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Electrospinning of sodium alginate with poly(ethylene oxide)

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Abstract

Another natural biopolymer, sodium alginate, has been electrospun from aqueous solution by blending with a non-toxic, biocompatible, synthetic polymer poly(ethylene oxide) (PEO). The interaction between sodium alginate and PEO has been evidenced by FTIR and conductivity change, which is thought to be the main reason for the successful electrospinning. The solution properties of sodium alginate/PEO blends have been measured, including viscosity, conductivity and surface tension. The morphology and mechanical properties of the electrospun mats have been investigated. Smooth fibers with diameters around 250 nm are obtained from 3% solutions of varied alginate/PEO proportions ranging from 1:1 to 0:1. Tensile strength around 4 MPa is found with smooth fiber mats. The anti-water property of the electrospun mats has been improved by a combination of hexamethylene diisocyanate and aqueous calcium chloride cross-linkings.

Keywords: Electrospinning; Sodium alginate; Poly(ethylene oxide)

1. Introduction

Electrospinning is a recently explored simple and effective fabrication technique for producing nano to microscale fibers. Since the electrospun mats consist of ultra-fine fibers with high specific surface area and high aspect ratio, and have a high porosity as a result of random deposition of the fibers, can therefore mimic the structure of natural extracellular matrix [1], they could have a great potential in biomedical applications such as tissue engineering scaffolds, drug delivery carriers, wound dressing, etc [2–4]. Applications in other fields such as filter, sensor and protective clothing are also promising [5–7].

So far, more than 50 different polymers have been successfully electrospun [1]. Although a few examples of polymers have been electrospun from polymer melt at high temperature under vacuum condition [8,9], most of the polymers have been electrospun from solution where the polymer must be dissolved in a suitable solvent before electrospinning. Synthetic polymers are relatively easy to dissolved in an organic solvent such as dimethyl formamide, dichloromethane and tetrahydrofuran, and therefore often electrospun from organic solutions, while in cases where they are water-soluble such as poly(vinyl alcohol) (PVA) and PEO, they can also be electrospun from aqueous solutions [10,11]. There are limited examples of natural biopolymers electrospun from organic solutions[12–14], since it is, in general, not easy to find an organic solvent for biopolymers. Biopolymers such as collagen, silk, chitosan and soluble eggshell membrane proteins (SEP) are usually soluble in aqueous solutions, however, electrospinning themselves alone from aqueous solutions seems difficult, and in fact their electrospinning from aqueous solutions has been achieved in polymer blend form by blending with a non-toxic, non-ionic and biocompatible synthetic polymer PEO or PVA [15–18], which improves their processability while maintaining their biocompatibility.

Alginate, which is obtained from marine brown algae, is a naturally occurring polysaccharide. It is the monovalent salt form of alginic acid comprising 1,4-linked β-D-mannuronic (M) and α-L-guluronic acid (G) units [19]. Alginate is a

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water-soluble polymer and forms gel in the presence of certain bivalent cation such as Ca^{2+} through ion exchange [20]. The industrial wet spinning process for manufacturing fibers relies on these useful characteristics. Alginate (sodium, ammonium or potassium salt) is firstly dissolved in water to make a viscous solution and then the degassed solution is ejected through a nozzle into a coagulating bath containing calcium ion, where the fiber forms as a result of cross-linking.

Alginate has some unique properties such as non-toxicity, biocompatibility, biodegradability, hydrophilicity and relatively low cost [21,22]. It is an important biopolymer in biomedical applications such as wound dressing, tissue engineering scaffold, drug delivery carrier, etc [23–26]. Traditionally manufactured fibers have a diameter of tens to hundreds microns. Electrospinning into ultra-fine fibers would greatly increase the efficiency of some specific biomedical applications. Some fiber-forming biopolymers such as chitosan and gelatin have been successfully electrospun, however, to the best of our knowledge, electrospinning involving alginate has not yet been reported.

In this paper, electrospinning of sodium alginate from aqueous solution is investigated. Sodium alginate alone did not electrospin. By blending with PEO, a non-toxic biocompatible synthetic polymer, smooth fibers were obtained. The properties of the aqueous blend solutions, and the morphology and mechanical properties of the electrospun mats were measured and discussed. Furthermore, a two-step cross-linking method was investigated to improve the anti-water property of the electrospun mats in order to facilitate their practical applications.

2. Experimental

2.1. Materials

Sodium alginate and PEO (100 kDa) were purchased from Xilong Chemical Engineering (China) and Alfa Aesar, respectively, and used without further purification.

2.2. Preparation of the electrospinning solutions

Aqueous solutions of sodium alginate/PEO with different concentration and ratio were prepared by dissolving sodium alginate and PEO in distilled water. The mixtures were stirred at room temperature with magnetic stirring for 6 h to obtain homogeneous solutions.

2.3. Electrospinning

Each solution was placed into a 10 ml glass syringe capped with a 9-gauge blunt needle. The positive lead from a high voltage supply was connected via an alligator clip to the external surface of the needle. A rectangular (20 × 10 cm) aluminum foil was used as a static collector and connected to the ground. The tip-to-collector distance was 20 cm. The flow rate of the solution is 0.5 ml/h, and dispensed manually. The voltage was kept at 15 kV.

2.4. Method of cross-linking

The electrospun mats were cross-linked by immersing in 2% hexamethylene diisocyanate (HMDI) containing a catalytic amount of dibutyltin dilaurate (DBTDL) in toluene at room temperature for 24 h, then washed thoroughly with toluene. The HMDI-treated mats were further cross-linked by soaking in 5% aqueous $CaCl_2$ for 24 h. To study the anti-water property of the electrospun mats, the cross-linked mats were immersed in distilled water for three days.

2.5. Characterization

Images of electrospun fibers were obtained with a JSM-7401 field emission gun scanning electron microscopy (SEM). Average fiber diameters were determined by measuring fibers randomly selected from SEM images. Infrared spectra were obtained with a Fourier transform spectrophotometer (Nicolet 560) with a resolution of $4\ cm^{-1}$ and a spectral range of $4000-600\ cm^{-1}$. The surface tension of solutions was measured with a tensiometer (DCAT 21, Dataphysics). The viscosity of solutions was measured in a rotating viscometer (Model NDJ-8S, Shanghai Rex Instruments) at 25 °C. The conductivity of the solutions was tested in a conductivity instrument (Model DDSNDJ-307, Shanghai Rex Instruments). Evaluation of the mechanical properties of the electrospun mats was performed on a universal testing machine (TCS2000, Gotech) with a 20 kg f load cell and an extension rate of 1.0 mm/min. Six specimens were tested and averaged. Specimens were cut into rectangular shape (100 mm × 10 mm) and dried in a vacuum oven at 50 °C for 24 h before testing.

3. Results and discussion

3.1. Electrospinning of sodium alginate/PEO aqueous blends

A few groups of researchers claimed that biopolymers, including collagen, silk, casein, chitosan, and SEP, did not electrospin from aqueous solutions, but can be successfully electrospun by blending with PEO or PVA [15–18,27]. In this work, we also had difficulty to electrospin aqueous sodium alginate, only after blending with PEO, smooth electrospun fibers can be obtained. We would wonder the reason behind this. Analyzing the published papers, it seems that for the cases of collagen, silk and SEP, the low viscosity of the aqueous biopolymer solutions is the most apparent reason for the unsuccessful aqueous electrospinning of those biopolymers alone. After blending with PEO or PVA, the viscosity can be increased to the appropriate values, making electrospinning successful. In fact, an all-aqueous process for electrospinning of silk fibroin was recently developed following an effort in preparing concentrated silk fibroin solution [28].

However, in the cases of casein and chitosan, viscosity seems not to be a problem since viscous solutions can be obtained at high concentrations. The high elasticity of casein resulted from its strong inter- and intra-molecular forces and

3D structure seems to be the key factor hindering its electrospinning [27]. The addition of PEO (or PVA) can reduce its elasticity by dissociating the interconnected chains through formation of secondary bonding between PEO and casein. Chitosan is a polyelectrolyte having high conductivity in aqueous solution, the strong repulsive force among the polycations along the chitosan chains, which prevent sufficient chain entanglement necessary for fiber formation, was thought to be the main reason for the unsuccessful aqueous electrospinning [29,30]. By blending with PEO or PVA, the repelling force among polycationic chitosan molecules could be reduced to a certain degree, favoring electrospinning [29]. It is proposed [31], in another work on electrospinning of polyelectrolytes, that the formation of nanofibers could be favored by hydrogen bonds between the polyelectrolyte and the non-ionogenic polymer such as PEO.

Sodium alginate, similar to chitosan, is a polyelectrolyte having high conductivity and can form solutions with a wide range of viscosity. Viscosity is not a limiting factor in this case. The repulsive force among the polyanions could be the key factor hindering electrospinning of sodium alginate. After blending with PEO, the interaction between PEO and sodium alginate, which is evidenced by conductivity change and FTIR, reduces the repulsive force among polyanionic sodium alginate molecules, and thus allows successful electrospinning of sodium alginate/PEO blends. The conductivity of a 2% solution of sodium alginate is reduced by 16% (from 4.40 ms/cm to 3.69 ms/cm) after adding half the amount of PEO, indicating reduced degree of ionization of carboxylate salt, which is a result of interaction between PEO and sodium alginate. In FTIR spectra (Fig. 1), as the proportion of PEO in blends increases from 0% to 50%, the asymmetrical band of carboxylate ion has shifted to lower frequencies from 1593 cm^{-1} to 1613 cm^{-1}, and the hydroxy band of sodium alginate has shifted from 3246 cm^{-1} to 3406 cm^{-1}, revealing interaction of sodium alginate and PEO through hydrogen bonding between the etheric oxygen of PEO and hydroxyl groups of sodium alginate.

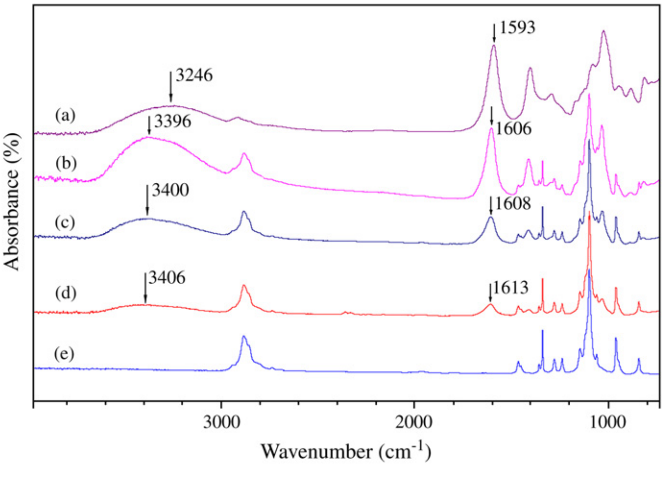

Fig. 1. The FTIR spectra of the electrospun mats with different sodium alginate/PEO ratio: (a) 1:0, (b) 3:1, (c) 2:1, (d) 1:1, and (e) 0:1.

3.2. Effect of solution concentration on morphology and mechanical properties of the electrospun mats

In this series of experiments, sodium alginate/PEO ratio was kept at 1:1, all other conditions were kept the same unless the overall solution concentration of the blend was changed. As shown in Fig. 2, beads-on-string structure was observed at low concentrations (1%–2%) and the shape of the beads changes from spherical to spindle-like as the concentration increases from 1% to 2%. At higher concentration (3%), smooth fibers were observed. At even higher concentration (4%), the electrospinning is difficult due to the high viscosity of the solution. From Table 1, it can be seen that the solution viscosity and conductivity increase and the surface tension decreases as the solution concentration increases. All the three parameters favor the formation of smooth fibers [32] when the concentration increases to 3%. It is noted that the fiber diameter increases with increasing solution concentration from 46 nm (1%) to 228 nm (3%). In general, the increase in viscosity increases the fiber diameter and the increase in conductivity shows opposite effect. In this case, the effect of viscosity is larger than that of conductivity, leading to an increase in fiber diameter with increasing solution concentration.

The mechanical properties of the electrospun mats can be affected by various parameters such as the composition, the interaction between the two components, processing conditions, beads and fiber diameter. From Table 2, it is obvious that the tensile strength increases and the elongation to break decreases when the solution concentration increases. It seems that the mechanical properties are related to the morphology of the electrospun mats since the composition and processing conditions of the blends were kept the same. The one without beads has the highest tensile strength. This seems understandable, since the beads can be regarded as defects which can cause stress concentration and thus lower the strength when the mat is stretched. It is rather surprising that the mat having the most beads has the highest elongation to break. The beads-on-string structure can probably deform and stretch out along the stress direction, making the elongation higher.

3.3. Effect of sodium alginate/PEO ratio on morphology and mechanical properties of the electrospun mats

Fig. 3 shows the morphology of the electrospun mats obtained from different sodium alginate/PEO ratio at the same overall concentration (3%). With high proportions of sodium alginate (75% and 66%), the fiber diameters are thinner than with low proportions of sodium alginate (50% and 33%) and there are spindle-like beads. Smooth fibers were observed with low proportions of sodium alginate (50% and 33%). As shown in Table 1, the viscosity and surface tension increase, and the conductivity decreases with decreasing proportion of sodium alginate. Usually, the increase in viscosity favors the formation of smooth fibers without beads, while the increase in surface tension and the decrease in conductivity show opposite effect. However, in this case, the reduction in the degree of ionization of carboxylate salt enhances chain entanglement,

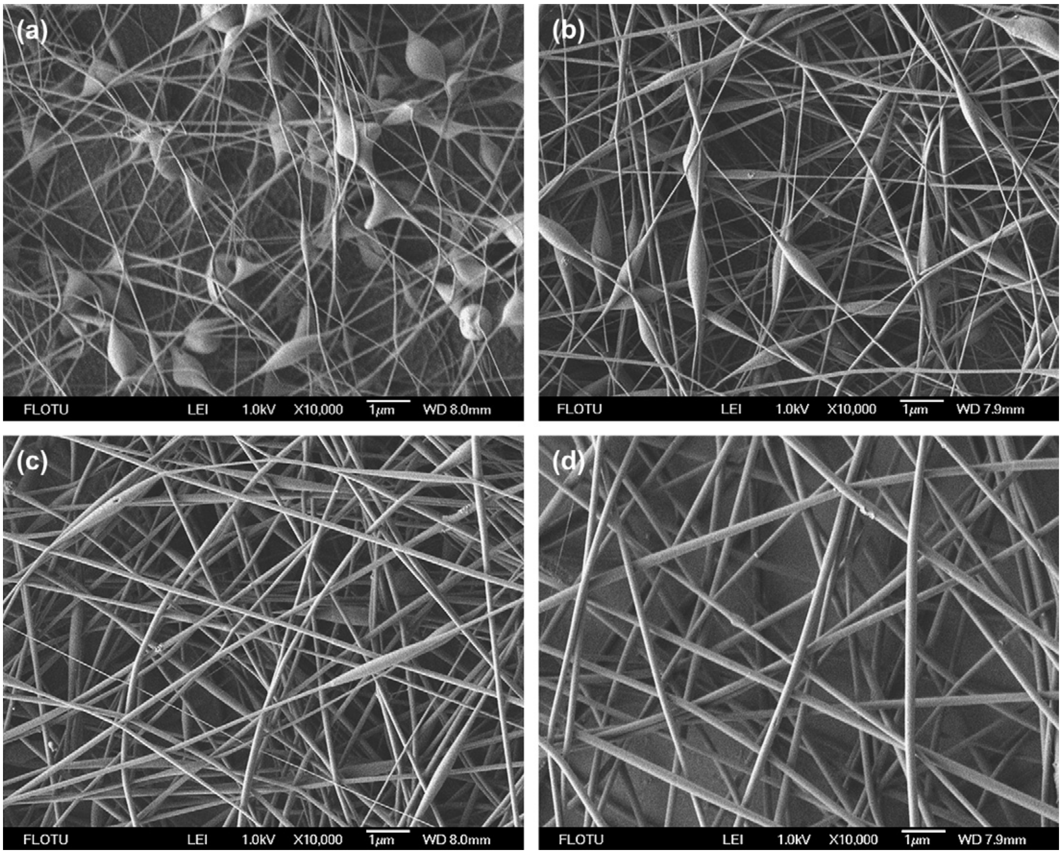

Fig. 2. The morphology of electrospun fibers with different solution concentrations: (a) 1%, (b) 1.5%, (c) 2%, and (d) 3%.

making the solution have better processability, favoring the formation of smooth fibers. The fiber diameter increases with decreasing proportions of sodium alginate as a result of combined effects of viscosity increase and conductivity decrease.

Table 3 lists the mechanical properties of the electrospun mats with different sodium alginate/PEO ratio and at the same overall concentration of 3%. With low proportions of sodium alginate (50% and 33%), the tensile strength is around 4 MPa, much higher than those of PEO and the electrospun mats with high proportions of sodium alginate (75% and 66%). However, the elongation to break does not have much increase compared to that of PEO, and is smaller than those at high proportions of sodium alginate. Similar to the discussion in the last section, the high strength may be related to the smooth fiber morphology, and the high elongation to break may be related to the presence of the beads.

Table 1
Properties of sodium alginate and PEO solutions

Entry	Sodium alginate/PEO ratio	Concentration (%)	Viscosity (cps)	Conductivity (ms/cm)	Surface tension (mN/m)
1	1:1	1	124	1.01	56.02
2	1:1	1.5	279	1.40	53.77
3	1:1	2	687	1.83	52.41
4	1:1	3	2219	2.43	50.72
5	1:0	3	1337	5.68	43.51
6	3:1	3	1741	4.16	46.22
7	2:1	3	2171	3.69	48.87
8	1:2	3	2423	1.77	54.19
9	1:3	3	2535	1.24	56.21
10	0:1	3	2672	0.09	57.09

3.4. Improvement of anti-water property

Since both sodium alginate and PEO are water-soluble, the sodium alginate/PEO electrospun mats dissolve instantly in water, therefore their anti-water property must be improved for practical applications. Previous research [18] on SEP/PEO electrospun mats has shown that the anti-water property can be improved slightly by soaking in methanol for 24 h due to an increase in degree of crystallinity (i.e. physical cross-links) of PEO as indicated by DSC. Thus, sodium alginate/PEO electrospun mats were soaked in methanol for 24 h at room temperature, and then dipped in water to test the

Table 2
Mechanical properties and morphology of electrospun sodium alginate/PEO mats with different solution concentrations

Entry	Concentration (%)	Tensile strength (MPa)	Elongation to break (%)	Morphology
1	1.0	1.0	8.2	46 nm, spherical beads
2	1.5	1.5	6.1	76 nm, spindle-like beads
3	2	2.9	5.6	152 nm, spindle-like beads
4	3	4.5	3.4	228 nm, smooth fibers

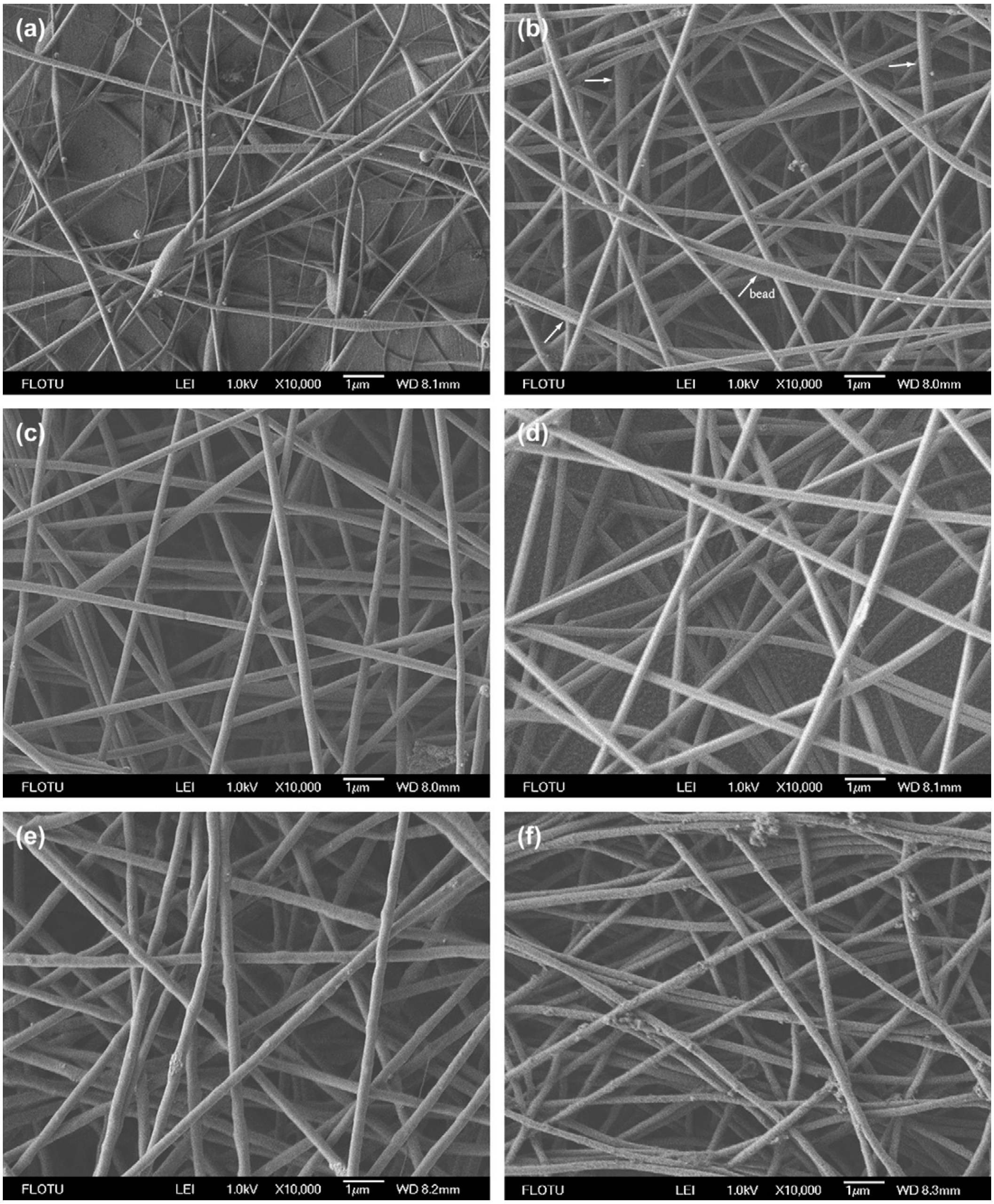

Fig. 3. The morphology of electrospun fibers with different sodium alginate/PEO ratio: (a) 3:1, (b) 2:1, (c) 1:1, (d) 1:2, (e) 0:1, and (f) entry 3 in Table 3 treated by HMDI and aqueous $CaCl_2$, dipped in water for three days.

Table 3
Mechanical properties and morphology of electrospun sodium alginate/PEO mats with different sodium alginate/PEO ratios

Entry	Sodium alginate/ PEO ratio	Tensile strength (MPa)	Elongation to break (%)	Morphology
1	3:1	0.9	8.5	114 nm, spindle-like beads
2	2:1	1.9	6.2	171 nm, spindle-like beads
3	1:1	4.5	3.4	228 nm, smooth fibers
4	1:2	4.0	3.3	266 nm, smooth fibers
5	0:1	1.2	2.9	308 nm, smooth fibers

anti-water property. The mat dissolved in less than 1 min in water. Cross-linking of sodium alginate in aqueous $CaCl_2$, like in traditional fiber-manufacturing process of sodium alginate, was then envisaged after soaking in methanol. The shape of the fibers on the above-treated mats completely disappeared after dipping in water for 1 h, as shown by SEM observation, due to the dissolution of PEO.

Xie and Hsieh [27] have used 4,4′-methylenebis(phenyl diisocyanate) treatment to improve the anti-water property of casein/PEO electrospun mats. The fibrous structure was rendered insoluble by covalent chemical cross-linking among the casein molecules and most likely also between PEO and casein, attributed to the high reactivity of isocyanate groups toward amino and hydroxyl groups. There are numerous hydroxyl groups on sodium alginate chains, and PEO has two end hydroxyl groups, we therefore adopted the same idea to render sodium alginate/PEO electrospun mats insoluble in water. A sodium alginate/PEO electrospun mat was immersed in a toluene solution of HMDI containing DBTDL as the catalyst for 24 h at room temperature, and then dipped in water to test the anti-water property. The HMDI-treated mat dissolved in water in less than 10 min, indicating that the degree of cross-linking is low. Since sodium alginate has no amino groups, its reactivity toward diisocyanate is much less than casein which contains amino groups. We then envisaged a further cross-linking of sodium alginate by soaking HMDI-treated mat in 5% aqueous $CaCl_2$ for 24 h. The shape of fibers on such treated mat was retained after dipping in water for three days as shown in Fig. 3f, indicating that PEO has been at least grafted, if not cross-linked, on sodium alginate during HMDI treatment. Therefore, a combination of HMDI and aqueous $CaCl_2$ cross-linkings can render sodium alginate/PEO electrospun mats insoluble in water.

4. Conclusions

Electrospinning of sodium alginate, a natural polymer, has been investigated. Sodium alginate alone cannot be electrospun from aqueous solution. The processability of sodium alginate can be improved by blending with PEO. Smooth fibers with a diameter around 250 nm were obtained with a solution concentration of 3% and sodium alginate/PEO ratio of 1:1–0:1. Higher tensile strength was found with electrospun mats having smooth fibers, while the higher elongation was found with electrospun mats containing beads. A combined cross-linking with HMDI and aqueous $CaCl_2$ can improve the water resistance of the electrospun fibers. The process investigated in this work provides a convenient approach for producing ultra-fine fibers of sodium alginate, which could have a good potential in biomedical applications.

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