Effect of Solvent on Morphology of Electrospinning Ethyl Cellulose Fibers

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ABSTRACT: The influence of the composition of a multicomponent solvent on the surface morphology and diameter distribution of ethyl cellulose fibers produced by electrospinning technology was investigated. The results showed that the average diameter of the fibers using the multicomponent solvent was thinner than when using either of the two components and the diameter distribution of the fibers became narrower. Tiny tubercles formed on the fiber surface, which may improve the specific surface area and broaden the applications. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1292–1297, 2005

Key words: electrospinning; fibers; morphology; ethyl cellulose; nanotechnology

INTRODUCTION

Electrospinning is a straightforward, convenient, and effective method to produce submicron diameter fibers compared to traditional methods to prepare thin fibers. It was first patented by Formhals in 1934.[1] Electrospinning employs high voltage electrostatics to propel the polymer solution and fiber formed by the splitting of the liquid jets, when they travel to the grounded collector. Since this method was invented, many polymer systems have been electrospun to produce ultrathin fibers, such as nylon 6,[2] polystyrene,[3] protein,[4] DNA,[5] and polycaprolactone,[6] which have many special properties and can be used in reinforced materials,[7] medical materials,[8] filter materials,[9] and so forth.

Cellulose is an abundant, reproducible, natural material, and it is considered as a potential material source to replace fossil oil, which has limited stores on earth. However, few studies has been reported on the fiber of cellulose and its derivates produced by the electrospinning method.[10] Ethyl cellulose (EC) is a kind of cellulose ether, and it shows good thermostability and electric properties. The film made from EC has quite good permeability, it has been widely used in the biomedical field. The fiber produced by elecrospinning has a large specific surface, which broadens the possible uses of EC.

In this study, EC was dissolved in a multicomponent solvent system with different mixing ratios, and the solution was used for electrospinning to produce EC fibers. The effects of the composition of the solvent on the diameter distribution and surface morphology of the fibers were investigated.

EXPERIMENTAL

EC, with number-average and weight-average molecular weights of (7.2 and 16) $\times 10^4$, respectively, and a substituted degree of ethyl of about 2.2, was provided by Luzhou Chemical Plant. Tetrahydrofuran (THF) and dimethylacetamide (DMAc) were chemically pure reagents that were used as the solvents in the experiments. Figure 1 shows the scheme of the electrospinning apparatus. The polymer solution was placed in an orifice. An electrode, which was connected to the electrostatic generator, was placed in the solution to impose an electrostatic field. The generator for high voltage electrostatics was made in our lab, and it generates electrostatics ranging from 0 to 100 kV. The voltage of the electrostatics was measured by an electrometer (EST101, Beijing Electrostatic Facilities Company, Ltd.). The current was measured with an ordinary ampere meter (maximum scale = 50 μA). The grounded collector was an aluminum lamella with a diameter of about 20 cm. The distance between the electrode and the collector could be adjusted from 1 to

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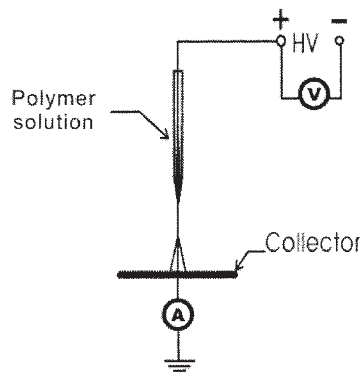


Figure 1 The scheme of the electrospinning apparatus.

40 cm. If not specified, in our experiments the diameter of the orifice was 1.2 mm, the polar distance was 15 cm, and the surrounding temperature was 22°C.

EC was dissolved in the solvent system with different mixing ratios of THF and DMAc at ambient temperature, and the volume ratio of these two components ranged from 100/0 to 0/100. The solution was allowed to sit for about 10 days, and the resulting homogeneous solution was then stored until used. The viscosity of the solution was measured with a rheometer (REOTEST II) at room temperature, and the surface tension was measured by a surface tension apparatus (JZhY1-18). The morphology of the fiber was observed with a polarized optical microscope (ORTHOPLAN-POL, Leitz) and two environment scanning electron microscopes (ESEMs, FEI XL-30 and ESCALab220I-XL) for elemental analysis.

RESULTS AND DISCUSSION

During electrospinning, the solution is charged after imposing an electric field. The solution droplet in the front of the orifice is distorted into the shape of a conical meniscus, known as the Taylor cone,[11] and a solution jet is ejected from the droplet when the voltage is above the critical value (V_c). As the jet travels to the grounded collector, it splits into a bundle of thinner ones. At the same time, the solvent volatilizes from the splitting jets and the fibers in the form of nonwoven mats are collected on the grounded collector.

In previous investigations, more attention was focused on the effects of different conditions on the morphology of the fibers during the electrospinning process, such as the applied voltage, solution concentration, distance from the electrode to the collector, and so forth. However, in our experiment the composition of the solvent also shows a great effect on the V_c and the current generated in the electrospinning process. In the EC/(THF–DMAc) solution, the ratio of THF and DMAc influences the viscosity of the solution and the viscosity of the solution and the surface tension decrease with increasing content of DMAc in the system (Table I). The V_c and the current are also varied with the variation of the mixing ratio of the THF and the DMAc, which are proportionally increased with the volume of DMAc in the multicomponent solvent. According to the Taylor equation,[12]

$$V_c^2 = 4\,\frac{H^2}{L^2}\left(\ln\frac{2L}{R} - \frac{3}{2}\right)(0.0117\pi R\gamma) \qquad (1)$$

where H is the distance between the electrode and the collector, L is the length of the capillary of the orifice, R is the radius of the capillary, and y is the surface tension of the solution. The V_c is proportional to the surface tension of the solution. Addition of DMAc in the system decreases the surface tension of the solution and the V_c is also decreased during the spinning. For the current, which is mainly produced by the charge carried by the solution in the electrospinning, the small surface tension and the viscosity of the solution result in a larger amount of solution electrospun within a unit of time. Therefore, there are more charges carried to the collector and the current is increased when increasing the volume of DMAc in the solvent system.

Effects of solvent composition on diameter and its distribution of fibers

Besides the V_c and the current, the composition of the solvent also affects the diameter of the fibers and its distribution. Figure 2 shows the diameter distribution of the fibers under the conditions of a 20-kV applied voltage, a 10-cm distance between the electrode and collector, and a 13 wt % solution concentration. Note that the diameter of the fiber has a broad distribution for the EC/THF system, and no predominant distribution diameter range is found, as shown in Figure 2(a). However, in the system with a multicomponent solvent, the diameter distribution of the fiber is unimodal; and as the composition of the DMAc in the

TABLE I
Composition of Solvent, Current, and Critical Voltage in Electrospinning and Viscosity and Surface Tension of Solution in 13 wt % EC/(THF–DMAc) Solution

Mixing ratio of THF/DMAc	Critical voltage (kV)	Current (μA)	Viscosity (cP)	Surface tension (10^{-3} N/m)
100/0	19	<0.1	635	37.3
80/20	17	0.5	420	36.7
60/40	16	1	416	34.5
50/50	13	1	416	32.9
40/60	9	2	467	32.8
20/80	5	5	388	31.9
0/100	4	10	317	32.6

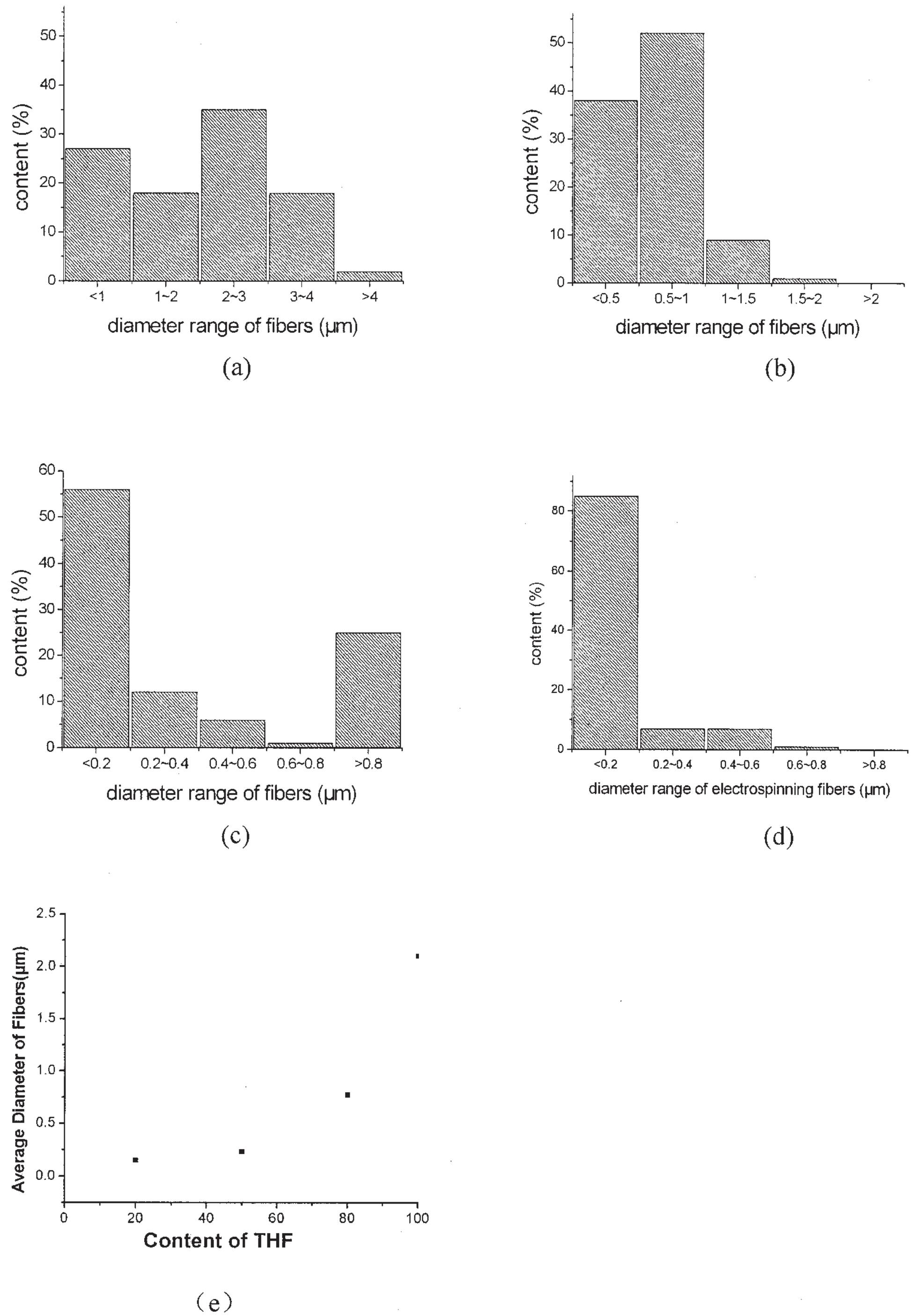


Figure 2 The diameter distribution of the fiber. The applied voltage is 20 kV, the distance between the polar electrode and the collector is 10 cm, and the concentration of the solution is 13 wt %. The mixing ratios of THF to DMAc in the solvent system are (a) 100/0, (b) 80/20, (c) 50/50, and (d) 20/80. (e) The variation of the average diameter with the composition of the solvent.

solvent increases, the peak moves to the smaller end. When the ratio of THF/DMAc is 20/80 [Fig. 2(d)], the over 80% (v/v) fibers are smaller than 200 nm in diameter. Figure 2(e) presents the variation of the fiber average diameter with the composition of the solvent. It shows that the addition of DMAc in the system results in the decrease of the fiber diameter and the average diameter of the fiber decreases with increasing content of DMAc. When the composition of the DMAc in the solvent is higher than 50% (v/v), the average diameter does not vary much, although the distribution has changed. The thinnest diameter of the fiber is about 70 nm (Fig. 3) when the ratio of the THF/DMAc is 20/80. Moreover, it can be seen from

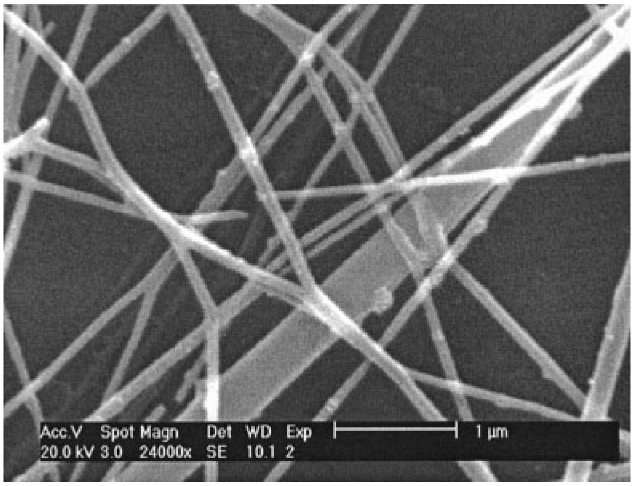


Figure 3 An SEM micrograph of the thinnest fibers produced in the experiment by electrospinning. The applied voltage is 7 kV.

Table I that the system shows the lowest surface tension and bigger current when the ratio of THF/DMAc is 20/80, which means that more charges are carried by the solution jet and, as we know, the charges carried by the jet play an important role in the splitting of fibers. Thus, thinner fibers are collected.

The differences in the solubility parameters for each component in the system may influence the fiber diameter and the diameter distribution. The solubility parameters of THF, DMAc, and EC are 9.9, 11.1, and 10.5, respectively. When EC is dissolved in THF or DMAc, the solubility parameter of the EC and the solvent is much different and THF and DMAc are not good solvents for EC. However, when THF is mixed with DMAc, the solubility parameter of the solvent system is close to the solubility parameter of the EC. In addition, when the ratio of THF/DMAc is 50/50, the solubility parameter of the solvent system is equal to that of the EC, which means that it is a good solvent for EC and the EC can be easily dissolved in this system. The molecular chains extend more freely in the EC/(THF–DMAc) solution than in the EC/THF or the EC/DMAc solution. At the same time, the polarity of DMAc is higher than that of THF. In the electrostatic field, the distortion of DMAc molecules is easier than that of THF molecules because of more charges carried by the jet. As far as we know, after the jet forms, the charges on it repel each other and the splitting of the jet occurs. When the surface tension is held constant, more charges are therefore carried by the jet and thinner fibers are formed.

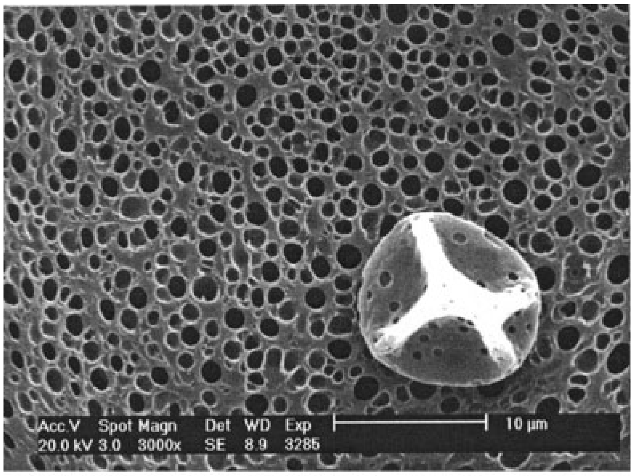
Effects of solvent composition on morphology of fibers

Many investigations have shown that different electrostatic field voltages and solution concentrations will result in different fiber morphologies, such as fibers with microholes[13] and beaded fibers.[14] In our experiments, we found that the morphology of the fibers was also influenced by the composition variation of the multicomponent solvent.

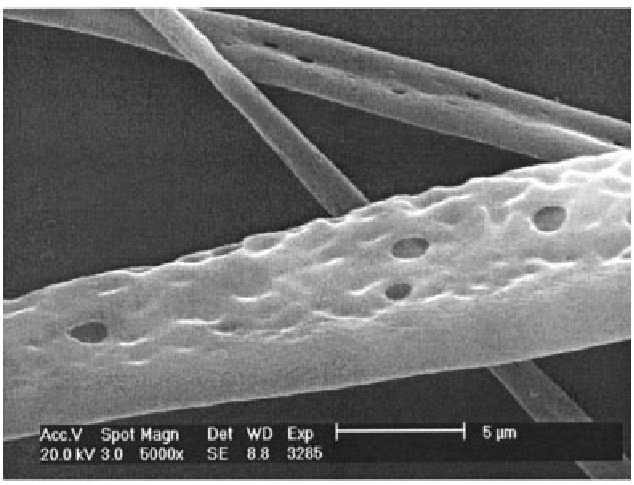
For the EC/THF solution, when the concentration is lower than 5 wt %, only a film composed of microholes can be collected because of the low viscosity of the solution [see in Fig. 4(a)]. With increasing concentration, beaded fibers and fibers with microholes are sometimes observed. When further increasing the concentration to 10 wt %, there are more fibers with microholes, but the diameter of the holes are almost the same. Figure 4(b) shows that microholes on the fiber surface are not concatenation, and the depth of these holes is about 50 nm. When the concentration of the solution increases to 13 wt %, the fibers with microholes are rarely observed again. According to the interpretation of Dzenis,[13] at low concentration, the content of solvent is relatively high and more solvent volatilizes, which leads to the formation of fibers with microholes. When the concentration of the EC/THF solution is high enough, the surface of jet can easily form a dense film after the solvent volatilizes, which hampers the volatilization of the solvent inside the jet (or fiber) and the solvent molecules have to be volatilized only by diffusion; thus, the surface of the fiber is smooth. Note from Figure 4(c), when the concentration of the EC/THF solution is high (above 20 wt %) and the distance from the electrode to collector is large (>20 cm), it is difficult to obtain a good fiber.

When the solvent is only DMAc, no fibers can be collected in the concentration range of 5–20 wt %, and the products are in the form of films with tiny holes, which usually aggregate in block mass for the higher volatilization temperature of DMAc, as shown in Figure 5.

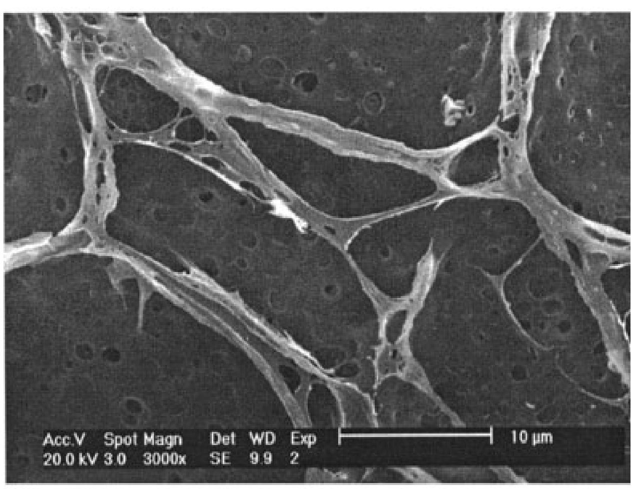
For the EC/(THF/DMAc) solution, fibers with beads and microholes are also observed, which depended on the variation of the concentration. Moreover, we found that the morphology of the fibers is also influenced by the composition of the multicomponent solvent. When the concentration of EC is kept at 13 wt %, if the content of THF is >20% (v/v) and <80% (v/v), fibers with tubercles are collected. A typical example of the fibers with tubercles is shown in Figure 6, and the diameter of the tubercles on the fiber surface is on the order of nanometers, which is about one-fifth to one-third of the diameter of the fiber (Figs. 3, 6). This is different from the beaded fibers reported by Feng et al.[15] The diameter of the tubercles on the fiber surface is smaller than that of the beads on the beaded fiber. Elemental analysis by the ESEMs shows that the composition of the tubercles is the same as that of the fiber, as shown in Table II, which is mainly composed of EC and part of the unvolatilized solvent. The formation of tubercles on the fiber



(a)



(b)



(c)

Figure 4 SEM micrographs of the fiber electrospun from EC/THF solution. The concentrations and voltages are (a) 5 wt % and 17 kV, (b) 20 wt % and 22 kV, and (c) 13 wt % and 20 kV, respectively.

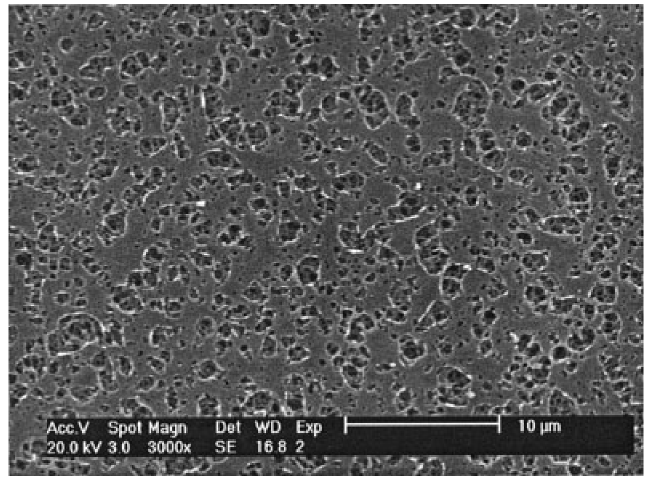


Figure 5 An SEM micrograph of the products of the EC/DMAc solution. The concentration is 13 wt % and the applied voltage is 18 kV.

surface may result from the difference of volatilization of the two components, THF and DMAc, in the multicomponent solvent system. The boiling points of THF and DMAc are 65 and 165°C, respectively. During electrospinning, the solution jet flies to the collector and the THF is volatilized first because of its lower boiling temperature. The volatilization of the DMAc in the solution jet is slow because of its higher boiling temperature and some EC/DMAc solution particles exist on the fiber surface when the jets arrive to the collector because the THF is almost totally volatilized. Finally, some tubercles are formed on the fiber surface after the DMAc is volatilized, the composition of which is the same as that of the fiber itself (Table II).

Moreover, we also found that the concentration region in which the electrospinning can be carried out

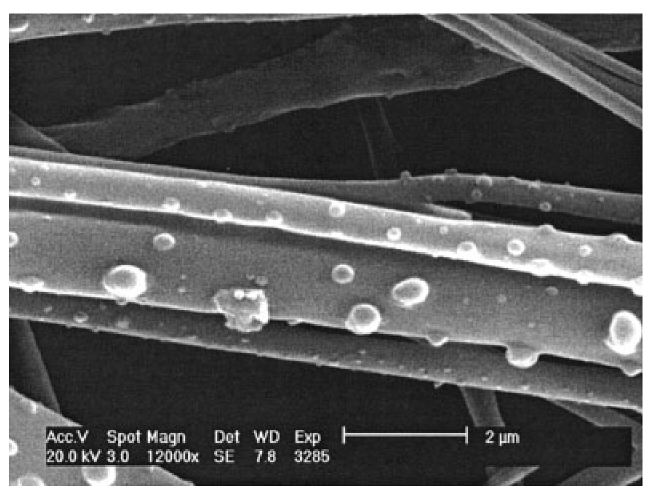


Figure 6 An SEM micrograph of the fibers with tiny tubercles electrospun from the 13 wt % EC/(THF–DMAc) solution. The ratio of THF/DMAc is 40/60 and the voltage in the electrospinning is 18 kV.

TABLE II
ESEM Results of Component of Tubercles and Fibers

Component (wt %)	Tubercles	Fibers
C	40.01	39.66
N	3.11	3.61
O	56.88	57.64

varies with the composition of the multicomponent solvent. For example, when the composition of the DMAc is increased from 0 to 50% (v/v) in the multicomponent solvent system, the concentration region in which the solution can be electrospun is changed from 7–20 to 7–27 wt %. This is probably because when DMAc is added and with increasing the DMAc composition in the multicomponent solvent system, the viscosity of the solution decreases, as shown in Table I, and the surface tension is lower.

CONCLUSION

The diameter and its distribution of the EC fiber manufactured by electrospinning are greatly influenced by the composition of the multicomponent solvent system (THF–DMAc). The mean diameter of the fiber manufactured with the multicomponent solvent system is smaller and the diameter distribution is narrower than that prepared with a single component solvent system, such as THF. The concentration range in which the solution can be electrospun is increased when the second component DMAc is added. Because of the difference in volatilization of the two components in the solvent system, tiny tubercles on the surface of the fiber are formed when the multicomponent solvent is used in electrospinning.

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