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Electrospinning of poly(styrene-*co*-maleic anhydride) (SMA) and water-swelling behavior of crosslinked/hydrolyzed SMA hydrogel nanofibers

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Abstract

Random and alternating poly(styrene-*co*-maleic anhydrides) (SMAs) with respective maleic anhydride (MAh) content of 32 and 48% were synthesized through radical polymerization. SMA nanofibers with diameter down to 180 nm were generated by electrospinning from solvents acetone, dimethylformamide (DMF), and their mixtures. Fiber diameter increased dramatically when the SMA concentration in the spinning solution reached to a critical point where the SMA chains are extensively entangled. The diameter of SMA nanofiber decreased with increasing DMF content in the mixture, but beads are often accompanied as DMF content is over 50%. The optimum acetone/DMF ratio was found to be 2:1, in which continuous electrospinning was achieved and bead-free nanofibers were obtained. SMA nanofibers with MAh content of 32 and 48% were crosslinked with diethyleneglycol and subsequently hydrolyzed in NaOH/EtOH to turn SMA into crosslinked sodium form SMA (SMA-Na) hydrogel nanofiber. These hydrogel nanofibers were able to retain fiber form after immersing in water for 24 h. Their water absorption ratio was up to 37.6 and 8.2 g/g in distilled water and 0.25 N NaCl aq. solution, respectively.

Keywords: Electrospinning; Poly(styrene-*co*-maleic anhydride); Nanofiber

1. Introduction

Electrospinning is a simple but versatile method in preparing fibers with diameter down to submicron [1]. One of the most important characters of nanofiber is its very large surface-to-volume and length-to-diameter ratios, which assure its promising applications in areas where super-large surface area is highly required [2–6]. Besides many factors such as solvent, viscosity, surface tension, solution conductivity, feeding rate, and electrical field affecting electrospinning [7], the choice of a proper solvent and composition in a mixed solvent is of great importance to the electrospinning process. For instance, the morphology of poly(ethylene oxide) nanofiber changed greatly with the change of ethanol/water ratio [8]. Chitosan nanofiber was obtained from solvent of concentrated acetic acid/H_2O instead of aqueous dilute acetic acid solution [9]. In our previous work, we studied the effect of solvent composition on electrospinning of cellulose acetate [10,11] and found that its optimal solvent is 2:1 (v/v) acetone/dimethylacetamide (DMAc) mixture. One purpose of this work is to use poly(styrene-*co*-maleic anhydride) (SMA) as a model polymer to further study the effect of solvent composition on electrospinning. Two solvents, i.e. acetone and *N*,*N*-dimethylformamide, and their mixtures having a wide range of solvent properties such as vapor pressure (0.34–24.53 kPa) and surface tension (23.33–36.45 mN/m) were used to prepare SMA solution for electrospinning (Table 1).

SMA is an important reactive thermoplastic polymer offering high heat resistance while maintaining good impact, rigidity and dimensional stability [12–14]. Though it is mainly applied as engineering plastics, crosslinked salt form of alternating SMA with MAh content of ca. 50% is good for

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Table 1
Solution properties of R-SMA-1 solutions

Acetone/ DMF ratio	γ (mN/m) at 22 °C	P (kPa) at 20 °C	Conc. of R-SMA-1 (wt%)	η (cp) at 30 °C
Acetone	23.33	24.53	20	20.2
			24	35.7
			30	96.0
			38	415.0
DMF	36.45	0.34	20	80.0
			30	347.5
			40	2062.5
3:1	25.33	19.64	20	29.0
2:1	26.45	17.76	20	34.1
1:1	28.33	13.90	20	35.2
1:2	30.50	9.77	20	43.3
1:3	31.75	7.61	20	46.7

absorbing fiber material [15]. The water absorption capacity of SMA type absorbing material varies with the solution's ionic strength [15]. Due to this particular property, it is very interesting and meaningful to make functional SMA hydrogel nanofiber through electrospinning and post-spinning treatment. It is reported that ultrafine hydrogel nanofiber would greatly improve its response time [16], and enhance mass transport of ions and chemicals from the solution to the enzymes and cells embedded in the hydrogel [17]. Most hydrogel nanofibers reported so far contain poly(acrylic acid) (PAA) component [18,19]. Judging from their SEM images, the most noticeable shortcoming of PAA containing hydrogel nanofibers is the large deformation of individual fiber after they were immersed in water, mainly due to their flexible backbone chain structure. In order to maintain fiber morphology as much as possible in the water immersion/drying cycles of hydrogel nanofiber, one simple approach is to employ a polymer with rigid chain structure. SMA molecular chain is relatively rigid because of the existence of phenyl side group; therefore it is highly possible that the deformation of SMA hydrogel nanofiber upon exposure to water may be limited to small extent.

In this work, we also aim to prepare SMA hydrogel nanofibers responsive to ionic strength. To this end, an alternating SMA and a random SMA with respective MAh content of 48 and 32% were synthesized. They were electrospun in the presence of crosslinker diethyleneglycol, followed by heat-induced crosslinking and subsequent hydrolysis. The water absorption of crosslinked/hydrolyzed SMA nanofibrous membrane as a function of MAh content, crosslinking density, and ionic strength in water is examined.

2. Experimental

2.1. Materials

Styrene was purified by washing with 5 wt% NaOH aq. solution twice and then with distilled water until neutralization, followed by distillation at reduced pressure. Maleic anhydride (MAh) was milled into powder and dried at 50 °C in a vacuum oven for 10 h. Then it was stored in a desiccator prior to use. Initiators 2,2′-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were recrystallized before use. Acetone, *N*,*N*-dimethylformamide (DMF), and crosslinking agent diethyleneglycol (DEG) were used as received. A commercialized random SMA copolymer, coded as R-SMA-1, was kindly provided by Shanghai Research Institute of Petrochemical Technology (Shanghai, China).

2.2. Synthesis of SMA

2.2.1. Preparation of random SMA copolymer

In a typical procedure, to a three-necked round bottle with 10.8 g of styrene, 50 ml of butanone containing 4.9 g of MAh and 9.7×10^{-3} g of BPO was added dropwise. The reaction was proceeded at 95 °C for 2 h under the purge of nitrogen gas. SMA was then obtained by precipitating and washing with methanol. The precipitate was dried at 50 °C in a vacuum oven for 10 h and was coded as R-SMA-2.

2.2.2. Preparation of alternating SMA copolymer

MAh (4.9 g) was added to a three-necked round bottle containing 100 ml of toluene. MAh was completely dissolved after the mixture was stirred at 75 °C for 30 min. A mixed solution of styrene:AIBN:toluene (5.4 g:2.46×10^{-3} g:20 ml) was then added dropwise. The polymerization was proceeded at 75 °C for 30 min, and at 85 °C for another 30 min. White precipitate was observed with the progress of polymerization reaction. The whole course of this reaction was performed under N_2 atmosphere. The SMA product was collected by filtration and washed thoroughly with toluene. SMA was dried at 50 °C in a vacuum oven for 10 h. It was labeled as A-SMA.

2.3. Electrospinning of SMA

SMA was dissolved in acetone, DMF, and their mixtures in different ratios to prepare electrospun solution with desired SMA concentrations (Table 1). SMA solution was placed in a syringe with a stainless needle of gauge 18. The feeding rate was 10 μl/min set by a syringe pump (TS2-60, Longer Precision Pump Co. Ltd, Baoding, China). An electrode was clamped on the needle and connected to a power supply (DW-P303-IAC, Tianjin Dongwen High Voltage Plant, China). Grounded counter electrode was connected to collector aluminum foil. The electrospinning conditions of voltage of 10 kV and tip-to-collector distance of 17 cm were used. The nanofibrous membranes on grounded collector were dried under vacuum at 80 °C for 10 h to remove any residual solvents.

In a typical procedure for the preparation of water-absorbing SMA nanofibers, into 40 wt% SMA in 2:1 (v/v) acetone/DMF solution, 5 or 10% (weight percent to SMA) crosslinking agent DEG was added, followed by vigorous stirring in an oil bath at 100 °C for 10 min. Then the solution was electrospun immediately under the processing conditions given above. Such-obtained SMA nanofibrous membrane was put in an oven at 145 °C [18] for 10 min to allow the crosslinking reaction to proceed completely.

The crosslinked SMA nanofibrous membrane was hydrolyzed in 1.5 N NaOH/ethanol solution for 24 h at room temperature, followed by washing with ethanol, and then dried in a vacuum oven at 50 °C for 10 h.

2.4. Characterization

Fourier transform infrared (FTIR) spectra of SMA products were collected on Nicolet Avatar 360 spectrometer in KBr form. ^{1}H NMR spectra were recorded on Bruker DRX-400 at room temperature by using solvent acetone-d_6 ($\delta = 2.06$ ppm) with internal standard tetramethylsilane (TMS). Molecular weight and molecular weight distribution of SMA were determined on Waters 1515 gel permeation chromatography (GPC) by using THF as solvent and eluent. Monodispersed polystyrene was used as calibration standard. Viscosity of SMA solution was measured by a rotational viscometer (NDJ-1, Shanghai Precision & Scientific Instrument Co., Ltd, China) at 30 °C. Solvent surface tension was measured via platinum plate method on a tensiometer (JK99C, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd) at 22 °C. Vapor pressures of solvents were calculated as follows:

$$P = n_1 P_{\text{acetone}} + (1 - n_1) P_{\text{DMF}}$$

where P, P_{acetone}, and P_{DMF} are vapor pressures of mixed solvents, acetone, and DMF, respectively, at 20 °C and 1 atm; n_1 is molar fraction of component acetone in the solvent mixture.

Morphology of the fibrous membrane was observed under scanning electron microscope (JEOL, JSM-6380LV). Average fiber diameter was obtained by measuring the diameter of ca. 10–20 nanofibers in its SEM images. Differential scanning calorimetry (DSC) was performed on NETZSCH DSC-204. Specimens were first heated to 150 °C at a heating rate of 25 °C/min and then cooled to 25 °C to eliminate thermal history. A second run from 25 to 400 °C at a heating rate of 20 °C/min under N_2 was recorded.

Hydrolyzed crosslinked SMA nanofibrous membrane strips with size of 1 × 1 cm^2 weighing 20–23 mg were used for water absorption measurement. The thickness of nanofibrous membrane was not measured due to its softness. Strips were put in distilled water and 0.25 N NaCl aq. solution for 24 h. Then the membrane was taken out and the free water on the membrane surface was absorbed by filter paper. It should be mentioned that two parts of water contribute to the total water absorption of SMA hydrogel nanofibrous membrane. One part is within the swelled SMA hydrogel nanofibers and the other part is from the filling of pores formed among fibers. In order to remove the latter part of water, water swelled membrane strip was placed into a specially designed centrifuge tube that prevents the strip from coming into contact with the supernatant during centrifuging. The tube was centrifuged at 5000 rpm for 10 min. Water absorption ratio was calculated as follows:

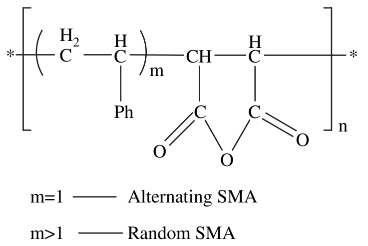
$$R = \frac{m_w - m_d}{m_d}$$

where m_w and m_d are the masses of wet and dry nanofibrous membranes, respectively.

3. Results and discussion

3.1. Synthesis of SMA copolymer

Styrene and maleic anhydride are readily copolymerized through free-radical polymerization. However, alternating SMA (A-SMA) of low molecular weight (Scheme 1) is favored to produce due to the formation of charge transfer complex (CTC) between St and MAh. With the increasing content of monomer styrene in the polymerization media and the elevation of reaction temperature to over 90 °C, random SMA (R-SMA) with high molecular weight (Scheme 1) is able to form because of the self-polymerization of styrene [20]. The molecular weight and its distribution of SMAs used in this work were measured by GPC (Fig. 1) and are summarized in Table 2. Characteristic absorption peaks at 1853 and 1779 cm^{-1} for $\nu_{c=o}$ maleic anhydride, and at 696 cm^{-1} for $\delta_{c=c}$ of the phenyl group are present in the FTIR spectrum of A-SMA (Fig. 2). In the ^{1}H NMR spectra of SMAs (Fig. 3), peak in the chemical shift range of 6.0–7.6 ppm is designated to aromatic ring protons of styrene, while broad and poor resolved peaks between 1.2 and 3.8 ppm belong to methylene and methine protons of MAh and St. The other peaks appearing in the spectrum of specimen R-SMA-1 were caused by the additives in the commercial product. The composition of MAh in copolymer SMAs was easily calculated from their ^{1}H NMR spectra since the resonance of phenyl group of styrene is well resolved from the others. The mole fraction of MAh was calculated by the following equation [13]:



Scheme 1. Repeating unit of SMA.

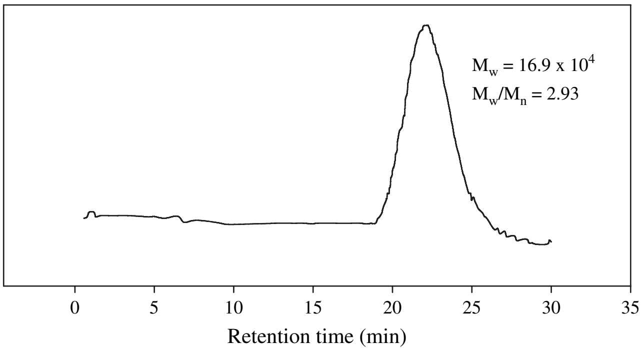


Fig. 1. GPC chromatogram of R-SMA-1.

Table 2
Molecular weight and content of MAh of SMA

Sample	Content of MAh (χ) (%)	M_w ($\times10^4$)	M_w/M_n	Source
R-SMA-1	19	16.9	2.93	Commercial product
R-SMA-2	32	23.2	2.84	Synthesized in this work
A-SMA	48	0.53	3.42	Synthesized in this work

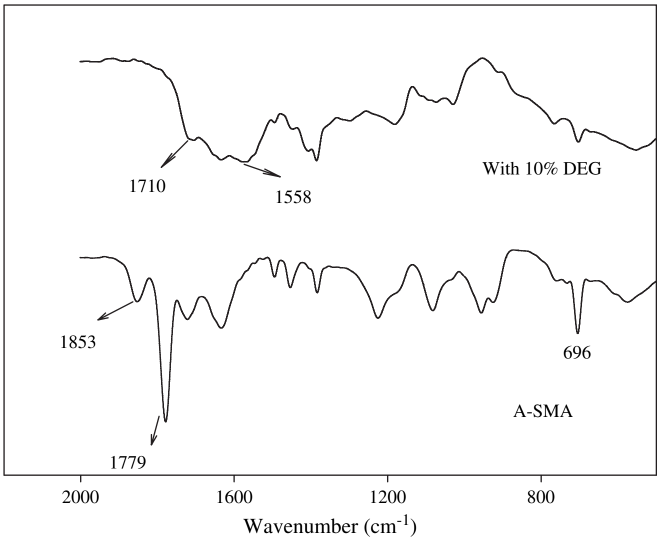


Fig. 2. FTIR spectra of A-SMA and crosslinked/hydrolyzed A-SMA nanofibers.

$$\chi = \frac{5I_{\text{total}} - 8I_{\text{phenyl}}}{5I_{\text{total}} - 6I_{\text{phenyl}}}$$

where χ is the mole fraction of MAh in SMA, I_{total} and I_{phenyl} are the integration intensities of the total protons and phenyl protons, respectively. The χ values are listed in Table 2. On the basis of these χ values, we conclude that a random SMA (R-SMA-2) with MAh content of 32% and a nearly alternating SMA (A-SMA) with MAh content of 48% were synthesized in this work as expected.

3.2. SMA nanofibers

R-SMA-1 was used as starting material to study the effect of solvent on the electrospinning process. The morphology of R-SMA-1 nanofibers from solvent acetone is shown in Fig. 4. 'Beads-on-string' morphology (Fig. 4A and B) was found for nanofibers from 20 and 24 wt% R-SMA-1 solutions. With increasing of R-SMA-1 concentration to 30 and 38 wt%, bead-free nanofibers were obtained (Fig. 4C and D). Beaded fiber is often observed in the electrospinning of many polymer solutions at their low concentration (or in their low viscosity) [10,21,22]. In electrospinning a charged polymer jet is ejected from the Taylor cone by electrostatic force once it overcomes the surface tension. In the course of the jet's traveling to the collector, jet breaks up and retracts into beads if it cannot withstand the surface tension and the electrostatic force [23]. Instead of forming individual beads like in the electrospraying of low molecular weight compound solution, a stable beads-on-string structure is formed. This can be explained by the fact that the extensional flow of the viscoelastic polymer jet resists breakup, and the solidification of jet due to quick solvent evaporation immobilizes the oriented, elongated chain to form fiber [8,24]. The toroids formed by the collapse of beads (Fig. 4A and B), as well as ribbon shape nanofibers are similar to the findings reported by Reneker et al., and these special morphologies result from the collapse of fiber skin because of fast evaporation of solvent acetone [25]. As to the variation of fiber diameter with R-SMA-1 concentration, it is found that mean fiber diameter gradually increased from 1.0 to 5.7 μm as concentration of R-SMA-1 increased from 20 to 30%, and it

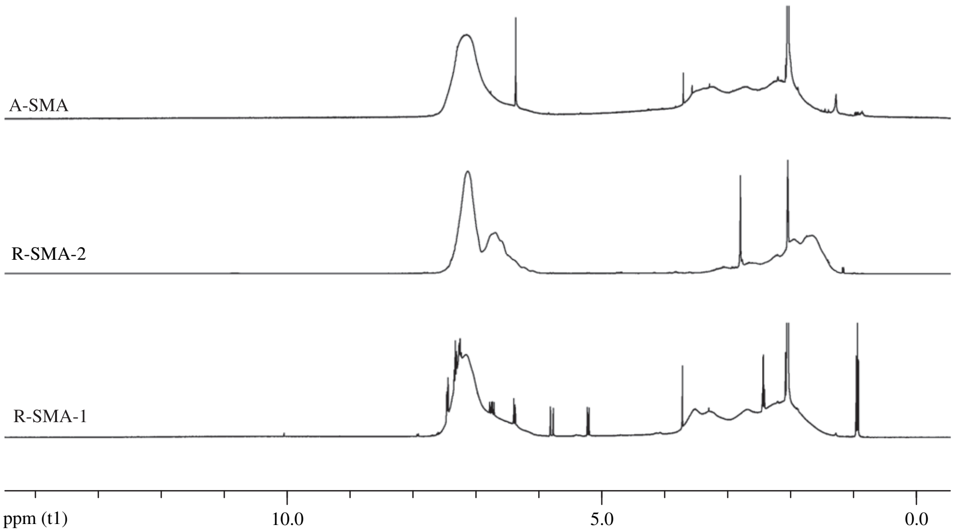


Fig. 3. ^{1}H NMR spectra of SMA specimens.

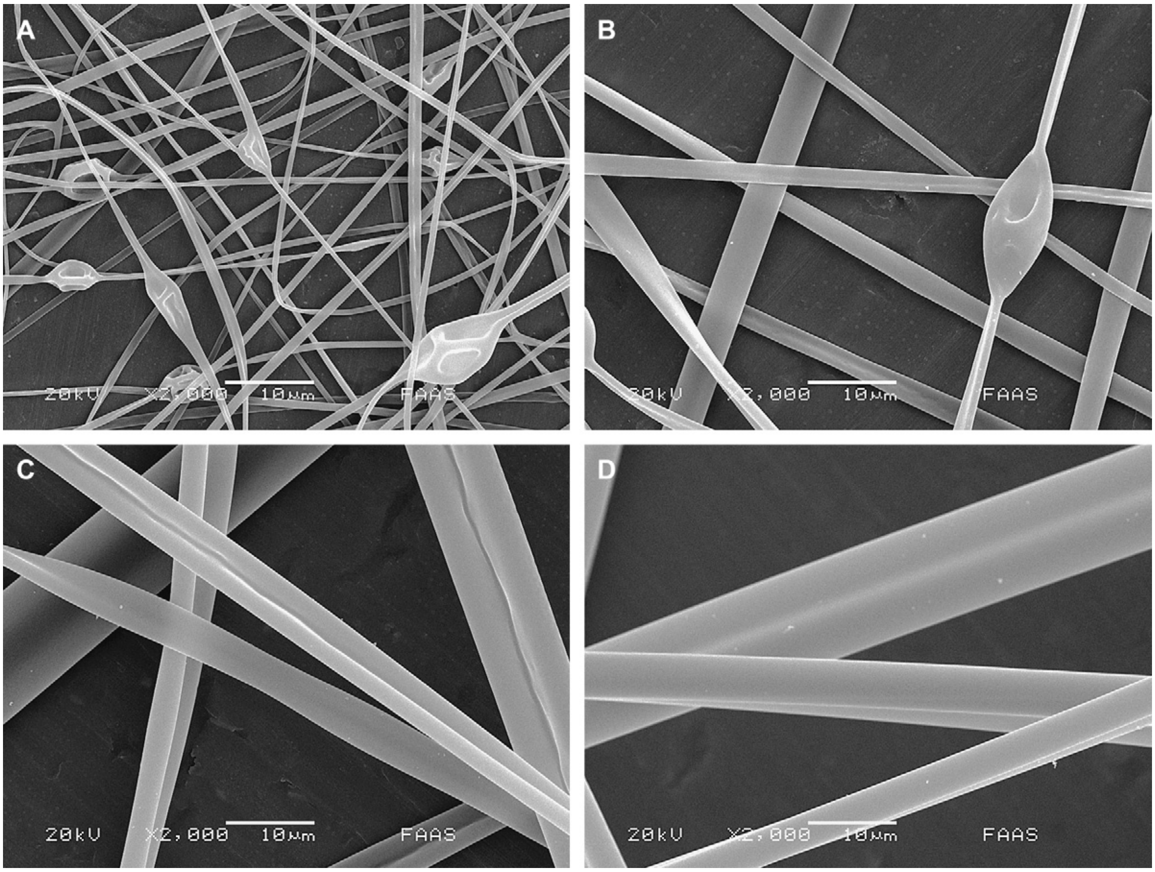


Fig. 4. SEM images of R-SMA-1 nanofibers from solvent acetone with R-SMA-1 concentrations of (A) 20%, (B) 24%, (C) 30%, and (D) 38%.

leapt to 11.7 µm when R-SMA-1 concentration was raised to 38 wt% (Fig. 5). This phenomenon is closely related to the change of solution viscosity with SMA concentration shown in Table 1. It has been reported that concentration exponents for the viscosity dependence in a good solvent in the semidilute entangled polymer solution follow $\eta \sim C^{4.25-4.5}$, and fiber diameter showed a ~3.0 power law dependence on solution concentration [23,26]. The dramatic viscosity increase of 38 wt% R-SMA-1 solution implies a large number of entanglement couplings of SMA chains, thereby generating larger electrospun fibers [23].

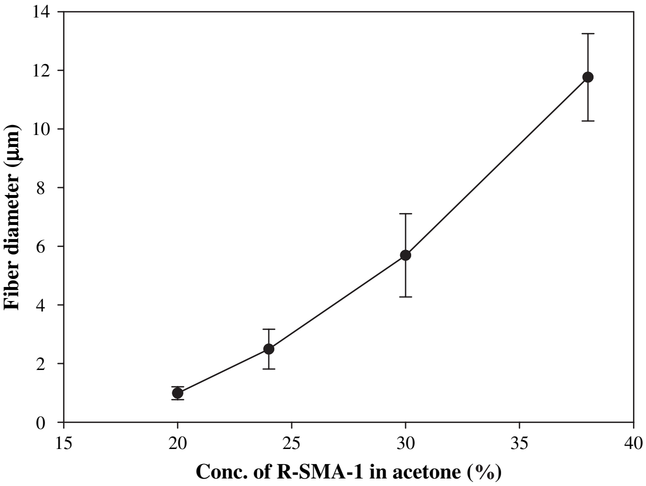


Fig. 5. Average diameters of nanofibers as a function of R-SMA-1 concentration in acetone shown in Fig. 4.

Fig. 6 shows R-SMA-1 nanofibers electrospun from its DMF solutions. Beaded fibers with average diameter of ca. 170 and 310 nm were obtained for 20 and 30 wt% SMA solution, respectively, but the size and amount of beads substantially decreased with increasing SMA concentration (Fig. 6A and B, and Fig. 7). From 40 wt% SMA solution, nanofibers in diameter of 1100 nm with relative narrow size distribution were generated. This non-linear relationship between fiber diameter and SMA concentration is caused by the fact that fiber diameter increases exponentially with polymer concentration, as shown for SMA nanofibers from solvent acetone. However, the exact exponent is not available because of limited data point in this study. The morphology and diameter change of nanofibers from DMF solution are similar to that from acetone solution. However, it is noticed that the diameter of nanofibers from DMF solutions is significantly thinner than that from acetone solution with corresponding SMA concentration. This is believed to be associated with the differences in the solvent vapor pressure (Table 1) governing the solvent evaporation from the electrospun fibers. To form nanofibers, SMA jet is elongated hundreds of thousands times in the course of traveling from tip to collector under the influence of electrical

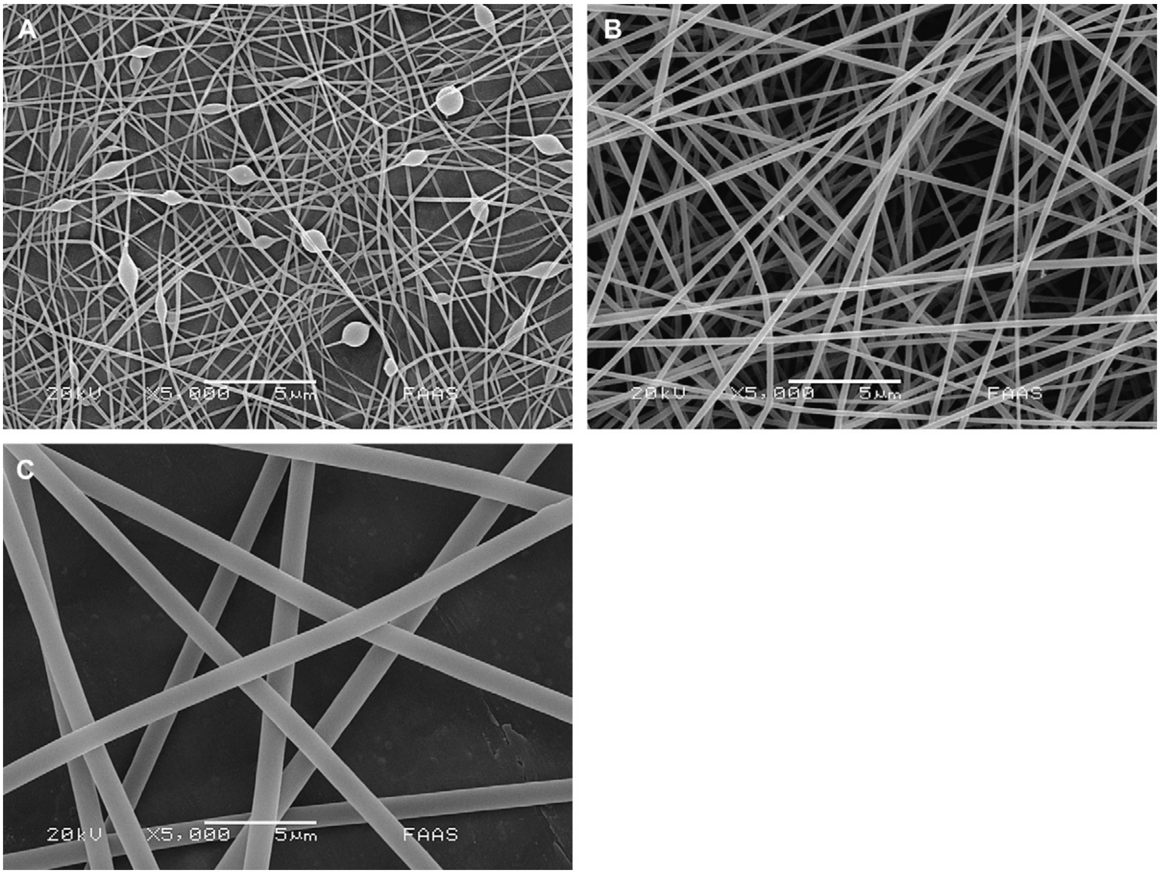


Fig. 6. SEM images of R-SMA-1 nanofibers from solvent DMF with R-SMA-1 concentrations of (A) 20%, (B) 30%, and (C) 40%.

forces, but the elongation is terminated once the fibers are solidified. Since the vapor pressure of acetone is high, the stretching of SMA/acetone jets is readily to be halted due to its solidification. The SMA/DMF jets may be stretched more times before it reaches the collector because of the slow evaporation of DMF, leading to much thinner fibers.

The effect of solvent composition in acetone/DMF mixture on fiber morphology and size is shown in Fig. 8. R-SMA-1 concentration was kept constant at 20 wt%. Uniform nanofibers with diameter less than 1 μm were obtained from 3:1, 2:1 and 1:1 acetone/DMF mixture (Fig. 8A–C), whereas fibers with a few elongated beads (Fig. 8D) were generated as the content of DMF exceeded 67% in the solvent mixture and more beads appeared along fiber with further increasing DMF content to 75% (Fig. 8E). Average fiber diameter decreased from 1000 to 170 nm as DMF content increased from 0 to 100% (Fig. 9). The reason for this change is identical to that described above.

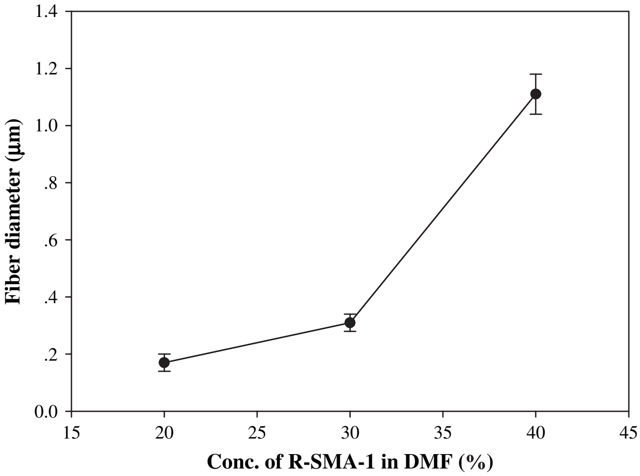


Fig. 7. Average diameters of nanofibers as a function of R-SMA-1 concentration in DMF shown in Fig. 6.

Among the three solvent systems, i.e. acetone, DMF and acetone/DMF mixture for the electrospinning of SMA, it was found that the continuous electrospinning process in acetone is limited because the needle tip is blocked in several seconds caused by the fast evaporation of acetone. The continuity of this process is guaranteed in DMF though fiber is often accompanied by beads. In acetone/DMF mixture, 2:1 acetone/DMF with respective surface tension (γ) and vapor pressure (P) of 26.45 mN/m and 17.76 kPa (Table 1), is the most proper solvent for the electrospinning of SMA not only due to its easy processibility, but also due to its bead-free nanofiber obtained. A similar optimum composition ratio was found for the electrospinning of cellulose acetate in mixed solvent acetone/DMAc [10], suggesting that an ideal solvent should have a proper balance between surface tension and vapor pressure. Thus 2:1 acetone/DMF was used for the following study.

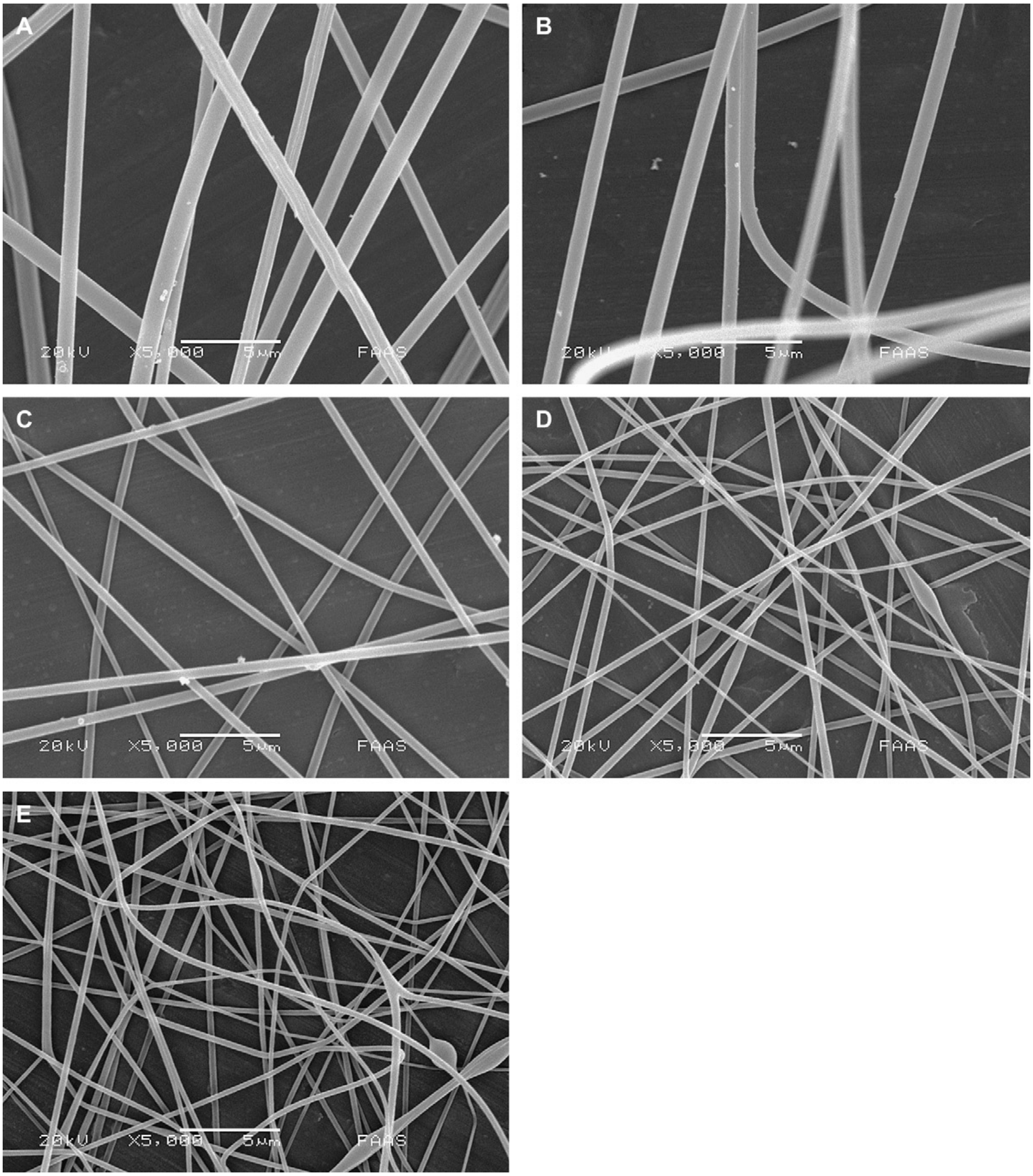


Fig. 8. SEM images of R-SMA-1 nanofibers from 20 wt% R-SMA-1 in mixed solvent acetone/DMF with volume ratio of (A) 3:1, (B) 2:1, (C) 1:1, (D) 1:2, and (E) 1:3.

3.3. Water-absorbing SMA nanofibrous membrane

The MAh units in SMA copolymers are readily hydrolyzed in basic condition. The fully hydrolyzed R-SMA-1 in NaOH/EtOH was still hydrophobic and showed little swelling in water due to the low MAh content (18%) in the copolymer. An initial experiment on the hydrolysis of R-SMA-2 and A-SMA nanofibers found that their hydrolyzed products were water soluble and could not retain their fiber form. In order to make fiber with water absorbance, fiber must be water swellable but insoluble. A crosslinking via heat-induced esterification between MAh units and DEG, followed by hydrolysis to turn SMA fiber into crosslinked polyelectrolyte (SMA-Na) (Scheme 2) was designed to achieve this goal. After treatment, characteristic peaks at 1853 and 1779 cm^{-1} for the carbonyl group of MAh disappeared, while new peaks appeared at 1710 cm^{-1} for $\nu_{c=o}$ of ester group, and at 1558 cm^{-1} for $\nu_{\text{as } c=o}$ of sodium carboxylate (Fig. 2), indicating crosslinking and hydrolysis reactions took place as shown in Scheme 2. Linear untreated A-SMA showed T_g and T_m at 49.1 and 216 °C, respectively. It has been reported that the T_g of SMA varies from several tens to 170 °C depending on the sequence of MAh and St units, MAh content and molecular weight [27,28]. After SMA chains were crosslinked with 5 and 10 wt% DEG (Fig. 10), T_m of SMA disappeared and their

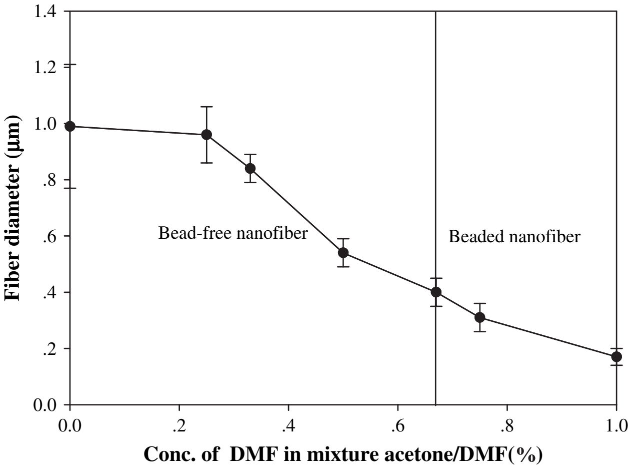


Fig. 9. Average diameters of nanofibers from 20 wt% R-SMA-1 as a function of acetone/DMF ratio shown in Fig. 8.

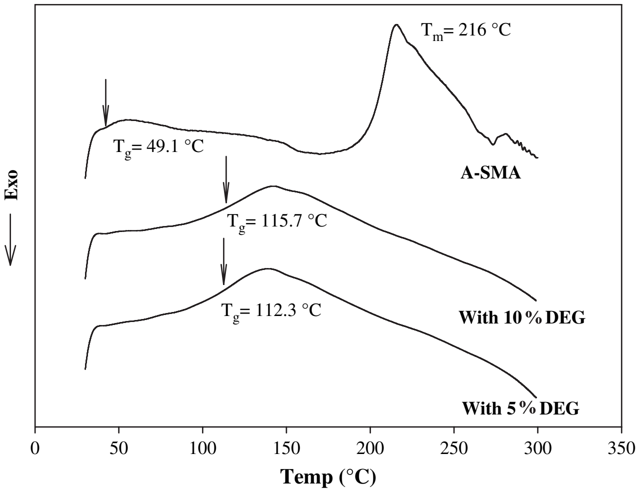
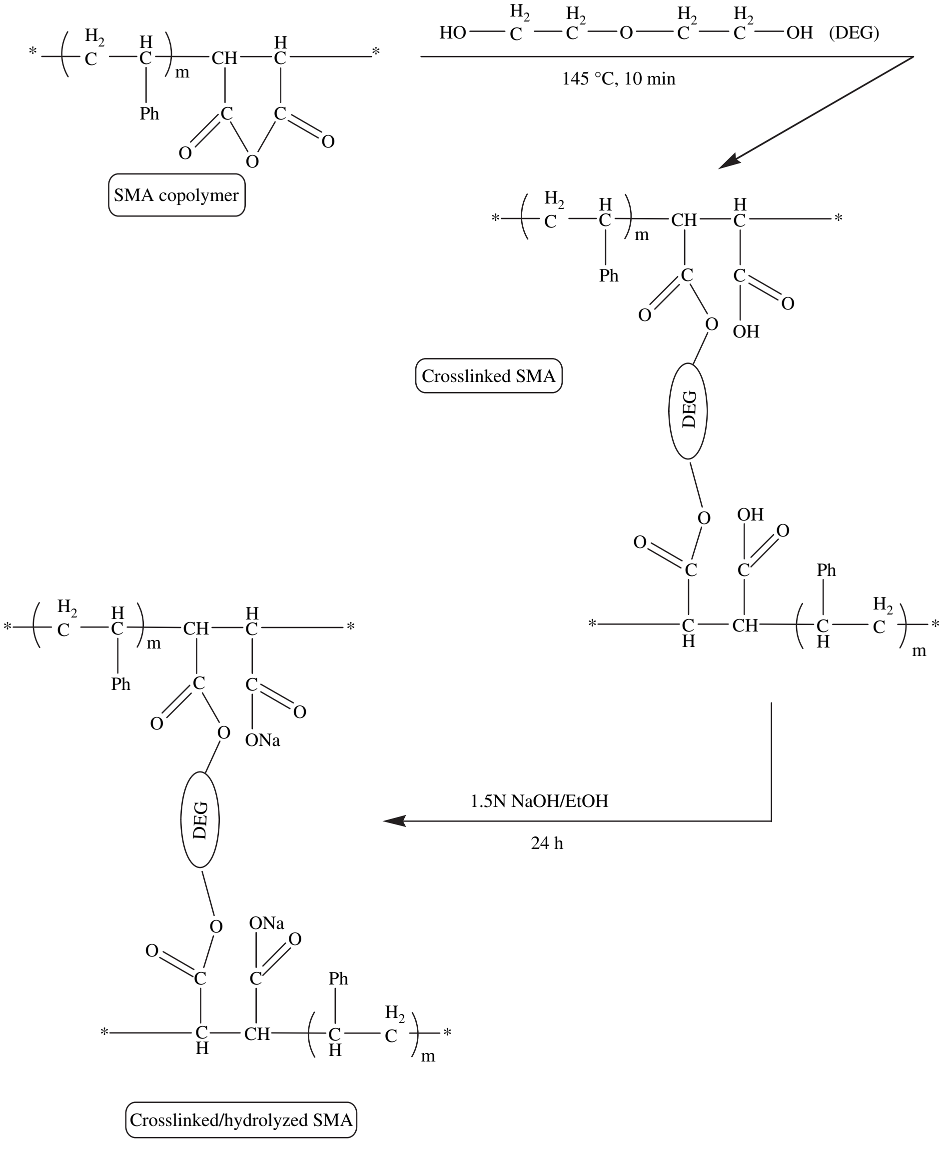


Fig. 10. DSC thermograms of A-SMA nanofibers and crosslinked A-SMA nanofibers.



Scheme 2. Crosslinking and hydrolysis of SMA.

T_g's greatly increased to 112.3 and 115.7 °C, respectively. Crosslinking would result in the increase of T_g because it limits the rotation of SMA molecular chain segments. In addition, the higher the crosslinking density, the higher the T_g is. The crosslinkage ester bond between MAh unit and hydroxyl group of DEG may be subjected to breakdown to some degree under the basic condition, but fortunately most of the crosslinkage ester bonds are kept intact in the mild hydrolysis conditions, as suggested by the disappearance of melting point, which is a characteristic of thermoplastic SMA copolymer, and by the retaining of fiber form after water treatment of the crosslinked/hydrolyzed SMA nanofibers as discussed below.

SEM images of pre- and post-water treated crosslinked/hydrolyzed SMA hydrogel nanofibers are shown in Fig. 11. Both A-SMA and R-SMA-2 retained their round fiber form very well though some fibers adhered together after water treatment. It is obvious that the mean size of water treated fibers was ca. 80–200 nm larger than the untreated one as shown in Fig. 11. This is attributed to fiber collapse from round to flat to some degree on loss of water from the swelled fiber, but in general the SMA hydrogel nanofiber surface is still smooth unlike the distorted and irregular surface of water exposed PVA or PVA/PAA hydrogel nanofibers [18,29]. Phenyl side group of SMA enhances the chain rigidity, leading to a good

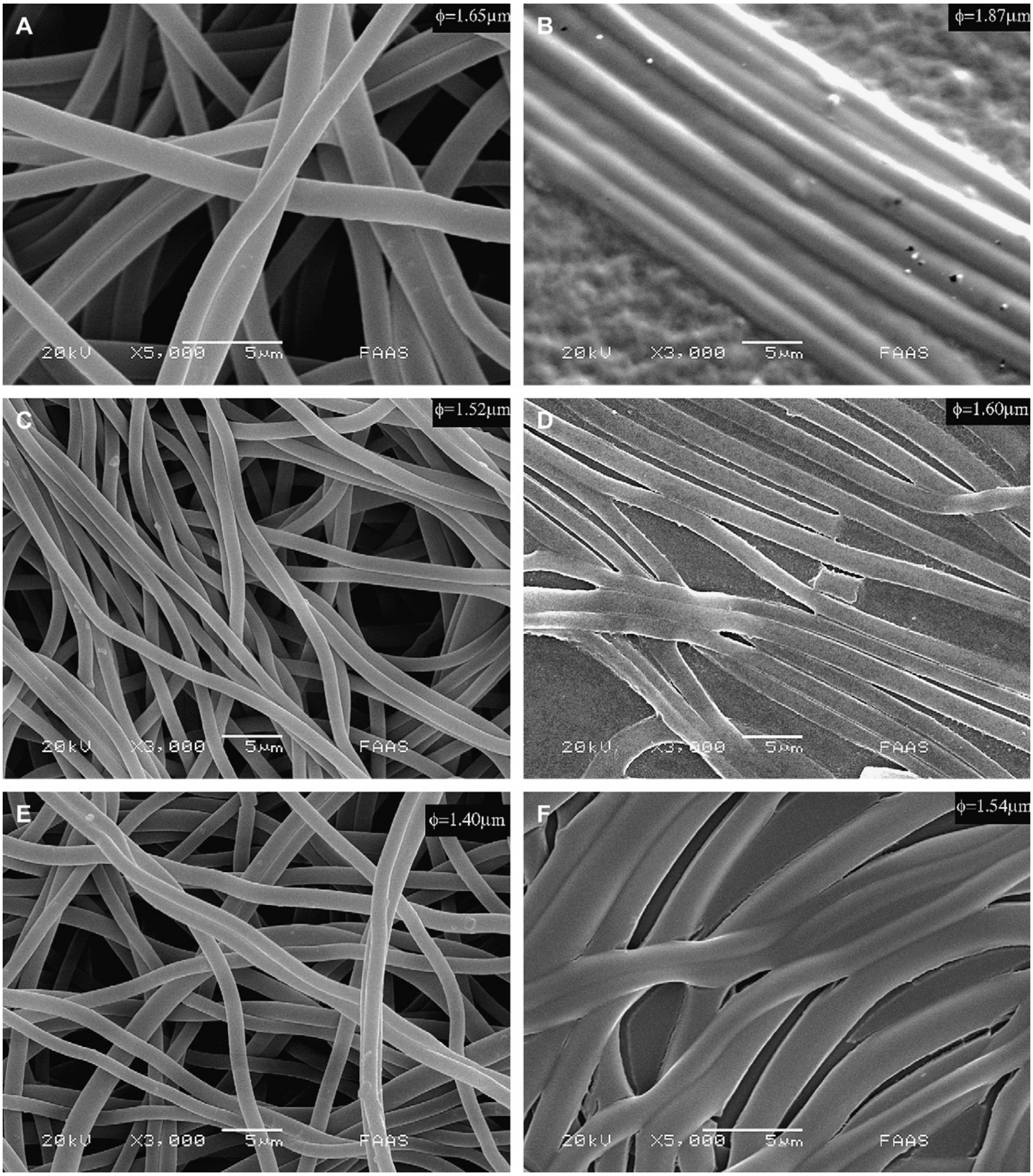


Fig. 11. SEM images of A-SMA hydrogel nanofibers with 10 wt% DEG (A) before and (B) after water immersion; R-SMA-2 hydrogel nanofibers with (C and D) 5 wt% and (E and F) 10 wt% DEG before (C and E) and after water immersion (D and F). Values on the upper right corner are the mean fiber diameter.

Table 3
Water absorption capacity of SMA hydrogel nanofibers

Specimen	Content of crosslinker DEG (%)	Water absorption ratio R (g/g)			
		H_2O		0.25 N NaCl aq. solution	
		Total[a]	Net[b]	Total	Net
R-SMA-2–5%	5	71.0	37.6	14.1	8.2
R-SMA-2–10%	10	42.2	24.5	10.2	5.7
A-SMA-5%	5	33.9	15.2	13.0	7.3
A-SMA-10%	10	13.6	6.4	7.9	4.6

[a] Measured after removal of water by filter paper.

[b] After centrifugation.

dimensional stability of SMA hydrogel nanofiber, while the flexible backbone structure of PVA and PAA results in easy deformation of their nanofiber under the influence of water.

Water absorption ratios of crosslinked/hydrolyzed R-SMA-2 and A-SMA nanofibrous membranes are listed in Table 3. Depending on the molecular structure, M_w and MAh content in the SMA copolymers, and crosslinking density, the total water absorption ratio varied in a wide range of 13.6–71.0 and 7.9–14.1 g/g for the absorption of distilled water and 0.25 N NaCl aq. solution, respectively; while the net ratio (without the contribution from water filling in pores) was about 45–60% of the total ratio, suggesting that the large pore areas of SMA hydrogel nanofibrous membrane hold large amount of free water. Generally random copolymer R-SMA-2 is capable of absorbing more water than alternating copolymer A-SMA; less crosslinking density leads to higher absorption; and the presence of electrolyte NaCl in solution results in less absorption ratio. Hydrolyzed SMA in sodium form (SMA-Na) is a type of polyelectrolyte, whose water absorption mechanism is strongly associated with chain conformation in the solution. If without crosslinking, the random-coil of SMA-Na chain is extended in distilled water because of the negative charge electrostatic repulsion. However, this chain extension is suppressed upon the addition of NaCl because counterion Na^+ may neutralize the negative charge along the SMA-Na chain. Consequently, chains are contracted to coils and its size is reduced. If crosslinked, the swelling of the network caused by chain extension would enlarge the container formed in the chain networks, leading to more water absorption. However, the limited chain extension by the addition of NaCl and higher crosslinking density would result in less water absorption. It should be pointed out that the water absorption ratio of A-SMA is less than that of R-SMA-2 with the same content of crosslinking agent, though the former has higher MAh content of 48%. This is possibly contributed to their structure difference and much lower molecular weight of the former than that of the latter. The chain elasticity and chain conformation change in water are limited by the short chain structure of A-SMA.

4. Conclusion

SMA nanofibers with diameter down to 180 nm were generated from electrospinning of SMA in solvents acetone, DMF and their mixtures. Due to the fast solidification on loss of acetone during electrospinning, large sized SMA fibers with diameter in several micrometers were often obtained from SMA/acetone solution, while ultrafine fibers were produced from SMA/DMF solutions because SMA/DMF jet can be stretched more times before it solidifies. The diameter of SMA nanofibers decreased from 1000 to 180 nm as DMF content increased from 0 to 100% DMF in the acetone/DMF mixture.

The hydrolyzed random SMA copolymer with MAh content as low as 18% is water insoluble, whereas those copolymers with MAh content of 32 and 48% are water soluble after hydrolysis. Crosslinking reaction with diethyleneglycol, followed by hydrolysis in NaOH/EtOH made water swellable but insoluble SMA hydrogel nanofibers. Water absorption ratio of crosslinked/hydrolyzed SMA nanofibers varied with molecular structure, molecular weight of SMA, crosslinking density and ionic strength in solution.

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