Encapsulation and Exfoliation of Inorganic Lamellar Fillers into Polycaprolactone by Electrospinning

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The present paper reports, for the first time, the successful fabrication of layered double hydroxide (Mg−Al LDH)-reinforced polycaprolactone (PCL) nanofibers by electrospinning. Either the LDH in carbonate form or an LDH organically modified with 12-hydroxydodecanoic acid (LDH-HA) were incorporated into PCL and electrospun using a voltage of 20 KV. The LDH-HA was prepared by an ionic exchange reaction from pristine LDH and encapsulated into PCL from acetone solutions at 15 wt %. The morphological analysis showed pure PCL fibers with an average diameter of 600 ± 50 nm, and this dimension was maintained in the fibers with LDH, with the inorganic component residing outside the fibers and not exfoliated. At variance, the fibers with the LDH-HA showed a significantly lower average diameter in the range of 350 ± 50 nm, indicating the improved electrospinnability of PCL. Moreover, the inorganic lamellae were exfoliated, as shown by X-rays and residing inside the nanofibers as demonstrated by energy dispersive X-ray spectroscopy analysis. The structural parameters, such as degradation temperature and crystallinity, were investigated for all the samples and correlated with the electrospinning process.

Introduction

The manufacturing of structured polymeric fibers with diameters in the submicrometer range down to a few nanometers has generated considerable technological interest. In this range of dimensions, there appear several amazing characteristics such as very large surface area to volume ratio, variations in the wetting behavior, modifications of the release rate, or a strong decrease in the concentration of structural defects on the fiber surface, leading to superior mechanical performance (e.g., stiffness and tensile strength) compared with any other known form of the material.

These outstanding properties make the polymer nanofibers optimal candidates for many important applications, such as ultrafiltration, protective clothing, composite-fiber-reinforced materials, biomedical applications (tissue engineering, drug release systems), fibers loaded with catalysts, core/shell fibers for optical applications (waveguides), or nanocables for microelectronics applications.

Traditional methods of polymer fiber production include melt spinning, solution spinning and gel state spinning. These methods rely on mechanical forces to produce fibers by extruding a polymer melt or solution through a spinneret and subsequently drawing the resulting filaments as they solidify or coagulate. By using these methods, typical fiber diameters in the range of 5−500 μm can be produced. The consistently producible minimum fiber diameter is on the order of a micron. At variance, the electrospinning technology allows the production of much lower dimension fibers.

Electrospinning is not a new technology for polymer fiber production, being known since the 1930s;[1] however, it is nowadays gaining renewed interest for filtration and biomedical applications. An important characteristic of electrospinning is the ability to make fibers with diameters in the range of nanometers to a few microns.[2−4] Consequently, these fibers have a large surface area per unit mass so that nanowoven fabrics of these nanofibers collected on a screen can be used, for example, for the filtration of submicron particles in separation industries and for biomedical applications,[5−6] such as wound dressing in the medical industry, tissue engineering scaffolds, and artificial blood vessels.

In the past decade, biodegradable and biocompatible polymers have received significant attention because they are environmentally friendly and are extensively used in biomedical applications. In this direction, poly(ϵ-caprolactone) (PCL) is one of the most promising polymers, and it can be used in many medical applications, such as drug delivery, scaffolds, and guided bone regeneration.[7−8]

On the other hand, there are few studies about the electrospinning of polymer/ layered inorganic nanocomposites. Poly(lactic acid),[9] Nylon 6[10] and poly(methyl methacrylate-*co*-methacrylic acid)[11] are some of the polymers that have been used for the preparation of nanocomposite fibrous membranes.

In the present work, membranes composed of nanosized fibers, either of neat PCL, or PCL in which inorganic and organomodified layered double hydroxides (LDHs) are encapsulated by electrospinning, are presented. The structure of LDHs originates from the packing of layers built up in a manner similar to that found in brucite, the naturally occurring $Mg(OH)_2$.[12−13] In this mineral, the Mg atoms are octahedrally coordinated by six oxygen atoms belonging to six OH groups; each OH group is, in turn, shared by three octahedral cations and points the hydrogen atom to the interlayer space. When some of the Mg(II) cations are isomorphously replaced by Al(III) cations, the

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substitution creates positive charges balanced by the presence of counteranions located in the interlamellar region.[14−15] The ability to replace these anions by simple ion-exchange procedures makes LDHs a unique class of layered solids to be used as a host of active molecules. We used both inorganic and organically modified LDH for introducing into PCL by electrospinning. The ability introduced into LDH to drug molecules makes these composites very attractive for many biomedical fields such as membranes and suture threads with controlled release. The fibrous structure, containing the inorganic samples, was investigated as a function of the solution concentration, the applied voltage, and the inorganic content.

Experimental

Materials. The PCL was kindly supplied by Solvay (CAPA 6501; $M_n = 50\,000$), as was the commercial hydrotalcite (carbonate form) (LDH) magnesium aluminum hydroxycarbonate $Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$ (basal spacing 3.83 Å) was purchased from Aldrich, and the hydrotalcite modified with the organic residue (12-hydroxydodecanoic acid) (LDH-HA) (basal spacing 22.7 Å) was obtained according to a previously reported procedure.[15] 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 ammonium carbonate from urea.[14] The precursor was converted in nitrate form, of formula $Mg_{0.66}Al_{0.34}(OH)_2\ (NO_3)_{0.34}\cdot 0.62H_2O$, 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.

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 THF. A 55.2 mmol (5.05 g) portion of LDH in nitrate form was added to the 12-hydroxydodecanoic acid 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 centrifuged two more times. The product was finally filtered and dried at 80 °C.

Processing for Obtaining the Nanocomposites: High-Energy Ball Milling (HEBM) Experiments. The powder mixtures were obtained using HEBM technology. Such a process has been revealed as an alternative and innovative strategy that ought to involve an efficient mixing of two or more species by mechanical milling, avoiding high temperatures and solvents.[16,17]

In every single experiment, hydrotalcite powder (1%, 5% wt/wt) and PCL were milled in the solid state in a Retsch (Germany) centrifugal ball mill (model S 100). Mass samples were milled in a 50 cm^3 cylindrical steel jar with five steel balls of 10 mm diameter. The rotation speed used was 580 rpm, and the milling time was fixed to 60 min.

Electrospinning Procedure. Electrospinning of PCL fiber was carried out at room temperature at a high voltage of 20 kV (HV Power Supply, Gamma High Voltage Research, Ormond, FL). The spinneret used in the experiments had an inner diameter of 0.8 mm. A copper wire was mounted in the spinneret and used as the positive electrode. Grounded aluminum foil was used as the counter electrode and mounted at a distance of 20 cm from the spinneret. Continuous PCL fibers were collected on the aluminum foil in the form of a fibrous mat. Electrospinning conditions were optimized to produce PCL nanofibrous mats composed of individual fibrils less than 1000 nm in diameter and without bead formation.

Also, 15% (wt/wt) of pure PCL, 15% (wt/wt) of composites formed by PCL, and 1% and 5% (wt/wt) of inorganics were stirred vigorously for 1 h until complete dissolution in acetone and then spun.

Methods. *X-ray Diffraction (XRD) Measurements.* XRD measurements were carried out on the spun samples with a Brucker diffractometer (equipped with a continuous scan attachment and a proportional counter) with Ni-filtered Cu Kα radiation ($\lambda = 1.54050$ Å).

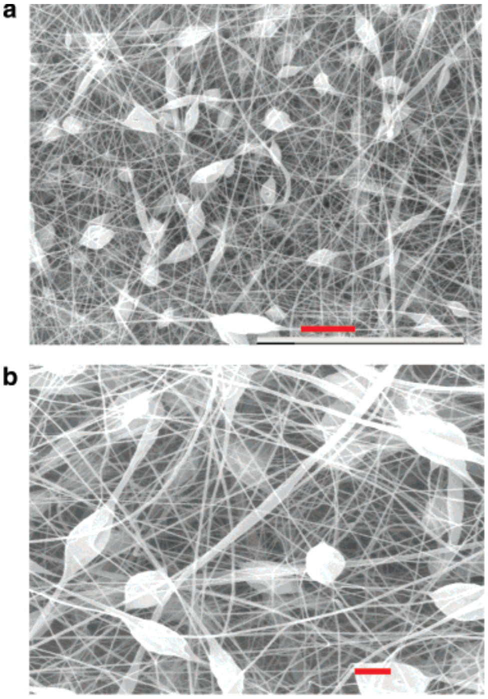

Figure 1. SEM micrographs of electrospun fibers: (a) 10 wt % PCL in acetone solution and (b) 12.5 wt % PCL in acetone solution, (magnification bar: 10 μm).

Thermogravimetric Analysis. Thermogravimetric analysis was performed with a thermogravimetric analyzer SDTQ TA Mettler with a 5 K·min^{-1} heating rate, under flowing air between 25 and 900 °C.

Differential Scanning Calorimetry (DSC). DSC measurements were carried out using a thermal analyzer Mettler DSC 822/400 at a heating rate of 10 °C/min between −50 and 200 °C.

Scanning Electron Microscopy (SEM). The morphology and diameter of the electrospun nanofibers were determined with a scanning electron microscope (SEM; JEOL JSM-T300). A small section of the fiber mat was placed on the SEM sample holder and sputter-coated with gold prior to the analysis.

Energy Dispersive X-ray Spectroscopy (EDX). Some samples were also characterized by microanalysis to investigate their chemical structure. Elemental analysis and element mapping were conducted with a field-emission scanning electron microscope (FESEM, model LEO 1525, Carl Zeiss SMT AG, Oberkochen, Germany) equipped with an EDX spectroscope (INCA Energy 350, Oxford Instruments, Witney, United Kingdom).

Results and Discussion

Morphology of the Pure and Composite Samples. As a first parameter, we investigated the type of solvent, choosing the solvents according to the solubility parameters that give indication of the interactions between polymer and solvent. Among the solvents used (dichloromethane−methanol, chloroform−methanol, THF, and acetone), the best was found to be acetone, which is a medium hydrogen-bonded solvent with a solubility parameter of 10 (cal/cm^3)$^{1/2}$. Dissolving PCL in this solvent, we tried different concentrations, with a distance of the needle from the screen of 10 or 20 cm, alternatively. The concentration of the PCL solutions influences the spinning of fibers and controls the morphology. The formation of beads along the fiber took place at low PCL concentrations (Figure 1a,b). As the concentration of PCL was increased, continuous nanofibers without beads formation were obtained by electrospinning from 15 wt % solutions.

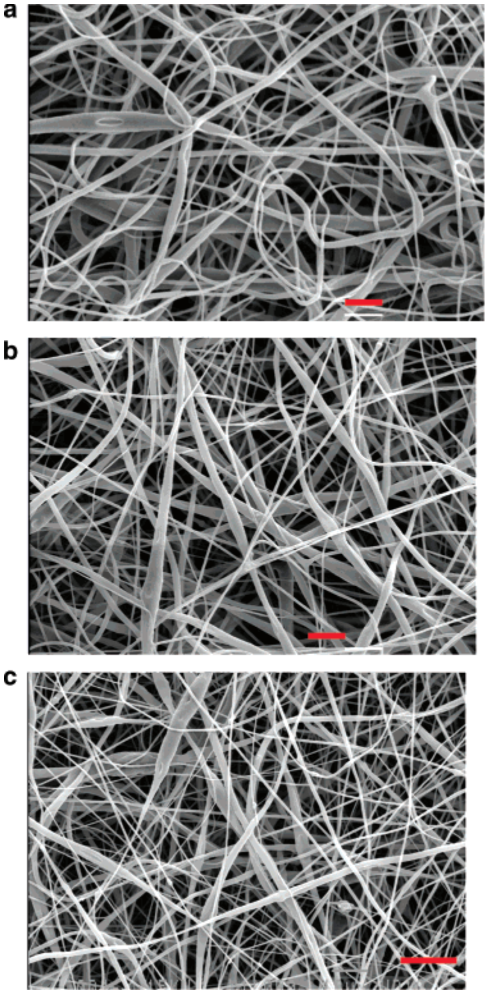

Figure 2. SEM micrographs of electrospun fibers (applied voltage 20 kV, solution concentration 15 wt %): (a) PCL, (b) PCL + 1% LDH, and (c) PCL + 5% LDH, (magnification bar: 10 μm).

Analyzing the experimental results, we chose a concentration of 15%, with a distance of 20 cm, to spin either the pure PCL or the composites, and in Figure 2a we show the obtained fibers.

The nanofibrous structure of the sample is evident, which is composed of individual, uniform, and randomly oriented fibers with an average diameter of 600 ± 50 nm.

Then LDH layers were dispersed into PCL solution, which was subsequently electrospun. Successful PCL in solution was spun with 1 wt % and 5 wt % LDH, as shown in Figure 2b,c. The presence of the inorganic component caused no noticeable change in the morphology and average fiber diameter of the nanofibers.

A series of PCL nanofibers with the addition of 1−5 wt % acid-modified filler (LDH-HA) were also fabricated by electrospinning processing. Figure 3a,b shows the electrospun nanofibers of composite PCL + LDH-HA with 1 wt % LDH-HA with different magnitudes. Figure 3c,d shows the composite of PCL + LDH-HA with 5 wt % LDH-HA with different magnitudes. The addition of the LDH-HA intercalation compound resulted in electrospun nanofibers with significantly lower average diameter, in comparison with PCL or PCL−LDH nanofibers, in the range of 350 ± 50 nm.

Thus, it is most probable that the dispersion of LDH-HA structures improved the electrospinnability of the mixture, as denoted from the lower average diameter of nanofibers obtained. LDH-HA is predominantly exfoliated and well distributed within the fiber and very likely oriented, as shown later.

To determine the structural organization of the inorganic component of either LDH or LDH-HA in the PCL fibers, we determined the chemical structures on the surface of the composite fibers with FESEM−EDX. In Figure 4 we show the EDX micrographs of electrospun fibers PCL + 5% LDH. Besides the elements always appearing in the micrographs (such as Fe and Cr due to the iron support of the samples and the coating of the samples with Cr), we observe the peaks of Mg and Al, indicating the presence of the inorganic component on the surface of the fibers. This means that LDH with carbonate does not interact with PCL in solution and is simply deposited

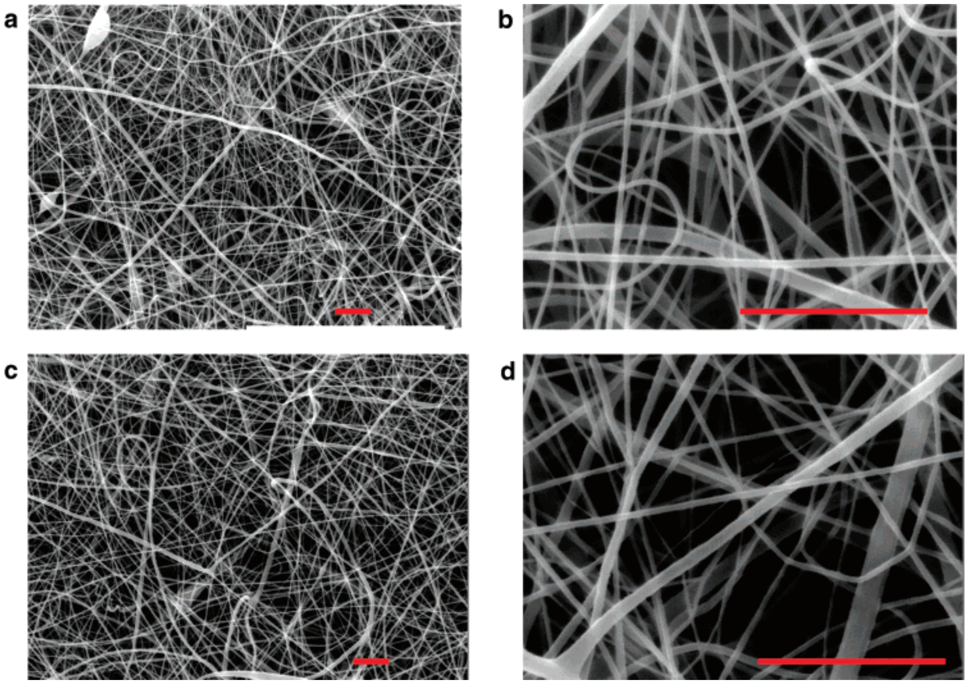

Figure 3. Electrospun nanofibers of composite PCL + LDH-HA with 1 wt % LDH-HA with different magnitudes (a,b). Panels c and d show the composite of PCL + LDH-HA with 5 wt % LDH-HA with different magnitudes, (magnification bar: 10 μm).

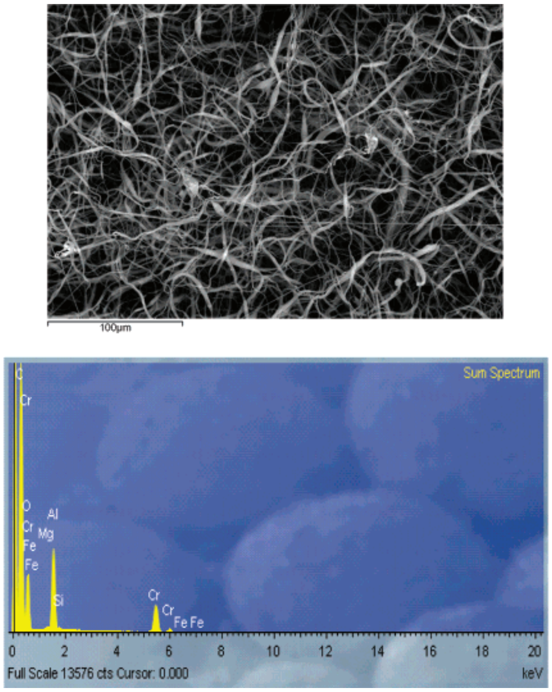

Figure 4. FESEM along with an EDX micrograph of electrospun fibers PCL + 5% LDH.

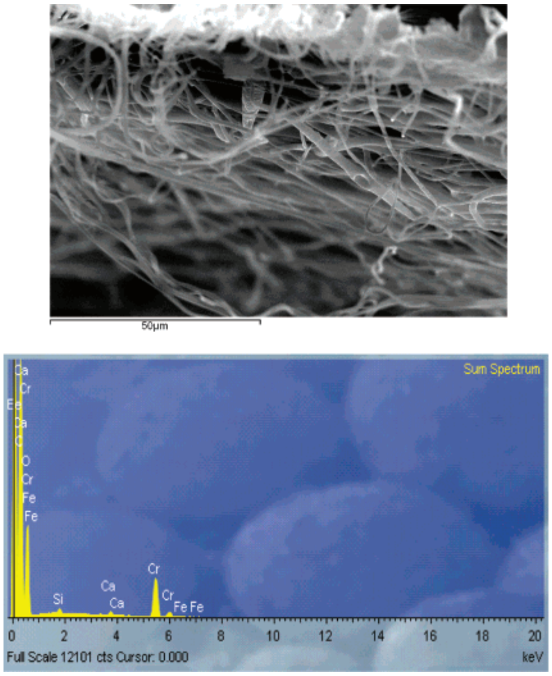

Figure 5. FESEM along with an EDX micrograph of electrospun fibers of the surface of PCL + 5% LDH-HA.

on the surface of the fibers during the PCL spinning. At variance, in Figure 5, where the fibers of PCL + 5% of LDH-HA are shown, we observe the absence of the peaks (Mg, Al) on the surface of the fibers. In this case, to ascertain whether the inorganic hybrid is located inside the fibers, we submitted the sample to a thermal oxidation up to 450 °C, followed by an EDX observation. In Figure 6 we show the result, pointing out the presence of Mg and Al. This is a clear indication that the hybrid LDH-HA is located inside the fibers. Therefore, when the inorganic component is modified with an organic molecule and able to interact with the polymeric chains in solution, it can be incorporated into the fibers, also changing the fiber dimensions. At variance, when the inorganic is not able to interact with the polymer chains in solution, the polymer is spun without changing the fiber dimensions, and the inorganic is simply deposited on the surface. Either way, we cannot exclude the presence of some microcrystals inside the fibers.

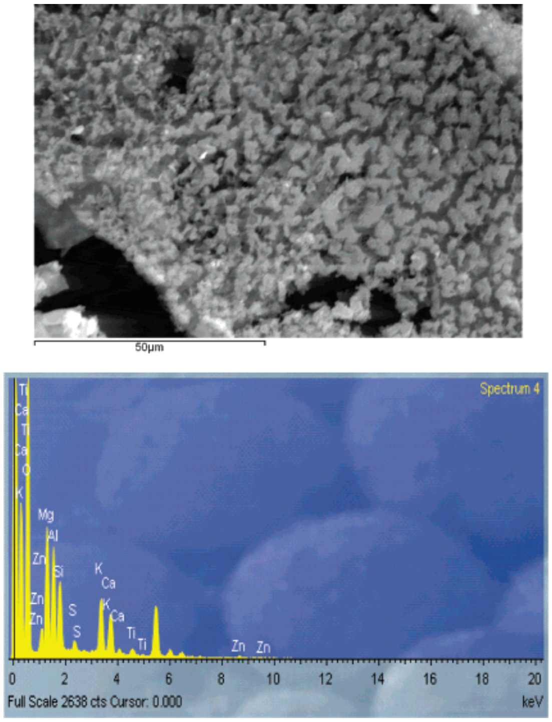

Figure 6. FESEM along with an EDX micrograph, after thermal oxidation up 450 °C, of PCL + 5% LDH-HA composites.

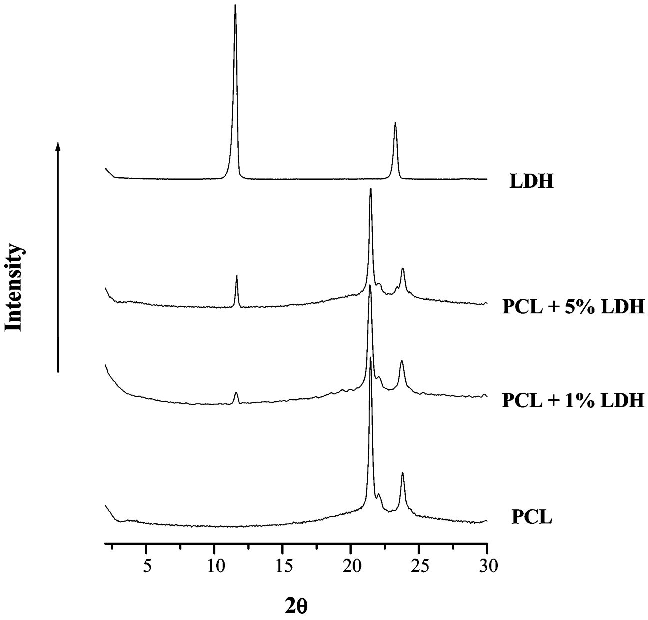

Figure 7. XRD diffractograms of pure PCL, PCL + 1% LDH, PCL + 5%LDH, and pristine LDH.

XRD Diffractograms. Figure 7 shows the XRD diffractograms of pure PCL, PCL + 1% LDH, PCL + 5%LDH, and pristine LDH.

The pure PCL, spun from the 15% solution in acetone, shows the crystalline structure well developed with the main peaks at 21.4° of 2θ and 23.8° of 2θ and a reduced amorphous fraction. The diffractograms of the composite samples show the peak of the LDH basal spacing at 11.6° of 2θ (as evident observing the

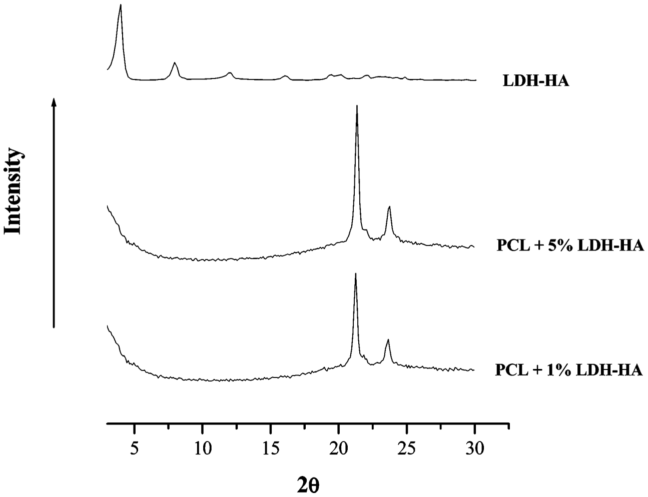

Figure 8. The diffractograms of PCL + 1% LDH-HA, and PCL + 5% LDH-HA, and LDH-HA.

diffractogram of pure LDH), with an intensity increasing upon increasing the inorganic content. This is an indication that the inorganic lamellae are neither exfoliated nor intercalated, but rather formed conventional microcomposites.

We have previously shown that the inorganic component, which is not exfoliated, is simply deposited on the surface of the fibers, and X-rays confirm this result.

In Figure 8 the diffractograms of PCL + 1% LDH-HA, PCL + 5% LDH-HA, and LDH-HA are shown. The LDH-HA shows the peak of the basal spacing at a lower angle with respect to the LDH, that is, 3.9° of 2θ ($d = 22.67$ Å) due to the enlargement of the inorganic lamellae to host the bigger organic molecular anion. However, this peak is not present in the composite samples, and this is a strong indication that the lamellae are exfoliated in the PCL matrix. Also in this case, the previous analysis showing that the inorganic hybrid is located inside the fibers is supported by the X-ray results.

We have thus obtained nanocomposites by electrospinning the polymer with the organically modified hydrotalcite. PCL is crystalline, showing peaks at 21.4° and 23.8° of 2θ, although it seems that there is a higher amorphous fraction.

Thermal Properties. The thermogravimetric analysis was performed for investigating both the degradation temperature and the inorganic content into the fibers. The thermal degradation of pristine PCL and its hybrids with different amounts of LDH and LDH-HA loadings in air atmosphere are presented in Figure 9 (panels a and b, respectively).

PCL thermally degrades to volatile products above 300 °C and ends above 500 °C. It appears that the introduction of even very small amounts (about 1 wt %) of inorganic material anticipates either the onset degradation or the inflection point. Upon increasing the inorganic content, no further decrease in the degradation temperature is observed. The effect of decreased thermal stability is due to the presence of the inorganic component, which decomposes at lower temperatures.

At variance, in the nanocomposites, in which the inorganic lamellae were modified with 5% of the organic molecule, we observe a decrease in the thermal stability either in the onset or in the inflection point. However, this decrease is much lower than that in the previous case. No substantial changes are observed for 1% of the organic molecule, except for a fluctuation in the inflection points.

Figure 10 reports the calorimetric curves (DSC) for all the samples.

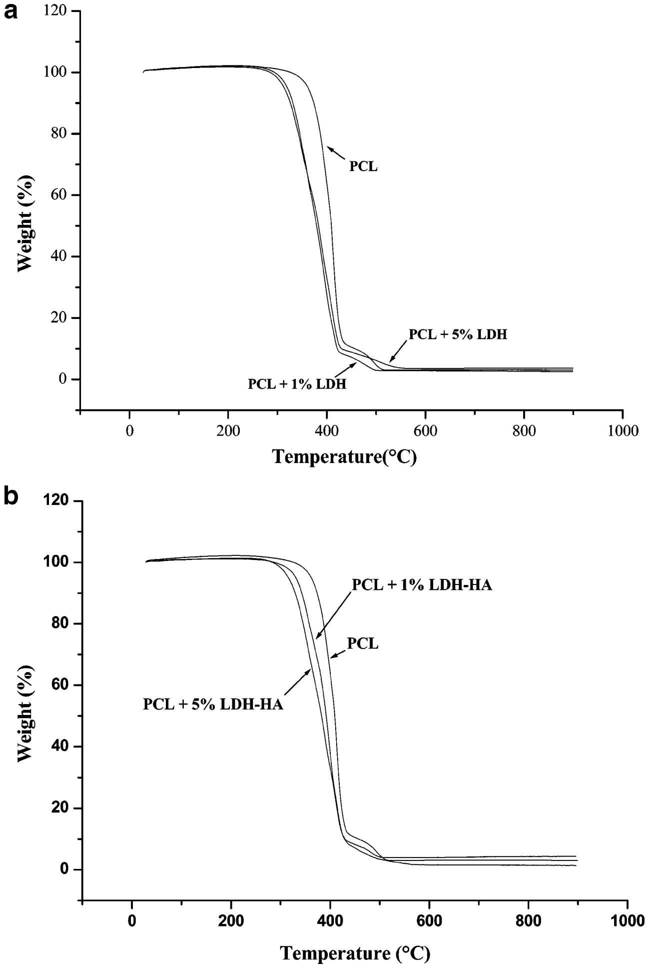

Figure 9. The thermal degradation of pristine PCL and its hybrids with different amounts of LDH (a) and LDH-HA (b) loadings in air atmosphere.

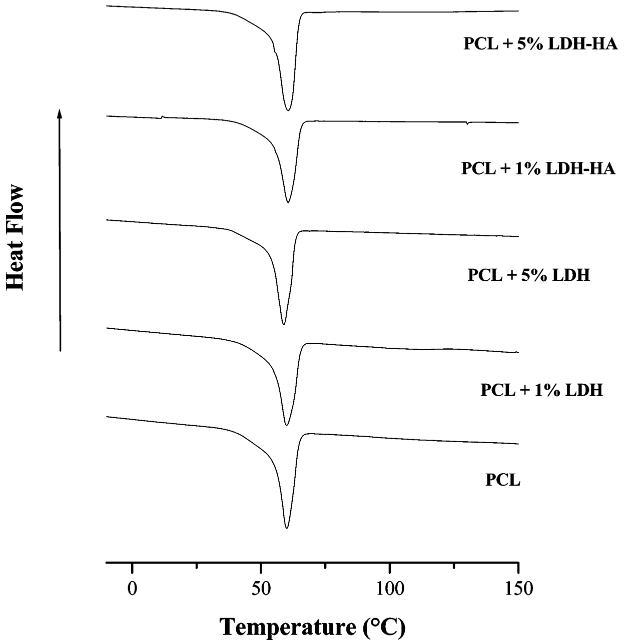

Figure 10. The calorimetric curves (DSC) for all the samples.

We observe the main melting range between 30° and 70 °C, with a peak centered at 60 °C for the pure PCL. Relevant changes are observed neither in the LDH nor in the LDH-HA samples. In Table 1 (Supporting Information), the calorimetric parameters and the results for the degradation temperature and the melting enthalpy are reported for all the samples. We observe a decrease in both parameters in the PCL−LDH microcomposites, whereas the nanocomposites show a lower decrease of the crystallinity and a smaller decrease in the degradation temperature.

Conclusions

We have obtained the successful fabrication of LDH-reinforced PCL nanofibers by electrospinning. Both a completely inorganic LDH carbonate and one organically modified with 12-hydroxydodecanoic acid (LDH-HA) were incorporated into PCL using HEBM, which has been proven to be an efficient and unconventional technique to produce composites and nanocomposites avoiding high temperatures and solvents. The organically modified LDH-HA was prepared by an ionic exchange reaction from pristine LDH and encapsulated into PCL from acetone solution at 15 wt %. The morphological analysis showed, in the case of pure PCL, fibers with an average diameter of 600 ± 50 nm, and this dimension was maintained in the fibers with LDH carbonate, with the inorganic component residing outside the fibers and not exfoliated. At variance, the fibers with the organically modified LDH-HA showed a significantly lower average diameter in the range of 300 ± 50 nm, indicating improved electrospinnability of PCL. Moreover the inorganic lamellae were exfoliated and residing inside the nanofibers, as shown by X-rays and EDX analysis.

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Supporting Information Available. Calorimetric parameters and complexive results for the degradation temperature and melting enthalpy of all samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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