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Thermosetting epoxy reinforced shape memory composite microfiber membranes: Fabrication, structure and properties

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ABSTRACT

The thermosetting epoxy-based shape memory composite microfibers are successfully fabricated by means of coaxial electrospinning. The PCL/epoxy composite fiber shows core/shell structure, in which epoxy as the core layer is for an enhancing purpose. By incorporating epoxy and PCL, the mechanical strength of composite fibers is greatly reinforced. The deformation is via the heating and cooling process, and the shape memory effect can be demonstrated from the micro level to the macro level. The whole shape recovery performance takes only 6.2 s when triggered by the temperature being at 70 °C. The porosity of woven microfibers changes in response to temperature. In addition, the PCL/epoxy composite microfiber membranes are analyzed in an in vitro cytotoxicity test, which proves that PCL as the shell layer provides the composite microfibers potential capabilities in biomedical science.

1. Introduction

Shape memory polymers (SMPs), due to their special ability to remember deformed shapes and recover these original shapes in response to external stimuli, such as temperature, electricity, magnetism and solutions are attractive in a wide array of fields [1–5]. Compared to shape memory alloys (SMAs), the advantages of SMPs include large deformation, light weight, large recovery ability, lower cost as well as superior process ability [2]. And their stiffness can be changed between the thermoplastic glass and the elastomer when actuated by temperature. SMPs filled with different particles and fibers can realize the multifunction and reinforcement which has been demonstrated in previous research [6]. On the basis of a fixed phase structure, SMPs are classified into thermosetting and thermoplastic SMPs [7]. Epoxy, as a kind of thermosetting SMPs with high strength and large deformation, is successfully used in aerospace, automobiles, robotics and so on [8,9]. A large variety of polymers have been added into epoxy matrix to realize different functions. In previous reports, some researchers combine epoxy with polycaprolactone (PCL) to realize the multifunction of composites. For instance, Mather and coworkers [10] have synthesized a shape memory composite, through incorporating non-woven PCL fibers into an epoxy-based SMP matrix. Such a composite is able to display triple-shape memory effect because it possesses two transition temperatures T_m and T_g respectively. Luo et al. [11] reported that they prepared electrospun thermoplastic PCL fibers which were distributed in a shape memory epoxy matrix. The mechanical damage was capable of being self-healed via heating. Oh and co-workers fabricated the meta-aramid/epoxy fibers with core/shell structure, the thermal and mechanical performances of which were investigated in the adhesive composites [12,13]. Although epoxy has been developed in so many fields, the applications of epoxy resin are still limited by the properties of itself, especially the application size at the micro- or nano- level. In addition, it cannot be used in biomedicalfield. In order to obtain the micro-size epoxy which can be used in biomedical fields, we design a system cooperating the thermosetting epoxy and thermoplastic PCL together through electrospinning.

Electrospinning, being recognized as an efficient technique, has been utilized for fabrication of fibers with micro-size or nano-size diameters [14–16]. Recently, an increasing number of SMPs have been electrospun into fibers, such as polycaprolactone [17,18], polyurethane [19,20], as well as Nafion [21,22], which will have potential application in the biomedical field [23,24]. PCL is a very attractive polymer, advantages of which include biodegradability, low cost, availability and physicochemical properties (semicrystallinity, hydrophobicity) tuned easily through chemical modification or copolymerization with other monomers [17]. The cross-linking of homo- and co-polymers often leads to superior

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mechanical performance of these materials, such as high modulus and dimensional stability. Besides, during the last decade, several strategies for the crosslinking of PCL derivatives have been taken. Very recently, it has been reported that PCL networks can exhibit excellent shape memory properties including shape fixity and recovery ratios [18]. Therefore, PCL shows biodegradability, biocompatibility, shape memory effect and in some cases, recyclability. These advantages open up new perspectives for biomedical applications (degradable stents and implants, drug carrier matrices, hard and soft tissues engineering, stem cell therapy, etc.) or for recyclability and reprocessing of cross-linked materials [25,26].

Coaxial electrospinning, being used to obtain fibers with more than one compound material, can turn some materials without spinnability into fiber structure to develop the properties and applications [27,28]. As we all know, thermoset polymers are not able to be electrospun into fibers because of the poor spinnability. In order to solve these problems, we design a kind of core/shell structure composite fibers system in which epoxy is the core layer and PCL is the shell layer. PCL as a template is easy to draw the epoxy into fibers. To electrospin epoxy into fibers is a challenge that has not been reported. The core/shell composite fibers have a reinforced inner layer with good mechanical properties capable of improving the PCL's low strength and stiffness. On the other hand, the outside layer PCL brings epoxy into potential biomedical applications.

In this paper, we describe a kind of core/shell composite fiber. PCL as shell material and epoxy as core material were electrospun into microfibers by co-electrospinning method. This new system was characterized by SEM, TEM, DSC, DMA and vitro cytotoxicity test, etc. to analyze the morphology, structure, thermal and mechanical properties, as well as biological behavior. Shape memory effect was also demonstrated from micro and macro perspectives. Thus, the strong and flexible polymer composite fiber films are developed and are promising for applications in smart materials and structures, especially in tissue engineering in the future.

2. Materials and experiment

2.1. Materials

Polycaprolactone (PCL, Mw = 50,000) was purchased from Perstorp UK. Benzophenone ($C_{13}H_{10}O$) as the UV agent, dichloromethane (CH_2Cl_2) and dimethylformamide (DMF) as the solutions were purchased from Tianjin guangfu fine chemical research institute and used as received. Epoxy-based shape memory polymer specimens were synthesized according to the procedure reported by Wu et al. [29]. Epoxy SMPs were fabricated by mixing epoxy resin and hardener which was 35 wt.% for EP06. Mouse schwann cells were purchased from American Type Culture Collection (ATCC), USA. CCK-8 was purchased from Dojindo, Japan. All biological experiment procedures were approved by the Ethics Committee of the First Affiliated Hospital of Harbin Medical University.

2.2. Electrospinning of PCL/epoxy composite microfibers

The PCL/epoxy composite microfibers were prepared as displayed in Fig. 1. CH_2Cl_2 and DMF were mixed together with a volumetric proportion of 4:1. PCL was dissolved in the mixed solvent with a concentration of 15 wt.%. And the 10 wt.% UV initiator benzophenone was added in the mixture. The polymer solution was stirred on a magnetic stirrer at room temperature until well mixed. Fig. 1a shows the schematic illustration of electrospinning setup to fabricate the core–shell fibers. The syringes we used for epoxy and PCL were 1 mL and 2.5 mL, respectively. The electrospinning parameters were listed in the following: the needle size was an inner diameter of 100 ím and outer diameter of 200 ím; the needle tip to collector distance and applied voltage were 18 cm and 15 kV, respectively. The feed rate of PCL was 0.002 mm/s and the feed rate of epoxy was 0.0005, 0.0008, 0.001 and 0.002 mm/s, respectively. The feed ratios between PCL and epoxy were named as 1:1, 2:1, 2.5:1, and 4:1, respectively. During the electrospinning process, the diameters of core fibers varied with the changes of the flow rate of epoxy. The composite microfibers specimens (as shown in Fig. 1b and c) were electrospun on aluminum for 30 min and cured at 70 °C for more than 75 h in the oven. Fig. 1d shows the morphology of the electrospun composite microfibers. During the electrospinning process as shown in Fig. 1e, the UV lamp, the wavelength of which was 365 nm (the power was 100 W), was used to radiate the PCL to form the networks for shape memory effect [30].

2.3. Characterization

SEM images of PCL/epoxy composite microfibers were collected by scanning electron microscopy (SEM, Quanta 200FEG). The specimens were coated with a thin layer Au metal for 10 min.

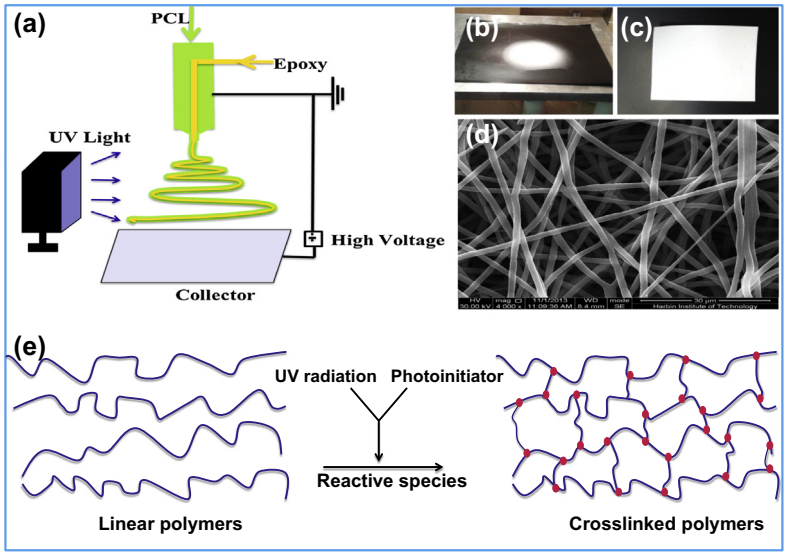

Fig. 1. Schematic illustration of co-electrospinning and UV photoinitiato process. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)