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Electrospun nanofiber membranes for electrically activated shape memory nanocomposites

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Abstract

A novel shape memory nanocomposite system, consisting of a thermoplastic Naion polymer and ultrathin electrospun polyacrylonitrile (PAN)-based carbonization nanofiber membranes, is successfully synthesized. PAN-based carbonization nanofiber networks that offer responses to deformations are considered to be an excellent actuation source. Significant improvement in the electrical conductivity of carbon nanofiber membranes is found by adjusting the applied voltage power in the electrospinning PAN process varying from 7.85 to 12.30 S cm\(^{-1}\). The porous structure of the carbon nanofiber membranes provides a large specific surface area and interfacial contact area when combined with the polymer matrix. Shape memory Naion nanocomposites filled with interpenetrating non-woven electrospun PAN carbonization membranes can be actuated by applying 14 V electrical voltage within 5 s. The results, as demonstrated through morphology, electrical and thermal measurements and a shape recovery test, suggest a valuable route to producing soft nanocomposites.

Keywords: actuation, carbon nanofiber membranes, electroconductibility, Naion, shape memory polymer

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

1. Introduction

A shape memory polymer (SMP) that is capable of remembering stable temporary shapes and reverting to its original shape when exposed to external stimuli, is highly significant in the development of smart materials [1, 2]. A kind of active polymeric material, SMPs have been utilized for a number of applications in various fields, such as automobiles, aerospace (hinge, variable camber wing), biomedicine (drug delivery system, smart surgical suture), self-healing composite systems, smart textiles and so on [3, 4]. Their stimuli-sensitive behavior enables SMPs to change certain properties when adjusted by an external signal [5]. However, shape memory behavior can be triggered by heating, which is a common method and is not feasible in some practical applications. In addition to direct heating, other methods including electricity [6], light [7], magnetism [8] or water [9] have been developed to achieve the multifunction in broad applications.

Electro-induced SMP composites have attracted the interest of researchers due to their capability of achieving remote control. Sensitivity to electricity in SMPs has been realized [10, 11]. In general, carbon materials in SMP composites are used to improve the conductivity and thermal properties. SMP composites filled with electrically conductive materials such as carbon nanotubes [12], carbon black [13], carbon nanotube nanopapers, carbon nanofibers [14, 15] and so on have previously been reported. Shape memory behavior has been demonstrated in various typical polymer matrices which include polyurethane, styrene-based and epoxy SMPs. For example, Jae Whan Cho \textit{et al} [16] have fabricated an electro-active SMP composite that is made of the multi-walled carbon nanotubes in a shape memory polyurethane matrix.
An order of $10^{-3}$ S cm$^{-1}$ has been obtained in samples with 5 wt% modified MWCNT content. Xiaofan Luo et al [17] have incorporated carbon nanofibers (CNFs) into an epoxy-based SMP matrix. The electrical conductivity of D50N50/CNF is about $30.59 \pm 0.81$ S m$^{-1}$. Jinsong Leng et al [18] have reported that an electroactive thermoset styrene-based shape memory polymer nanocomposite filled with nanosized (30 nm) carbon powders shows good electrical conductivity with a percolation of about 3.8%. To the best of our knowledge, a Nafion polymer system that can be triggered by electricity has not been reported.

Compared with other types of polymers, Nafion exhibits many advantages and has been adopted to investigate the shape memory matrix. DuPont’s Nafion® is a commercial thermoplastic polymer possessing a shape memory effect which has been demonstrated in [19–21]. A polytetrafluorethylene backbone and perfluoroether side chains terminated by a sulfonate ionic group have been researched since 1962. In addition, Nafion has excellent chemical properties, thermostability, mechanical properties, ionic conductivity, ion selectivity and biocompatibility that make it attractive for many uses in electrochemistry, fuel cells, catalysts, and in various types of chemical, humidity and biological sensors [22]. In order to expand the application fields and efficiency of shape memory Nafion, we use carbonization nanofiber membranes to actuate it, and the research shows the potential for bringing this type of composite into remote control, high speed recovery process and emerging biomedical devices. It is significant to develop the stimulus method of Nafion, which may lead to more specific uses.

Due to the softness of Nafion films, the conductive particles dispersed in the Nafion matrix could affect the shape recovery behavior. Therefore, a conductive composite is designed by introducing electrospun PAN carbonization nanofiber membranes into shape memory Nafion. Apart from their good electrical and thermal conductive properties, electrospun carbonization nanofiber membranes are ultrathin and soft. Compared with other conductive fillers [23, 24], carbon nanofiber membranes have many advantages. Continuous, smooth and non-woven carbonization nanofiber membranes via electrospinning with a conductive network and with a porous structure effectively increase the specific surface areas which can improve the permeability and the interfacial strength between fillers with a polymer matrix. The nanofiber membranes can disperse homogeneously in the polymer composite and noticeably enhance the heating transfer and mechanical properties. Various nanofiber sizes are needed to realize different conductivity with the changing electrospinning conditions to meet the requirements of all applications and to achieve high speed actuation in the shape recovery process. This is significant for extending applications of Nafion and its composites.

Figure 1. Demonstration platform for the SMP composite. (a) Schematic illustration of the electrospinning equipment. (b) Image showing the DMA of Nafion. (c) Schematic illustration of the SMP composite. (d) Image of sample size.
Here, we report a new type of shape memory composite system with electrical responsiveness. The electrospun PAN carbonization nanofiber membranes are embedded in the soft Nafton matrix, which is investigated as a functional material. Two major strategies are established to incorporate carbon nanofiber membranes into a Nafton matrix: (1) fabrication of PAN-based carbonization nanofiber membranes (electrospinning, stabilization, and carbonization), and (2) integrating the conductive nanofiber membranes with shape memory Nafton and characterization of electrically actuated shape memory behavior. Carbon nanofibers possessing excellent electronic and thermal properties have been used in a number of fields. The conductivity of PAN-based carbonization nanofiber membranes can be adjusted by optimized fabrication and processing methods. Changing the electrospinning applied voltage also influences the conductive network of fibrous membranes. Furthermore, the shape recovery behavior of Nafton/PAN-based carbonization nanofiber membrane composites is controlled. The combination of high speed electrical actuation with easy fabrication renders this electrically responsive Nafton polymer an excellent candidate in sensing, biomimetics, actuating, smart devices, and so on.

2. Experimental section

2.1. Materials

The polyacrylonitrile (PAN) used in this study, possessing a molecular weight of 150 000 (Mw), was purchased from Sigma-Aldrich. Nafton® with a polymer content of 5.0 wt% was purchased from DuPont. N,N-dimethylformamide (DMF) was used as the solvent. All the chemicals were used without any further treatment.
2.2. Electrospinning of PAN

The PAN polymer was dissolved in DMF to obtain the 10 wt% solution. The mixture was stirred at room temperature for 24 h before becoming a homogeneous electrospun solution. The basic setup for electrospinning was shown in figure 1(a). The distance between the needle tip and collector was 15 cm. The feed rate of the syringe pump was 20 μl min$^{-1}$. The high voltages were 20, 25 and 30 kV, respectively. The PAN was electrospun on an iron plate for 30 min. The electrospun PAN nano fiber membranes were annealed at 70 °C for 2 h in air.

2.3. Preparation of carbon nanofiber membranes and shape memory composites

The resultant non-woven and high quality fibrous membranes were stabilized and carbonized to obtain carbon nanofiber membranes (with a thickness of 0.05 mm). The stabilization of PAN nanofiber membranes was carried out in a box furnace (Lenton ECF12/4) which was heated in air at a heating rate of 1 °C min$^{-1}$ from room temperature to 290 °C and held at 290 °C for 3 h. For carbonization, the stabilized PAN nanofiber membranes that were subsequently heated in a tube furnace were carbonized in argon at a heating rate of 5 °C min$^{-1}$ from room temperature to 1000 °C and held at 1000 °C for 1 h. During the stabilization and carbonization process, the fibrous network was formed between intersecting nanofibers. The electrospun PAN-based carbonization nanofiber membranes were cooled down to room temperature for further use.

Nafion as a kind of thermoplastic polymer with a broad transition temperature (with a tan δ peak at 120 °C) in its dynamic mechanical analysis (DMA) curve (figure 1(b)), was chosen as the shape memory system matrix. The PAN-based carbon nanofiber membrane incorporated with shape memory Nafion was investigated through the following steps. The carbon nanofiber membrane was placed on the bottom of a glass plate. The shape memory Nafion solution was then poured over the carbon nanofiber membrane. Another glass plate was placed on the composite and pressed to make the Nafion penetrate into the membrane at room temperature for 48 h to obtain the SMP composite. The sandwich-like structure of the composite made the shape memory Nafion run through the whole network of the fibrous membrane (figure 1(c)). The prepared sample was cut into a ‘U’ shape and its size is shown in figure 1(d). The PAN-based carbonization nanofiber membrane weight fraction was measured to be 1.07% according to thermogravimetric analysis.

2.4. Characterization

Scanning electron microscopy (SEM, Quanta 200FEG) was carried out to characterize the morphology and structure of the nanofiber membranes. The Images J software was used to analyze the diameters and their distribution. 50 fibers were randomly selected from each SEM image.

Raman spectra were obtained from a LabRAM XploRA laser Raman spectroscope (HORIBA Jobin Yvon Co. Ltd). The 532 nm laser was applied as the source with incident power of 0.15 mW.

A nitrogen adsorption test (Micromeritics ASAP 2020) was applied to determine the specific surface area, pore volume, and average pore diameter.

![Figure 3. Raman spectra of PAN nanofibers: (a) stabilization; (b) carbonization.](image)

![Table 1. The surface area and pore size of PAN carbonization nanofiber membranes under different electrospinning applied voltages.](table)
A dynamic mechanical analyzer (DMA, Mettler Instruments) was used to study the thermal-mechanical behavior at a constant frequency of 1 Hz from 0 °C to 180 °C at a heating rate of 5 °C min$^{-1}$.

Infrared thermography (JENOPTIK Infra Tec) was used to estimate the temperature distribution of the conductive fiber membranes.

A four-point probe measuring instrument (Napson RT-70V/RG-7C) was employed to test the resistivity of the PAN-based carbonization nano fiber membranes.

3. Results and discussion

The carbon nano fiber membrane has been successfully fabricated via three steps, electrospinning, stabilization, and carbonization [25–27]. Photos of the PAN fibrous membrane at different stages are shown in figures 2(a)–(c). They are shown in different colors: white (original PAN nanofibers), brown (stabilization nanofibers) and black (carbonization nanofibers). Scanning electron microscopy (SEM) images, as shown in figures 2(d)–(f), demonstrate the microstructures and morphologies of fibrous membranes. The resultant nanofibers were uniform and continuous. The combining of nanofibers formed a network which provided a large contact area for the material composite. Figures 2(g)–(i) show histograms of the nanofiber diameter distribution. The average nanofiber diameters decreased from 618 ± 67 nm to 327 ± 38 nm at different stages. During the carbonization process, chemical changes that caused the nanofibers to shrink included dehydrogenation, cyclization, pre-oxidation, oxidation and deoxidization. Finally, the carbon nano fiber membranes formed a turbostratic graphite structure, which possessed electroconductive and diathermanous properties.

Applied voltage is a key element in the electrospinning process, which influences the diameter and morphology of the resultant fibers. When the electric field is strong enough, the polymeric droplets can overcome the surface tension to fabricate the smooth and uniform fibers. SEM images of PAN-based carbonization nano fiber membranes and histograms of the nanofiber diameter distribution are shown in figure 3 for the electrospinning with different applied voltages (20, 25 and 30 kV). The average diameter of PAN-based carbonization

![Figure 4](image1.png) (a)–(c) SEM images of PAN-based carbonization nano fiber membranes. (d)–(f) Histograms of PAN-based carbonization nano fiber diameter distribution.

![Figure 5](image2.png) The conductivity of PAN-based carbonization nano fiber membranes with different applied voltages.
fibers increased from 343 ± 49 nm to 483 ± 48 nm with the increasing applied voltage. Increasing the electrostatic force may draw more solution from the needle. Demir et al reported that increasing the electrospinning applied voltage would increase the fiber diameter [28–31]. The resultant fibrous membranes were of high quality. In addition, the results of the nitrogen adsorption test show the specific surface area and pore sizes of the different nanofibers in table 1.

Figure 4 shows strong Raman spectra of (a) stabilization PAN nanofibers and (b) carbonization PAN nanofibers at different temperatures in the range of Raman shift from 1000 cm⁻¹ to 3000 cm⁻¹. The sharp peaks at 1350 cm⁻¹ and 1590 cm⁻¹ are attributed to the D peak and G peak respectively [26, 32]. Compared with the stabilization, the peak positions did not shift after carbonization. However, the intensity of the D peak decreased and the intensity of the G peak increased after carbonization at 1000 °C. As observed, the intensity of the G peak in different electrospun voltages is varied. With the increase of the electro spun applied voltage the intensity of the G peak decreased. This may be caused by...
the nanofiber structure and diameters. This result indicates that the electrospun PAN nanofibers had a varying degree of carbonization which could lead to different electrical conduction.

The electrical resistivity of PAN-based carbonization nanofiber membranes was measured by a four-point probe. As seen in figure 5, the test results of resistivity are converted into electrical conductivity. It is found that with the increase of the electrospinning voltages, the conductivity of PAN-based carbonization nanofiber membranes decreases. Based on this result, it is revealed that the electrospinning technology influenced the structure and diameters of the electrospun nanofibers, which may affect the conductivity of fibrous membranes after carbonization. This result indicates that the applied voltage of the electrospinning method played an important role in the success of obtaining controllable nanofiber membranes.

Figure 6 shows the temperature distribution conducted by infrared thermography under different applied voltages including 8, 12 and 16 V respectively. It demonstrated that the distribution of temperature was uniform with different direct voltages. The temperature of the specimen was 66 °C under 8 V. Increasing the applied voltage to 16 V, the temperature reached 165 °C. It was observed that the higher the applied voltage, the faster the heating temperature. Therefore, as compared with low voltage, high voltage could bring about a quicker shape recovery process, which may lead to a high speed actuation.

The temperature distribution and shape recovery behavior of SMP composites being actuated by electrical resistance heating is shown in figure 7. The electrical conductivity of the composite was approximately 12.3 S cm⁻¹. As shown in figure 7(a), the temperature increases when a 14 V direct current circuit is applied. After 5 s, the SMP composite reaches a temperature of 130 °C. The temperature was uniformly distributed. At this stage, the sample was bent into a ‘U’ shape and remained this shape until it cooled down to room temperature. When a 14 V constant electrical current was applied again, the deformed SMP composite began to recover its permanent shape. As seen in figure 7(b), the speed of shape recovery progress is high and it takes only 5 s. High speed electrical actuation may provide a broad application in smart materials and structure.

The shape memory effect of the SMP composites was investigated in this study. The Nafion can be actuated by low voltage. As shown in figure 8, the electrical and thermal conductivity of the electrospun PAN-based carbonization nanofiber membranes in the actuation of SMP composites were demonstrated. The SMP composite specimen was bent as ‘0 s’ (temporary shape) during the application of electric field and the shape was kept at room temperature. A constant voltage of 14 V was applied to actuate the Nafion composite. The shape recovery process of the Nafion/electrospun carbon nanofiber membrane composite was recorded by a video camera. The sample displayed an approximately 100% shape recovery ratio within 5 s. This result may be attributed to the interfacial effect, high electrical conductivity and temperature distribution. These observations suggested that the speed of electro-induced SMP composites improved significantly with an electrospun PAN-based carbonization nanofiber membrane.

The electrical responsive behavior can be observed when the SMP composite has access to electricity. Figure 9 is a plot of shape recovery angle vs time using a voltage of 14 V. The better the electrical conductivity of the Nafion/electrospun PAN-based carbonization nanofiber membrane composites, the faster the shape recovery of the composites. The conductivity is essential for the observed electrically responsive property.

4. Conclusions

In summary, a series of composites that combine shape memory Nafion with electrospun PAN-based carbonization nanofiber membranes are investigated. The SEM characterization demonstrates that the network structure of nanofiber membranes and pore size can be adjusted by changing the applied voltage in the electrospinning process. More importantly, the conductivity of the electrospun carbon nanofiber membranes increases with the decrease of the diameter. The interactions between Nafion and carbon nanofiber membranes
affect the electrical and thermal properties of composites. Shape memory nanocomposites can be triggered quickly by applying low voltage and the complete shape recovery behavior only takes 5 s. The electrically induced method will play an enormous role in the success of remote control, which facilitates the applications of SMP composites as smart materials.

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References

[22] Carla H W 1996 Recent advances in perfluorinated ionomer membranes: structure, properties and applications J. Membrane Sci. 120 1–33
[28] Demir MM, Yilgor I, Yilgor E and Erman B 2002 Electrospinning of perfluorine fibers Polymer 43 3303–9
[29] Deitzel J M, Klemmeyer J and Harris D T 2001 The effect of processing variables on the morphology of electrospun nanofibers and textiles Polymer 42 261–72