eXPRESS Polymer Letters Vol.5, No.2 (2011) 182–187
Available online at www.expresspolymlett.com
DOI: 10.3144/expresspolymlett.2011.16

Coaxial electrospun polyurethane core-shell nanofibers for shape memory and antibacterial nanomaterials

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Received 25 July 2010; accepted in revised form 26 October 2010

Abstract. A novel kind of shape memory polyurethane (SMPU) nanofibers with core-shell nanostructure is fabricated using coaxial electrospinning. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) results show that nanofibers with core-shell structure or bead-on-string structure can be electrospun successfully from the core solution of polycaprolactone based SMPU (CLSMPU) and shell solution of pyridine containing polyurethane (PySMPU). In addition to the excellent shape memory effect with good shape fixity, excellent antibacterial activity against both gram-negative bacteria and gram-positive bacteria are achieved in the CLSMPU-PySMPU core-shell nanofiber. Finally, it is proposed that the antibacterial mechanism should be resulted from the PySMPU shell materials containing amido group in γ position and the high surface area per unit mass of nanofibers. Thus, the CLSMPU-PySMPU core shell nanofibers can be used as both shape memory nanomaterials and antibacterial nanomaterials.

Keywords: *nanomaterials, smart polymers, electrospinning, shape memory, antibacterial*

1. Introduction

Smart polymer ultrafine fibers have gained much attention due to their great potential applications, such as textiles, filtration, catalysis, reinforcement and biomedical use [1–3]. Particularly, polymeric micro/nanofibers with core-shell structure have been attractive in the past decades [4, 5]. Co-axial electrospinning provides an effective and versatile way to fabricate core-shell micro/nanofibers [4, 6, 7]. This technique can not only be used to spin the unspinnable polymers into ultrafine fiber, but also be used to keep the functionalizing agents like biomolecules and antibacterial agents in the core-shell nanofibers. For example, Liu *et al.* [8] had developed core-shell nanofibrous mats with a controllable drug-releasing capability for the tissue engineering scaffold. Jiang *et al*. [9] encapsulated BSA and lysozyme in polycaprolactone (PCL) nanofibers and found the released lysozyme maintained its structure and bioactivity. Therefore, it is desirable to achieve various functionalizations in the core-shell micro/nanofibers using the coaxial electrospinning.

In addition, shape memory polymers (SMPs) in particular shape memory polyurethanes (SMPUs) were widely studied in the past decades [10–12]. In addition to the excellent shape memory effect, the SMPUs demonstrate functional biocompatibility and had been used in various medical interventions such as vascular stents [13]. Recently, antibacterial activity was reported in the SMPU ionomers by Zhu *et al*. [14]. Most recently, Chen *et al*. [15–17] had also synthesized one novel kind of supramolecular SMPUs containing pyridine moieties. Not only thermal-induced shape memory effect (SME) [17], but moisture-sensitive shape memory effect are also achieved in the pyridine containing SMPUs (PySMPUs) [16]. A preliminary investigation sug-

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gests that the nanofibers based on the PySMPUs exhibits antibacterial activity. However, it is difficult to spin the pure PySMPU/dimethylformamide (DMF) solution into fibers with the conventional electrospinning.

Therefore, the coaxial electrospinning is introduced to fabricate antibacterial nanofiber with core-shell structure in this experiment. The PCL based SMPUs (CLSMPU) or the elastic polyurethanes (TPUs) are designed to provide the certain mechanical properties as the core materials while the PySMPU is introduced as the sheath to exhibit additional properties including antibacterial activity. The preparation and antibacterial activity of SMPU-PySMPU core-shell nanofibers are reported in this communication.

2. Experimental section

2.1. Materials

DMF bought from Sigma-Aldrich Corporation (U.S.A) was used without any treatment. CLSMPU containing 75% soft segment content was synthesized by bulk polymerization in our lab according to the literature procedure [18, 19]. The PySMPU containing various contents of pyridine moieties was synthesized by solution polymerization in our lab according to the literature procedure [15]. For comparison study, TPU based on polytetramethylene glycol with glass transition temperature of –30°C are selected in this study. CLSMPU (M_n = 180 000), TPU (M_n = 200 000, bought from Hong Kong HI-Tec Enterprises Limited), PySMPU containing 53wt% pyridine moieties (named PUPy53, M_n = 40 000) and PySMPU containing 35wt% pyridine moieties and 35wt% hard segment (named PUPyMDI35, M_n = 70 000), were prepared to 10wt% DMF solutions for electrospinning.

2.2. Coaxial electrospinning

In this experiment, for comparison, the CLSMPU-PUPy53 and TPU-PUPyMDI53 core-shell nanofibers were prepared using the co-axial electrospinning. The experimental setup for coaxial electrospinning is shown in Figure 1. Both the shell solution and core solution were fed independently with a programmable syringe pump. The feed rates are both set at 0.015 ml/min. A collecting plate was placed on a rotating drum controlled by a stepping motor. The applied voltage was 20 kV.

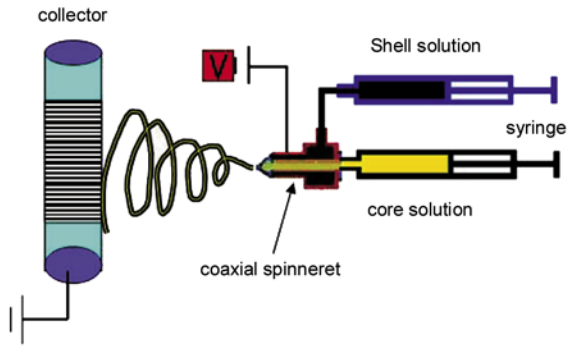

Figure 1. Experimental setup for coaxial electrospinning

2.3. Characterization

The surface morphology was observed using a scanning electron microscopy (SEM, S-4700 Hitachi, Japan) with an accelerating voltage of 20.0 kV. The core-shell structure was characterized using a transmission electron microscopy (TEM, Tecnai G2 F20 Philips, The Netherlands).

Antibacterial activity against gram-positive bacteria *Staphylococcus aureus* (*S.aureus*, ATCC6538) and gram-negative bacteria *Klebsiella pneumoniae* (*K.pneumoniae*, ATCC31488) was evaluated qualitatively according to the AATCC test method AATCC147 [14]. In this test, the specimens including corresponding untreated controls of the same material were placed in intimate contact with growth agar which had been previously streaked with test organism. After incubation, a clear area of interrupted growth underneath and along the sides of the test material indicated the antibacterial activity of the specimen. The size of the zone of inhibition and the narrowing of the streaks caused by the presence of the antibacterial agent permitted an estimate of the antibacterial activity.

Thermal-induced shape memory behaviors were characterized with cyclic tensile test method according to the literature method [17]. The test specimens with a width of 5.0 mm and length of 4.0 mm for cyclic tensile test are cut directly from the nanofibrous mat. The low temperature (T_{low}) for specimen stretching is about 45°C while the high temperature (T_{high}) for recovering is about 70°C.The test was done using an Instron 4466 apparatus with a temperature-controlled chamber; and a personal computer was used to control and record all data. The shape fixity and shape recovery were calculated from the recorded cyclic strain-stress curves [17].

3. Results and discussion

3.1. Structure and morphology

Figure 2 shows the SEM images of CLSMPU-PUPy53 and TPU-PUPyMDI35 core-shell nanofibers; and Figure 3 shows their TEM images. It is found in Figure 2 that uniform nanofibers with a diameter ranging from 600 to 1000 nm are fabricated in the CLSMPU-PUPy53 nanofiber. The TEM images confirm that the resultant CLSMPU-PUPy53 nanofibers have core-shell structure. The diameter of CLSMPU core nanofiber is changed from 250 to 320 nm while the sheath has a diameter of more than 600 nm. The interface between core material and sheath materials is clear since they are spun from different polymer. However, when the core material is spun from TPU/DMF solution and the shell material is spun from PUPyMDI35 materials, the resultant nanofibers not only form core-shell structure, but beads with average diameters of 1.5 μm are also observed on the core nanofibers. The distance within one bead is changed from 2.5 to 3.5 μm. It is also observed in Figure 2b. that clear interface is formed between the bead and the continuous core fiber. The core fiber threads the beads like a string. In this system, the core material is TPU while the shell material is PUPyMDI35. Thus, the beads should be formed by the PUPyMDI35 material due to their bad spinnability. Therefore, the coaxial electrospinning method can be used to fabricate core-shell micro/nanofibers and beads-on-string micro/nanofibers by adjusting the composition of core materials and shell materials. Comparing with the bulk film, the surface area per unit mass is improved greatly in both core-shell structure and bead-on-string structure nanofibers.

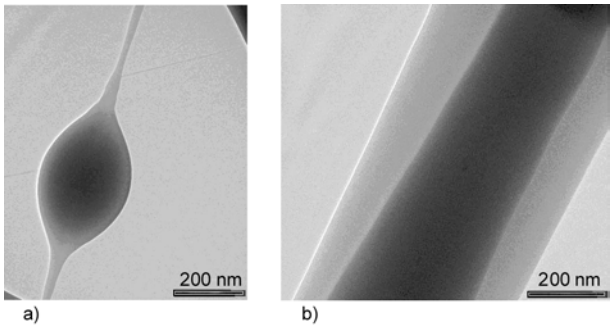

Figure 3. TEM images of (a) SMPU-PUPy53 and (b) TPU-PUPyMDI35 core-shell nanofiber

3.2. Thermal-induced shape memory properties

Figure 4 shows the cyclic strain-stress curve of CLSMPU-PUPy53 core-shell nanofibrous mat. It

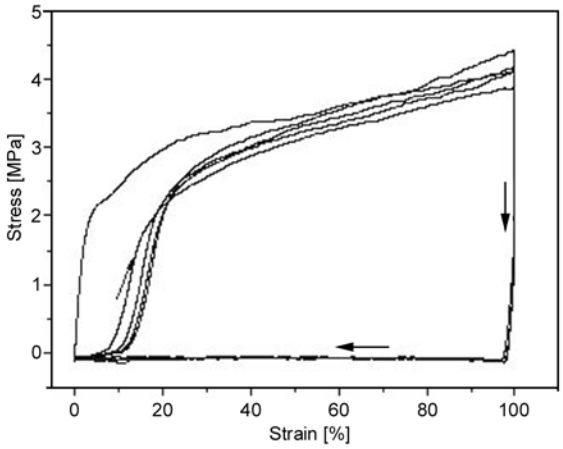

Figure 4. Stress-strain curve of CLSMPU/PUPy53 core-shell microfibrous mat

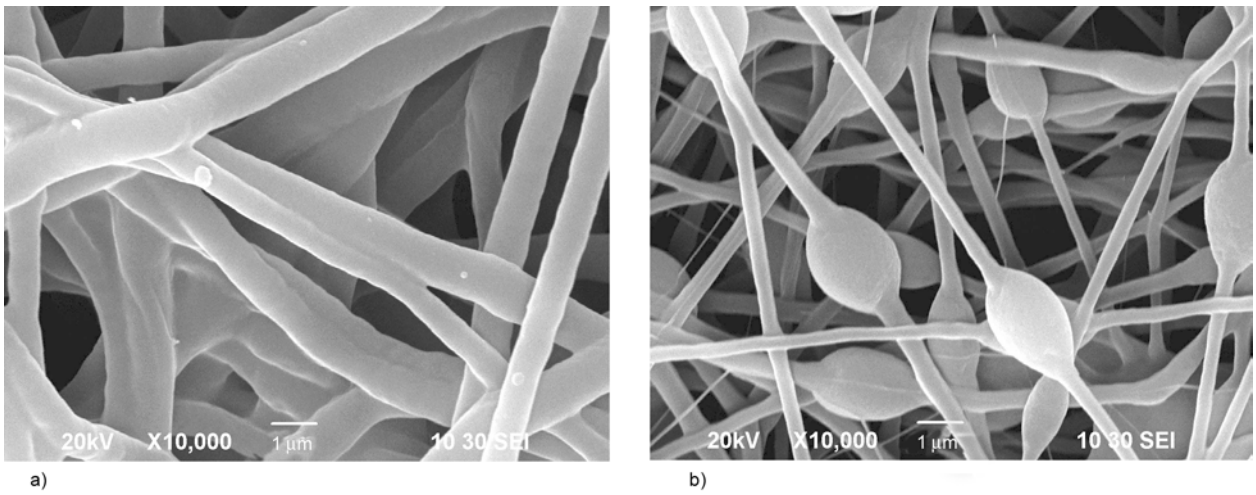

Figure 2. SEM images of (a) SMPU-PUPy53 and (b) TPU-PUPyMDI35 core-shell nanofiber

was reported that the transition temperature of CLSMPU nanofiber is about 46.83°Cwhile the transition temperature of PUPy53 is about 56°C [17]. The CLSMPU nanofiber usually shows unsatisfying shape fixity, less than 80% [20, 21]. However, when the CLSMPU nanofiber is coaxial electrospun into core-shell nanofibers with the sheath of PUPy53, the shape fixity is increased significantly to above 95% as shown in Figure 4. The shape recovery at the first cycle is still beyond 90% in the CLSMPU-PUPy53 core-shell nanofiber under the recovery temperature of 70°C. This behavior is very similar to the thermal-induced shape memory behavior of PUPy53 bulk film, which exhibits not only high shape fixity , but also good shape recovery [17]. This is due to the fact that the PUPy53 polymer has much high glassy modulus as reported by Chen *et al.* [17]. The PUPy53 sheath plays key role on the thermal-induced SME in this CLSMPU-PUPy53 core-shell nanofiber mat.

3.3. Antibacterial activity

Table 1 summarizes the result of antibacterial activity of CLSMPU-PUPy53 core-shell nanofibrous mat as compared with the pure CLSMPU nanofibrous mat and the PUPy53 bulk film. It is found that no growth of *S. aureus* and *K. pneumoniae* bacteria is observed directly underneath the CLSMPU-PUPy53 core-shell nanofibrous mat. However, growth of *S. aureus* and *K. pneumoniae* bacteria is observed directly underneath the PUPy53 bulk film and the pure CLSMPU nanofibrous mat. Additionally, 0 mm clear zone of inhibition is observed in the CLSMPU-PUPy53 core-shell nanofibrous mat. This observation suggests that the CLSMPU-PUPy53 core-shell nanofibrous mat has the acceptable antibacterial activity against both gram-positive and gram-negative bacteria while the CLSMPU nanofibrous mat and PUPy53 bulk polymer show unacceptable antibacterial activity. Moreover, there is no detectable diffusion of antibacterial agent from the CLSMPU-PUPy53 core-shell fibrous mat, *i.e.* the coaxial electrospinning provides a versatile method to encapsulate immobilized antibacterial agents in the core-shell micro/nanofibers. The antibacterial mechanism of this new kind of core-shell nanofibers may be different from the mechanism of Ag-doped antibacterial nanofibers [22, 23]. One reason is that the PySMPU like PUPy53 and PUPyMDI35 contains large fraction of BINA unit which have an amido group in γ position, and has important anti-tubercular, anti-pyretic and antibacterial properties [24]. Moreover, the microorganism contact surface area has been improved greatly after the PySMPU was electrospun into micro/nanofibers with core-shell structure or beads-on-string structure.

4. Conclusions

Novel core-shell micro/nanofibers are fabricated from the SMPU/DMF core solution and PySMPU/DMF shell solution using the coaxial electrospinning method in this experiment. Results show that both core-shell structure and bead-on-string structure can be formed in the core-shell micro/nanofiber by adjusting the core solution and shell solution. In addition to the excellent shape memory behaviors with good shape fixity, the CLSMPU-PySMPU core-shell nanofibrous mat is tested to show excellent antibacterial activity against both gram-negative bacteria and gram-positive bacteria. The antibacterial mechanism should be resulted from the PySMPU shell materials and the high surface area per unit mass of nanofibers. Thus, the CLSMPU-PySMPU core shell nanofibers are proposed for both shape memory nanomaterials and antibacterial nanomaterials.

Table 1. Antibacterial activity testing result using AATCC 147-2004

Test microorganism	Antibacterial activity		
	PUPy53 bulk film	**CLSMPU nanofiber mat**	**CLSMPU-PUPy53 core-shell nanofiber mat**
Staphylococcus aureus	**Growth** was observed directly underneath the tested specimen	**Growth** was observed directly underneath the tested specimen	**No growth** was observed directly underneath the tested specimen with 0 mm clear zone
Klebsiella pneumoniae	**Growth** was observed directly underneath the tested specimen	**Growth** was observed directly underneath the tested specimen	**No growth** was observed directly underneath the tested specimen with 0 mm clear zone

Acknowledgements

This work was financially supported by the Hong Kong RGC project G-T881 and the Hong Kong Polytechnic University Niche Area Research Funding Scheme project J-BB6M. The authors wish to express their gratitude for the generous support.

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