

Electrospinning of Ethyl–Cyanoethyl Cellulose/Tetrahydrofuran Solutions

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ABSTRACT: In this study, electrospinning was used to fabricate ethyl–cyanoethyl cellulose [(E-CE)C] fiber from a solution of (E-CE)C/tetrahydrofuran. The diameter of the thinnest fiber fabricated during the electrospinning was about 200 nm. It was found that the diameters of the fibers and their distribution depend on the processing parameters and properties of the solution, such as viscosity, tempera-

ture, and concentration, for example. The morphology of the fiber was also observed by SEM. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 242–246, 2004

Key words: solutions; fibers; morphology; electrospinning; viscosity

INTRODUCTION

In the past few years there has been growing interest in investigation of electrostatic spinning (electrospinning). Electrospinning is a convenient, cheap, and less-polluting method of producing fibers. Although Fomhals¹ first patented the method of electrospinning in 1934, it has not received much attention until recently. In 1971 Baumgarten reported visual evidence of a charged solution jet sent out from polyacrylic acid solution in the presence of an electrostatic field.² From that time, some materials have been reported to be electrospun from polymer solution or melt.^{3–7}

Compared with traditional spinning methods, such as melt spinning, solution spinning and so on, electrospinning is a unique process that is capable of producing fibers with diameters ranging over several orders of magnitude, from the micrometer range typical of conventional fibers to the nanometer range. Electrospun fibers also possess unusually large surface-to-volume ratios because of their small diameter and are expected to display morphologies and properties different from those of their conventional counterparts. Some applications of electrospun fibers were previously investigated, such as biomedical⁸ and functional materials.⁹

Cellulose is a cheap, renewable biomacromolecule. Few investigations concerning the fabrication of cellulose and its derivative fibers by using electrospinning have been reported.¹⁰

In this report, the electrospinning method was used to prepare ethyl–cyanoethyl cellulose [(E-CE)C] fibers. The morphology of the fibers and the factors that influence the diameter of the electrospun fibers are the main focus of this study.

EXPERIMENTAL

The (E-CE)C was prepared by reaction of ethyl cellulose (from Luzhou Chemical Plant, China) and acrylonitrile.¹¹ The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.37, determined by elemental analysis (CHN-O-RAPID, Heraeus, Germany). The number-average molecular mass of (E-CE)C, measured by gel permeation chromatography (GPC; Waters-ALC-244-GPC; Waters Chromatography Division/Millipore, Milford, MA), calibrated by standard polystyrene, was 9.7×10^4 g/mol. Tetrahydrofuran (THF) was a chemically pure reagent.

The electrospinning apparatus, equipped with variable high-voltage power (0–100 kV), was made in our lab (Fig. 1). The anode connected to the variable high-voltage transformer was attached to a copper wire that was inserted into the (E-CE)C/THF solutions kept in a glass pipette. The collector was attached to a round piece of aluminum foil as the collector that was electrically grounded. The distance between the anode and the collector was adjustable. The diameter of the orifice was 1.2 mm and, under the appropriate conditions, fibers were collected on a thin piece of glass placed on the collector.

The electrospun fibers were freeze-fractured to reveal fresh cross sections of their internal structure in

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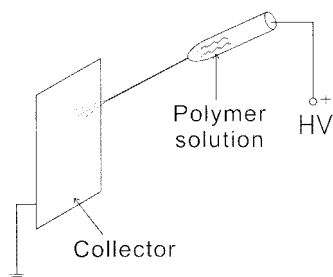


Figure 1 Schematic of the electrospinning device.

liquid N_2 , after which the fractured surface was sputtered with a thin layer of gold (IB-5 gold sputterer, Giko, Japan). The morphology of the fractured surface of the fibers was observed by a scanning electron microscope (SEM; Hitachi, S-430, Ibaraki, Japan). The crystallinity of the fibers was measured by use of an X-ray diffraction instrument (Rigaku, C/MAX-1200, Japan). The surface tension of the solutions was measured by interfacial tensiometer (JZHY-180, Chende Equipment Ltd., China) at room temperature.

RESULTS AND DISCUSSION

Without the effect of the electrostatic field, a spherical drop of the solution was suspended from the orifice of the pipette. However, the surface of the drop was distorted into the shape of a cone known as the Taylor cone¹² when an electrostatic field with high voltage was applied. When the voltage of the electrostatic field was increased to 20 kV, a charged solution jet erupted from the apex of the cone and was accelerated toward the collector by the effect of the electrostatic field. As the solution jet traveled through the air, the solvent was evaporated and the polymer fibers were collected on a collector. When the concentration of the (E-CE)C/THF solutions was lower than 15 wt %, the fibers could not be formed by electrospinning because of the low viscosity. At solution concentrations greater than 22 wt %, on the other hand, the solution jet also could not erupt because of the high viscosity and surface tension of the solution.

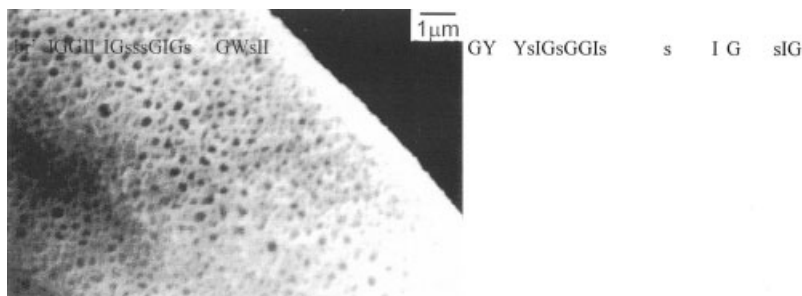


Figure 2 SEM micrograph of electrospun fiber fabricated from the solution with a concentration of 17 wt % at the temperature of 22°C; applied voltage is 30 kV and the polar distance is 15 cm.

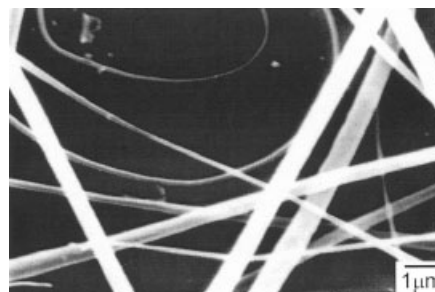


Figure 3 SEM micrograph of electrospun fibers.

SEM observations, as shown in Figures 2 and 3, indicate that there are many pores on the surface of the fiber and the thinnest fiber was about 200 nm, respectively. The cross-section shape of the fiber is round or ellipse (Fig. 4) and there are also many cavities. As indicated by the morphology of the fibers, the structure of the fibers is not compact. It is believed that these pores or cavities inside the fiber or on the surface of the fiber are formed by evaporation of the solvent during the electrospinning.¹³

From the X-ray diffraction data, it can be concluded that the crystallinity of the fiber varies with the voltage of the electrostatic field in the spinning. Figure 5 shows the variation of the crystallinity of the fibers with the voltage of the electrostatic field. The crystallinity of the fibers is initially increased with increasing voltage of the electrostatic field, reaching a maximum when the voltage of the electrostatic field is 50 kV. However, the crystallinity then decreases with further increases in the voltage from 50 kV. The crystallinity of the fibers is mainly influenced by both the degree of ordering induced by the effect of the electrostatic field and the time of crystallization during the flight of the jet. Increases in the potential of the electrostatic field will result in a greater effect of the electrostatic field on the polymer molecules. The polymer molecules will be more ordered when the effect of the electrostatic field is greater and thus the crystallinity of the fibers will be higher; thus the crystallinity of the fiber is increased with the increasing field stress. The time of the jet

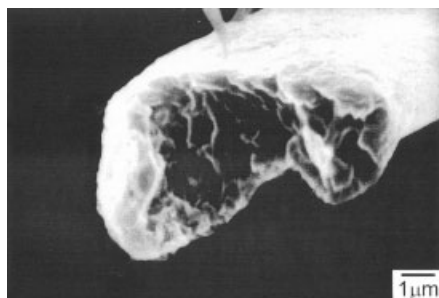


Figure 4 SEM micrograph of an electrospun fiber.

flight from the anode to the collector, however, is shortened with increases in the voltage of the electrostatic field, which means that the time of crystallization of (E-CE)C is shortened, and the crystallinity of the fibers is thus decreased. The degree of ordering of the (E-CE)C molecules is thus increased with increases in the voltage of the field and there is sufficient time to crystallization in the spinning when the voltage of the electrostatic field is lower than 50 kV, although the time is too short for the fiber to crystallize when the voltage of the field is greater than 50 kV; the crystallinity of the fiber is decreased with further increases in the voltage of the field.

Table I presents the relationship between the diameter distribution of the fiber and the voltage of the electrostatic field. It may be observed that the average diameter of the fiber is decreased and the distribution of the diameters becomes narrower with decreasing voltage of the electrostatic field. The decrease of the voltage of the field results in the decrease of the effect of the electrostatic field on the charged solution jet and the flight speed of the jet becomes slower, so the time the jet takes to travel from the anode to the collector becomes longer. Therefore, opportunities increase for the charged jet to split and elongate, and thus the thin fibers with narrow diameter distribution can be easily formed. However, the voltage of the electrostatic field

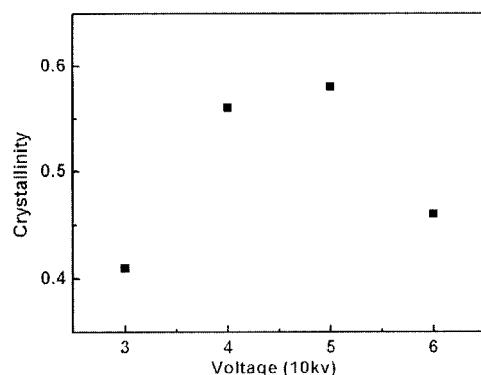


Figure 5 Relationship between applied voltage and the crystallinity of fibers.

TABLE I
Diameter Distribution of Fibers Fabricated with Different Applied Voltages

Diameter distribution range of fibers (μm)	Percentage in different voltage of electrostatic field (%)			
	20 kV	30 kV	40 kV	50 kV
0-2	32	11	14	8
2-4	15	15	11	9
4-6	11	18	15	7
6-8	14	22	8	13
8-10	9	15	8	8
10-12	7	8	9	12
12-14	4	2	11	6
14-16	8	5	2	13
16-18	0	4	8	12
18-20	0	0	14	12
Average diameter of fibers (μm)	5.6	6.2	9.2	10.7

must be greater than the critical value at which the solution can be erupted. As a result the fibers with small diameter and narrow diameter distribution can be easily formed when the voltage of the electrostatic field is close to the critical value in the electrospinning.

From Table II, it may be observed that the average diameter of fibers is decreased and the diameter distribution of the fiber becomes narrower with increasing polar distance. Increase of the polar distance may result in a depreciation of the effect of the electrostatic field on the charged solution jet. The flight speed of the jet decreases with increasing polar distance and the time of the jet flight from the anode to the collector is longer. Therefore, an increase of the polar distance results in greater opportunities for the charged solution jet to split and elongate. This means that the thin fibers with narrower diameter distribution are more easily formed with greater polar distance. However, when the polar distance is too long (>25 cm), the

TABLE II
Diameter Distribution of Fibers Fabricated with Different Polar Distances

Diameter distribution range of fibers (μm)	Percentage in different polar distance (%)			
	5 cm	10 cm	15 cm	20 cm
0-2	52	35	50	66
2-4	17	20	13	26
4-6	3	17	13	3
6-8	6	12	10	5
8-10	1	7	11	0
10-12	1	6	0	0
12-14	0	1	0	0
14-16	11	0	1	0
16-18	3	2	1	0
18-20	6	0	1	0
Average diameter of fibers (μm)	5.1	4.4	3.8	1.9

TABLE III
Diameter Distribution of Fibers Fabricated with Different Spinning Temperatures

Diameter distribution range of fibers (μm)	Percentage in different temperature (%)				
	18°C	22°C	26°C	30°C	34°C
0–2	15	22	26	11	18
2–4	37	55	27	40	25
4–6	19	12	14	14	18
6–8	20	6	13	13	12
8–10	9	5	20	6	10
10–12	0	0	0	16	17
Average diameter of fibers (μm)	4.5	3.5	4.5	5.4	5.6

fibers cannot be collected on the collector even if the voltage of the field is very high. Thus an optimum polar distance of 20 cm in electrospinning should be used to prepare thin fibers with narrow diameter distribution for the (E-CE)C/THF systems.

Table III gives the diameter distribution of the fibers prepared at different spinning temperatures. It is shown that the percentage of the fiber with a diameter smaller than 4 μm is 77% when the spinning temperature is 22°C, which is higher than that of the fiber prepared at temperatures both higher and lower than 22°C. It may also be observed from Table III that the diameter distribution is also narrowest when the spinning temperature is 22°C. When the spinning temperature is low, the speed of the solvent evaporation is also low and the solvent cannot be completely volatilized when the charged solution jets travel to the collector; moreover, the solution jets on the collector may be agglutinated, which will result in increases of the fiber diameter and a wider diameter distribution. When the temperature is higher, the speed of the solvent volatilization is fast and the charged solution jets have less time to split and elongate during the flight of the jets because of the fast evaporation of the surface solvents. Finally, the diameter of the fibers is also larger and the diameter distribution is higher. It is suggested, therefore, that when the spinning temperature is optimal—here in our case, 22°C—the solution jets are solidified by the solvent volatilization when they have arrived at the collector and the jets have enough time to split during their flight to the collector.

Table IV shows the variation of the diameter distribution of fibers at different concentrations of (E-CE)C. It may be observed that with increasing concentration, the average diameter of the fibers is increased and the diameter distribution becomes wider. The number of macromolecular chains in the (E-CE)C/THF solution is increased with increasing (E-CE)C concentration and the entanglement of macromolecular chains is increased, which may result in greater difficulty for the charged solution jet to split during the electrospin-

TABLE IV
Diameter Distribution of Fibers Fabricated with Different Concentrations of (E-CE)C

Diameter distribution range of fibers (μm)	Percentage in different concentration (%)			
	16 wt %	17 wt %	18 wt %	19 wt %
0–2	55	57	46	43
2–4	28	29	24	26
4–6	8	11	17	13
6–8	9	3	6	14
8–10	0	0	7	4
Average diameter of fibers (μm)	2.2	2.0	2.9	3.2

ning. Moreover, the surface tension of the (E-CE)C/THF solution is increased with increasing the concentration (Fig. 6). The increase of the surface tension can also prevent the charged solution jet from splitting because the repulsion among the charges in the jet have to be greater than the surface tension when the jet is split. Therefore, the average diameter of the fibers significantly increases and the diameter distribution becomes wider with increasing the concentration of the (E-CE)C/THF solution.

Table V indicates the relationship between the diameter distribution of the fibers and the diameter of the pipette orifice. The surface tension of the droplet is increased with decreases in the radius of the droplet.¹⁴ It is thus suggested that the surface tension of the droplet is increased with decreasing the diameter of the orifice. When the strength of the electrostatic field is constant, the initial acceleration is decreased with increasing the surface tension and the average velocity is also decreased. The time of jet flight from the anode to the collector is increased. Opportunities are increased for the charged solution jet to split and elongate. Thus fibers with small diameter and narrow distribution can be obtained by using a narrow orifice. However, the suspended droplet cannot be formed

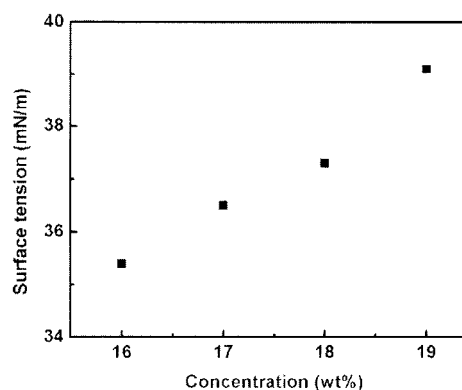


Figure 6 Variation between surface tension of the solution and the concentration of (E-CE)C.

TABLE V
Diameter Distribution of Fibers Fabricated with
Different Orifice Diameters

Diameter distribution range of fibers (μm)	Percentage in different diameter of orifice (%)		
	0.7 mm	0.9 mm	1.2 mm
0–1	62	46	19
1–2	25	48	34
2–3	9	6	8
3–4	3	0	15
4–5	1	0	13
5–6	0	0	5
6–7	0	0	6
Average diameter of fibers (μm)	1.0	1.1	2.6

when the diameter of the orifice is less than 0.5 mm because the surface tension of the solution is too large.

CONCLUSIONS

(E-CE)C fibers were prepared from (E-CE)C/THF solutions by electrospinning at the proper concentrations. There are many pores and cavities inside and on the surface of the electrospun fibers. The crystallinity of the fibers was initially increased with increases in the voltage of the electrostatic field but then decreased with further increases in voltage.

The average diameter of the fibers was increased and the diameter dispersion was broadened with increases in electrostatic field voltage, the polar distance, the solution concentration, and the diameter of the orifice of the pipette. The diameter and its distribution were also influenced by the spinning temperature.

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