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Fabrication of polymeric microfibers containing rice-like oligomeric hydrogel nanoparticles on their surface: A novel strategy in the electrospinning process

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ABSTRACT

In this work, nonwoven fiber mats of poly(ε-caprolacton) (PCL) and PCL blended with methoxy poly(ethylene glycol) (MPEG) oligomer were generated by electrospinning. The electrospinning was carried out in two different conditions depending upon the collector medium i.e. with and without water bath. It was found that the addition of MPEG increased the diameter of PCL microfibers when the electrospun mat was collected without water bath. However, the collection of microfibers into the water bath produced rice-like nanoparticles (NPs) of MPEG on the surface of PCL microfibers. The formation of hybrid mat containing hydrophobic PCL microfibers with hydrophilic MPEG hydrogel NPs is not only beneficial in future drug and gene delivery system but also useful in tissue engineering.

1. Introduction

Nanofibers and nanoparticles of biodegradable polymers have attracted great interest in recent years for clinical administration such as drug and gene delivery, cancer therapy, tissue scaffold, and biosensor [1–3]. Electrospinning is regarded as a simple and versatile method for generating nano to micrometer structure [4]. The obtained fibers from electrospinning offer a unique advantage as they have high surface area which makes them a best candidate in many different applications.

PCL is a semi-crystalline biodegradable polyester, commonly used for tissue engineering and drug delivery due to its good biocompatibility and mechanical properties [5], longer degradation time and high permeability to many drugs [6,7]. PCL electrospun fibers have been widely used as various scaffolds for bone [8], cartilage [9], skin [10], and blood vessel [11]. Nonetheless, its hydrophobicity and the considerable crystallinity greatly inhibit its fast biodegradation and limited cell adhesion, migration, proliferation, and differentiation. On the other hand, MPEG presents outstanding properties, e.g., hydrophilicity, miscibility with water and organic solvents, nontoxicity, and absence of antigenicity [12]. Therefore many research groups copolymerized PCL with MPEG and reported its efficiency in drug delivery as well as its potentiality for cell adhesion, proliferation, and differentiation. Herein, we demonstrated a novel type of polymer blending in which MPEG NPs were uniformly deposited on the surface of PCL microfibers via a one-step electrospinning process which can suppress the crystallization of PCL chains and increase the hydrophilicity of mat. The composite mat having hydrophilic MPEG NPs on the surface of hydrophobic PCL microfibers is not only able to encapsulate both the water soluble and insoluble drugs but also becomes an ideal candidate for their sustainable release by the same mat. Furthermore, the modification of PCL microfibers from hydrophobic to hydrophilic was carried out by the simple blending of PCL and MPEG without any polymerization reaction. This cost effective process can simply enhance the biocompatibility of composite mat for different biomedical applications.

2. Experimental

PCL ($M_w = 80{,}000$) was purchased from Aldrich (USA) and 10 wt.% solution was prepared using chloroform as solvent. Polymer blend was prepared by simple mixing of 4 g of MPEG (MW = 550, Aldrich, USA) into 25 g of 10 wt.% PCL solution. Electrospinning was carried out at 22 kV and 20 cm distance between the collector and the tip of the syringe which was clamped at about a 20° angle relative to the horizontal axis. Pristine PCL mat was collected without water bath whereas MPEG/PCL blend mat were collected with and without water bath at the same electrospinning condition (Fig. 1a). After vacuum drying for 24 h, the mates were further analyzed.

The morphology of the as-spun microfibers and the size of NPs on them were observed by using scanning electron microscopy (GMS 5900, JEOL Co., Japan). The thermal stability of the mat was investigated using

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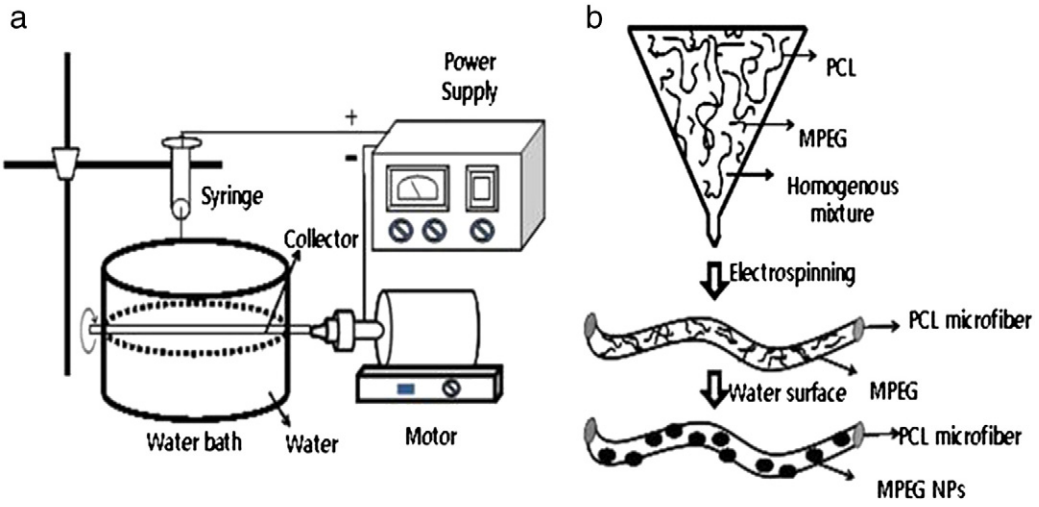

Fig. 1. Schematic illustration of (a) a water bath electrospinning setup, (b) the mechanism of the formation of MPEG NPs on the surface of PCL microfibers during water bath electrospinning.

thermogravimetric analysis (TGA, Perkin-Elmer Co., USA) by heating from −100 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) measurement was performed on a Perkin-Elmer Pyris-1 differential scanning calorimeter in a dry nitrogen atmosphere. Information about the phase and crystallinity was obtained by using a Rigaku X-ray diffractometer (XRD, Rigaku, Japan) with Cu K_α ($\lambda = 1.540$ Å) radiation over the Bragg angle ranging from 10 to 80°.The hydrophilicity of the electrospun mats was measured with deionized water contact angle measurements using a contact angle meter (GBX, Digidrop, France). Deionized water was automatically dropped (drop diameter was 6 μm) onto the mat. The measurement was carried out three times at different places of the same mat and the average was taken for comparison.

3. Results and discussion

Fig. 2 shows the morphology of pristine PCL fibers (a), MPEG/PCL composite fibers (b), and hybrid fibers decorated by MPEG NPs (collected on water surface) (c). It shows that the diameter of PCL microfibers (collected without water bath) is increased in the presence of MPEG. The mean fiber diameter of pristine PCL and MPEG/PCL blended microfibers was found to be 3.6 μm (standard deviation was 1.12) and 4.3 μm (standard deviation was 0.81), respectively. The fiber collected into the water bath became irregular with various diameters in the same fiber (mean fiber diameter was 2.7 μm and standard deviation was 1.31). Furthermore, the collection of fibers on the surface of water showed the decoration of PCL microfibers by rice-like MPEG NPs (≈800 nm) on their surface. The formation of such an interesting structure may be due to the fast phase separation of the two polymers during electrospinning. PCL is water insoluble whereas MPEG has more affinity towards water than that of used chloroform solvent. Therefore, when electrospun blend polymer has reached to the surface of water, the MPEG molecules escape from the fiber surface and attaché on the fiber in the form of NPs as shown in the schematic diagram (Fig. 1b). The attachment of NPs on the surface of PCL fiber may be due to the interaction of two polymers by means of hydrogen bonding between MPEG and PCL.

To investigate the proper condition for the formation of rice-like NPs of MPEG on the surface of PCL microfibers, we performed the electrospinning of different amounts of MPEG with 10% PCL solution. Low amount of MPEG (2 g MPEG with 25 g PCL solution) gave porous microfibers rather than the formation of rice-like NPs. 3 g of MPEG with 25 g PCL solution gave porous fibers containing small and

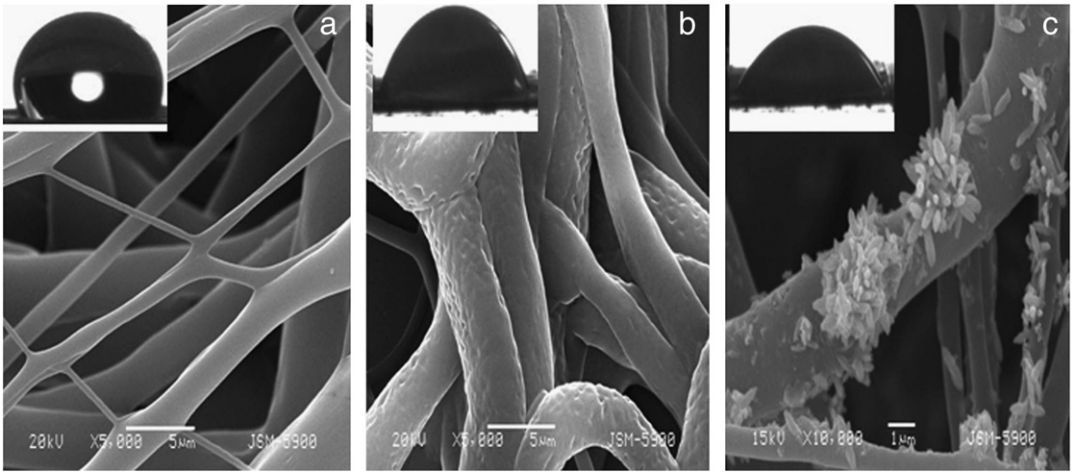

Fig. 2. SEM images and corresponding water contact angles of electrospun microfibers: (a) Pristine PCL mat (b) MPEG/PCL mat collected without water bath (c) MPEG/PCL mat collected into the water bath.