

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.

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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/H₂O 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 $\times 10^{-3}$ 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 N₂ 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 μ l/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-absorbent 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.

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