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The quintuple-shape memory effect in electrospun nanofiber membranes

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Abstract

Shape memory fibrous membranes (SMFMs) are an emerging class of active polymers, which are capable of switching from a temporary shape to their permanent shape upon appropriate stimulation. Quintuple-shape memory membranes based on the thermoplastic polymer Nafion, with a stable fibrous structure, are achieved via electrospinning technology, and possess a broad transition temperature. The recovery of multiple temporary shapes of electrospun membranes can be triggered by heat in a single triple-, quadruple-, quintuple-shape memory cycle, respectively. The fiber morphology and nanometer size provide unprecedented design flexibility for the adjustable morphing effect. SMFMs enable complex deformations at need, having a wide potential application field including smart textiles, artificial intelligence robots, bio-medical engineering, aerospace technologies, etc in the future.

(Some figures may appear in colour only in the online journal)

1. Introduction

Shape memory polymers (SMPs) possess unique memory and thermo-mechanical properties and have attracted significant interest in recent years [1–6]. Dual-shape SMPs can memorize pre-set temporary shapes and recover to an original shape when they are triggered by an external stimulus [7–11]. Due to this shape memory property, SMPs have been considered as biometrically-functional materials [12], sensors and actuators [13], smart textiles [14] and smart composites for aerospace engineering applications [15]. Dual-memory properties have attracted extensive research interest [16]. In contrast to dual-shape memory polymers, more and more attention is focused on the multi-shape memory effect upon heating [17]. Multi-shape capability requires the polymer to have a broad transition temperature. The transition temperature is determined by the molecule design and chemical composition. Xie has reported that thermoplastic Nafion with a broad transition temperature from 55 to 130 °C exhibits excellent quadruple-shape memory performance [18].

DuPont's Nafion® PFSA polymer as a commercial thermoplastic polymer possesses excellent super-selective, acidity and electrical conductivity, chemical stability, thermal stability, and mechanical properties. Although a great deal of research on SMPs has appeared in the last couple of years, it has mostly focused on bulk films. With the recent trend of miniaturization of smart materials and devices, it is a challenge to study micro/nano-sized polymeric fibers with tunable multi-shape memory behaviors.

Compared with Nafion bulk films, electrospun Nafion nanofiber membranes have some advantages, such as large specific surface area, high aspect ratio (length to diameter ratio), strong and mutual penetration of the other substances, fine fabric structure, and high porosity (better adsorption and filtration properties). Due to their special structure, shape memory nanofiber membranes have been applied in many important areas [19–21]. Shape memory nanofiber membranes as a novel smart material have garnered research interest. For example, Hu *et al* [22, 23] reported the manufacture of polyurethane nanofibers with a dual-shape memory effect by the electrospinning method. Their shape memory performance was achieved by adjusting their soft and hard segments. Chen *et al* [24] prepared a shape memory film via electrospinning of a triethoxysilane endcapped precursor solution, and the fibrous structure was stably reversible for shape memory test. Chung *et al* [25] fabricated an electrospun web to investigate its applicability as an intelligent clothing material using shape memory polyurethane. Compared with the dual-shape memory property of electrospun fibrous membranes, if the multi-shape memory effect can be realized, it will be more significant and interesting. To date, the memorability of shape memory nanofiber membranes that can achieve adjustable quintuple-shape memory effect under heat stimulation has not been reported.

In general, electrospun Nafion nanofiber membranes (ENNMs) have been used in a variety of applications including fuel cell membranes [26], photocatalysis and chemical catalysts [27], sensors [28], and functional composite materials [29]. The novel multiple morphing properties can bring new functions to ENNMs. For instance, for catalysts, ENNMs will obtain large specific surface area and pore diameter to increase the catalytic efficiency by adjusting shape upon different temperatures; the porosity of the porous diffusion layer in a proton exchange membrane fuel cell will be improved by changing the shape of the fibrous membrane in appropriate condition. In addition, ENNMs as catalysts can be used to increase the specific surface area, high porosity and catalytic activity via adjusting the shape of the fiber under multiple reaction temperatures. ENNMs have potential application prospects in smart textiles, artificial intelligence robots, bio-medical engineering, aerospace technologies, etc in the future. It is worthwhile to investigate the tunable multi-shape memory effect of electrospun polymeric fibrous membranes.

Here, based on Nafion with a broad transition temperature range, a little poly(ethyleneoxide) (PEO) as carrier polymer is added to improve the spinnability and to obtain the nanofiber membranes. Nafion nanofiber membranes as a kind of soft morphing material are fabricated using the electrospinning method, and possess the multi-shape memory property. The triple-, quadruple-, and quintuple-shape memory effects are demonstrated in a shape memory cycle.

2. Experimental section

2.1. Materials

Nafion® PFSA with polymer content 5.0 wt% was purchased from DuPont. Poly(ethyleneoxide) (PEO) ($Mn = 900\,000$) was purchased from Changchun Jinghua Co., Ltd. All the chemicals were used as received without any further treatment.

2.2. Electrospinning of Nafion

The 1.0 wt% PEO solution for electrospinning was prepared by magnetic stirring of PEO particles in 5.0 wt% Nafion solution at room temperature for 24 h to obtain the uniform electrospun solution.

Electrospinning was conducted using an apparatus (Nanospider, Elmarco) that was based on recent efforts to elevate electrospinning technology to an industrial level by simultaneously provoking innumerable polymeric jets from a sufficiently large liquid surface to increase productivity.

Nafion solution with 1.0 wt% PEO polymer concentration was electrospun with the following conditions: 30 kV applied voltage between the spinneret electrode and the collector, 16 cm electrode-to-collector distance, and 0.9 rpm constant electrode rotation rate.

The electrospun nanofiber membranes were annealed at 160 °C for 120 min. All obtained membranes were annealed under air conditions. During the annealing process, a network was formed between intersecting fibers.

2.3. Characterization

The morphology of the nanofiber membranes was determined through field emission environmental scanning electron microscopy (SEM, Quanta 200FEG). The diameters were measured by the software Image J.

Nicolet AVATAR 360 Fourier transform infrared (FT-IR) spectroscopy was applied to analyze the interaction between different materials. The samples were conducted from 400 to 4000 cm^{-1} in reflection mode at room temperature.

A thermo gravimetric analysis (TGA, Mettler Instruments) was conducted from 25 to 700 °C with an air flow rate of 20 ml min^{-1} and a heating rate of 10 °C min^{-1}.

X-ray diffractometer (XRD) analysis was applied using a Rigaku D/max-rb rotating anode XRD with Cu Kα radiation, Kα = 1.5418 Å at a generator voltage of 40 kV and a current of 50 mA. The data were collected from 5° to 80° intervals.

Nanotensile testing was performed on a commercial nanotensile testing system (Nano UTMTM Universal Testing System T150, Agilent Technologies) with the method of 'UTM-Bionix Standard Toecomp CDA'. The nominal maximum load of this system is 500 mN, and the maximum crosshead extension is 150 mm. Two individual samples were prepared and tested in each category. The tensile strain rate was set as 1.0×10^{-3} s^{-1}, and the harmonic force and frequency were typically 4.5 mN and 20 Hz, respectively.

The mechanical properties were tested with a dynamic mechanical analyzer (DMA, Mettler Instruments) at a constant frequency of 1 Hz from 0 to 180 °C at a heating rate of 3 °C min^{-1}.

The shape memory effect tests were evaluated in a fixed force controlled mode. Strain was monitored as follows. (1) The sample was heated at a high temperature T_{high}. Then the deformation occurred under a tensile load. (2) The deformed sample was cooled down to a lower temperature T_{low}, where the deformation was fixed. (3) The external force was removed at T_{low}, holding for a period of time under the no stress condition. (4) The deformation was recovered by reheating to T_{high}. Then the same process was repeated three, four and five times to achieve triple-, quadruple- and quintuple-shape memory cycles, respectively.

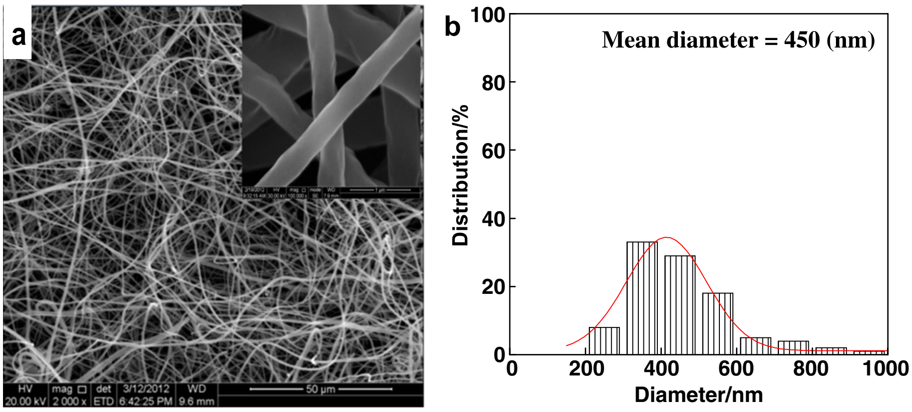

Figure 1. (a) SEM images of the electrospun nanofiber membranes. (b) The histograms of electrospun Nafion nanofiber diameter distribution. A total of 100 fibers were randomly and evenly picked from the SEM image (a) and their diameters were measured using ImageJ.

The following equations were used to calculate R_f and R_r for the multi-shape memory effect [18]:

$$R_f(X \to Y) = \frac{\varepsilon_y - \varepsilon_x}{\varepsilon_{y,\mathrm{load}} - \varepsilon_x} \times 100\% \quad (1)$$

$$R_r(Y \to X) = \frac{\varepsilon_y - \varepsilon_{x,\mathrm{rec}}}{\varepsilon_y - \varepsilon_x} \times 100\% \quad (2)$$

where X and Y denote different shapes, $\varepsilon_{y,\mathrm{load}}$ is the maximum strain under load, ε_y and ε_x are the fixed strains after cooling and load removal, and $\varepsilon_{x,\mathrm{rec}}$ is the strain after recovery.

3. Results and discussion

Nafion fibrous membranes were prepared by means of the electrospinning method; the PEO concentration was 1.0 wt%. The scanning electron microscopy (SEM) images of the obtained electrospun fibrous membranes are shown in figure 1(a). The resultant nanofibers were of good quality with no beading. In addition, the histograms of nanofiber diameter distribution are shown in figure 1(b); the average fiber diameter was approximately 450 nm.

The interaction between the Nafion and the PEO can be investigated by FTIR spectroscopy. As shown in figure 2, it is clearly observed that the characteristic absorption peaks at 1236 and 1155 cm^{-1} belong to $–CF_2–$. The absorption peaks at 637 and 528 cm^{-1} are attributed to the bending vibration of $–CF_2–$ and the stretching vibration of C–S [30]. Additionally, a band at about 1060 cm^{-1} is assigned to $–SO_3H$ groups [31]. The results showed that no new characteristic absorption peak appeared. This also showed that the addition of PEO could not change the Nafion's structure. From a material perspective, PEO is added into the eletrospun solution to increase the electrospinnability. Some papers have reported that hydrogen bonds can be produced between the sulfonic acid groups of Nafion and the lone-pair electrons of the ether oxygens in PEO [32]. These may provide some advantages for the shape memory properties of electrospun Nafion nanofiber membranes.

In order to discuss the decomposition temperatures of the different contents in the samples, thermal gravimetric

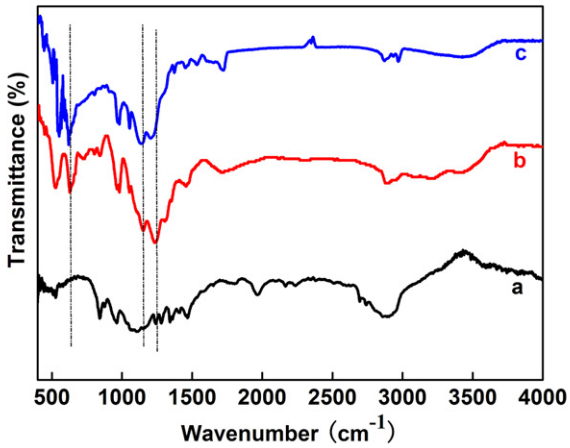

Figure 2. FTIR spectra of Nafion nanofibers: (a) PEO, (b) Nafion with 1.0% PEO, (c) Nafion.

analysis (TGA) was conducted. For pure Nafion and Nafion with 1.0% PEO mixture polymer, figure 3 revealed that the loss of mass observed for ENNMs up to 200 °C corresponded to traces of water, whereas the mass loss in the 280–375 °C temperature range was caused by degradation of sulfonic groups due to the decomposition of Nafion side chains $–OCF_2CF_2–SO_3H$. The rather sharp weight loss taking place in the range 375–550 °C resulted from degradation of the polymer backbone [30, 33]. As good thermal stability until 300 °C was found for the Nafion nanofiber, and taking into account that typical operation temperatures were between 50 and 200 °C, no degradation of the Nafion nanofiber was expected for widespread applications. Therefore, the physical properties of the samples were obviously influenced.

Thermal annealing was used to obtain an equilibrium length. In addition to water loss, annealing also caused the removal of residual strain/stress from the polymer processing steps. X-ray diffractometer (XRD) analysis was used to identify the crystalline structure of the samples. Figure 4 shows the XRD patterns of the ENNMs. For all samples, there are two peaks in the 5°–60° range and the peaks at 17.5° and 39.5° are the crystallization peak and the

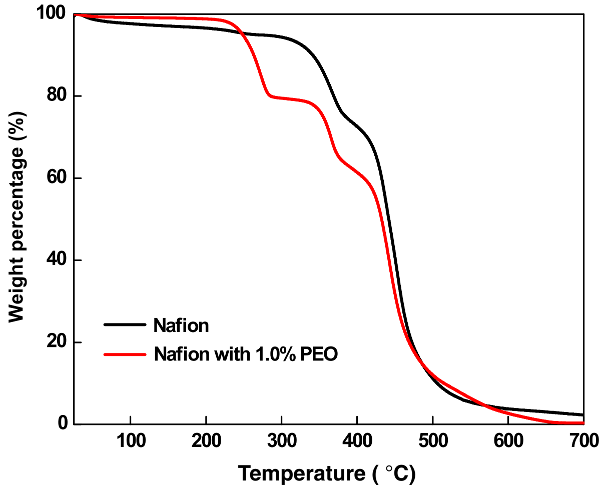

Figure 3. TGA curves of the Nafion nanofibers.

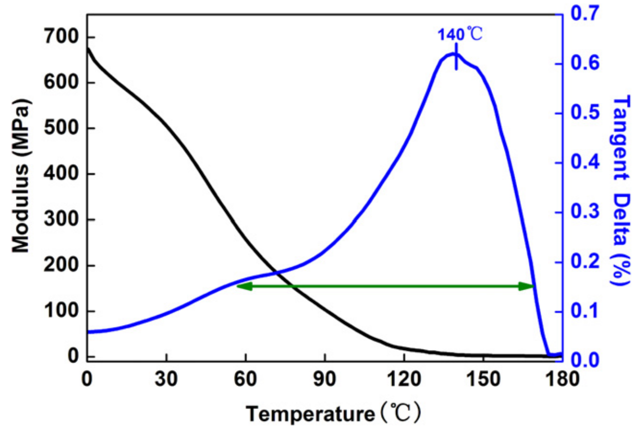

Figure 5. Storage modulus and tangent delta curves of Nafion at an oscillation frequency of 1 Hz: (a) electrospun Nafion nanofiber membranes, (b) Nafion N117 film.

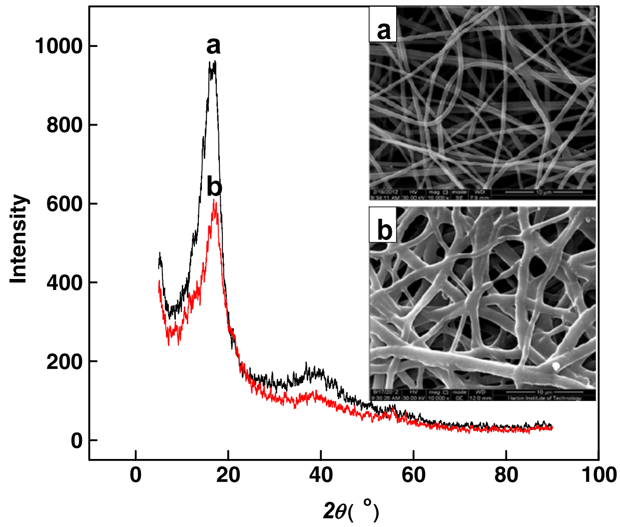

Figure 4. XRD patterns of electrospun Nafion nanofiber membranes: (a) SEM image of original electrospun nanofiber membrane and (b) SEM image of annealed electrospun nanofiber membrane at 160 °C.

amorphous peak, respectively. XRD results indicated that the stress relaxation occurred in the ionic phase of the nanofiber membranes and the ionomer peak intensity of the annealed nanofiber membranes greatly reduced as compared with pristine nanofiber membranes [18]. Accordingly, SEM images of original and annealed ENNMs are shown in figures 4(a) and (b), respectively. For the ENNMs, intersecting fibers could be welded to each other during the annealing stage. The effects of annealing temperature on interfiber welding and structure are presented in figure 4(b). It was found that the diameter of the nanofiber increased as compared with an original fiber (figure 4(a)). The morphology of the non-woven fibers was changed from a circular shape to a ribbon-like structure. Heat treatment could alleviate the stress concentration and heat history of the fibers and, thus, it could result in change of the mechanical properties.

A dynamic mechanical analyzer (DMA) was used to determine the dynamic thermal mechanical properties. The tensile mode results are presented in figure 5. A drop in the storage modulus (E') is observed over a wide range of temperature from 30 to 130 °C. Raising the temperature would lead to the mobility of the sulfonate groups increasing and the cross-linking decreasing, so that the elastic modulus of the material would decrease. The reduction in the storage with increase of temperature is associated with softening of Nafion at high temperature. As expected, the $\tan\delta$ curve exhibits a broad transition temperature range which is from 60 to 170 °C. It also shows the transition peak located at approximately 140 °C. During the electrospinning process, poly(ethyleneoxide) (PEO) as a carrier with lone-pair electrons interacts with the sulfuric acid groups of Nafion, which generates hydrogen bonding [32]. The glass transition temperature (T_g) could be markedly enhanced by increasing the intermolecular hydrogen bonding. At the same time, the transition behavior of the polymer was basically identical during heating and cooling processes under the specified rate conditions. The DMA results could supply some information for the realization of the quintuple-shape memory effect for ENNMs.

To examine the static mechanical behavior of the ENNMs, nanotensile testing was conducted at room temperature. The engineering stress–strain relationship for the Nafion nanofiber membranes is plotted in figure 6. The letters Y and B locate the positions of yield strain and break point. In the diagram, all samples show linear elastic response up to the point Y and follow Hook's elastomeric behavior. After releasing the load, the samples returned to their original shape. Thus, the Young's modulus can be calculated by measuring the slope of the curve from the origin to the point Y. The stress was no longer proportional to strain in the strain hardening region (between the Y point and peak stress). Then the constriction or neck began to form at some point and fracture ultimately occurred at the neck (between peak stress and the B point). In general, the strain corresponding to the linear region is only a few per cent. In microlevel view, the elastomeric behavior such as the higher modulus and small deformation was caused by the bond lengths and angles of polymer change.

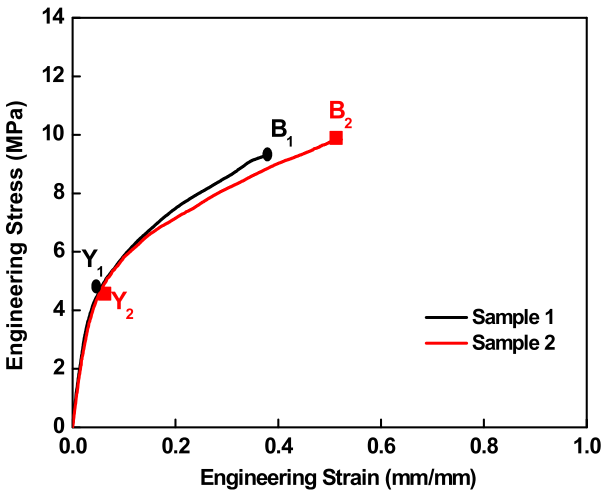

Figure 6. Engineering stress–strain responses for Nafion nanofiber membranes at a strain rate of 10^{-3} s^{-1}.

Table 1. The Young's modulus (E), offset yield strain (ε_y), fracture strength (F_s), and fracture strain (ε_f) of Nafion nanofiber membranes with 1.0 wt% PEO.

Sample	E (GPa)	ε_y (%)	F_s (MPa)	ε_f (%)
Nafion membranes	0.139 (0.008)	2.552 (0.276)	8.777 (1.397)	0.392 (0.125)

Ductile fracture occurred in the ENNMs at the breaking point after the yield point. Permanent deformation was found after the yield point when a load was continuously applied to the sample. However, if the ambient temperature was above its T_g, the sample was able to return to its original shape. Obviously, it was essentially a high-elastic deformation. Therefore, the molecular mechanism of the large deformation after the yield point was primarily caused by the motion of polymer chain segments. In general, SMPs experience elastic deformation, yielding, and cold drawing until failure. Nafion as a shape memory polymer has similar behavior upon loading with other SMPs. In table 1 some key mechanical properties for Nafion nanofiber membranes are shown.

The shape memory effect of ENNMs was under investigation. Triple-shape memory polymer can switch from a first shape (A) to a second shape (B) and from there to a third shape (C) by loading with a different force, with the shapes recovered by subsequent temperature stimulation. The triple-shape memory behavior of ENNMs is illustrated in figure 7(a). First, the sample was deformed at 160 °C (above both T_g and T_m) by loading with a force of 0.1 N. Then the sample was cooled to 100 °C, while holding the external force constant, followed by an isothermal hold for 10 min. Then the force was unloaded, keeping at 100 °C for 10 min. Thus, the first temporary shape was fixed. Second, the sample was reloaded with a force of 0.2 N at 100 °C. Then the sample was reduced to 40 °C. The load was kept at 40 °C for 10 min and then the load was removed. This led to the second temporary shape fixing. Sequentially the two fixed deformations recovered by heating the sample to 100 °C and keeping this temperature for 10 min, heating to

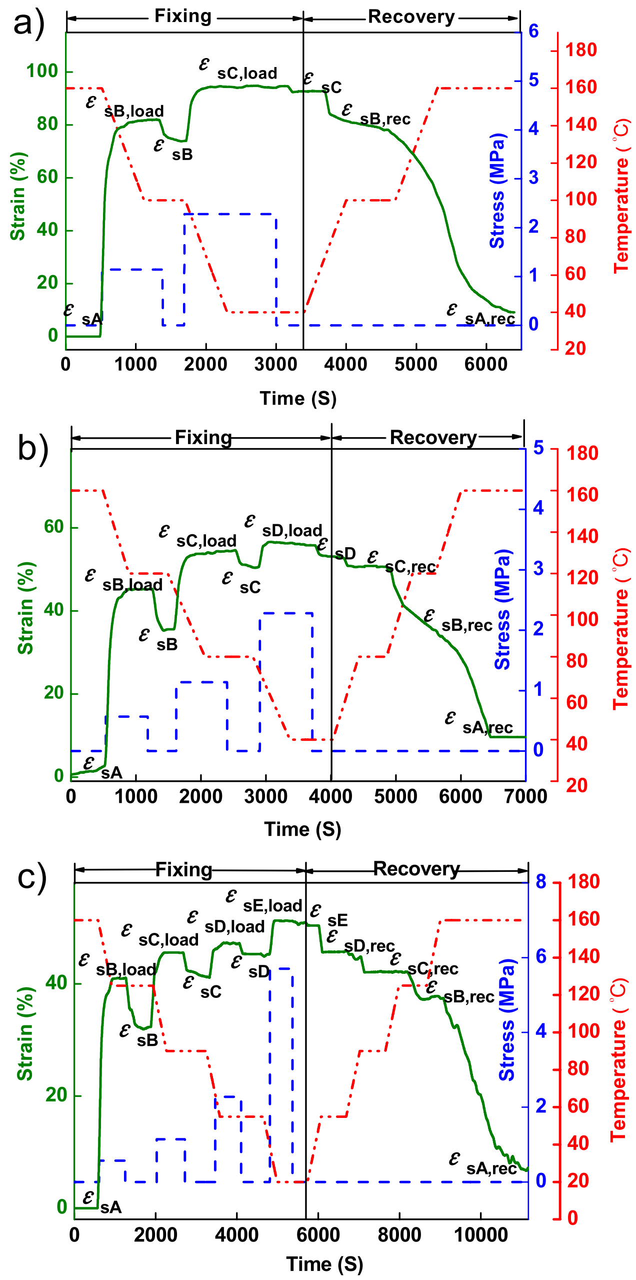

Figure 7. Multi-shape memory cycle of electrospun Nafion nanofiber membranes: (a) triple-shape memory cycle ($T_{dB} = T_{rC} = 160\,°C$, $T_{dC} = T_{rB} = 100\,°C$); (b) quadruple-shape memory cycle ($T_{dB} = T_{rD} = 160\,°C$, $T_{dC} = T_{rC} = 120\,°C$, $T_{dD} = T_{rB} = 80\,°C$); (c) quintuple-shape memory cycle ($T_{dB} = T_{rD} = 160\,°C$, $T_{dC} = T_{rC} = 125\,°C$, $T_{dD} = T_{rB} = 90\,°C$, $T_{dD} = T_{rB} = 55\,°C$).

160 °C and keeping the temperature. The shape recoveries were $R_r(SC \to SB) = 93.20\%$ and $R_r(SB \to SA) = 87.71\%$, respectively. The shape fixity was above 90% in all cases.

Accordingly, the data presented in figure 7(b) clearly demonstrate the relationship between the strain, stress and temperature. Heating at 160 °C leads to a motion of polymer chain segments, which causes the strain to increase from its initial value to ε ($T = 120\,°C$) under the constant stress conditions. Holding the temperature and stress, the strain does not change. The strain is decreased with the stress level

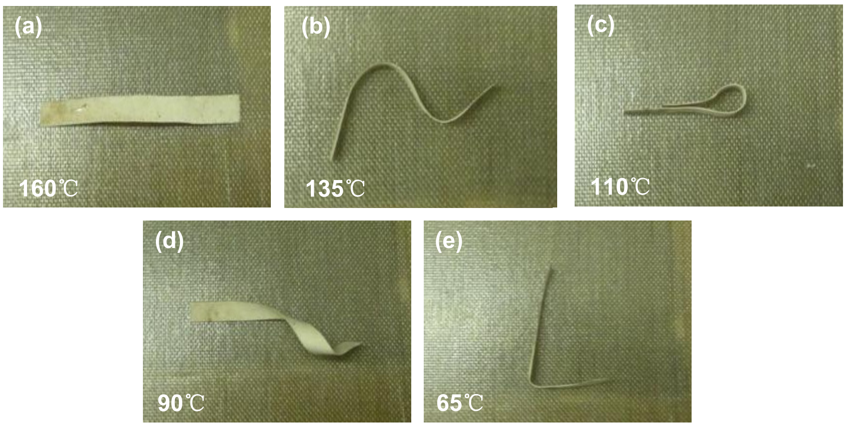

Figure 8. Photos of electrospun Nafion nanofiber membranes with quintuple-shape memory effect.

increasing. When the temperature cools down from 120 to 80 °C, the stress level is kept at 1.14 MPa; this results in a decrease of strain from ε_B to ε_C. Similarly to the process addressed above, the strain decreases from $\varepsilon_{C.load}$ to ε_C when the stress is removed. Then the sample is cooled to low temperature, $T = 40$ °C. While keeping the stress level at 2.28 MPa, the strain increases from ε_C to $\varepsilon_{D.load}$. The strain is reduced again after removing the stress. Ultimately, the stress level returns to zero and the strain $\varepsilon_{A.rec}$ is obtained when the temperature is reheated to 160 °C. The results for shape fixity and shape recovery ratio of the whole process show that $R_f(\text{SA} \rightarrow \text{SB})$, $R_f(\text{SB} \rightarrow \text{SC})$ and $R_f(\text{SC} \rightarrow \text{SD})$ were around 80%. $R_r(\text{SD} \rightarrow \text{SC})$ and $R_r(\text{SC} \rightarrow \text{SB})$ are above 80%, whereas $R_r(\text{SB} \rightarrow \text{SA})$ is above 70%.

It was exciting that the quintuple-shape memory effect of ENNMs was realized by using four temporary temperatures (160, 125, 90 and 55 °C). As shown in figure 7(c), ENNMs can memorize five shapes (one permanent shape A and four temporary shapes B–E) in a shape memory cycle. A stress of 0.57 MPa was applied to the ENNMs, which elongated the sample to shape B during the cooling down process from 160 to 125 °C. Shape B was changed to shape C when the temperature was decreased from 125 to 90 °C and a stress of 1.14 MPa was applied to the sample. Then, cooling from 125 to 90 °C, shape C was deformed to shape D, keeping the stress level at 2.28 MPa on the sample until cooling to 55 °C. The ENNMs were subjected to a stress of 5.7 MPa, and the shape change occurred at 55 °C. Reducing the temperature to 20 °C, the shape E was fixed. Subsequently, when the sample was reheated to 55 °C, 90 °C, 125 °C and 160 °C respectively, the temporary shapes gradually recovered to the original shape A. From the whole process, the Nafion nanofiber membranes showed an excellent quintuple-shape memory property with high shape fixity and recovery rate. The shape fixity and shape recovery of the Nafion nanofiber membranes are shown in table 2.

The quintuple-shape memory effect also reflected the tunable shape memory properties for ENNMs. As demonstrated in figure 8, ENNMs can memorize one permanent shape (A) and four temporary shapes (B–E) at different temperatures in a shape memory cycle. Subsequent heating to the relevant temperatures led to the recovery shapes. Furthermore, temporary shapes could be predesigned into different shapes to suit practical applications. It was also confirmed that the quintuple-shape memory effect could be realized at any two temperatures above the onset of the glass transition, provided that the two temperatures were not too close.

The tunable multi-shape memory effect demonstrated for ENNMs stemmed from the broad temperature transition. Throughout the entire process above, recovery of the four temporary shapes was obtained, confirming that the electrospun Nafion membranes can be actuated selectively and actually controlled in multiple recovery applications. The pore structure and nanometer size made the resultant membranes have light weight, easy morphing, soft property and good permeability. This is a versatile method to increase the potential applications in smart clothing, bio-medicine engineering, and biomimetic robot and intelligence actuators.

Table 2. The shape memory behavior of the Nafion nanofiber membranes.

Multi-shape memory cycle	Shape fixity (%)	Shape recovery (%)
Triple-shape memory cycle	SA → SB = 91.37 SB → SC = 91.99	SB → SA = 87.71 SC → SB = 93.20
Quadruple-shape memory cycle	SA → SB = 78.37 SB → SC = 79.06 SC → SD = 74.30	SB → SA = 74.23 SC → SB = 80.05 SD → SC = 87.19
Quintuple-shape memory cycle	SA → SB = 77.87 SB → SC = 67.73 SC → SD = 68.40 SD → SE = 84.44	SB → SA = 78.63 SC → SB = 76.17 SD → SC = 84.05 SE → SD = 92.94

4. Conclusions

In summary, tunable shape memory effect is achieved for Nafion nanofiber membranes by means of the electrospinning method. The morphing fibrous membranes are found to be capable of shape fixity and shape recovery in an independent quintuple-shape memory cycle. Additionally, ENNMs possess a broad transition temperature range from 60 to 170 °C. This is suitable for many application fields. More significantly, the tunable multi-shape memory fibrous membranes which combine their abilities to adjust shapes, nanofiber diameters, pore diameters, and multi-stage effect, can provide a pathway for novel potential applications.

Acknowledgment

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