

Interface Hydrogen-bonded Core-Shell Nanofibers by Coaxial Electrospinning*

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Abstract Core-shell nanofibers were prepared by coaxial electrospinning technology, with poly(ethylene oxide) (PEO) as the core while poly(acrylic acid) (PAA) as the shell. PEO and PAA can form polymer complexes based on hydrogen bonding. In order to avoid forming strong hydrogen bonding complexes at nozzle and blocking spinning process, a polar aprotic solvent, *N,N*-dimethylformamide (DMF), was selected to dissolve PEO and PAA respectively. SEM, TEM and DSC were utilized to characterize the morphology and structure of PEO-PAA core-shell nanofibers. FTIR spectra demonstrated that hydrogen bonding was formed at the core-shell interface. In addition, the PAA shell of the nanofibers can be cross-linked by ethylene glycol (EG) under heat treatment, which increases the stability and extends the potential applications in aqueous environment.

Keywords Coaxial electrospinning; Core-shell nanofibers; Hydrogen bonding

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INTRODUCTION

Core-shell structured nanofibers have drawn considerable attention due to various potential applications, like drug delivery^[1–4], battery electrodes^[5–7], photocatalysts^[8, 9], super-capacitors^[10–12], solar cells^[13], and optoelectronic devices^[14]. Different methods have been reported to prepare core-shell nanofibers, including laser ablation^[15], γ irradiation^[16], fibers template^[17], and electrospinning^[18–28]. Simple electrospinning of emulsion or blend solutions also has possibility to prepare core-shell structure fibers^[18–20], but coaxial electrospinning is a more reliable approach^[21–30].

Electrospinning is an effective technology to produce continuous nanofibers^[31–36]. Coaxial electrospinning is a development of the conventional electrospinning^[37, 38]. The coaxial electrospinning device uses concentric spinneret instead of single capillary. During the process, two different solutions are fed simultaneously through the core and the shell capillary separately, which will not encounter until they are pushed to the nozzle. The compound pendent drop formed at the nozzle is stretched at the high voltage to form the stabilized coaxial jet. The jet flow is further stretched and whipped by the electrostatic force to become thinner and solidified as the solvents rapidly evaporate. During electrospinning, the outer fluid forms a sheath around the core component, which suppresses the Rayleigh instability of the core fluid^[22]. Some fluids without spinnability, such as oil, can

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also be used as core component of the coaxial electrospinning^[39].

In this work, we prepared poly(ethylene oxide)-poly(acrylic acid) (PEO-PAA) core-shell nanofibers by coaxial electrospinning. Different to many reported core-shell fibers, the core-shell interface of PEO-PAA nanofibers is hydrogen-bonded. Hydrogen bond is an important secondary interaction and exists in many polymer systems, such as polyamide and polysaccharide^[40, 41]. PEO and PAA are widely-used water soluble polymers and have been electrospun to nanofibers, respectively^[42, 43]. PEO and PAA can form polymer complexes based on hydrogen bonding, and hence mixing PEO solution and PAA solution generally leads to precipitation^[44, 45]. If we want to conduct coaxial electrospinning of PEO solution and PAA solution, we need to select proper solvent to avoid strong polymer complexation by hydrogen bonding, and otherwise the complexes would block the nozzle of the electrospinning. We tried several solvents, and found that DMF was a suitable solvent for coaxial electrospinning of PEO and PAA. With DMF as the solvent, the coaxial jet was erected and core-shell nanofibers were prepared successfully. More interestingly, the core-shell interface of the nanofibers was hydrogen-bonded, which is different to the general core-shell nanofibers. Furthermore, the PAA shell of the nanofibers was cross-linked by ethylene glycol (EG) under thermal treatment to improve the stability in aqueous environment. The cross-linked core-shell nanofibers would show potential applications in various areas, such as drug release, membrane separation, and chemical sensors.

EXPERIMENTAL

Materials

Poly(acrylic acid) (PAA, $M_v \sim 4.5 \times 10^5$), and poly(ethylene oxide) (PEO, $M_w \sim 6.0 \times 10^5$) were purchased from Aldrich. Ethylene glycol (EG), *N,N*-dimethylformamide (DMF), ethanol (EtOH), dimethylsulfoxide (DMSO), and sulfuric acid (H_2SO_4) were of analytical grade. All materials were used as received.

Preparation of PEO-PAA Core-Shell Nanofibers

DMF was used as solvent. PEO solution (5 wt%) was used as core component while PAA solution (10 wt%) was chosen as shell component. The coaxial spinneret comprised two concentrically metallic capillaries. The inner and the outer diameters of the core capillary were 0.3 and 0.5 mm respectively while those of the shell capillary were 1.0 and 1.4 mm respectively. PEO and PAA solutions were separately added into 10 mL plastic syringes that were loaded on two independent pumps (JDF 04, Changsha Nano Machine Co., Hunan, China). PEO solution and PAA solution were pumped into the core capillary and the shell capillary respectively. The flow rate of PAA solution in the shell channel was fixed at 10 μ L/min, while the flow rate of PEO solution in the core channel was set to 3, 5 or 8 μ L/min. The collector was rotating drum and the distance from the spinneret to the collector was 20 cm. The voltage range of 14–19 kV was supplied by high voltage power supply (DW-P303-1ACF0, Dong Wen Co., Tianjin, China).

Cross-linking of PEO-PAA Core-Shell Nanofibers

EG was used as a cross-linking agent for PAA shell. EG was added into PAA solution and the weight of EG was 12% of PAA weight. PAA solution containing EG was pumped unto shell channel while PEO solution was injected into core channel to prepare core-shell fiber. The as-spun PEO-PAA core-shell nanofibrous mats were heat-treated at the temperature of 130, 140 or 150 °C under vacuum condition for 1 h. After this treatment, the samples were immersed into water for 12 h to check cross-linking effect.

Measurements and Characterization

Scanning electron microscopy (SEM, JSM-5600LV, JEOL Co., Ltd., Japan) was used to characterize the morphologies of nanofibrous mats. The SEM samples were dried in vacuum and coated with gold by sputtering. Image J software (supported by National Institutes of Health, U.S.A.) was used to analyze the ranges of nanofibers diameters. At least 100 fibers were selected to calculate the average diameter for each electrospun mat. Transmission electron microscopy (TEM, HT 7700, Hitachi High-Technologies Co. Japan) was conducted with a Hitachi machine. The core-shell nanofibers were collected on carbon-coated copper grids for TEM

observation. To strengthen the images contrast between the core and the shell, copper salt (0.1%) was added into the core component solution. Two-dimensional X-ray diffraction (WAXD) measurements were carried out with Bruker D8 Discover diffractometers (Cu-K α 0.15418 nm, 40 kV and 40 mA, VANTEC-500 area detector).

Fourier transform infrared spectroscopy instrument (FTIR, 8700, Thermo Nicolet Co., USA) equipped with diamond ATR attachment was utilized to evaluate chemical characteristics at ambient conditions. Differential scanning calorimetry (DSC, 204 F1, Netzsch Co., Germany) measurement was performed with a Netzsch instrument. Under nitrogen atmosphere, samples were sealed in an aluminum pan and heated at a heating rate of 10 K/min. Mechanical properties were tested by using a fiber tensile instrument (XS (08) XG-3, XuSai instrument Co., Ltd., China) with an elongation speed of 30 mm/min. The electrospun nanofibrous mats were cut into rectangular shape (10 mm $\times$ 30 mm) for tensile measurement.

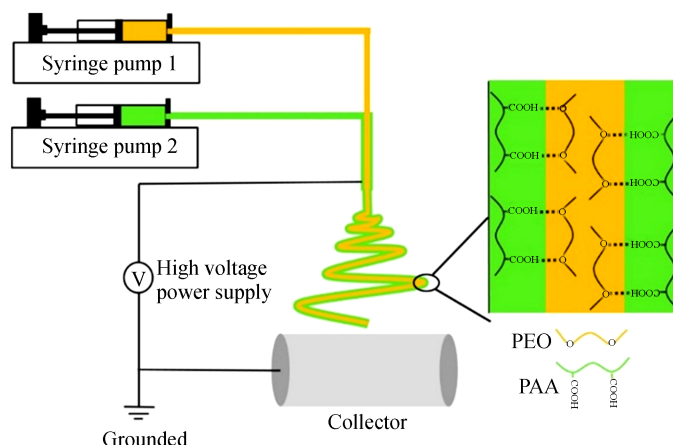
RESULTS AND DISCUSSION

Four solvents, ethanol, water, DMF and DMSO were tried to dissolve PEO and PAA to prepare spinning solutions (Properties of four solvents were listed in Table S1 in supporting information, SI.). PAA could be dissolved in these four solvents at room temperature. However PEO only could dissolve in water at room temperature, while dissolution in the other three solvents needed to be heated. Using ethanol as solvent, PEO precipitated out when the solution was cooled to room temperature. With DMF or DMSO as solvent, PEO solution remained homogenous even when the temperature was lowered.

The same weight of PEO and PAA powder were separately dissolved in water, DMF or DMSO, and then PEO solution and PAA solution were mixed (the total weight content 5 wt%, Fig. S1 in SI). For PEO/PAA mixed solution system, there was interaction equilibrium among PEO-PEO, PAA-PAA, solvent-solvent, PEO-solvent and PAA-solvent, and entropy also played an important role for PEO and PAA complexation^[46, 47]. With water as the solvent, PEO and PAA showed strong association and the complexes precipitated out from the solution. With DMF as the solvent, the mixed solution exhibited liquid-liquid phase separation, which was different to the system using water as the solvent. With DMSO as the solvent, the mixed solution was homogenous and there was no phase separation. The mixing experiments indicated that solvent had significant effect on PEO and PAA association. PEO and PAA have the strongest association in water, the weakest association in DMSO, and the middle in DMF.

For coaxial electrospinning, two solutions merged at the nozzle. If water was chosen as the solvent, the spinning nozzle would be blocked due to the strong complexation of PEO and PAA in water. DMSO and DMF both are aprotic polar solvents. With DMF or DMSO as solvent, there was no strong association to form solid complexes, and the jet would be erupted, stretched and whipped by the electrical field. During the stretching and the whipping, the jet becomes thinner and gradually solidifies as the solvent evaporated. The solvent evaporation is important for fiber formation. DMF (bp, 153 °C) is easier to evaporate than DMSO (bp, 189 °C). In DMSO, hydrogen bonding between PEO chains and PAA chains was almost restricted, which meant that DMSO had strong interaction with PEO and PAA. The strong interaction between DMSO and polymer chains made DMSO hard to be removed from polymers. Dissimilarly, PEO chains and PAA chains showed weak hydrogen bonding association in DMF, which was helpful for them to form hydrogen bonding at core-shell interface during the fiber formation. So DMF was selected as the solvent for coaxial electrospinning instead of DMSO.

Polymer solutions with high conductivity as the shell component flow is beneficial to obtain concentric core-shell structure^[22]. PAA solution has higher conductivity than PEO solution, so PAA solution was injected into the outer capillary, as shown in Scheme 1. PAA solution (10 wt%) was injected into the outer capillary while PEO solution (5 wt%) was pumped into the core capillary. High voltage (14–19 kV) was applied, and the rotation drum was used to collect core-shell nanofibers. SEM and TEM were utilized to observe the morphology of nanofibers, as shown in Fig. 1. SEM image exhibited the nanofibrous texture of the collected mats while TEM image clearly showed the core-shell structure of single nanofiber.



Scheme 1 A schematic procedure to fabricate PEO-PAA core-shell nanofibers by coaxial electrospinning

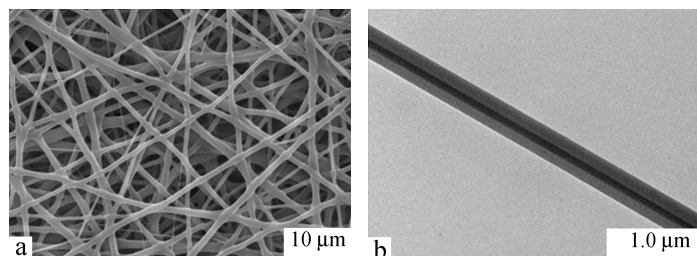


Fig. 1 SEM image (left) and TEM image (right) of coaxial electrospinning fiber composed of PEO core (flow rate, 5 $\mu\text{L}/\text{min}$) and PAA shell (flow rate, 10 $\mu\text{L}/\text{min}$)

We used DSC to characterize PEO-PAA core-shell nanofibers. The DSC curve showed that PEO-PAA core-shell nanofibers had a small melting peak of PEO at 63 $^{\circ}\text{C}$ (Fig. 2). For comparison, the single component nanofibers, PEO nanofibers and PAA nanofibers, were prepared by electrospinning and measured with DSC too, as shown in Fig. 2. The PEO nanofibers exhibited a broad endothermic peak, and the melting peak was located at 71 $^{\circ}\text{C}$. The melting enthalpy of PEO in the core-shell nanofibers (28.5 J/g) was much lower than that of PEO nanofibers (158.1 J/g). The melting enthalpy for 100% crystal PEO is 213.7 J/g^[48], and hence PEO crystallization degree in the core-shell nanofiber and the pure nanofibers was 13% and 74%, respectively. XRD showed that PEO had weak crystallization (Fig. S2 in SI). The results indicated that the crystallization of PEO in the core-shell nanofibers was restrained.

PAA is hard to crystallize. DSC curve showed that the glass transition of PAA nanofibers was at about 120 $^{\circ}\text{C}$. The DSC curve of PEO-PAA core-shell fibers did not show a clear glass transition like PAA nanofibers, but there were several small steps at the temperature region from 70 $^{\circ}\text{C}$ to 120 $^{\circ}\text{C}$. Our previous work studied hydrogen-bonded PEO/PAA complexes fibers, in which PEO chains and PAA chains were highly miscible and PEO crystallization was completely restricted^[49]. The DSC curves of PEO/PAA complexes fibers did not show PEO crystal melting but only a glass transition. The glass transition values of PEO/PAA complexes fibers were ranged from 10 $^{\circ}\text{C}$ to 85 $^{\circ}\text{C}$ depending on weight content of PEO and PAA^[49]. There was a hydrogen-bonded interface between the PEO core and the PAA shell. The hydrogen-bonded interface imposed influence both on the PEO core and the PAA shell. So the crystallization of PEO in the core and the glass transition of PAA in the shell were both affected.

FTIR spectra of nanofibers are shown in Fig. 3. The IR spectrum of pure PEO nanofibers displayed sharp vibration peaks. Triplet peaks at 1149, 1103 and 1062 cm^{-1} were attributed to C—O—C stretching vibrations, and the peaks at 1360, 1342, 1280 and 1241 cm^{-1} were assigned to the deformation of CH_2 ^[50]. The sharp vibration peaks of PEO nanofibers were related with the crystal structure of PEO^[51]. However, on the IR

spectrum of PEO-PAA core-shell nanofibers, the vibration peaks in region from 800 cm^{-1} to 1200 cm^{-1} became broad compared with the spectrum of the pure PEO nanofibers, indicating that the crystallization of PEO was restricted in PEO-PAA core-shell fibers.

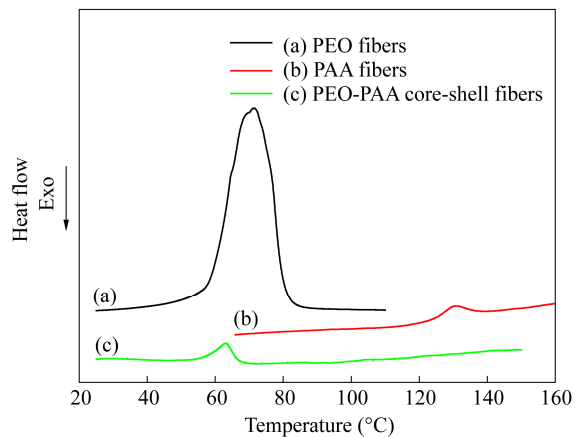


Fig. 2 DSC curves of PEO nanofibers (a), PAA nanofibers (b) and PEO-PAA core-shell nanofibers (c)

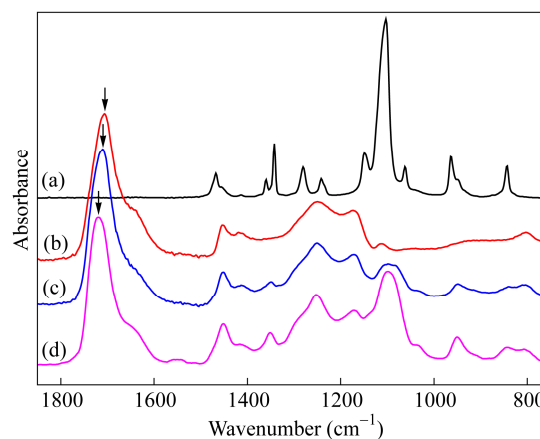


Fig. 3 FTIR spectra of the PEO fibers (a), PAA fibers (b), PEO-PAA core-shell fibers (PEO content: 20 wt%) (c) and PEO/PAA complexes fibers (PEO content: 38 wt%) (d)

The strongest vibration peak of pure PAA nanofibers was located at 1706 cm^{-1} , which was assigned to C=O stretching of carboxylic acid group in PAA^[52, 53]. In theory, the C=O stretching vibration peak of free COOH (not hydrogen bonding) is located at $1740\text{--}1745\text{ cm}^{-1}$ ^[54]. Hydrogen bonding among COOH themselves in PAA fibers made the C=O vibration peak show red-shift to 1706 cm^{-1} ^[54]. Our previous work used wet spinning technique to prepare PEO/PAA complexes fibers. In PEO/PAA complexes fiber, PEO and PAA had high level miscibility and hydrogen bonding mainly happened between PEO and PAA, which induced C=O peak move to 1720 cm^{-1} ^[49]. However, in PEO-PAA core-shell fibers, hydrogen bonding was formed not only in PAA shell among COOH groups but also at the core-shell interface between PEO and PAA, so C=O vibration peak of the PEO-PAA core-shell fibers shifted to 1710 cm^{-1} , the middle position between peaks of the pure PAA nanofibers and the PEO/PAA complexes fibers.

In order to further prove the formation of hydrogen bonding at the core-shell interface, we prepared PEO-PAA core-shell fibers by varying the flow rate of PEO solution. FTIR spectra of the core-shell nanofibers prepared with different PEO solution injection rates are shown in Fig. 4. Increasing PEO solution injection rate,

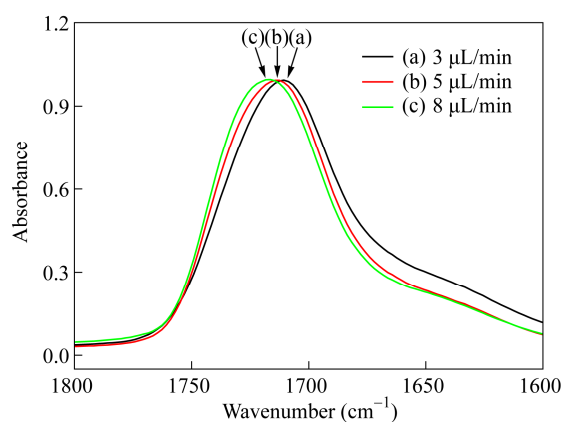


Fig. 4 FTIR spectra of PEO-PAA core-shell nanofibers prepared with fixing PAA injection rate ($10\text{ }\mu\text{L/min}$) while changing PEO injection rate as $3\text{ }\mu\text{L/min}$ (a), $5\text{ }\mu\text{L/min}$ (b), $8\text{ }\mu\text{L/min}$ (c)

the C=O stretching vibration shifted to higher frequency. With the same voltage and collection distance, increasing the feeding rate of PEO solution produced larger core-shell interface. The larger interface area meant that there was more hydrogen bonding between PEO and PAA.

As mentioned above, the highly miscible PEO/PAA system C=O vibration stretching peak was located at the higher wavenumber than that of the pure PAA system. In the highly miscible PEO/PAA system, hydrogen bonding mainly took place between PEO and PAA, and the C=O stretching vibration peak was at 1720 cm^{-1} . In the pure PAA system, hydrogen bonding formed among COOH groups and the C=O stretching vibration peak was at 1706 cm^{-1} . For PEO-PAA core-shell fiber, hydrogen bonding existed not only at core-shell interface between PEO and PAA but also at the shell among COOH groups of PAA. As the injection rate of PEO solution increased, the area of the core-shell interface became larger, and hence there was more hydrogen bonding between PEO and PAA, which made C=O stretching vibration shift to the higher wavenumber (Fig. 4).

Water is the most common solvent. PEO and PAA are both water soluble polymers and hence the water resistance of PEO-PAA nanofibers is very weak. As shown in Fig. 5(a), the mat of PEO-PAA core-shell nanofibers was quickly dissolved when immersed into water. However many practical applications are in aqueous environment, and hence the stability of PEO-PAA core-shell fibers against water should be considered. Heat treatment can make PAA shell cross-linked based on anhydride reaction (Fig. S3 in SI). The mats of PEO-PAA core-shell fibers were heated at $150\text{ }^{\circ}\text{C}$ for 1 h, and then were immersed into water. The mats did not dissolve (Fig. 5b). After immersed in water for 12 h, the mats were picked out, and dried in vacuum at $60\text{ }^{\circ}\text{C}$ for 24 h. The morphology of mats was characterized by SEM, as shown in Fig. 5(c). Though the mats kept integrity at macro level, the stacked nanofibers became smeared due to high level swelling.

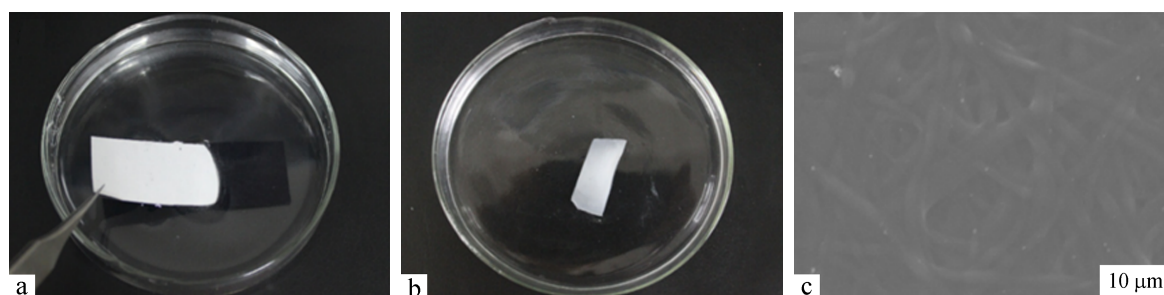


Fig. 5 Photographs (a, b) and SEM image (c) of PEO-PAA core-shell nanofibers mats

(a) The as-prepared PEO-PAA nanofibers mat was immersed into water; (b) The mat that treated at $150\text{ }^{\circ}\text{C}$ for 1 h was immersed into water for 12 h; (c) Immersed in water for 12h and then dried at $60\text{ }^{\circ}\text{C}$ for 24 h.

Figure 5(c) indicated that simple heat treatment did not have good cross-linking effect. EG, as cross-linking agent, was introduced into the shell of the nanofibers for heat treatment. The prepared mats of PEO-PAA core-shell nanofibers containing EG were treated at 130, 140 and $150\text{ }^{\circ}\text{C}$ separately in vacuum oven for 1 h, and then immersed into water for 12 h. As shown in Figs. 6(a)–6(c), the heat-treated mats did not dissolve in water. The mats were drawn out from water and dried at $60\text{ }^{\circ}\text{C}$ in vacuum for 24 h. SEM images of the dried mats are presented in Figs. 6(d)–6(f). The mat that was treated at $130\text{ }^{\circ}\text{C}$ had the highest degree of swelling and the fibrous structure became blurry after immersed in water for 12 h. However, when the heat treatment temperature was elevated to $140\text{ }^{\circ}\text{C}$, the mat exhibited a small degree of swelling, showing somewhat fiber fusion, but fibrous morphology was almost retained. The swelling degree was dependent on cross-linking degree. The higher the cross-linking degree was, the lower the swelling degree would be. When the heat treatment temperature was further elevated to $150\text{ }^{\circ}\text{C}$, the mat exhibited much better cross-linking effect. By comparing Fig. 6 with Fig. 5, we found that introducing EG made the better cross-linking effect under the same heat-treated conditions. The PAA was cross-linked both by esterification and anhydride reaction (Fig. S4 in SI).

The tensile strength of PEO-PAA core-shell nanofibrous mats was tested (Fig. S5 in SI). The tensile strength of the as-prepared nanofibrous mat was 3.5–4.0 MPa while breakage strain was about 10%. After

introducing EG into PAA shell, the tensile strength of the nanofibrous mats showed (51 ± 34)% increment but breakage strain decreased about (40 ± 28)%. However the cross-linking only made a small change of the break elongation and the tensile strength of the mats.

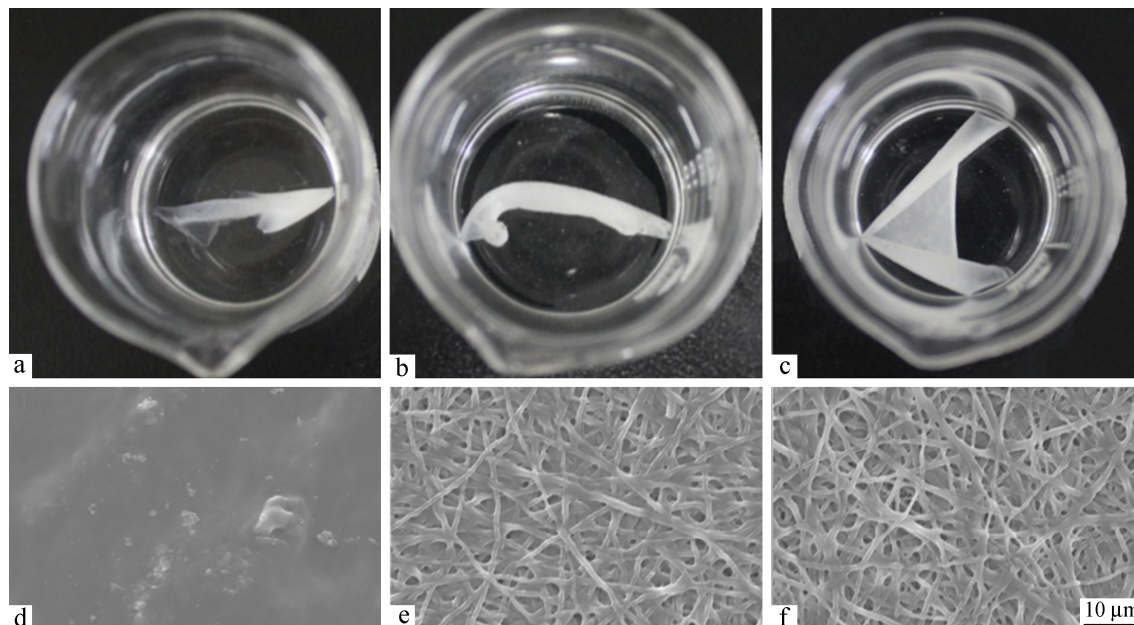


Fig. 6 Photographs (above, a–c) and SEM images (below, d–f) of PEO-PAA core-shell nanofibers mats which had been heat-treated at different temperatures for 1 h at 130 °C (a, d), 140 °C (b, e) and 150 °C (c, f). Photographs: the mats were immersed into water for 12h. SEM images: the mats were picked out from water and then dried at 60 °C for 24 h.

CONCLUSIONS

Through coaxial electrospinning, PEO-PAA core-shell nanofibers were prepared. With heat treatment, the PAA shell was cross-linked, which improved water resistance of the fibers. Special components, such as small molecules and metal ions can be introduced into the shell or the core of the nanofibers. For example, EG has been successfully introduced into PAA shell, which was useful for cross-linking the shell by heat treatment, while copper ions have been added into PEO core, which was helpful to enhance the core-shell density contrast for TEM observation.

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