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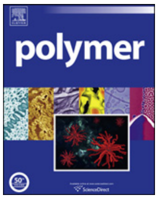

Effect of poly(ethylene oxide) with different molecular weights on the electrospinnability of sodium alginate

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ABSTRACT

Although sodium alginate (SA) could not be electrospun from its aqueous solution, SA-based electrospun nanofibers can be fabricated with the help of polyethylene oxide (PEO). In this study, the influence of PEO on the electrospinnability of SA aqueous solution was investigated and the roles of chain entanglements and conformations of the blend system were emphasized. It was found that a little amount of PEO100 with high molecular weight could improve the electrospinnability of SA aqueous solution. However, a large amount of PEO2 with low molecular weight had no positive effect on the electrospinnability of SA aqueous solution. Dynamic laser light scattering (DLLS) results showed that only when the PEO molecular chains in aqueous solution were in an entangled state, PEO can enhance the electrospinnability of SA aqueous solution. The further study on rheological measurements showed that SA molecular chains could not form significant entanglements for the electrospinning even when the SA solution concentration approached concentrated regime. SA molecular chains are closely “overlapped” due to its rigid and extended conformation and cannot form effective chain entanglement. The main contribution of PEO100 to improve SA electrospinnability is offering entanglement sites and thereby enhancing the applicable entanglement degree of the blend system. Whereas, although the chain interaction between PEO2 and SA may improve slightly the flexibility of SA chains, the significant chain entanglements of the blend solution is not achieved. Three molecular models are proposed to depict visually the effect of PEO with different molecular weights on chain conformations and entanglements of SA.

1. Introduction

Polymer nanofibers could offer a broad range of applications in the fields of composites, protective clothing, catalysis, electronics, filtration and biomedicine [1]. Electrospinning has been accepted as an effective technique available for the production of ultra-thin fibers from various synthetic and natural polymers [2]. Up to date, more than one hundred polymers have been successfully electrospun into ultrafine fibers using the electrospinning technique. In terms of the sustainability of resources, natural polymers are generally favored over synthetic polymers with the fact that they are readily available and renewable resources. Therefore, the electrospinning of natural polymers has become a hot issue in recent years [3–12]. Water is sometimes a good solvent for natural polymers, so electrospinning of these polymers from their aqueous solutions should be a good choice from the reasons of environmental protection, economic cost and practical application. However, it was reported that most natural polymers are either difficult or impossible to be electrospun from their aqueous solutions [13–18]. Meanwhile, water-soluble synthetic polymers, such as polyethylene oxide (PEO) and polyvinyl alcohol (PVA) were often found to be helpful in fiber fabrication of natural polymers from their blend solutions. Alginate is a typical example [15–18].

Alginate consists of mannuronate (M) and guluronate (G) arranged in a nonregular block wise pattern with varying

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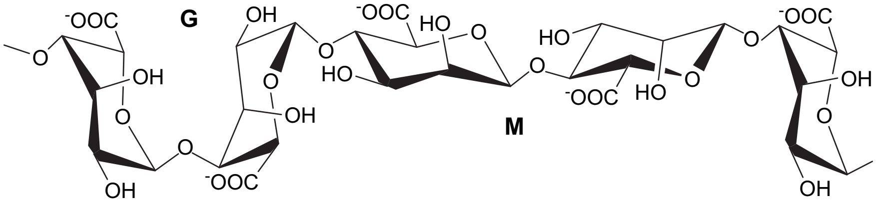

Fig. 1. Chemical structure of alginate.

proportions of GG, MG, and MM units (Fig. 1) [19]. It is an abundant, nontoxic, nonimmunogenic, and biodegradable polymer, which makes it one of the most commonly used natural polymers in the biomedical field [20–25]. Hence, many research groups have focused on the fabrication of SA nanofibers by electrospinning [15–18,26]. However, electrospinning of SA from its aqueous solution is not possible till now, and the previously electrospun SA fibers are all based on the blend solutions of SA and PEO [15–18]or SA and PVA [18]. Bhattarai et al. [15] ascribed the major challenge in electrospinning SA to the gelation of SA solution at a low concentration (2 w/v% in deionized water). The SA solution could not contain sufficient material to generate fibrous structures at a lower polymer concentration, but the solutions are too viscous to be injected at a higher concentration. Therefore, PEO (M_W, 900,000) was used to decrease the solution viscosity by associating with SA through hydrogen bonding. Lu et al. [16] considered the strong repulsive force among the polyanion chains might be the key factor hindering the electrospinning of SA, and proposed that the main function of PEO is to decrease the conductivity of the solution. Recently, in our group, electrospinning of the pure SA solution at a very low concentration (below 2 w/v%) had been successfully carried out by introducing glycerol as cosolvent [26]. We ascribed the key reason that hindering the electrospinning of SA aqueous solution to the insufficient chain entanglement between SA molecular chains.

In order to further understand the physical reason in the difficulties of electrospinning of SA, we also studied the electrospinnability of the blended systems of SA and PEO. Therefore, this study can be regarded as an extension of the work of Bhattarai, Lu and our above work with the aim to understand the intrinsic role of PEO on the improvement of SA electrospinning process. In this study, two kinds of PEO with different molecular weights, and alginate with medium viscosity were used. The electrospinnability of SA/PEO solutions and their physical properties were investigated in detail. By comparing the changes of the solution properties and the spinnability before and after the addition of PEO, we demonstrated that the failure in electrospinning SA was caused by the insufficient chain entanglements for its rigid and extended chain structures and consequent lack of elasticity to stabilize the electrospinning jet. The role of PEO on the improved electrospinnability of SA was explained by the rheological measurements, DLLS and molecular model.

2. Experimental

2.1. Materials

Sodium alginate (SA, ~3500 cps for a 2% solution at 25 °C) was purchased from Sigma. PEO (PEO100, $M_W = 1000$ kDa) was purchased from Alfa Aesar. PEO (PEO2, $M_W = 20$ kDa), was obtained

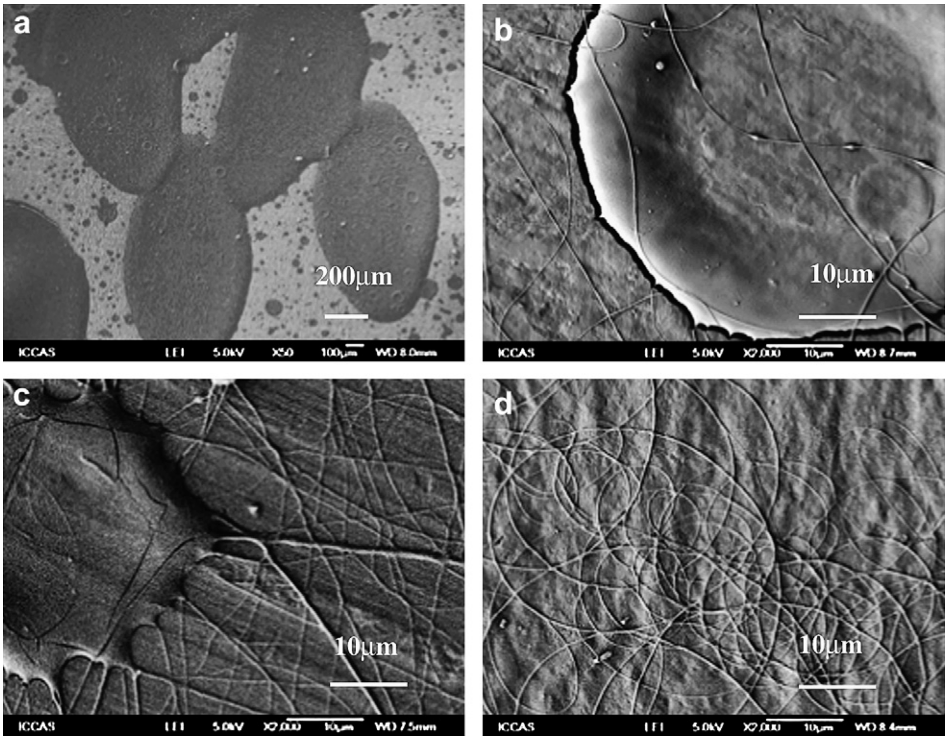

Fig. 2. SEM images of SA based fibers electrospun from the blended solutions of SA/PEO100 with different mass ratio: (a) 100/0, (b) 95/5 (c) 90/10 and (d) 80/20. The total concentration was constant (3.5 w/v%).

from Beijing Chem. Co. (Beijing, China). All the reagents were used without further purification.

2.2. Electrospinning

All transparent solutions were prepared by dissolving a precise amount of SA or PEO (PEO100 or PEO2) in the double distilled water through gentle stirring. The mixed solutions were obtained by mixing SA aqueous solutions and PEO aqueous solutions together with proper volume ratios. A high voltage power supply (The Beijing Machinery & Electricity Institute, China) was employed to generate the electric field (0–50 kV). The applied voltage was fixed at 20 kV and the tip-to-collector distance was 15 cm. The electrospinning temperature including polymer solution and the environment was controlled at 50 ± 2 °C. The electrospinning solutions were placed into a 5 mL syringe with a capillary tip which has an inner diameter of 0.3 mm. A syringe pump was used to feed the polymer solution into the needle tip at a feeding rate of 50 μL/min. The alginate fibrous membranes dried at 50 °C overnight to remove the remaining solvent.

2.3. Characterization

The morphologies of the electrospun fibers were observed using scanning electron microscope (SEM, JEOL JSM-6700F, Japan) at an accelerating voltage of 5 kV. Each sample was sputter-coated with platinum for analysis. The conductivities of the spinning solutions were measured by the conductivity meter (DDS-307A, Rex Shanghai). FTIR spectra were recorded on an infrared spectrometer (IR, BRUKER TENSOR 27, Germany) at 4 cm^{-1} resolution with 32 scans in the range of 4000–400 cm^{-1}. Dynamic laser light scattering (DLLS) measurements were carried out by a commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He–Ne laser ($\lambda_0 = 632.8$ nm). The LLS cell is held in a thermostat index matching vat filled with purified and dust-free toluene, with the temperature controlled at 25 ± 0.02 °C. In dynamic LLS, the intensity–intensity time correlation function $G^{(2)}(t, q)$ in the self-beating mode was measured, where t is the decay time and q is scattering vector ($q = (4\pi n/\lambda_0)\ \sin\ (\theta/2)$). $G^{(2)}(t,\ q)$ can be related to the normalized first-order electric field time correlation function $|g^{(1)}(t, q)|$via the Siegert relation as

$$G^{(2)}(t,q) = A\left[1 + \beta|g^{(1)}(t,q)|^2\right]$$

where $A(\equiv\langle I(0)\rangle^2)$ is the measured baseline.

The concentrations of the polymer solutions were in the range of 0.04 w/v%–4 w/v%. Steady shear measurements were carried out in a range of shear rates from 0.01 to 100 s^{-1}at 25 °C on a TA2000 controlled-stress rheometer with a couette cup geometry. To prevent water evaporation, the measuring system was surrounded with a solvent trap. The values of zero-shear viscosity were determined by steady-state experiments.

3. Results and discussion

3.1. Electrospinning of the SA/PEO100 blended solutions

It has been reported that SA alone in its aqueous solution cannot be electrospun. However, the electrospinnability of SA can be improved greatly with the addition of PEO [15–18]. In this study, two kinds of PEO with different molecular weights (PEO100, $M_w = 1{,}000{,}000$; PEO2, $M_w = 20{,}000$) were used to blend with SA. Firstly, the spinnability of SA/PEO100 solutions was investigated. The total polymer concentration was fixed at 3.5 w/v% and the mass ratio of SA to PEO100 was varied. As shown in Fig. 2a, no continuous jets were observed and only irregular droplets were collected under the applied voltage (0–30 kV) for SA aqueous solution. However, as the PEO100 was added, spindle-on-string morphologies with a few droplets were collected although the mass ratio of SA to PEO100 was 95/5 (Fig. 2b), that is, the concentration of PEO100 was only 0.175 w/v%. Fig. 2c shows that more fibers were collected when the mass ratio of SA to PEO100 reached 90/10. Finally, as the mass ratio of SA to PEO100 was 80/20, a continuous stable jet was observed and smooth uniform fibers were also obtained (Fig. 2d). It can be concluded that PEO100 played a positive role on improving the electrospinnability of SA, and the SA/PEO100 bi-component nanofibers could be fabricated through a stable electrospinning process.

3.2. Electrospinning of the SA/PEO2 blended solutions

As a comparison, the low molecular weight PEO, namely PEO2, were also used to mix with SA. The total concentration of the blended solution of SA and PEO2 was fixed at 3.5 w/v%, and the electrospinnability of the SA/PEO2 blended solutions was investigated. It was found that the blended solutions of SA/PEO2 with the mass ratio of SA to PEO2 in the range of 0.35 w/v%–1.75 w/v% could not be electrospun at all and only irregular droplets were collected as shown in Fig. 3(a–c). It has been reported that the molecular chains of alginate are extended in water, even under a very high salt concentration such as in 0.2 M NaCl solution and the chain rigidity of alginate is similar to that of the cellulosic chain [27]. The inclusion of glycerol or poly(ethylene glycol) can improve the flexibility of alginate chains [28]. In our earlier work, we certainly utilized this viewpoint and obtained SA electrospun nanofibers by adding glycerol into SA aqueous solution [26]. Therefore, in the following study, an improved chain flexibility of SA is expected by increasing the amount of PEO2 in SA aqueous solution. The concentration of SA was fixed 2.8 w/v%, and the concentration of PEO2 was varied from 4 w/v% to 35 w/v% in the blended solution of SA/PEO2. The electrospinnability of SA/PEO2 was investigated. However, although the electrospinning parameters were changed, none of the blended solutions can be electrospun (Fig. 3 (d,e)), even when the concentration of PEO2 reached a very high concentration of 60 w/v%. It is obvious that PEO2 cannot improve the electrospinnability of SA.

3.3. Electrospinning of PEO aqueous solutions

In order to understand the critical role of PEO on the electrospinnability of SA, the spinnability of pure PEO was studied in this work. Here, the concentration of PEO electrospun solution was equal to that of PEO in SA/PEO blend solutions for electrospinning. All the morphologies of the PEO after electrospinning were summarized in Fig. 4. Fig. 4a shows that some beads with short tails, a small number of beads and bead-on-string structure were obtained when PEO100 aqueous solution was electrospun at a very low concentration (0.175 w/v%). With the concentration increased, bead-on-string morphology (Fig. 4b) and then spindle-on-string morphology (Fig. 4c) were obtained. For all PEO2 solutions, electrospinning was impossible, even when the concentration approached 35 w/v% (Fig. 4d–h).

During the electrospinning process of polymer solutions, it has been established that beads, beaded-on-string, and fibers may be gradually obtained with an increase in polymer concentration. The formation of chain entanglements has been acknowledged as the primary effect in this progress [29]. Eda reported [30] that at a certain molecular weight, the effect of concentration on the electrospinning process can be described by two critical concentrations, C_i (a transition concentration from bead-only structure to

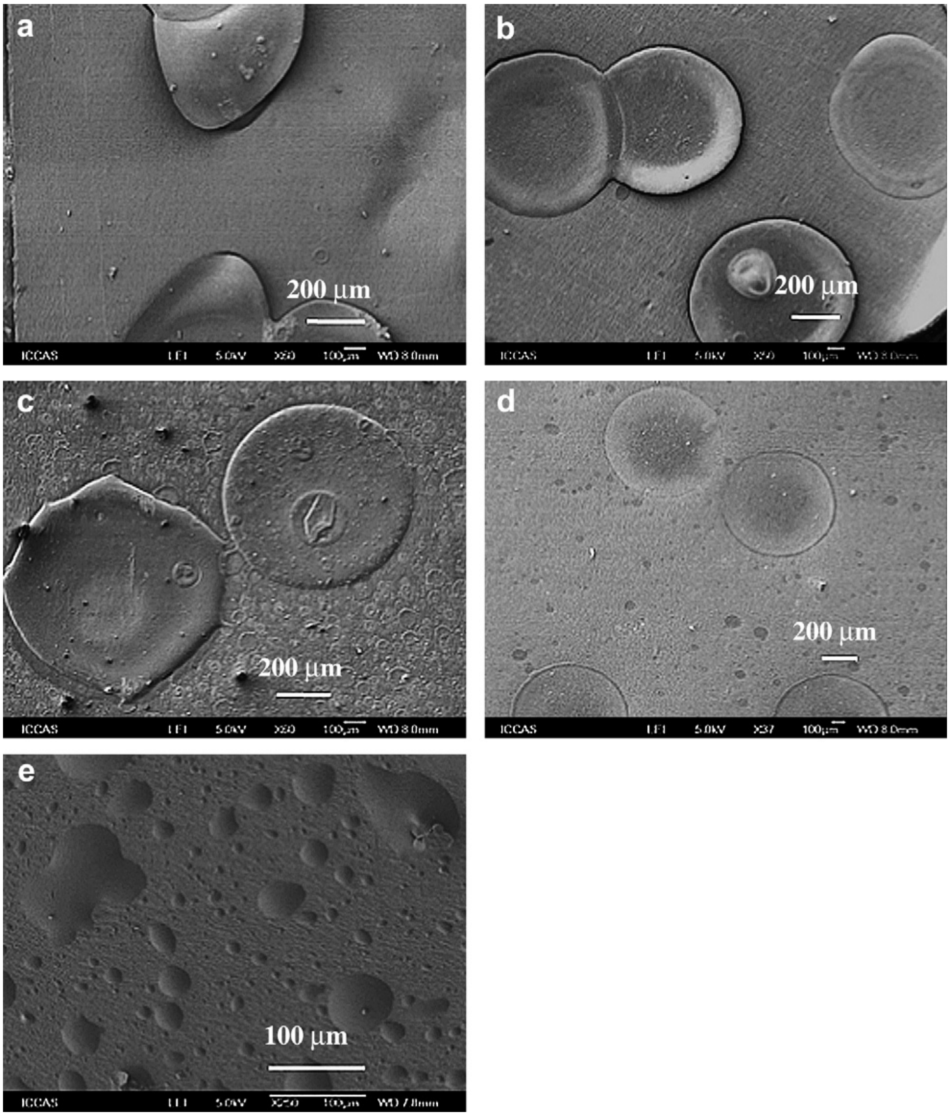

Fig. 3. SEM images of SA based fibers electrospun from the blended solutions of SA/PEO2 with different mass ratio: (a) 90/10, (b) 80/20 and (c) 50/50, as the total concentration was 3.5 w/v%; (d) 7 w/v% and (e) 35 w/v% represent the concentration of PEO2 as the concentration of SA was 2.8 w/v%.

bead-on-string structure) and C_f (a transition concentration from bead-on-string structure to bead-free fiber). Below $C_{i,}$ only beads can be produced due to insufficient chain entanglements in the solution. Above C_i, a combination of beads and fibers is observed and when the concentration is increased above C_f, complete fibers are produced. C_i is typically near the entanglement concentration C_e (the boundary concentration between the unentangled and semidilute entangled regimes, defined as the point at which significant overlap of the polymer chains topologically constrain the chain motion, causing entanglement couplings). Therefore, based on above observation, 0.175 w/v% should be close to C_i, and 0.35 w/v% should be above C_i of PEO100 aqueous solution. But for PEO2 aqueous solutions, the corresponding chain entanglements apparently did not exist even at a relative high concentration (1.75 w/v%) due to its low molecular weight.

3.4. Dynamic laser light scattering (DLLS) of PEO aqueous solutions

To understand the onset concentration of molecular chain entanglements in PEO aqueous solution, dynamic laser light scattering measurement was carried out. Fig. 5a shows typical plots of the intensity–intensity correlation function for the PEO100 aqueous solution in both the dilute and semidilute regimes, and Fig. 5c shows the corresponding plots of characteristic relaxation time distribution function analyzed by the CONTIN method. When $C < C^*$ (C^*, the critical overlap concentration), a single relaxation mode is observed, which is related to the mutual diffusion of individual polymer chains. As the concentration increases and enters the semidilute regime, the chains begin to overlap and entangle, and new dynamical processes involving chain entanglement begin to occur besides the fast relaxation mode. The fast mode measures the cooperative diffusion of the polymer between entanglement points. Therefore, as its decay time becomes shorter and shorter, more and more entanglement points can be formed for one chain. Therefore, it is not surprising that some bead-on-string structure was observed when PEO100 with the concentration of 0.175 w/v% was electrospun. This means the chain entanglement of PEO100 at this concentration is not tight enough to withstand the elongation and capillary instability during the spinning process, then the jet still broke up into droplets. Fig. 5b shows typical plots of the intensity–intensity correlation function for the PEO2 aqueous solution in both the

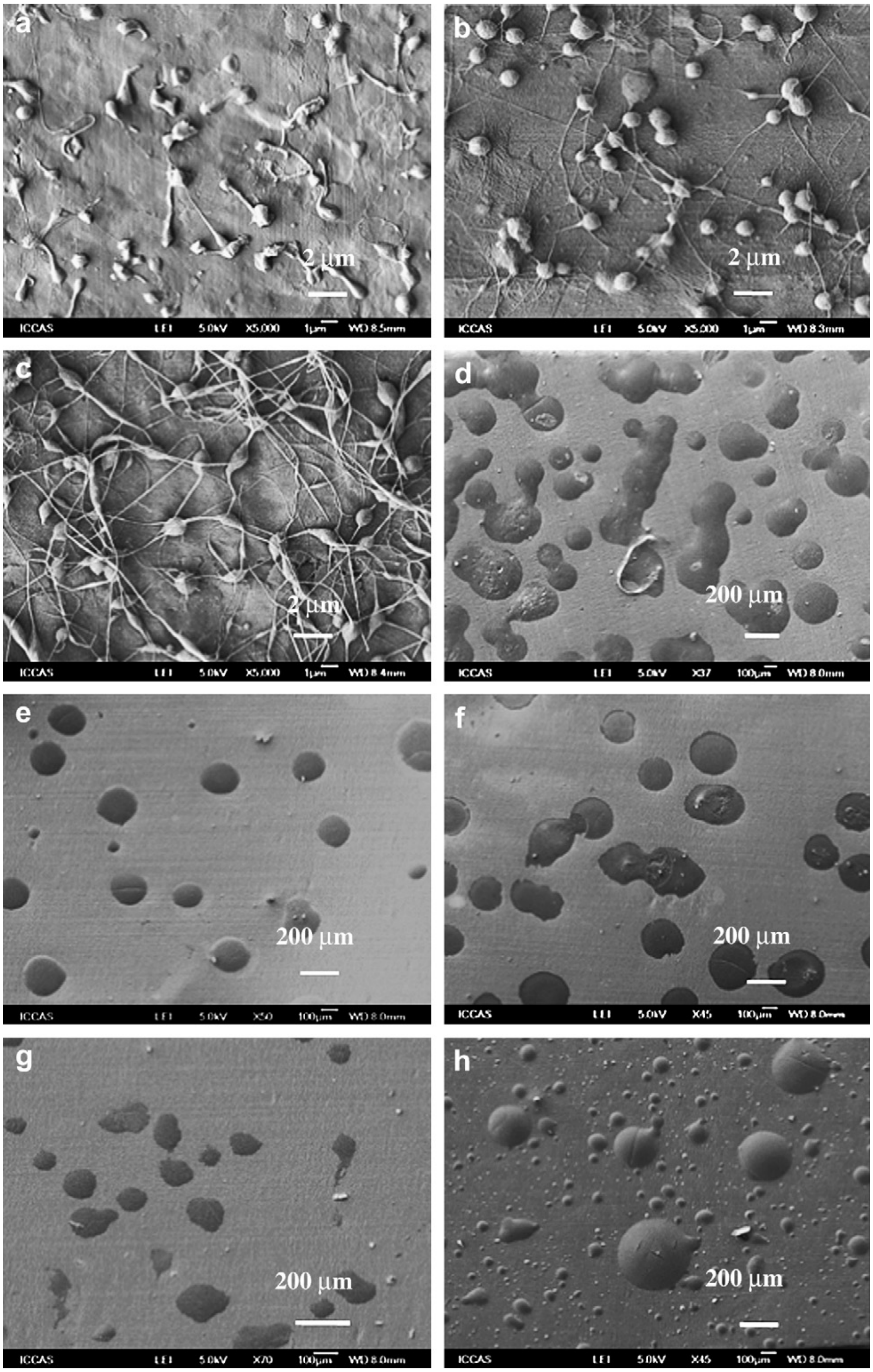

Fig. 4. SEM images of pure PEO membranes (a) PEO100 (0.175 w/v%), (b) PEO100 (0.35 w/v%), (c) PEO100 (0.7 w/v%); (d) PEO2 (0.35 w/v%), (e) PEO2 (0.7 w/v%) (f) PEO2 (1.75 w/v%), (g) PEO2 (7 w/v%) and (h) PEO2 (35 w/v%).

dilute and semidilute regimes, and Fig. 5d shows the corresponding plots of characteristic relaxation time distribution function analyzed by the CONTIN method. However, for PEO2 aqueous solution, slow mode is not observed when the concentration was changed in a wide concentration range. This may be caused by the low molecular weight of PEO2, which is below its entanglement molecular weight (M_e), so it would not form an entanglement system. Solutions used for electrospinning should be concentrated enough and the polymer chains should also be highly entangled. This is why PEO2 solutions with the concentrations varied from 1.75 w/v% to 60 w/v% cannot be electrospun at all.

When comparing Figs. 1 and 2, we found that the addition of SA can improve the chain entanglements in the blend solutions, and uniform SA/PEO100 fibers can be collected (Fig. 2c), while only bead-on-string structures can be obtained from pure

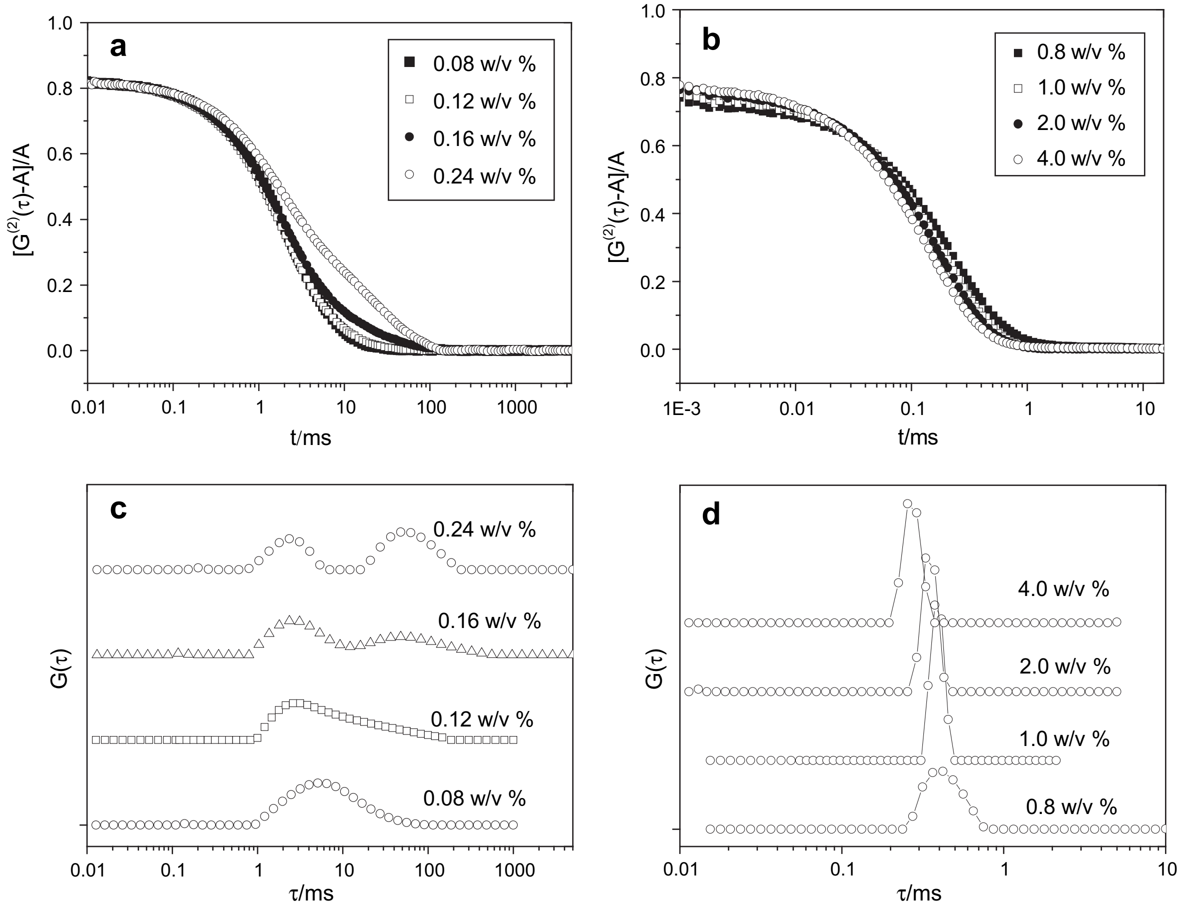

Fig. 5. Concentration dependence of intensity-intensity time correlation function $[G^{(2)}(t, q) - A]/A$ of (a) PEO100 and (b) PEO2 aqueous solutions; (c,d) the corresponding characteristic relaxation time distribution function $G(\tau)$ of (a and b).

PEO100 solution via electrospinning at this concentration (Fig. 4b). This implies that there may have an interaction between SA and PEO100 chains, which makes the chain entanglements of the blended solutions tighter than that of PEO100 aqueous solutions. Fig. 6 shows the FT-IR spectra of original SA, PEO100 and SA/PEO100 fibers in the wave number ranges of 4000–400 cm^{-1}. The IR spectrum of SA showed some characteristic absorption bands at 3385 cm^{-1} (OH stretching), 1608 cm^{-1} (COO^{-} asymmetric stretching), and 1410 cm^{-1} (COO^{-} symmetric stretching). The characteristic band of PEO100 was observed at 1120 cm^{-1} and 843 cm^{-1} due to the C–O–C asymmetric stretch and bending vibrations. For SA/PEO100 blend fibers, a significant difference in the region of the C–O–C asymmetric stretch was observed. The absorption band at 1120 cm^{-1} for original PEO shifted to a lower wave number with the addition of SA. This indicates that the interaction between SA and PEO can be formed through the hydrogen bonding between the hydroxyl groups of SA and the ether oxygen groups of PEO.

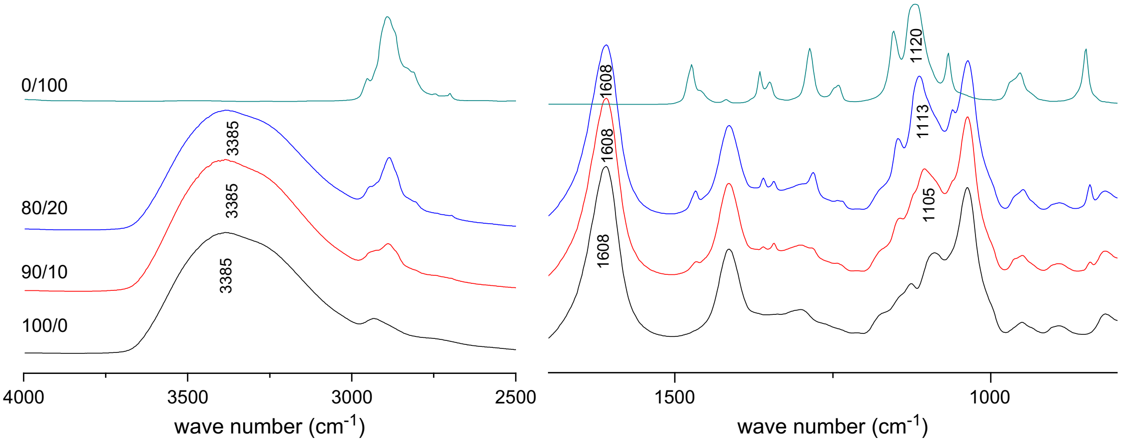

Fig. 6. IR spectra of original SA, PEO100, and SA/PEO100 fibers. 100/0, 90/10, 80/20 and 0/100 represent the mass ratio of SA to PEO100.

Table 1
The physical properties of SA/PEO solutions.

SA/PEO	Conductivity (mS/cm)	Viscosity[b] (pa s)	Spinnability[a]
100/0[c]	6.87	8.74	–
95/5[c]	6.49	9.23	±
90/10[c]	6.20	10.77	±
80/20[c]	4.88	12.40	++
90/10[d]	6.31	6.22	–
80/20[d]	4.94	4.44	–
50/50[d]	3.87	0.10	–
8/100[e]	1.18	61.09	–

Note: + stable jet without fiber; ± fiber without stable jet; ++ fiber with stable jet.

[a] No stable jet or no fiber, only splashed liquid.

[b] Zero shear viscosity determined by steady shear measurements.

[c] SA/PEO100, the total concentration was 3.5 w/v%.

[d] SA/PEO2, the total concentration was 3.5 w/v%.

[e] SA/PEO2, the concentration of SA was 2.8 w/v%, the concentration of PEO2 was 35 w/v%.

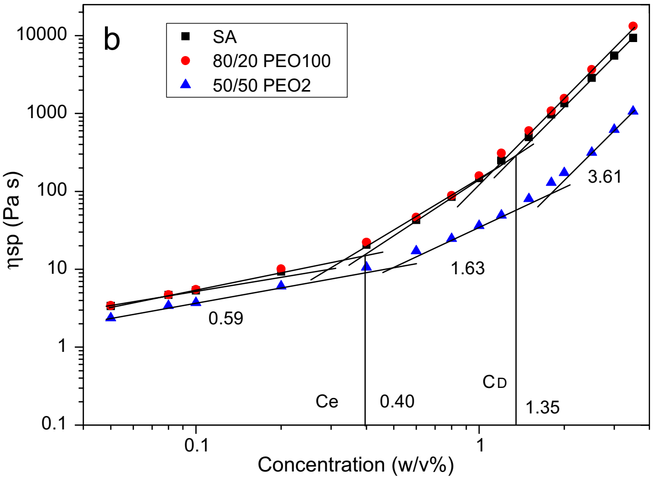

Fig. 7. The dependence of specific viscosity (η_{sp}) on concentration of SA/PEO blended solutions. 80/20 and 50/50 respectively represent the mass ratio of PEO100/SA and PEO2/SA.

3.5. *Physical properties of the SA/PEO aqueous solutions*

The physical properties of SA/PEO solutions were investigated in detail as shown in Table 1. For the blended solutions of SA/PEO, the conductivity decreased with the increase in PEO content. However, only the blended solutions of SA/PEO100 can be electrospun instead of SA aqueous solution and the blended solution of SA/PEO2. It seems that the decreased conductivities cannot assure an improved electrospinnability of SA aqueous solution. The viscosities of the blended solutions SA/PEO100 are all higher than that of SA aqueous solution. As Lu reported, SA is a polyelectrolyte and can form solutions with a wide range of viscosity. Viscosity should not be a limiting factor in this case. Therefore, it can be deduced that neither the viscosity nor the conductivity can be the main obstacle in the electrospinning of SA. The zero shear viscosity of 2.8 w/v% SA aqueous solution was 4.21 Pa s. However, when 35 w/v% PEO2 was added in SA aqueous solution, the viscosity of the blended solution increased to 61.09 Pa s. The viscosity of PEO2 itself at this concentration (0.2 Pa s) cannot affect the viscosity of SA/PEO2 system enough. Therefore, it can be deduced that the major contribution of the addition of PEO2 into the SA solution was to change the SA chain conformation through the interaction between PEO2 and SA chains. Consequently, the SA chain entanglements must have been enhanced which led to the increase in viscosity of the blended solution. However, in this system, the improved flexibility of SA chains was not enough to form effective chain entanglement for electrospinning.

Shear rate sweeps from 0.01 to 100 s^{-1}were performed at 25 °C on the polymer solutions to determine the dependence of specific viscosity (η_{sp}) on concentration. For alginate, a natural polyelectrolyte, its viscosity η_{sp} at low concentrations should be proportional to the square root of polymer concentration $\eta_{sp} \sim C^{1/2}$. In this semidilute unentangled regime ($C^* < C < C_e$), no chain entanglements are formed. The viscosity scaling relationships for polyelectrolyte solution without salt added in the semidilute entangled ($C_e < C < C_D$) and concentrated regimes ($C > C_D$) are $\eta_{sp} \sim C^{1.5}$ and $\eta_{sp} \sim C^{3.75}$, respectively. C_D marks the onset concentration of the concentrated regime [31]. As shown in Fig. 7, the concentration of 3.5 w/v% of SA is much higher than the measured entanglement concentration ($C_e = 0.4$ w/v%). However, SA aqueous solution in its concentrated regime cannot be electrospun at all. It seems that the traditionally defined molecular chain entanglement cannot be directly applied to the electrospinnability of SA, although it is very important to PEO as described earlier. This might be caused by the special chain structure and chain conformation of SA in aqueous solution. It can be speculated that if one molecular chain of SA occupies a domain, then the other molecular chains of SA can "enter" this domain when the concentration approaches the entanglement concentration. However, due to their rigid and extended chains, the molecular chains of SA cannot entangle each other to form an interpenetrating network as occurs with flexible molecular chains of PEO. The SA chains just exhibit closely spaced "overlap" even at its concentrated regime. The SA molecular chains just slide against each other during the electrospinning process. This is why electrospinning of alginate aqueous solution is very difficult or impossible, which was demonstrated in our earlier work [26]. Although the electrospinning concentration of SA/PEO2 was also above its measured C_e, the blended solution of SA/PEO2 cannot be electrospun. It is obvious that the chain entanglement of SA/PEO2 system which is mainly contributed by SA chains is not tight enough for electrospinning.

It is known that the formation of uniform fibers always requires proper chain entanglements [29]. Previous electrospinning results showed that the effective chain entanglements in SA/PEO100 solutions with a ratio of 90/10 or 80/20 at a concentration of 3.5 w/v% have been formed. The concentration of SA/PEO100 solution with a ratio of 80/20 (3.5 w/v%) is also higher than its C_e (Fig. 7). However, rheological results have already showed that the closely overlapped chains of SA did not contribute to its electrospinnability. Therefore, the effective chain entanglement in SA/PEO100 solutions must be mainly coming from the contribution of PEO100.

PEO is a flexible polymer. PEO100 chains begin to entangle each other at a concentration less than 0.16 w/v% determined by DLLS. With the concentration increased, the entanglement degree of PEO100 chains increased greatly. Therefore, when more and more PEO100 was added into SA aqueous solution, more and more molecular chains of SA were included in the network formed by PEO100 molecular chains. This is why the production of electrospun fiber from the SA/PEO100 solution increased as the ratio of PEO100 to SA was increased. As a result, the electrospinnability of SA/PEO100 solutions was improved greatly. PEO2 with low molecular weight cannot form effective chain entanglements even at a very high concentration of 4 w/v%. In SA/PEO2 solutions, the measured chain entanglements were mainly coming from the closely overlapped SA molecular chains. Therefore, the electrospinnability of SA/PEO2 solutions was not improved.

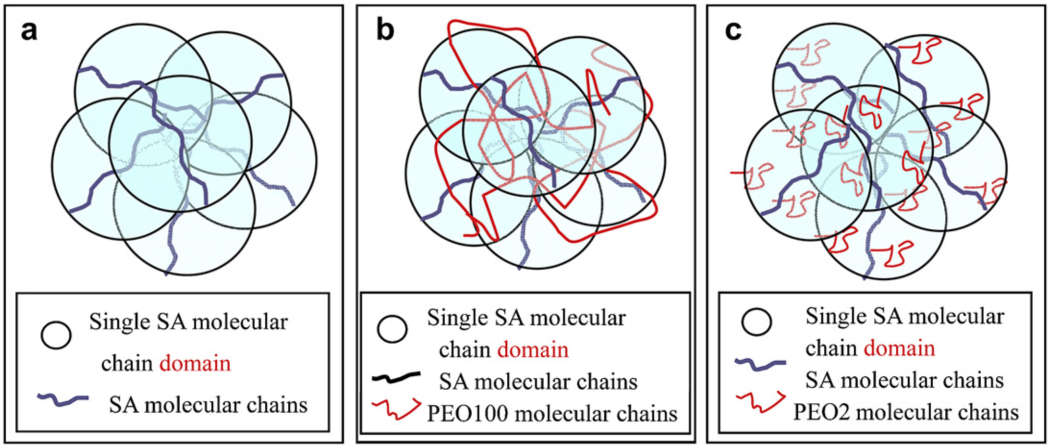

Fig. 8. The schematic drawing of the chain conformation in SA and SA/PEO systems (a) pure SA solution; (b) SA/PEO100 blended solution; (c) SA/PEO2 blended solution.

3.6. *Model illustration for the contribution of PEO to the electrospinnability of SA*

Fig. 8 depicts the role of PEO on the chain entanglements of SA aqueous solution in schematic view. Although the concentration of SA has approached its concentrated regime and the molecular chains of SA are closely "overlapped" each other, they cannot entangle each other due to the rigid and extended chain conformation of SA. Therefore, we make a circle to depict the domain of each SA molecular chain occupied, although SA molecular chains have entered the domains of each other as the concentration increased, however, SA chains cannot really entangle each other, they just pack-like planks (Fig. 8a). For PEO100, its long and flexible molecular chains can easily form a physical network even at a lower concentration. Therefore, when SA was added in PEO100 aqueous solution, the SA molecular chains were definitely enclosed in the PEO100 network. It seems that the role of PEO100 is offering a cage to enclose SA molecular chains into its large physical networks. In addition, this makes the chain entanglements of the blended solution of SA/PEO100 tighter than those of PEO100 aqueous solution (Fig. 8b). For PEO2, the molecular chains of PEO2 in its aqueous solution cannot form effective chain entanglements and they may exist in the form of short random coils. When SA was added, PEO2 chains just spread around the SA molecular chains and endowed the SA chains an enhanced flexibility. However, this changing of the SA chains has no ability to form an effective entanglement network (Fig. 8c).

4. Conclusions

SA alone cannot be electrospun from its aqueous solution, but its electrospinnability was greatly improved by adding high molecular weight PEO100. The low molecular weight PEO2 cannot improve the electrospinnability of SA. The properties of the SA solutions revealed that the failure of electrospinning from SA solutions cannot be simply attributed to their polyelectrolyte characteristics or their high viscosity. DLLS results showed that when the molecular chains of PEO in SA aqueous solution reached the entangled regime, they have the ability to improve the electrospinnability of SA. The rheological measurements of SA solutions showed that even when the concentration of SA approached its concentrated regime, no effective chain entanglements could be formed to achieve the electrospinning requirement. The molecular chains of SA closely overlap each other and no entanglement network can be formed due to the rigid and extended chain conformation of SA. The molecular chains of PEO100 in SA aqueous solution played an important role to provide entanglement site to SA molecular chains and to incorporate them into the overall physical networks, so that SA was included in the fiber during the electrospinning of the blend solution of SA and PEO100. However, PEO2 chains cannot form a physical network in its solutions due to its low molecular weight. Therefore, PEO2 has no ability to improve the SA electrospinnability even though PEO2 could enhance the flexibility of SA chains. Three schematic pictures were used to depict the role of PEO with different molecular weight on the chain entanglements of SA.

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