitrate form with formula $[Mg_{0.65}Al_{0.35}(OH)_2](NO_3)_{0.35}\cdot 0.56H_2O$ was obtained by the titration, at room temperature, of the carbonate form dispersed in a 1.0 M $NaNO_3$ aqueous solution with a 1.0 M HNO_3 solution. The solid, after the exchange reaction, was washed with CO_2 free deionized water and dried over phosphorus pentoxide.

Grafting Reaction. The grafting reaction was carried out in the melt by using a Rheocord mixer from Haake, equipped with two roller blades. A powder mixture of 45 g of PCL, 2.5 g (0.025 mol) of MA, and 0.5 g (2.1 mmol) of BPO was first fed into the mixer at 100 °C, and then 2.5 g (0.018 mol) of GMA was added dropwise. The reaction was carried out at 100 °C for 20 min at a rate of 32 rpm. Modified PCL (PCLgMA) was dissolved in 500 mL of chloroform ($CHCl_3$) and then precipitated twice in a large excess of *n*-hexane, to remove all of the ungrafted components (residual monomers and glycidyl methacrylate oligomers). The obtained product was dried under nitrogen stream at room temperature overnight until constant weight (average yield 80%). It was further purified by extractions with diethyl ether to remove plain PCL (average yield 90%).

Exchange Reaction. Two solutions were prepared by adding 1 mL of a 1 M KOH water solution to 0.5 g of PCLgMA previously dissolved in 50 mL of tetrahydrofuran. Two mixtures were then prepared by adding to the solutions 0.0525 and 0.1260 g of LDH in nitrate form, respectively. Each mixture was then stirred at reflux for 48 h at 80 °C. The solid obtained was isolated by centrifugation, suspended in THF, and centrifugated twice. The product was finally filtered and dried. The resulting powder were then molded in a Carver laboratory press, at the temperature of 75 °C, followed by a quick quenching in an ice−water bath (samples PCLgMA/LDH1 and PCLgMA/LDH2). To have a control sample, the same procedure was followed with nonmodified PCL (0.5 g in 50 mL of tetrahydrofuran, 1 mL of KOH 1 M, and 0.12 g of LDH at reflux at 80 °C), obtaining sample PCL-LDH.

Techniques. FTIR spectra were obtained by using a Perkin-Elmer spectrometer, model Paragon 500 (average of 20 scans, at a resolution of 4 cm^{-1}). Polymer samples were dissolved in chloroform and cast onto a KBr disk to obtain a thin film.

For ^1H NMR spectroscopy, the samples were dissolved in deuterated dimethylsulfoxide, and one-dimensional ^1H NMR spectra were recorded with a BRUKER AVANCE DPX300 apparatus operating at 300 MHz.

Thermograms were recorded with a differential scanning calorimeter Mettler DSC 30. Samples, sealed in an aluminum pan, underwent three consecutive runs: first, heated from 25 to 150 °C, kept at 150 °C for 2 min, then cooled from 150 to −100 °C, and finally reheated from −100 to 200 °C under a nitrogen stream at a rate of 20 °C/min.

Thermogravimetric analysis (TGA) was carried out in air atmosphere with a Mettler TC-10 thermobalance from room temperature to 800 °C at a heating rate of 5 °C/min.

Wide-angle X-ray diffractograms (WAXD) were obtained using a Philips PW 1710 Powder diffractometer (Cu Kα-Ni filtered radiation). The scan rate was 2° θ/min.

The atomic force microscopy (AFM) data were acquired at room temperature in an ambient atmosphere (30−40% humidity) in tapping mode (TMAFM) with a NanoScope III multimode AFM (Digital Instruments), Santa Barbara (CA), using microfabricated silicon tips/cantilevers. All of the images have been recorded simultaneously in height and in amplitude. The height images show the profile of the sample surface quantitatively (assuming that the oscillation of the cantilever is damped similarly at all locations), and the amplitude images provide in some cases much clearer contrast of the feature imaged as compared to the height images. The two samples investigated (pristine PCLgMA and PCLgMA/LDH2) were initially etched. The etching reagent was prepared by stirring 1.0 g of potassium permanganate in a solution of 95 mL of sulfuric acid (95−97 vol %) and 48 mL of orthophosphoric acid (85 vol %). The films were immersed into the fresh etching reagent at room temperature and held under agitation for 1 and 3 h, respectively. Subsequent washings were done using a cold mixture of 2 parts by volume of concentrated sulfuric acid and 7 parts of water. Furthermore, the samples were washed successively with 30 vol % aqueous hydrogen peroxide to remove any manganese dioxide. The samples were washed with distilled water and kept under vacuum for 2 days.

Determination of the Grafted Maleic Anhydride Content. The content of grafted maleic anhydride was determined by infrared spectroscopy on samples of PCLgMA in chloroform solutions. The band at 1777 cm^{-1}, corresponding to the symmetric stretching of the anhydride group, was taken as the analytical band in the spectrum. A preliminary calibration curve was built with different amounts of succinic anhydride in chloroform. The results obtained in the test are reported as the average of three determinations.

Results and Discussion

Synthesis of PCLgMA and Structural Characterization. PCL has been functionalized by insertion of maleic anhydride molecules. As the direct grafting of MA onto PCL is reported to give low degrees of functionalization[29] and, as a matter of fact, an attempt to graft MA directly onto PCL in the same experimental conditions led just to PCL degradation, a new approach of synthesis has been here adopted, based on the use of a second comonomer, glycidylmethacrylate (GMA). The choice of GMA resides on its boiling temperature (compatible with the conditions of reactive processing) and on literature reports[30] that demonstrate a good reactivity of GMA toward grafting on PCL without leading to long grafted chains, which may disturb the crystallization of PCL.[31,32] Moreover, GMA acts also as electron donor toward MA, thus inducing its insertion. As MA is keen to copolymerize, we may hypothesize that GMA grafts directly onto PCL chains, and MA can successively insert on GMA growing chains.

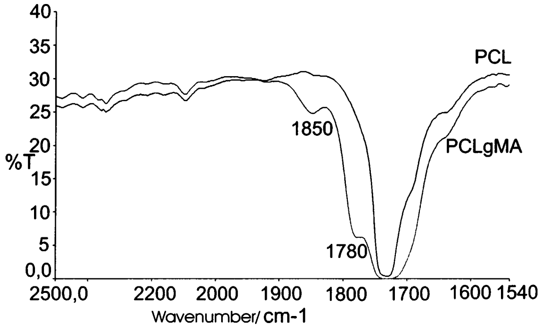


Figure 1. Infrared spectra in transmittance of PCL and PCLgMA.

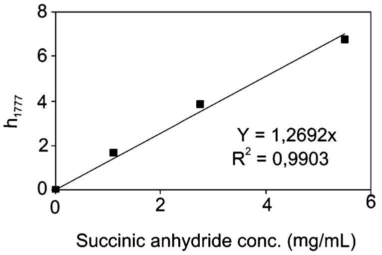


Figure 2. Calibration curve built on succinic anhydride solutions in chloroform.

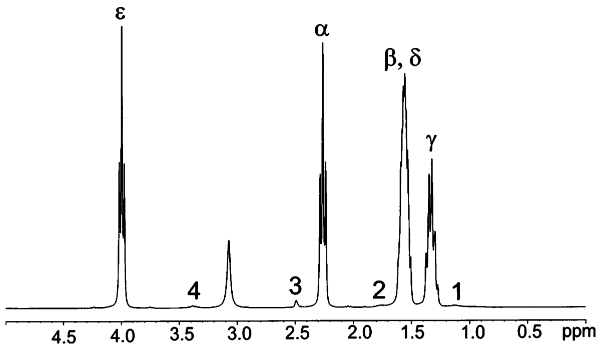


Figure 3. ^{1}H NMR spectrum of PCLgMA (solvent: d_6-DMSO).

The outcome of the grafting reaction, after purification, was investigated by FTIR. As compared to PCL, the PCLgMA spectrum shows the presence of new peaks at 1777 and 1850 cm^{-1} (see Figure 1), respectively, attributed to symmetric and asymmetric stretching of the carbonyl groups of the grafted anhydride. Unfortunately, the characteristic glycidyl methacrylate bands all overlap the polycaprolactone ones, such as the epoxy stretching vibration at 1170 cm^{-1}, which overlaps with the symmetric C−O−C stretching of PCL. Hence, infrared analysis does not provide evidence of glycidyl methacrylate grafted onto polycaprolactone.

The quantitative determination of grafted maleic anhydride,[32−34] obtained by measuring the absolute height of the band at 1777 cm^{-1} in the infrared spectrum of a chloroform solution of PCLgMA of known concentration, and using a calibration curve built on succinic anhydride solutions in chloroform, shown in Figure 2, has revealed a grafting weight percentage of 9.5 ± 0.9.

The structure of PCLgMA was elucidated by ^{1}H NMR spectroscopy. Several small peaks appear in the spectrum of PCLgMA (see Figure 3), attributed to grafted molecules.[35] The signal at δ 2.49 is typical of the −CH− protons of the anhydride moieties, while the signals at δ 1.13, 1.75, and 3.39 can be reasonably attributed to GMA moieties. As, according to literature, characteristic signals relative to $-CH_2$ protons of the GMA epoxy rings are found at δ 2.8 and 2.6, we explained the differences in GMA signals with the outcoming of a condensation reaction between GMA and MA molecules, leading to the opening of the epoxy and anhydride rings with the formation of an ester bond. This reaction is well documented in the literature[36] in experimental conditions similar to ours. The molar excess of MA as compared to GMA confirms the possibility that part of the MA gives rise to a condensation reaction with the epoxy of GMA in the course of the grafting process, and part is grafted as cyclic anhydride.

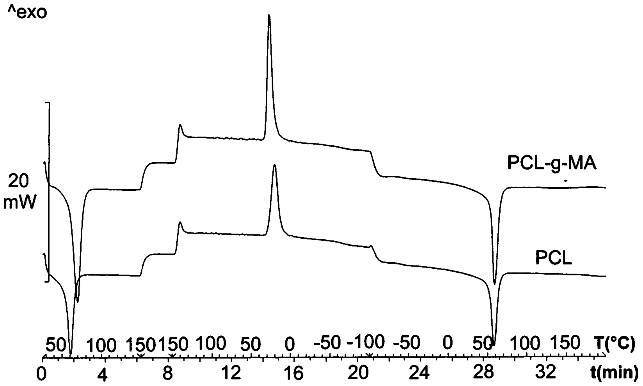
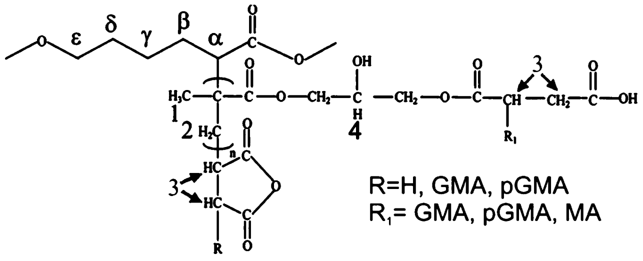


Figure 4. DSC curves of PCL and PCLgMA.

Table 1. Melting Temperature, T_m (°C), Melting Enthalpy, ΔH_m (J/g), and Crystallinity, X_c (%), of PCL, PCLgMA, PCLgMA/LDH1, and PCLgMA/LDH2

sample	T_m (°C)	ΔH_m (J/g)	X_c (%)
PCL	61.0	73.5	55
PCLgMA	61.3	77.3	57
PCLgMA/LHD1	61.8	75.1	56
PCLgMA/LHD2	60.7	70.2	52

Scheme 1. Schematic Structure of PCLgMA



According to the above considerations, we hypothesized the schematic structure in Scheme 1 for our modified PCL.

DSC curves for PCL and PCLgMA are reported in Figure 4. No relevant differences are found between PCL and PCLgMA polymers for what concerns the melting enthalpy (ΔH_m) when normalized by the sample weight as shown in Table 1. The insertion of short grafted chains onto PCL does not influence the crystallization, as one could expect in the case of grafting of long chains. Even an increase of T_c from the melt is observed for modified PCL, and it seems to indicate that the increased polar interactions among chains act as nucleating sites for crystallization.

In Figure 5, we show the X-ray diffractograms of both PCL (a) and the modified PCL (b). Pristine PCL shows the peaks at 21.5° and 24.5° of 2θ, corresponding to the 100 and 200 crystallographic planes, characteristic of the PCL crystalline structure. In addition to the main peaks at 21.5° and 24.5° of 2θ, PCLgMA shows in the diffractogram (b) low-intensity peaks at 20.3° and 22.2° of 2θ, also characteristic of the crystalline structure. They correspond to the 004 and 111 crystallographic planes and appear in more crystalline samples. Indeed, the

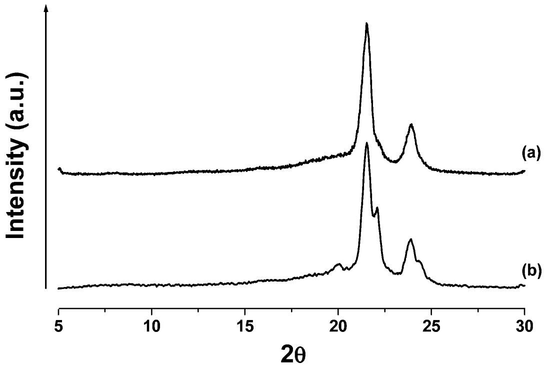


Figure 5. X-ray powder diffraction patterns of (a) PCL and (b) PCLgMA.

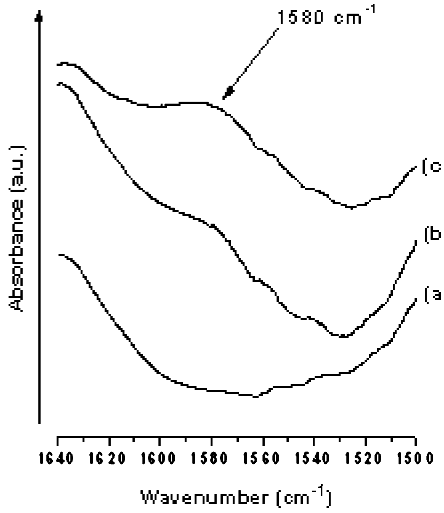


Figure 6. Infrared spectra in absorbance of PCLgMA (a), PCLgMA/LDH1 (b), and PCLgMA/LDH2 (c).

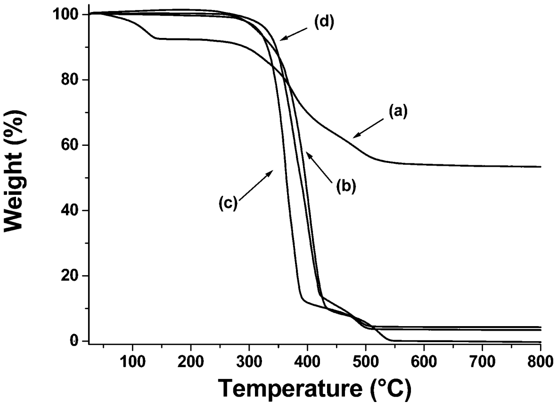


Figure 7. Thermogravimetric curves of LDH (a), PCLgMA (b), PCLgMA/LDH1 (c), and PCLgMA/LDH2 (d).

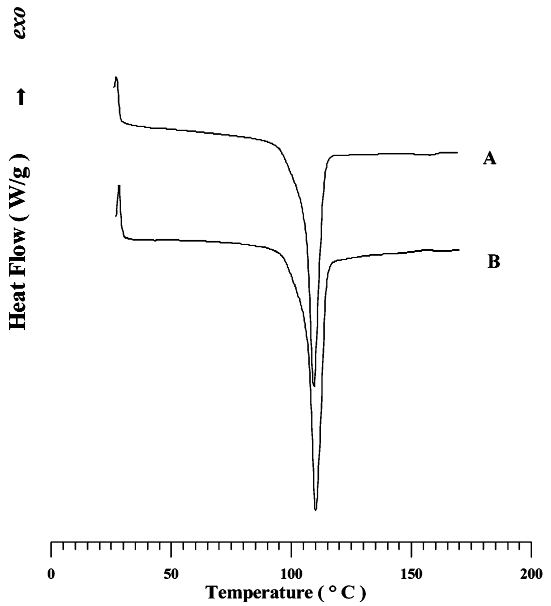


Figure 8. DSC curves for PCLgMA/LDH1 (A) and PCLgMA/LDH2 (B).

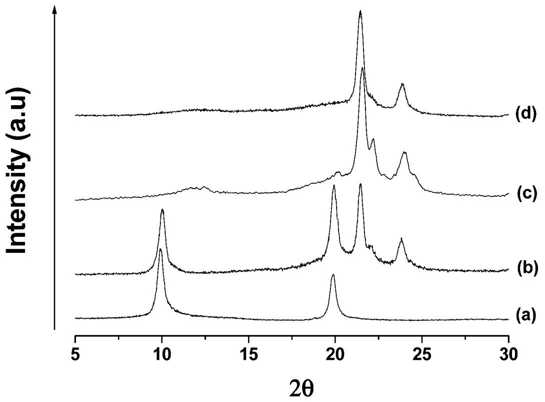


Figure 9. X-ray powder diffraction patterns of LDH (a), PCL/LDH (b), PCLgMA/LDH1 (c), and PCLgMA/LDH2 (d).

sample appears well crystallized, with a crystallinity even better that the pristine PCL, confirming the DSC results.

Composites of PCL and PCLgMA with LDH. LDHs are able to exchange the counteranions in the interlayer galleries with other anions present in a solution in which they are dispersed. The exchange reaction is regulated by the selectivity of the host for the various counteranions, the concentration, and the temperature. Early studies have demonstrated the following selectivity scale: $CO_3^{2-} > SO_4^{2-} \gg OH^- > F^- > Cl^- > Br^- > NO_3^- > ClO_4^-$.[15]

Nitrate or perclorate anions are the less held counterions, and so LDHs containing these counteranions are the most suitable precursors for the uptake of long-chain carboxylate anions. On the basis of this observation, the original carbonate form of Mg/Al LDH was converted into the nitrate form, which, in turn, was equilibrated with a basic solution of PCLgMA at the reflux temperature, to perform the ion-exchange reaction. To investigate if this reaction occurred with the hydrolyzed maleate, we performed an infrared analysis, and in Figure 6 we show the FTIR spectra, in absorbance, for samples PCLgMA (a), PCLgMA/LDH1 (b), and PCLgMA/LDH2 (c) in the interval 1500−1640 cm^{-1}. In this range, the spectra of the composite samples show the antisymmetric $\nu_{C=O}$ mode of the carboxylate group at around 1580 cm^{-1}, absent in the pristine PCLgMA sample. This absorbance peak, visible in both composite samples, testifies the presence of COO^- anions and therefore suggests an ionic bond with the positively charged inorganic lamellae of the hydrotalcite.[37] The symmetric $\nu_{C=O}$ mode between 1300 and 1420 cm^{-1} is hidden by PCL bands in this range. The presence of the antisymmetric $\nu_{C=O}$ mode supports the hypothesis that the carboxylic functionalities grafted to the polycaprolactone chains were bond to the inorganic lamellae through ionic bonds.

The composites were analyzed by thermogravimetric analysis to determine either the content of the inorganic component after the thermal degradation in air up to 800 °C or the degradation temperature. In Figure 7, we show the thermogravimetric curves of the initial LDH in nitrate form (a), PCLgMA (b), PCLgMA/

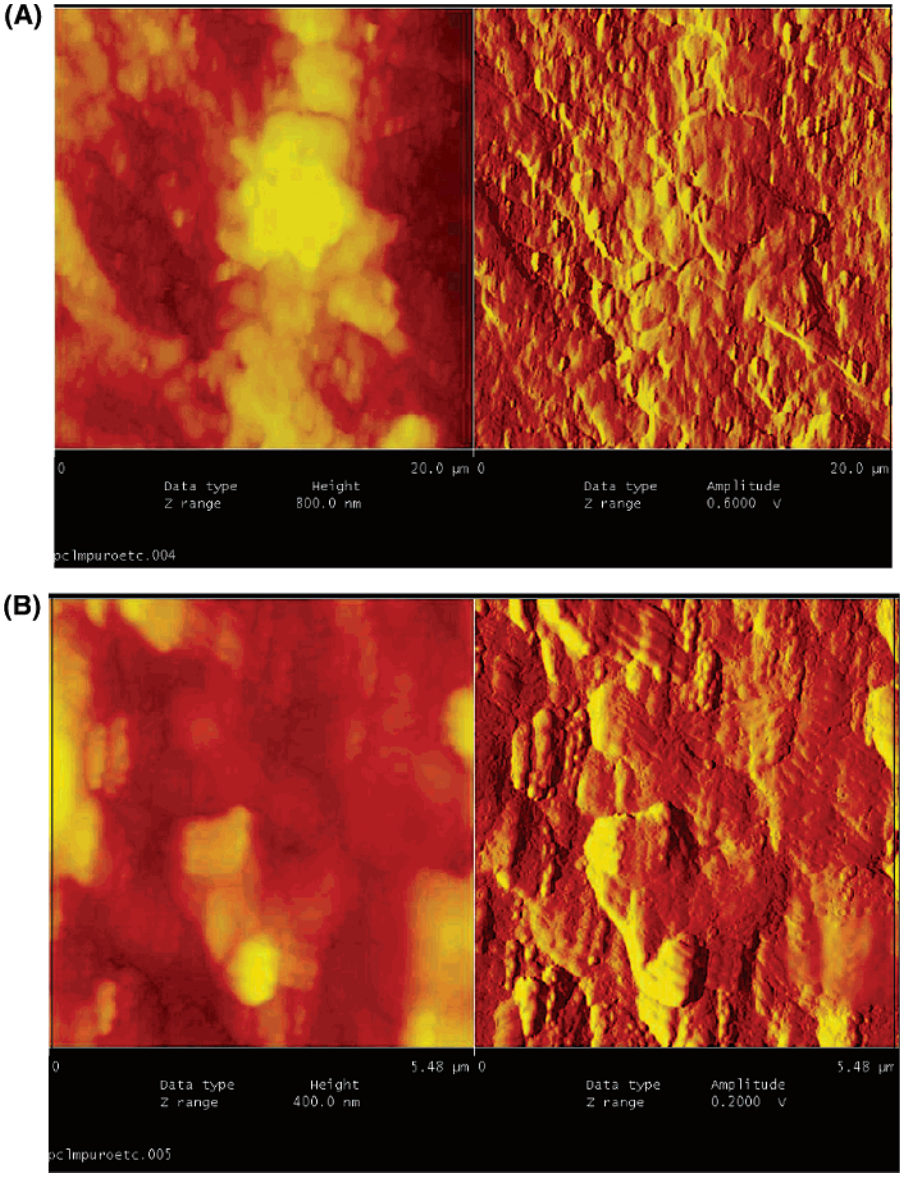


Figure 10. Tapping mode AFM images of PCLgMA at two magnifications: 20 μm (A) and 5 μm (B).

LDH1 (c), and PCLgMA/LDH2 (d). In the analysis conditions, it was shown that LDH material is transformed in Mg−Al oxides. The curve of LDH nitrate shows a first weight loss attributable to the loss of cointercalated water (8 wt %) and a second broad weight loss step, between 300 and 500 °C, corresponding to the degradation of the sample up to the formation of metal oxides (58 wt %). The degradation of PCLgMA occurs in two steps centered at 400 and 480 °C, respectively. The shape of the curve for the composites is very similar to that of the parent polymer, although the temperature of the decomposition step is slightly lower. This is due to the presence of LDH, which starts to decompose at a lower temperature. In fact, by increasing the inorganic content (d), we observe a further decrease of the decomposition temperature, even though the behavior is very similar to the pristine polymer, occurring in two stages. The Mg−Al oxides content resulted in 3 and 5 wt % for PCLgMA/LDH1 and PCLgMA/LDH2, respectively.

The thermal transitions of the composites were analyzed by differential scanning calorimetry, and in Figure 8 we report the DSC curves for PCLgMA/LDH1 (A) and PCLgMA/LDH2 (B).

The two composite samples show a much narrower melting range than the pristine polymer (see Figure 4), although at a similar temperature.

Although the quenching temperature and the crystallization conditions were similar for the samples, in the pristine sample a broader distribution of crystal thickness is present, particularly at the lower temperature side.

The values of crystallinity, obtained by dividing the melting enthalpy by the thermodynamic melting enthalpy[39] $\Delta H_o = 136$ J/g, are reported for all of the samples in Table 1. Both the melting temperatures and the crystallinities are alike for all of the samples.

Figure 9 shows the X-ray diffraction patterns of the pure inorganic LDH, with nitrate as counterions (a), the control sample PCL/LDH (b), and the two composites PCLgMA/LDH1 (c), and PCLgMA/LDH2 (d). The diffractogram of pure LDH shows the reflection due to the interlayer distance positioned at $2\theta = 10°$. This value indicates that the sheet−sheet distance in the lamellar sample, perpendicular to the sheet plane (d_{003}), is 0.884 nm. The second peak corresponds to the higher harmonics of the interlayer distance. The diffractogram of not-modified PCL/LDH (control sample) is a superposition of the LDH nitrate

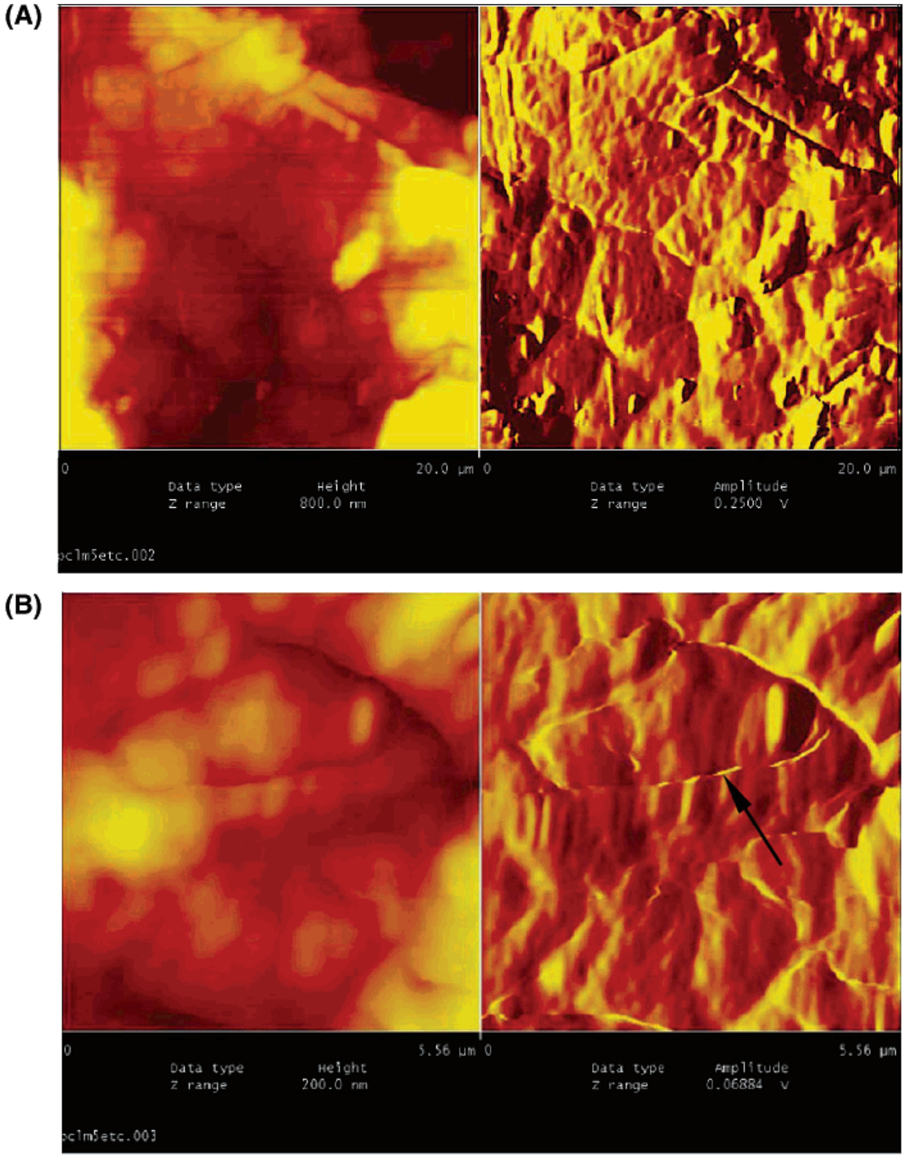


Figure 11. Tapping mode AFM images of PCLgMA/LDH2 at two magnifications: 20 μm (A) and 5 μm (B).

pattern, with the peaks at 10° and 20° of 2θ, and the pattern of PCL, with the peaks at 21.6°, 22.1°, and 24.1° of 2θ, all typical of crystalline PCL. At variance, in the diffractograms of the composite with PCLgMA, the peaks of LDH nitrate are completely absent, and only in sample PCLgMA/LDH2 is a very broad and low-intensity peak observable in the interval 11.5−12.5° of 2θ. This peak is possibly due to a small fraction of carbonate anions exchanged with nitrate ones during the reaction. As a matter of fact, LDH carbonate shows its interlayer distance at 12.3° of 2θ. The X-ray results could indicate that PCLgMA went into the LDH structure, exfoliating the lamellae and forming ionic bonds with the positive charges. This phenomenon did not occur with non-modified PCL (control sample), in which no groups are present that can be transformed in anions. However, because in the X-ray diffractogram we are not able to detect peaks at angles lower than 2° of 2θ, we cannot exclude the formation of ordered structures, in which the polymer intercalated the inorganic lamellae, increasing their basal spacing to values higher than 4.5 nm, corresponding to 2° of 2θ. Also, in this case, we would not see any peak in the wide angle diffractogram. In any case, however, this result is a strong support to the suggestion that the two samples PCLgMA/LDH1 and PCLgMA/LDH2 were able to exchange the anions present into the lamellae of the pristine sample, by a direct insertion of the modified polymer on the inorganic positively charged lamellae, forming nanocomposites either intercalated or exfoliated.

To better study the morphology and the dispersion of the inorganic compound in PCLgMA, we performed an atomic force microscopy characterization on the initial PCLgMA and on the nanocomposite PCLgMA/LDH2.

The AFM images of the reference sample PCLgMA are shown in Figure 10 at two magnifications (A and B). The etching procedure erased the amorphous component on the surface, enlightening the lamellar structure of the reference sample. The lamellae are well visible at a higher magnification (B), where groups of parallel lamellae are assembled in bigger domains with different orientation. The thickness of the lamellae varies between 100 and 130 nm. No spherulitic morphology is apparent in the reference sample.

The morphology of the nanocomposite PCLgMA/LDH2 is interesting and is shown at two magnifications in Figure 11. Also, in this case, we observe a lamellar morphology, characterized by groups of parallel crystals, in some cases scaled off in terraces. They appear of larger dimensions and generally more homogeneous than the reference PCLgMA, confirming the DSC results. They range between 130 and 150 nm. Some crystalline domains, characterized by different orientation of the lamellae, show narrow fissures at the edge, due to the inorganic LDH removed by the oxidant solution. These fissures are homogeneously distributed in the polymeric matrix, marking the boundary between lamellae with different orientation, and are clearly visible in the higher magnification picture (see the arrow in B). They are very thin and well separated, indicating that intercalated groups of lamellae are present in the composite sample.

Considering that in the X-ray diffractogram the basal spacing of the lamellar inorganic is not present, this AFM result indicates that stacked hydrotalcite sheets containing the polymer must have spacings higher than 4.5 nm, as discussed in the X-ray section. The lateral dimension of these fissures varies in a narrow range, between 100 and 140 nm, and therefore they could contain 20−25 intercalated lamellae. It is worth recalling that the AFM resolution is not able to show exfoliated lamallae that have dimensions lower than 1 nm. In conclusion, AFM demonstrates that nanometer stacks of these sheets embedded in a highly textured PCLgMA matrix were present in the composite sample. No large hydrotalcite aggregates are visible in any place of the sample, and this result corroborates the suggestion that the ionic exchange reaction led to either exfoliated or intercalated nanocomposites.

Conclusions

We succeeded in incorporating a hydrotalcite-like solid constituted of magnesium−aluminum hydroxide layers, by an ionic exchange procedure into a chemically modified polycaprolactone. Polycaprolactone (PCL) was chemically modified by grafting maleic anhydride on it, through a radical reaction induced by benzoyl peroxide as initiator. To improve the grafting degree, a second unsaturated comonomer such as glycidyl methacrylate (GMA) was added, demonstrating a good reactivity in melt grafting without leading to long grafted chains. The exchange reaction was led with mild conditions, and two samples characterized by 3 and 5 wt % of LDH (determined as oxides at 800 °C) were obtained. The infrared spectra of the composites showed the antisymmetric $\nu_{C=O}$ mode of the carboxylate group, absent in the pristine PCLgMA sample. This absorbance peak, visible in both composite samples, unequivocally testifies the presence of COO^- anions and therefore suggests an ionic bond with the positively charged inorganic lamellae of the hydrotalcite. This result supported the hypothesis that the maleic anydride, grafted to the polycaprolactone chains, was hydrolyzed and the anions were bond to the inorganic lamellae. This was confirmed by X-ray analysis that showed the absence of the peaks of the basal spacing of the inorganic component. At variance, the control sample PCL-LDH showed the peaks of LDH in the X-ray diffractogram and the absence of the carboxylate absorbance in the infrared spectrum. The AFM analysis showed ordered stacks of LDH sheets embedded in a highly textured PCLgMA matrix. The ionic exchange reaction between an inorganic layered double hydroxide and a chemically modified PCL led to the formation of nanocomposites, either exfoliated or intercalated, characterized by a well-developed crystallinity of the polymeric matrix and a good dispersion degree of the inorganic lamellae.

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