Fabrication of Polycaprolactone-Cellulose Acetate Hybrid Electrospun Fiber Blends

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Abstract- Series of Poly(ε-caprolactone) (PCL)/Cellulose Acetate(CA) hybrid electrospun fibers mats (EFMs) were prepared via electrospinning process. The EFMs were characterized by X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), field emission-Scanning electron microscopy (FE-SEM) and water contact angle (WCA) measurements. XPS analysis revealed that the carbon content (%) was gradually decreased and the oxygen content (%) was enhanced steadily with the increasing composition of the CA present in the PCL/CA hybrid EFMs. Better thermal stability of the PCL/CA hybrid EFMs was found in comparison to the neat PCL EFM and the neat CA EFM, as revealed by TGA analysis. The fiber morphology under FE-SEM showed that the surface of EFMs were smooth and beadless. The WCA results revealed that EFMs were hydrophobic. The PCL/CA hybrid EFMs may be used as scaffold in tissue engineering and in other biomaterials where low wetting properties are required.

Keywords- Poly(ε-caprolactone), Cellulose Acetate, Electrospinning, Thermal Stability, Smooth Surface

I. Introduction

The rapid evolution of nanotechnology has paved the way for researchers worldwide to explore the unique properties of nanoscale materials [i]. Electrospinning is a well-known method for producing polymer fibers in the submicron to nanometer diameter ranges [ii]. Electrospun fibers and mats offer several advantages including high surface to volume ratio, tunable porosity and good physico-mechanical properties making them a suitable substrate for various applications [iii]. Significantly, desired properties in electrospun fibers and mats can be achieved by manipulating the polymer solution and process parameters [iv].

Poly(ε-caprolactone) (PCL) is a non-toxic polyester having good biocompatibility and environmental degradability, as well as good mechanical properties [v-vii]. It has poor thermal properties due to its low melting temperature preventing wide scale use [viii-ix]. However, PCL can be blended with other polymers to achieve improved properties [vi]. Significantly, PCL is suitable for blending with other polymers due to its good processability and blend compatibility [v].

Cellulose acetate (CA) is an important organic ester of cellulose and is extensively used to make fibers, plastics and coatings [vi], [x]. It is a cost-effective organic polymer with limited water absorption property due to the presence of acetyl groups in its chemical structure [xi]. Furthermore, CA offers higher melting temperature making its processability difficult [viii].

There are various reports available in which PCL was successfully blended with different polymers to enhance the desired properties of either one or both constituent polymers. We are providing three such examples here. Firstly, the blend of long-chain cellulose ester (LCCE) and PCL showed that the addition of PCL into LCCE raised the tensile stress at break slightly as well as enhanced the thermal stability of LCCE in the blends [xii]. Secondly, the PCL-PLLA blend was prepared to make nanofibers tubes. In the blend, PCL provides a better physical and mechanical stability, and the PLLA enhances the biodegradability [xiii]. Thirdly, cellulose/PCL blends were prepared successfully. The blends showed considerable enhancement of thermal stability in comparison to the regenerated cellulose when the proportion of PCL content is more than 40 wt% [xiv].

In this study, we prepared PCL-CA hybrid EFMs by blending different proportions of the PCL and CA polymer solutions followed by electrospinning. Furthermore, the surface and thermal properties of the EFMs were characterized by X-ray photoelectron spectroscopy (XPS), Field emission-Scanning electron microscopy (FE-SEM) and thermal gravimetric analysis (TGA) respectively. The wetting property of EFMs was also evaluated by water contact angle (WCA) measurements.

II. Experimental

A. Materials

Poly(ε-caprolactone) (PCL, weight average molecular weight = 80,000) and Cellulose acetate, CA (39.8% acetyl content having weight average molecular weight = 30 kDa) were obtained from Sigma-Aldrich (USA), and used as-received.

B. Preparation of the polymer solutions

A 9 % (w/w) PCL solution in dimethylformamide/

chloroform and a 17% (w/w) CA solution in acetone/ dimethyl formamide were prepared to fabricate the neat PCL electrospun fibers mat (EFM) and the neat CA EFM respectively. For PCL/CA hybrid EFMs, four different blend ratios were prepared as 4:1, 3:1, 2:1 and1:1 (w/w). Each PCL/CA polymer solution was stirred at 50°C for 24 h before electrospinning. All the PCL/CA polymer solutions were clear and homogeneous.

C. *Electrospinning*

The electrospinning set up (NanoNC, Korea) was used as reported previously [xv]. The polymer solutions were pumped with a 10 mL plastic syringe at a controlled feeding rate of 0.1 mL/h (KD Scientific, Korea) through a 23 gauge needle. The voltage of 12 kV was applied and the tip-to-collector distance was fixed at 15 cm. Electrospun fibers were collected over the metallic drum covered with aluminum foil. The average thicknesses of EFMs were in the range of 40-50 µm; measured by Digital Micrometer MCD130-25 with a measuring sensitivity of 1 µm.

D. Measurements

The chemical compositions of the EFMs were examined by XPS (Theta Probe Base System, Thermo Fisher Scientific Co.) with Al Kα radiation. Survey spectrum was recorded over the 0-1350 eV binding energy range at detector pass energy of 200 eV. TGA (PerkinElmer TGA-7,Korea) was performed to investigate the thermal properties of EFMs from 30°C to 500°C at a heating rate of 10°C per minute under a nitrogen gas atmosphere. The morphology of EFMs were examined under FE-SEM (JSM 6701F, JEOL Japan). All samples were sputtered with platinum under vacuum before assessment. WCA of the EFMs was measured by sessile drop measurements using a Drop Shape Analysis System, DSA 100 (Krüss, Hamburg, Germany). Five contact angle measurements were averaged to get a reliable value.

III. Results and Discussion

A. XPS analysis of EFMs

Fig. 1 depicts the average chemical composition of the surfaces of the EFMs at a 10 nm depth. The C 1s peaks and O 1s peaks are present at 285 eV and 532 eV respectively. The elementary compositions of the EFMs obtained from the survey spectrum are also compiled and given in Table I. The PCL EFM showed greater carbon content (77.49%) in comparison to the carbon content (62.54%) of CA EFM. In contrast, PCL EFM showed lower oxygen content (22.51%) in comparison to the oxygen content (37.46%) of CA EFM. The results showed that carbon content (%) was gradually decreased and the oxygen content (%) was enhanced with the increasing composition of the CA present in the PCL-CA EFMs as given in Table I.

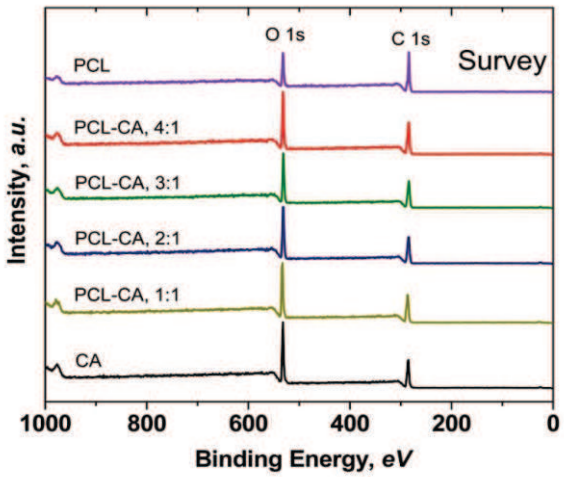

Fig. 1. XPS results of PCL, CA and PCL-CA hybrid EFMs.

B. TGA analysis of EFMs

Sample	Carbon (%)	Oxygen (%)
PCL	77.49	22.51
PCL-CA, 4:1	68.61	31.39
PCL-CA,3:1	67.91	32.09
PCL-CA,2:1	65.61	34.39
PCL-CA,1:1	65.7	34.3
CA	62.54	37.46

Fig. 2. TGA results of PCL, CA and PCL-CA hybrid EFMs.

The TGA thermal curves of PCL, CA and PCL-CA hybrid EFMs are shown in Fig.2. All the EFMs exhibited a single step in the loss of their weight. Significant weight loss occurred at around 350-400°C, and continued to decrease until the temperature reached up to 500°C. The thermal stability of the PCL-CA hybrid EFMs was found better than the PCL EFM and the CA EFM. Hence, blending PCL with CA resulted into a higher thermal stability than the neat PCL and the neat CA EFMs.

Fig. 4 shows the results of WCA of EFMs. It can be seen from Fig.4 that all the EFMs remained hydrophobic producing WCA results in the range of 110-115°. Therefore, blending of CA and PCL did not produce significant effect on the surface wetting of the EFMs.

C. *FE-SEM analysis of EFMs*

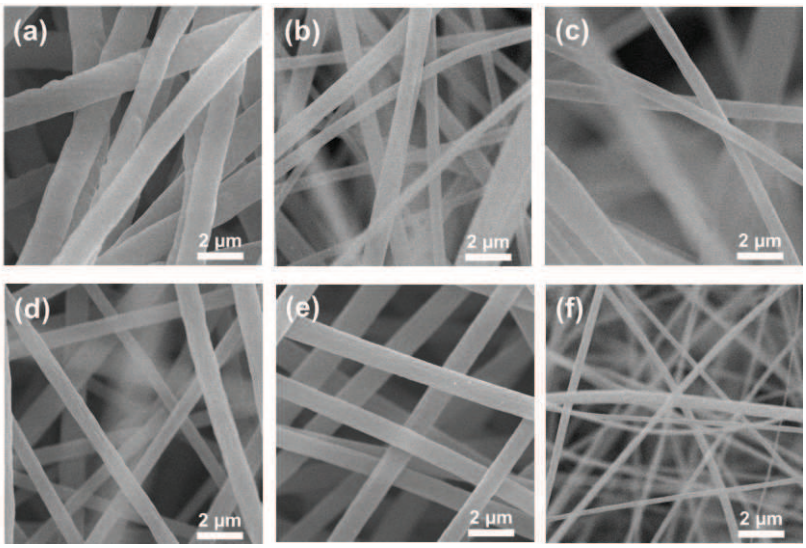

Fig. 3. FE-SEM images of as-spun EFMs. *(a)* PCL, (1:0), *(b)* PCL-CA, (4:1), *(c)* PCL-CA, (3:1), *(d)* PCL-CA, (2:1), *(e)* PCL-CA, (1:1) and *(f)* CA, (0:1).

Figure 3 demonstrates the morphologies of the PCL, CA and PCL-CA hybrid EFMs. All the samples showed a beadless and smooth morphology, which suggests that the polymer concentrations used, the selection of solvent system as well as the electrospinning parameters used were optimal. Moreover, FE-SEM images showed that the CA electrospun fibers are finer than PCL electrospun fibers Fig. 3.

D. WCA analysis of EFMs

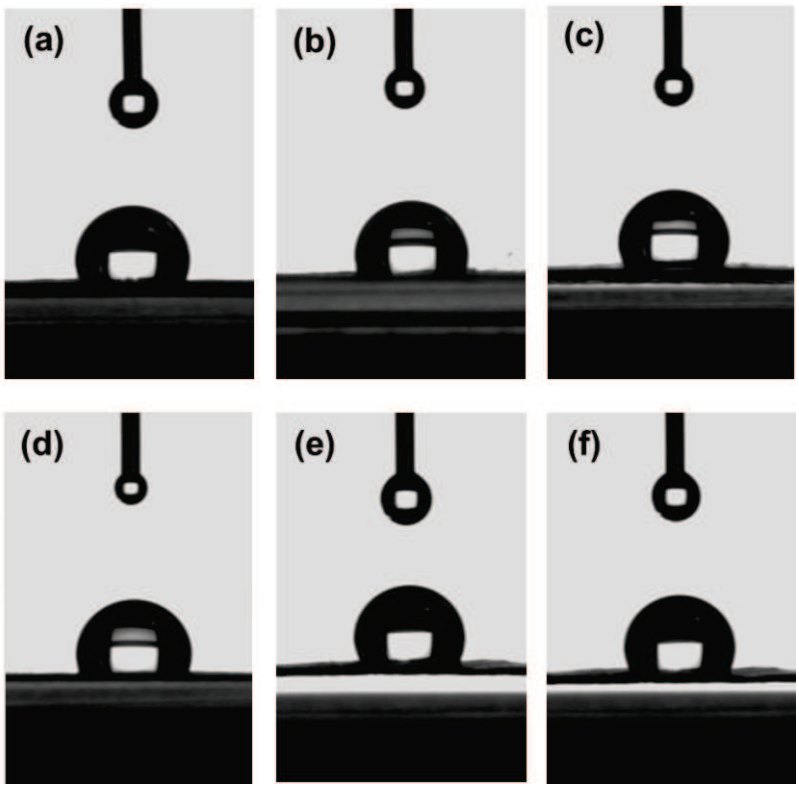

Fig. 4. WCA (°) of EFMs *(a)* PCL, (1:0), *(b)* PCL-CA, (4:1), *(c)* PCL-CA, (3:1), *(d)* PCL-CA, (2:1), *(e)* PCL-CA, (1:1) and *(f)* CA, (0:1).

IV. Conclusions

PCL/CA hybrid EFMs were successfully fabricated via electrospinning process. XPS analysis showed that the carbon content (%) was gradually decreased and the oxygen content (%) was enhanced steadily with the increasing composition of the CA present in the PCL/CA hybrid EFMs. TGA analysis revealed better thermal stability for PCL/CA hybrid EFMs in comparison to the neat PCL EFM and the neat CA EFM. FE-SEM results demonstrated the bead-free surface morphology of EFMs. The WCA results revealed that EFMs were hydrophobic. The potential application of PCL/CA hybrid EFMs include scaffold in tissue engineering and in other biomaterials.

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