Fibrous Scaffolds by Electrospinning of Poly(ε-caprolactone)/Layered Silicate Nanocomposites

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Abstract–Polymer nanocomposites, based on poly(ε-caprolactone) (PCL) with various contents of organically modified montmorillonite, were fabricated by the solvent casting method. The morphology of the prepared materials was investigated by X-ray diffraction (XRD) and their thermal behavior was analyzed by thermogravimetric analysis (TGA). Membranes consisted of nanosized fibers of pure and nanocomposite PCL were prepared by electrospinning. The effect of the solution concentration, the applied voltage, and the clay content on the final fibrous structure was investigated by scanning electron microscopy (SEM).

I. INTRODUCTION

In the past decade, biodegradable and biocompatible polymers have received significant attention because they are environmentally friendly and are extensively used in biomedical applications [1].

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 and guided bone regeneration [2].

Guided bone regeneration approach to repair mandible and bone defects infected by periodontal diseases is based on the use of polymeric membranes that encourage the bone growth and prevent the growth of non-functional scar tissues [3]. These membranes are usually utilized along with dental implants or bone grafting materials.

Nowadays, conventional, non-biodegradable polymers, such as polytetrafluoroethylene, but also biodegradable polymers, such as polylactic acid, are used. The main advantage of using biodegradable polymers is that no second surgery procedure is needed in order to remove the membrane [3].

These membranes must meet some basic requirements such as (a) proper degradation rate, (b) osteoconductivity and (c) proper mechanical properties. In order to achieve these requirements composite materials have attracted considerable attention. The introduction of some inorganic fillers (such as calcium phosphate and calcium carbonate) can improve the osteoconductivity of the polymer matrix [3]. Also the incorporation of a small quantity of inorganic nanosized materials with a high aspect ratio, such as clay platelets, can significantly improve mechanical and physical properties of the polymer [4].

Recently, the potential of electrospinning has been introduced as an alternative technique in fabrication of scaffolds for soft tissue cell transplantation and hard tissue regeneration. This technique provides membranes with fiber diameter ranging from few nanometers to few micrometers. The final fibrous structure can be tailored by altering the concentration of the polymer solution, the applied voltage, the distance between the injection and the collecting point, the spinneret geometry, and the solution flow rate [5].

During the last decade various polymers, mostly dissolved in solvents but some also from melts, have been successfully electrospun into ultra fine fibers [6]. On the other hand, there are few studies about the electrospinning of polymers/layered silicate nanocomposites. Poly(l-lactic acid) [7], Nylon 6 [8] and Poly(methyl methacrylate-co-methacrylic acid) [9] are some of the polymers that were used for the preparation of nanocomposite fibrous membranes.

In the present work, membranes consisted of nanosized fibers, of neat PCL and PCL reinforced by organomodified montmorillonite were prepared by electrospinning. The final fibrous structure was investigated as a function of the solution concentration, the applied voltage and the clay content.

II. EXPERIMENTAL

A. Materials

PCL (Mn=80000) was obtained from Aldrich (PCL 440744), dichloromethane (>99.9% purity) from Fluka Chemie. The organically modified montmorillonite, Cloisite 25A, was purchased from Southern Clay Products, Inc.. It was prepared by ion exchange reaction of natural montmorillonite with dimethyl, hydrogenated tallow, 2-ethylhexyl ammonium salt. This modified clay contains 32-33% of organic material.

B. Preparation of nanocomposites

Nanocomposites were fabricated by the solution casting technique. Initially, the organomodified clay was dispersed in dichloromethane. Then the polymer was added and the mixture was sonicated for 1h, using a Branson Sonic Power s125 sonicator. Eventually, the mixture was cast onto Petri dishes and kept for 24 h in a dichloromethane atmosphere achieving a slow solvent evaporation. Then, nanocomposite films were dried under vacuum at 40°C for 24h. The clay content of the produced film was 1, 3, 5, 9 and 15 wt %.

B. Electrospinning processing parameters

The electrospinning setup consists of a syringe pump for the injection of the polymer solution, a rotating drum for
the collection of the fibers and a high voltage supply.

All experiments were performed using a glass syringe of 10 mL internal volume and 1 mm (18G) needle diameter. The flow rate was controlled by the syringe pump and was equal to 0.38 ml/hr. The needle was connected to a high voltage supply and the ground electrode was connected on the conductive surface of the rotating drum. The distance between the needle and the drum surface was 7 cm and the applied voltage was ranged between 5-20 kV. Dichloromethane was used as a solvent for the preparation of the neat polymer and nanocomposite polymer solutions.

**D. Characterization**

The morphology of the nanohybrids was investigated by XRD analysis using a Siemens D 500 diffractometer and Ni-filtered CuKα radiation (λ=0.154nm). The scanning range was varied from 2θ=2° to 30°.

Thermal degradation studies were conducted with a Shimadzu TGA-50. Temperature scans were carried out at a heating rate of 10 °C/min under constant nitrogen flow of 20 cm³/min. The samples were heated up to 750 °C.

The membrane structures were explored by Scanning Electron Microscopy (SEM, JEOL, mod. JSM-840A). All surfaces were coated with graphite to avoid charging under the electron beam. The fiber size distributions were obtained using image analysis with the use of appropriate software.

**III. RESULTS AND DISCUSSION**

**A. Nanocomposite structure**

Fig. 1 describes the results of XRD analysis in the range of 2θ=2-30°. The mean interlayer spacing d_{(001)} for organically modified montmorillonite is 1.96 nm. In the case of nanocomposites, the peak referred to the basal spacing of the inorganic material, is shifted to 2θ=3.4° indicating that polymer chains have diffused into the layered silicate galleries expanding the (001) plane of the silicate layers to 2.6 nm.

With increasing the clay content the intensity of the peaks increases and a small angle appears at 2θ=6.65° which is due to the spacing d_{(002)} of the intercalated silicate sheets [10].

**B. Thermal stability**

The thermal degradation of pristine PCL and its hybrids with different organoclay loadings in inert atmosphere are presented in Fig. 2. PCL thermally degrades to volatile products above 300°C. Fig. 3 describes the relation of the clay content with the onset decomposition temperature (T_{onset}) of the hybrid. T_{onset} is considered to be the temperature that the material loses 2% of its weight. It appears that introduction of very small amounts (about 1 wt %) of organophilic inorganic material improves the thermal stability of the polymer delaying the polymer mass loss. Increase of the clay loading destabilizes the polymer matrix decreasing the temperature of the decomposition initiation. This must be attributed to the increment of the ammonium cation content, which decomposes at lower temperatures compared to the pristine polymer [11].
C. Effect of solution concentration

The effect of solution concentration on the membrane morphology and the average fiber diameter was studied for four different solutions (4, 7.5, 10 and 13 wt %). All the experiments were performed using pure PCL at constant voltage equal to 15 kV. SEM micrographs of the produced membranes are presented in Fig. 4, while Fig. 5 shows the dependence of the average fiber diameter on the solution concentration. For 4 wt % solution concentration big spherical beads in combination with thin fibers were observed (Fig. 4a). Membranes with fine fiber structure were observed for all other concentrations (Fig. 4b-d). In all cases the increment of the solution concentration resulted in the increase of the average fiber diameter (Fig. 5). These findings were observed in many studies and were attributed to the solution viscosity, which is proportional to the solution concentration [6].

![Fig. 4 SEM micrographs of electrospun PCL fibers, applied voltage 15 kV, solution concentration: (a) 4 wt %, (b) 7.5 wt %, (c) 10 wt %, (d) 15 wt % (magnification bar: 5 μm)](image)

![Fig. 5 Effect of the solution concentration on the average fiber diameter, applied voltage 15 kV](image)

D. Effect of applied voltage

The effect of the applied voltage on the membrane morphology and the average fiber diameter was studied in the range of 7.5–20 kV. All the experiments were performed using nanocomposite PCL with 9 wt % clay content and 7 wt % solution concentration. Fig. 6 presents the SEM micrographs of the produced membranes, while Fig. 7 shows the dependence of the average fiber diameter on the applied voltage. In all cases, membranes with fine fiber structure, without beads were produced. The results indicated that the applied voltage had no major effect on the average fiber diameter. The latter was slightly increased with increasing voltage (Fig. 7). In general, when a higher voltage is applied, more fluid is ejected, resulting in larger diameter fibers [6].

![Fig. 6 SEM micrographs of electrospun fibers, PCL with 9 wt % clay content, solution concentration 7 wt %, (a) 7.5 kV, (b) 10 kV, (c) 15 kV, (d) 20 kV, (magnification bar: 10 μm)](image)

![Fig. 7 Effect of applied voltage on the average fiber diameter: PCL with 9% wt. clay content, solution concentration 7 % wt.](image)
IV. CONCLUSIONS

In this work, nanosized layered silicates were incorporated into PCL matrix. The thermal analysis revealed that the introduction of very small amounts of clay particles increases the thermal stability of the material. Furthermore, fibrous scaffolds of pure and nanocomposite PCL were successfully prepared by electrospinning. It was observed that fine fibrous structures are not obtained at low solution concentrations. It was also confirmed that increment of applied voltage results only in a slight increase in diameter of the fibers. Finally the presence of the inorganic nanosized filler proved to have a major influence on the final fibrous structure. Introduction of small quantities of clay (up to 5 wt %) leads to more uniform fibrous structures with smaller fiber diameters.

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V. REFERENCES

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