Electrospun Shape Memory Film with Reversible Fibrous Structure

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The thermoplastic SMP film in cycles of shape memory test (stretching-recovery):

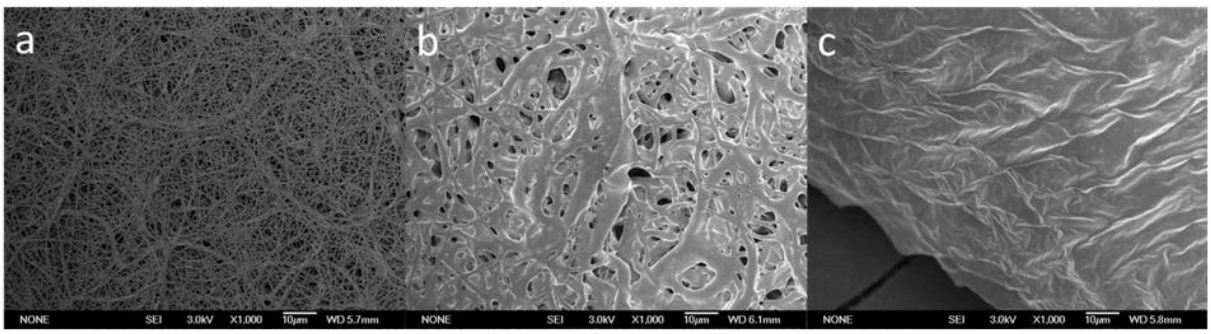


Fig. S1 SEM images of the electrospun film from the thermoplastic SMP in cycles of shape memory test. a) the as prepared film; b) film after the first cycle of the shape memory test; c) film after the third cycle of shape memory test.

Fig. S1 shows the micro/nano-structure of the electrospun thermoplastic SMP film before and after cycles of shape memory test. The sample was prepared according to literature. [S1] The as prepared film gives a typical electrospun fibrous structure with the fibers's diameter between ~200 nm to 2 μm. After only one cycle of stretching-recovery test, the fibers tend to stick together and the fibrous structure almost completely lost after three cycles of test. It should be due to the thermoplastic essence of the polymer adopted. During the shape memory tests, the thermoplastic SMPs would become viscous liquid and the micro/nano-structure would collapse and stick together in these processes.

Sample preparation and characterization:

Materials:

Polycaprolactonediol (PCL, $\bar{M}_n$ = 3000 g mol^{-1}) was purchased from Perstorp (Sweden). Polyvinylpyrrolidone (PVP, $\bar{M}_w$ = 1,300,000 g mol^{-1}) was purchased from Sigma-Aldrich. 4, 4'-Diphenyl-methane-diisocyanate (MDI) and γ-Aminpropyltriethoxysilane (APS) were purchased from Alfa Aesar and Hubei Wuhan University Silicone New Material Co., Ltd, respectively. All the solvents were purchased from Beijing Chemical Works.

Synthesis of Precursor-ASPU and SMPU solution:

a) Synthesis of Precursor-ASPU: Precursor-ASPU was prepared from PCL, MDI and APS by a

two-step method. (1) A given amount of dehydrated PCL, MDI and freshly distilled 1,4-dioxane were introduced into a three-neck flask equipped with a nitrogen inlet and a mechanical stirrer, and stirred at 80 °C for 2 hrs under N_2. (2) An appropriate amount of APS (the molar ratio of PCL/MDI/APS = 1/1.4/0.8) was added, and the reaction was continued at 70 ℃ for another 1h.

b) Preparation of SMPU solution: SMPU solution was obtained by adjusting the hydrolysis and condensation reaction. Water and HCl (10% aqueous solution) were added into the Precursor-ASPU solution. The molar ratio of Precursor-ASPU/HCl/H_2O was around 1/0.05/10, and the solid content was about 35 % in 1, 4-dioxane. The mixture solution was stirred at room temperature for about 2 hrs.

Preparation of bulk and micro/nano-fibrous SMP film:

a) Bulk SMP film: The bulk SMP films were prepared by casting the SMPU solution into a Teflon mold, and kept at room temperature for 12 hrs and another 24 hrs in a vacuum oven. Then it was treated in liquid paraffin at 80 °C for 24 hrs. The films were then washed by dehydrate ether and dried.

b) Micro/nano-fibrous SMP film: PVP (10 wt % in absolute ethyl alcohol) was added into the SMPU solution with the weight ratio of 1: 1. The elctrospinning apparatus included a high voltage power supply, a syringe with a flat-end metal needle, a syringe pump and a collecting screen covered with an aluminum foil. The prepared electrospinning solution was added into a syringe and delivered to the tip of the needle by the syringe pump at a feeding rate of 0.0015 mm s^{-1}. Electrospinning was carried out under an applied voltage of 23 kV with fiber collecting distance of 20 cm. The SMPU/PVP film was first treated as the same procedure as that of the bulk film, and then was thoroughly washing by water/ethanol to remove the PVP and dried resulting the micro/nano-fibrous SMP film.

Characterization:

Instruments and measurements:

Fourier transform infrared spectra (FTIR) was measured on a FTIR spectrometry (Tensor-27, Bruker Co., Germany) in TR mode. ^{1}H-NMR and ^{29}Si-NMR were carried out on Avance III, 400 MHz Digital Nuclear Magnetic Resonance Spectrometer (Bruker Co., Germany). The morphology and microstructural evolution of the electrospun film were observed by scanning electron microscopy (SEM, JSM-6700F, Hitachi Co., Japan).

The dynamic mechanical analysis (DMA) was conducted by tensile test at a Q800 DMA (TA Instruments, Inc., America) with a frequency of 1 Hz and a heating rate of 3 °C min^{-1}. The differential scanning calorimetry (DSC) was measured by a Perkin-Elmer diamond differential scanning calorimeter with a heating rate of 10 °C min^{-1}.

Water contact angle (CA) was measured using a contact angle system OCA20 (DataPhysics, Germany) at room temperature (296 K). Water droplets used for all measurements were about 2 μL. Each datum was obtained by at least five measurements at different positions.

Shape memory tests:

The sizes of the films were 12 mm × 2 mm × 0.8 mm. In the stretching-recovery tests, the

samples were stretched at 60 °C, and then cooled at 0 °C for 3 min to fix the temporary shape. To allow the shape recovery, the samples were heated to 60 °C again. In the bending-recovery tests, the samples were bent to a same temporary shape at 60 °C with the assistance of a polyethylene pipe, and then cooled at 0 °C to fix the temporary shape. Then the fibrous and the bulk SMP film was fixed by one end on a Teflon plate respectively. The set was put on a hot stage, and warmed up by ~ 0.3 °C s^{-1}. The shape recovery progress was recorded by a camera, and the temperature was recorded by a thermometer.

Results and analysis

Precursor-ASPU was characterized by FTIR, ^{1}H-NMR and ^{29}Si-NMR.

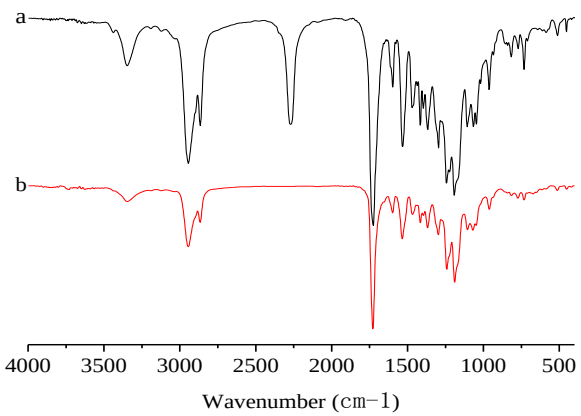
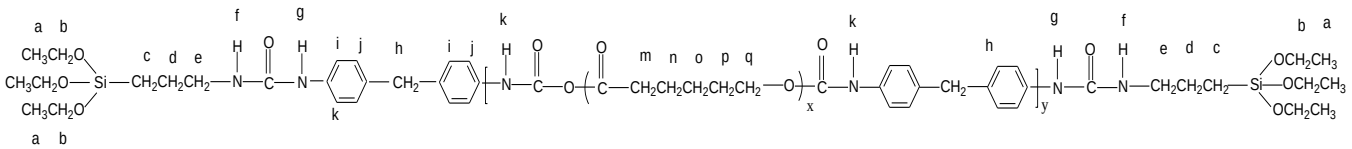


Fig. S2 FTIR spectra of the synthesis product a) from step (1), before APS was added; b) from step (2), after APS was added and reacted.

The FTIR spectra (Fig. S2) show that the synthesis reaction was carried out as expected. In FTIR spectrum, the peak at 2200~2300 cm^{-1} is the asymmetric stretching mode of –NCO group, and the peak disappeared after APS was introduced.

The molecular structure of Precursor-ASPU is shown in Scheme S1. The average value of "x" and "y" is 26.1 and 2.5 respectively according to the ^{1}H-NMR data (Table S1).



Scheme S1 The molecular structure of Precursor-ASPU.

Table S1 The data of ^{1}H-NMR spectrum of Precursor-ASPU

Precursor A	δ (ppm)	Theoretical value (the number of hydrogen atom)	Actual value (the number of hydrogen atom)
a:-CH_3	1.121-1.155	18	18
b:-CH_2	3.562	12	12.52
c:-CH_2	0.539-0.560	4	3.39
e: -CH_2	3.002-3.047	4	4.05
f:-NH	6.079	2	2.07
g:-NH	9.476	3.5	4.19
h:-CH_2	3.730-3.765	7	19.67
i:-CH	7.251-7.350	14	14.57
j:-CH	7.004-7.073	14	13.9
k: -NH	8.272	2	1.91
m:-CH_2	3.957-3.988	130.5	130.0
o: -CH_2	1.283-1.300	130.5	130.5
q: -CH_2	3.324	130.5	130.0
d、n、p: -	1.522-1.539	261+4	265.2

The result of ^{1}H-NMR measurement of Precursor-ASPU is listed in Table S1.

The ^{29}Si-NMR spectrum of the Precursor-ASPU only shows one sharp peak at -45.9 ppm, which is corresponding to the Si atoms with three ethoxy groups.[S2] The ^{29}Si-NMR spectrum of the final micro/nano-fibrous SMP film shows multiple peaks from -50 ppm to -70 ppm indicating different types of Si atom because the Si–OEt groups are hydrolyzed and partially condensed. The degree of condensation of the micro/nano-fibrous SMP film is ca. 67 %, calculated according to the peaks' area ratio.[S3]

The SEM observation of the electrospun film before and after removing of PVP:

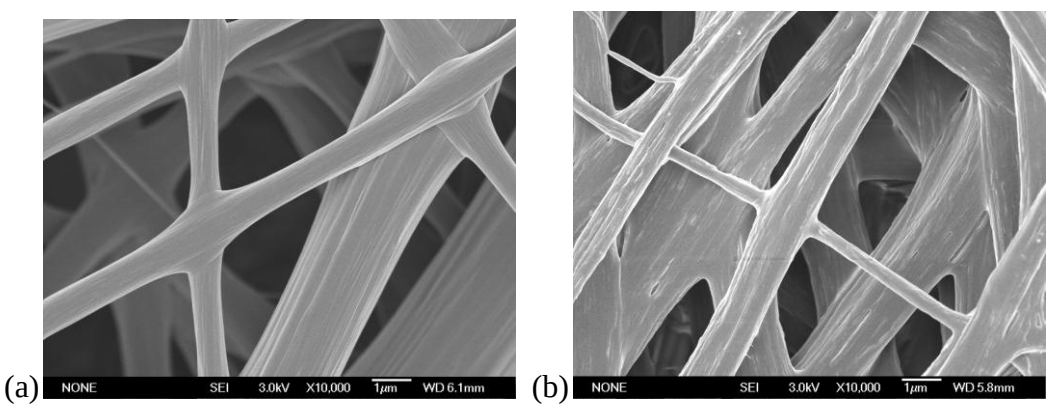


Fig. S3 SEM images of the electrospun film fibers before (a) and after (b) PVP was removed.

The stretching/Bending-recovery shape memory tests for the electrospun film

Table S2 The shape recovery ratios (R_rs) and shape fixting ratios (R_fs) in three cycles of stretching/bending-recovery tests

Model	R_f (%)		R_r (%)	
Stretching recovery test	R_{f1}	99.1	R_{r1}	80.5
	R_{f2}	98.8	R_{r2}	82.0
	R_{f3}	99.5	R_{r3}	81.4
	Average	99.1±0.4	Average	81.3±0.8
Bending recovery test	R_{f1}	81.3	R_{r1}	100.0
	R_{f2}	79.9	R_{r2}	100.0
	R_{f3}	80.6	R_{r3}	100.0
	Average	80.6±0.7	Average	100.0

R_{fn} or R_{rn}, where n = 1, 2, or 3, refers to the R_f or R_r in the first, second and third cycle of shape memory test respectively.

The R_f and R_r in each cycle of stretching-recovery (elongated to 150 %) or bending-recovery test are all 100 %.

References:

S1. J. N. Zhang, Y. M. Ma, J. J. Zhang, D. Xu, Q. L. Yang, J. G. Guan, X. Y. Cao and L. Jiang, *Mater. Lett.*, 2011, 65, 3639.

S2. J. W. Xu, W. F. Shi and W. M. Pang, *Polymer*, 2006, 47, 457.

S3. H. J. Dong, R. F. Reidy and J. D. Brennan, *Chem. Mater*, 2005, 17, 6012.