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Fabrication of hybrid membrane of electrospun polycaprolactone and polyethylene oxide with shape memory property

Yongtao Yao [a], Hongqiu Wei [a], Jingjie Wang [a], Haibao Lu [a, *], Jinsong Leng [a, **], David Hui [b]

[a] National Key Laboratory of Science and Technology for Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin 150080, China

[b] Composite Material Research Laboratory, Department of Mechanical Engineering, University of New Orleans, LA 70148, USA

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ABSTRACT

Hybrid materials with nanostructure could exhibit a diverse range of applications as advanced functional materials. This research work, composite membranes with shape memory property based on biocompatible polycaprolactone and polyethylene oxide were successfully fabricated by using electrospinning technique. Electrospun fiber configuration is strongly related to the concentration of polymer and electric field strength. The hydrophilic property of hybrid membrane has been improved and water play a critical role in resulting lower its responsive temperature compared with dry membrane. The mechanism of shape memory PCL/PEO hybrid membrane at wet condition has been proposed.

1. Introduction

Shape-memory polymers (SMPs) are one kind of stimuli-responsive materials which could be triggered by external stimulus, such as electricity, thermal, light, magnetism and water (or solvent) [1–5]. More and more researchers are attracted by SMP due to the feature of the shape memory effect (SME). It could be deformed under external stimulus and fixed into a temporary shape, and then, can recover to its original shape when it is exposed to an appropriate external stimulus. The potential uses for SMPs are actuators due to its capabilities of changing shape, stiffness and natural frequency in response to external stimuli [6–9]. This advanced functionality potentially makes SMPs as a promising candidate for engineering applications, including biomedicine, automobile, aerospace and textiles, etc. [10–15].

In the recent years, for manufacturing SMPs, electrospinning is a mature technology being used for fabricating woven or nonwoven fibrous structure at nano or micro-scale, such as fibers, tubes, belts, etc. [16–23] The advantage of electrospinning was a wide range of materials prepared as a polymer solution, sol–gel, particulate suspension or melt could be electrospun into fibers under high electric fields. Spun woven structure is fascinating due to the feature of high porosity, light weight, high strength to weight ratios, flexible and controlled microarchitecture, etc [24–26]. In this point of view, hybrid membranes with different polymer content could be achieved, which is a promising candidate for many biomedical applications, such as scaffolds, wound dressing and medical prostheses, etc.

Recently, a variety of materials has been reported for electrospuning into fibrous structures and applied in biomedical field. Among them, synthetic polycaprolactone (PCL) is a semi-crystalline polymer, which is one of the most investigated polymers in tissue engineering research due to its biodegradable and biocompatible feature. Especially, PCL has relatively slow degradation rate, which is suitable candidate for manufacturing fibrous scaffolds with micro- and nanofibrous structures [27–29]. But, hydrophobic feature of PCL may obstruct its applications as scaffolds both in Vitro and in Vivo with requiring faster absorption rates or drug release systems; meanwhile, PCL with shape memory property could broaden its applications in biomedical field [30,31]. In last decades, more research focused on copolymerization of ε-caprolactone with other monomers to modify its mechanical and chemical properties. For example, the synthesis of polyester–polyether type block copolymer has been reported due to its excellent biodegradable and biocompatible feature, which could be used as controlled-release drug carriers [32–38].

* Corresponding author. Tel.: +86 45186403786.
** Corresponding author. Tel.: +86 45186403786.
E-mail addresses: luhb@hit.edu.cn (H. Lu), lengjs@hit.edu.cn (J. Leng).

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When electrospinning method was employed to fabricate PCL nonwoven structure, the chemical properties has been improved through modifying structural and topological features of several polymeric meshes [39]. In addition, blending techniques have also been widely used to enhance physical and chemical properties of PCL. Such as, water-soluble poly(N-vinyl-2-pyrrolidone) was selected to blend with PCL to fabricate scaffolds with tunable fibrous surface morphology and controllable degradation rates via electrospinning technology [40,41].

In this study, as a water soluble component, plastic PEO was chosen according to its excellent biocompatibility, remarkable solubility in water and most organic solvents. To the authors' knowledge, there is limit of investigation on electrospinning PCL/PEO hybrid membrane with shape memory behavior. Providing a systematic investigation on how to manufacture non defect fiber with desired microarchitectures based on electrospinning method and study the water influence on SME of hybrid electrospun membrane.

This work presents the development of bio-compatible membrane with shape memory property based on PCL and PEO, fabricated via electrospinning technology. Cross-linked PCL was prepared though free radical reaction under ultraviolet (UV) irradiation, which could endow its shape memory property. PEO has been selected to increase the hydrophilic property of electrospun hybrid membrane. The effect of water on shape memory property and mechanical property has been investigated. The hybrid methodology based on electrospinning technique applied to this study has the potential to increase the potential application in biomedical field.

2. Experimental details

2.1. Preparation of electrospun composite nanofiber

2.1.1. Materials

Poly (ε-caprolactone) (PCL) pellets were purchased from Perstorp Chemical Trading Co., Ltd. (CaPa 6500, $M_n = 40{,}000–50{,}000$; density: 1.146 g/mL). Polyethylene oxide (PEO, $M_n = 900{,}000$) was obtained from changchun jinghua company, china. Benzophenone was purchased from Sigma–Aldrich LTD. Dichloromethane was procured from beijing chemical company. All chemicals involved in preparing electrospun fibers were used as received.

2.1.2. Electrospinning of the shape memory hybrid membrane

The shape memory hybrid membranes were fabricated as follows. Firstly, PCL and benzophenone (PCL: BP = 100:10 wt.%) sols with 10, 12 and 16 wt.% CH_2Cl_2 content were prepared and kept under stirring for 2 h to get the complete dissolved solution. Then, PEO was diluted into a 5 wt.% solution in de-ionized water, which were used for electrospinning. Finally, the first and the third layer were spun by using PCL and BP sols. The second layer was formed with hybrid nanofibers of PCL and PEO, which was obtained by two needles spinning together. Solution concentrations, applied electrical field, flow rate and collector distance were found to result in defect and morphology of electrospun nanofiber. The PCL electrospun process conditions were optimized at the flow rate 0.002 mL/min, needle to collector distance 20 cm, and voltage 18 kV. The electrospun hybrid membranes were cured by UV radiation with 365 nm of wavelength and dried at room temperature.

2.2. Methods of characterization

2.2.1. FT-IR spectroscopy

The electrospun hybrid membranes were prepared by drying at room temperature in a vacuum oven for 12 h. The chemical structures and infrared absorbing efficiency of electrospun nanofiber and hybrid membranes were determined by Fourier Transform Infrared (FTIR) spectroscopy (Nicolet AVATAR 360) in a range from 400 to 4000 cm^{-1} at room temperature in a transmittance mode.

2.2.2. The morphology and structure of electrospun nanofibers

Scanning electron microscopy (SEM, VEGA3 TESCAN) was employed to characterize the configuration of electrospun nanofibers by varying processing parameters.

2.2.3. The mechanical properties characterization

The mechanical performance of the electrospun membrane was quantitatively examined with a nano tensile system (Agilent UTM T150) and the test samples were regular rectangles with dimensions of $20 \times 1 \times 0.27$ mm^3. Meanwhile, the influence of water on the tensile properties of electrospun membrane was investigated at a temperature of 25 °C.

2.2.4. Thermal stability and melting temperature analysis

T_m plays an crucial role in influencing the shape recovery behavior of the electrospun membrane. In this study, Differential scanning calorimetry (DSC 204F1, Netzsch, Germany) was employed to measure T_m of electrospun hybrid membranes in a nitrogen environment within a temperature range from 25 to 200 °C at a constant heating rate of 10 °C min^{-1}.

2.2.5. X-ray diffraction (XRD) studies

X-ray diffraction (XRD) was employed to characterize UV cured electrospun PCL membrane based on a PANalytical X'Pert Pro diffractometer (Almelo, The Netherlands) using Cu-Kα radiation and a 1.00 arcmin step size.

2.2.6. Thermal actuation with temperature sensing

In order to investigate the effect of water on the shape memory properties of electrospun membranes, the tested specimens were stimulated by heat-treatment at wet and dry condition, respectively. The shape memory test processing was recorded by an infrared video camera (VarioCAM HiRessl, JENOPTIK Infra Tec.) to monitor the temperature distribution in electrospun membranes. The tested electrospun composite nanofiber mat was prepared with a dimension of $8 \times 30 \times 0.3$ mm^3, which was bent into a "U" shape at 55 °C. Six snap-shots of the tested SMP composite sample were presented to characterize the effect of water on the shape memory property of electrospun membranes.

3. Results and discussion

3.1. Morphology and structure of electrospun fiber

In order to investigate the effect of polymer solution and process parameters on the morphology of spun nanofibers, Scanning Electron Microscopy (SEM, VEGA3 TESCAN) was conducted in this study. Fig. 1 shows SEM images of UV cured spun nanofibers based on PCL concentration of 14 wt.% for applied electric field strength with 10 kV, 12 kV, 14 kV, 16 kV, 18 kV and 20 kV, respectively. It reveals that nanofibers were easily produced for applied electric field strength from 10 kV to 20 kV. The fiber diameter increased with increasing electric field strength from 10 kV to 16 kV and decreased from 18 kV to 20 kV. The smooth fibrous configuration with narrow diameter distribution was observed at applied electric field strength of 18 kV (Fig. 1(a)–(g)). For varying concentration of PCL, electrospun fibers having uniformly diameter without beads were observed above 10 wt.%, and the range of diameter distribution decreased as increasing PCL concentration from 12 wt.% to