World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:6, No:2, 2012

Physical and Chemical Investigation of Polycaprolactone, Nanohydroxyapatite and Poly (Vinyl Alcohol) Nanocomposite Scaffolds

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***Abstract*—**Aligned and random nanofibrous scaffolds of PVA/PCL/nHA were fabricated by electrospinning method. The composite nanofibrous scaffolds were subjected to detailed analysis. Morphological investigations revealed that the prepared nanofibers have uniform morphology and the average fiber diameters of aligned and random scaffolds were 135.5 and 290 nm, respectively. The obtained scaffolds have a porous structure with porosity of 88 and 76% for random and aligned nanofibers, respectively. Furthermore, FTIR analysis demonstrated that there were strong intramolecular interactions between the molecules of PVA/PCL/nHA. On the other hand, mechanical characterizations show that aligning the nanofibers, could significantly improve the rigidity of the resultant biocomposite nanofibrous scaffolds.

***Keywords*—**Electrospinnig; Nanofibrous scaffold; poly (vinyl alcohol); Polycaprolactone

I. Introduction

ELECTROSPINNING is a highly versatile method to process polymer solutions or melts, into continuous fibers with diameters ranging from a few micrometers to a few nanometers. In the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field and an electric charge is included on the liquid surface due to this electric field. When the electric field applied reaches a critical value, the repulsive electrical forces overcome the surface tension forces. Eventually, a charged jet of the solution is ejected from the tip of the Taylor cone and an unstable jet occurs in the space between the capillary tip and collector which leads to evaporation of the solvent, leaving a polymer fiber [1, 2]. With smaller pores and higher surface area than regular fibers, electrospun fibers have been successfully applied in various fields such as, nanocatalysis, tissue engineering scaffolds, filtration, biomedical, pharmaceutical, optical and environmental engineering [3-9]. There are a wide range of polymers that used in electrospinning and are able to form nanofibers within the submicron range and used for varied applications. For nonwovens produced by electrospinning, the fiber arrangement is of great importance. The orientation of nanofibers along a preferred direction is of interest for structural reinforcement with nanofibers or for tissue engineering to give the cells a preferred growth direction. Aligned fibers can, for example, be obtained by the use of rapidly rotating cylindrical collectors, which either serves as counter electrode or are combined with an electrode [10-12]. The objective of this study was to prepare aligned and random nanofibrous scaffolds of poly (ε-caprolactone) (PCL), Poly (vinyl alcohol) (PVA) and nanohydroxyapatite (nHA) and investigate their chemical and physical characteristics.

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II. Materials and Methods

A. Materials

PVA with molecular weight of 72 KD and 98% degree of hydrolysis was obtained from Merck and used without further purification. PCL with molecular weight of 80 KD and nHA (≤200 nm) were obtained from Sigma-Aldrich. N,N-dimethylformamide (DMF) and chloroform were purchased from Merck.

B. PVA Solution preparation

To obtain electrospinnable solution, 10 % (w/w) PVA was dissolved in de-ionized water and vigorously stirred with a magnetic stir bar at 80 ° C for 5 h, then cooled to room temperature and stirred for 3 h at room temperature to ensure homogeneity.

C. PCL/nHA Solution Preparation

The two-solvent system was exploited to obtain a spinnable PCL/nHA dispersion. HA nanoparticles (10.0 (w/w) %) were dispersed in chloroform/ DMF (85/15 v/v) to form a suspension, then PCL pellets were added to the suspension, and the suspension was homogenized by using ultrasonic vibrator.

D. Nanofibrous Scaffolds Preparation

A double-spinnert electrospinning was used for the preparation of composite nanofibrous scaffolds (Fig.1). The solutions were fed into 5 mL standard syringes attached to a 21-gauge blunted needle using a syringe pump with a rate of 0.5 mL/hr and 0.3 mL/hr for PCL/nHA and PVA solution, respectively. A steel grounded collector was used to collect the electrospun nanofibers in a distance of 15 cm from the needle. Aligned nanofibers were formed using a rotating disk setup

with the same parameters and this rotating disk operated at a speed of 3000 rpm for obtaining well-aligned nanofibers.

E. Morphological Characterization

The morphology of electrospun scaffolds was characterized by scanning electron microscopy (SEM; Vega II XMU instrument Tescan, Czech Republic). Specimens were sputter-coated with gold for 20s and imaged with a back-scattering detector. Fiber diameters of scaffolds were calculated from their respective SEM images using image analysis software (Image J, NIH).

F. Porosity

The apparent density and porosity characteristics of the electrospun scaffolds were calculated using Eqs.(1) and (2), respectively [13].

$$\text{Apparent density of scaffold (g/ cm}^3\text{)} = \frac{\text{Mass of scaffold (g)}}{\text{Area of scaffold (cm}^2\text{)} \times \text{Thickness of scaffold (cm)}} \quad (1)$$

$$\text{Porosity of scaffold (\%)} = \left(1 - \frac{\text{apparent density of scaffold (g/ cm}^3\text{)}}{\text{bulk density of scaffold (g/ cm}^3\text{)}}\right) \times 100 \quad (2)$$

The thickness of aligned and random scaffolds was measured by micrometer. The bulk density of PCL/PVA nanofibrous membrane is known to be 1.24 g cm^{-2} [14].

G. Mechanical Testing

Mechanical properties of aligned and random nanofibrous scaffolds were determined using a universal testing machine (Galdabini, Italy) at ambient temperature using a 10-N load cell under a cross-head speed of 50 mm/min. All samples were prepared in the form of rectangular shape with dimensions of 60 × 10 mm^2 from the electrospun fibrous membranes. At least five samples were tested for each type of scaffolds.

H. ATR-FTIR Spectroscopy

Chemical analysis of electrospun PCL, PVA, PCL/nHA and PCL/nHA/PVA nanofibrous scaffolds was performed by ATR-FTIR spectroscopy. ATR-FTIR spectra of scaffolds were obtained on an Equinox 55 spectrometer (Bruker optics, Germany).

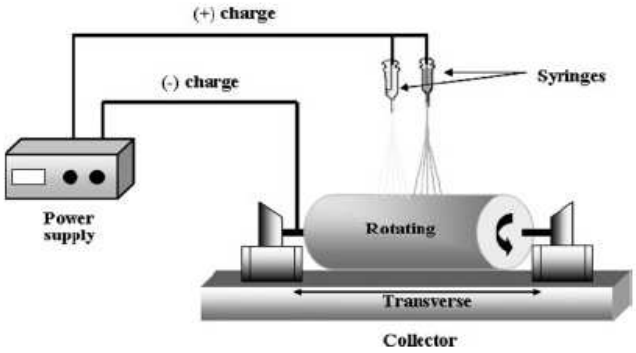


Fig. 1 Schematic diagram of the double-spinneret electrospinning

III. Results and Discussion

A. Morphology of Nanofibrous Scaffolds

SEM micrographs of electrospun nanofibrous scaffolds revealed porous, nanoscaled fibrous structures formed under controlled parameters (Fig.2). Randomely oriented PCL/nHA/PVA nanofibrous scaffold was obtained uniform, bead free nanofibers with mean fiber diameter of 290 nm. Aligned PCL/nHA/PVA nanofibers showed the average fiber diameter of 135.5 nm, comparatively lower than the random fibers. Use of high speed rotating disk setup for the production of aligned nanofibers imparted a smooth surface morphology with highly aligned and fine fibers.

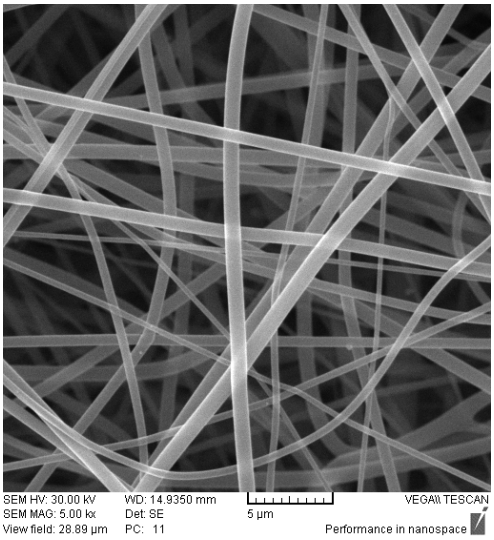
B. Porosity

The porosity of the scaffolds was calculated and it was observed that random fibers had a porosity of 88%, whereas aligned fibers had 76% porosity. The different orientation of the aligned and random fibers leads to different shape of pores between the fibers. Jose et.al [15] reported similar results in the electrospinning of PLGA/HA nanofibrous nanocomposite scaffolds. The porosity of random scaffolds was 77 %, whereas aligned scaffolds had 72 % porosity. As shown in Fig. 2, smaller and narrower pores are commonly seen on aligned nanofibrous scaffold; but bigger and rounder pores are shown on random ones. By aligning the fibers, aligned nanofibers exhibit a denser structure and a lower porosity than random nanofibers.

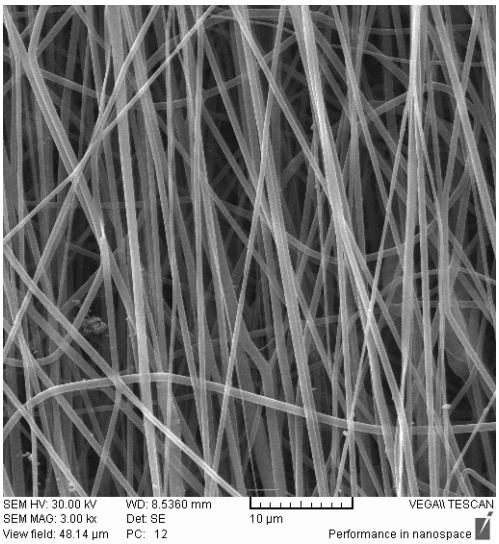
C. Mechanical Properties

The mechanical properties of biocomposite nanofibrous scaffolds were evaluated by tensile testing. The stress-strain curves of the samples are shown in Fig.3. It is observed that the tensile strength for random PVA/PCL/nHA nanofibers is 2.66 MPa and the elastic modulus is 5.22 MPa. By aligning of nanofibers, the tensile strength increases to 5.82 MPa with an elastic modulus of 12.2 MPa. Yin et.al [16] found that the alignment of PLLA nanofibers significantly increased the mechanical properties of prepared nanofiberous scaffolds. The increment of elastic modulus and tensile strength is attributed to the highly porous nature of the random

nanofibrous scaffolds. Moreover, during tensile loading, only the fibers oriented along the loading direction experience the stretching force, while the fibers that are oriented perpendicular to the loading direction do not experience any force.



(a)



(b)

Fig. 2 SEM images of nanofibrous scaffolds (a) random, (b) aligned

D. Fourier Transform Infrared Spectroscopy

Infrared spectroscopic analysis was done to characterize functional groups in the fibers in order to confirm the presence of the scaffold component phases and to discern any possible chemical modification or interaction between phases. Figure 4 shows FTIR spectra for PCL, nHA, PCL/HA, PVA and PCL/nHA/PVA scaffolds. Typical infrared bands for PCL-related stretching modes are observed for the PCL and PCL/HA scaffolds. These include 2923 cm^{-1} (asymmetric CH2 stretching), 2857 cm^{-1} (symmetric CH2 stretching), 1720 cm^{-1} (carbonyl stretching), 1293 cm^{-1} (C–O and C–C stretching in the crystalline phase) and 1240 cm^{-1} (asymmetric COC stretching). Characteristic PO_4^{-3} absorption bands attributed to HA nanoparticles are seen for each of nHA, PCL/nHA and PCL/nHA/PVA scaffolds. These PO_4^{-3} bands are seen at 569 cm^{-1} and 1031 cm^{-1}. PCL/nHA/PVA nanofibers also showed a characteristic broad absorbance at 3265 cm^{-1} (–OH stretching), at 2917 cm^{-1} (symmetric –CH2–), and at 1422 and 1088 cm^{-1} for C–O group of PVA.

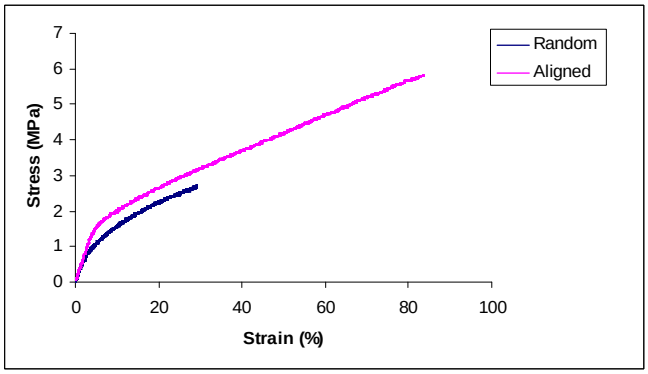


Fig. 3 stress–strain curves for electrospun nanocomposite scaffolds

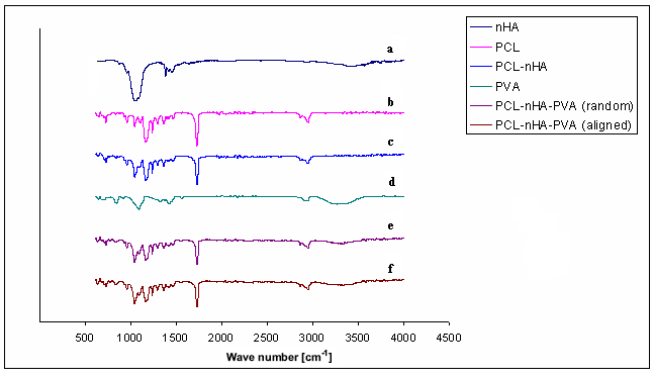


Fig. 4 FTIR spectra for (a) nHA, (b) PCL, (c) PCL- nHA, (d) PVA, (e) PCL- nHA-PVA (random), (f) PCL- nHA-PVA (aligned)

IV. CONCLUSION

In study, aligned and random biocomposites of PVA/PCL/nHA nanofibrous scaffolds were prepared via electrospinning techniques. The results reported in this study demonstrated that the mean fiber diameter and porosity of aligned nanofibers was lower than random nanofibers. Also, it was found that the mechanical properties of aligned nanofibrous scaffolds were higher than randomly oriented scaffolds. The results indicate that aligned nanocomposite scaffolds are good candidates for tissue engineering applications.

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