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Ultrafine Cellulose Triacetate Mats Electrospun by Using Co-solvent of DMSO/Chloroform System

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ABSTRACT: Cellulose triacetate (CTA) nanofiber nonwoven mats were continuously electrospun by using mixed solvent of DMSO/chloroform system. The size and morphology of CTA nanofibers were investigated. It was found that CTA fibers with diameters in the range of 98 nm–1.81 μm were obtained from 8 wt % CTA solutions in 1 : 1, 3 : 2, 2 : 1, 3 : 1, 5 : 1 and 7 : 1 (v/v) DMSO/chloroform. The average diameter of CTA nanofiber was decreased and size distribution was narrowed with increasing the DMSO content in the mixed solvent. Smooth and uniform nanofibers with mean diameters of about 260 nm could be obtained from a solution of CTA in the binary system DMSO/chloroform 5 : 1(v/v) at a polymer concentration of 8 wt %. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40373.

KEYWORDS: electrospinning; cellulose triacetate; DMSO/chloroform; fiber diameter; nanofibers

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INTRODUCTION

Nowadays, electrospinning technique is an attractive process capable of fabricating polymeric fibers having diameters ranging over several orders of magnitude, from micrometer range to the nanometer range.[1–3] This technology is perhaps the simplest and most straightforward way to produce polymeric fibers by forcing a polymer melt or a solution through a spinnerette and subsequently drawing the resulting filaments as they solidify or coagulate. Due to the exceptionally high surface area to mass ratio of the fibers obtained and high density of pores on the submicron-meter length scale of the electro-spun products are in areas where these properties are fully utilized, such as reinforced composite system,[4] filtration,[5] chemical, and biological protection sensors,[6] solar cells, and fuel cells,[7] tissue engineering and tissue repair,[8] and drug delivery.[9]

In the electrospinning process, a polymer solution is held by its surface tension at the end of a capillary. When a sufficiently large electric field is applied, the solution at the tip of the capillary elongates to form a cone because of coupled effects of the electrostatic repulsion within the charged droplet and attraction to a grounded electrode of opposite polarity. As the intensity of the electric field is increased, the charge overcomes the surface tension, the fiber deposits randomly to form a fused fiber mat. During electrospinning of polymer solutions, the microstructure and morphology of electrospun polymeric nanofibers are dependent on three classes of electrospinning parameters which involve solution properties (conductivity, viscosity, surface tension, and solvent volatility), machine parameters (field strength, distance between tip, and collector, flow rate), ambient conditions (temperature, humidity).[10] Among these parameters, the solution property is one of the most influential parameters on the structure of resulting fibers. Therefore, selection of an appropriate solvent system for dissolution of polymer is the first and foremost setup in electrospinning process.[11,12]

Cellulose, the most abundant biopolymer resource on the planet and also a renewable resource, can be chemically modified to produce cellulose esters or ethers because of its particularly molecular structure.[13] Among these cellulose derivatives, cellulose triacetate (CTA) is an important cellulose ester in industry because of its desirable physical properties, which can be easily processed into films, membranes, and fibers from either melts or solutions.[14] In recent years, a wide variety of solvents can be mixed into a binary or ternary system, which is used to prepare a cellulose diacetate solution that results in electrospun fibers with diameters ranging from nano-meter to micrometer. Such solvent systems are acetone/dimethylacetamide (DMAc),[15] acetic acid/acetone,[16] acetic acid/water,[17] acetone/water,[18] chloroform/methanol,[19] EtOH/dimethylsulfoxide (DMSO),[12] dichloroform/

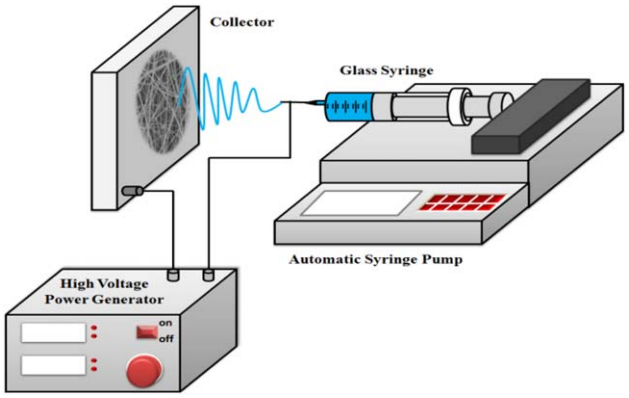

Figure 1. Schematic diagram of electrospinning apparatus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

methanol,[19] acetone/dimethylformamide (DMF)/trifluoroethanol.[20] Compare with cellulose diacetate, CTA has higher content of acetyl groups (exceed 2.8–2.9) that limited the solubility in common organic solvent, e.g., CTA can be swelled in solution in acetone only. So far little research effort has focused on developing various kinds of co-solvent systems for electrospinning of CTA nanofibers. HAN et al. prepared ultrafine porous CTA fibers by electrospinning with methylene chloride (MC) and a mixed solvent of MC/ethanol.[21] Yoon et al. fabricated a superhydrophobicity of cellulose triacetate fibrous mats, which had a fiber diameter ranging from 0.23 to 3.41 μm. They also suggested that fiber diameter was more important in imparting hydrophobicity to the CTA mats than the surface structure.[22]

With the objective of exploring a new co-solvent system for prepare ultrafine and uniform CTA nanofiber mats, this work therefore focused on relevant research which summarized that the important factors determining the electrospinnability of the solutions were high enough values of conductivity both of the solvent and of the resulting solutions, high enough vapor pressure of the solvent, and not very high values of both the surface tension and the viscosity of the resulting solutions.[23] Hence, a new mixed solvent of dimethylsulfoxide (DMSO)/chloroform was developed for the continuous electrospun CTA nanofibers. It was found that the mean diameter and diameter distribution of the resulting CTA nanofibers could be easily controlled by varying the composition of this mixed solvent.

EXPERIMENTAL

Materials

Cellulose triacetate (CTA) (DS = 2.96, Mw = 350,000) was purchased from ACROC ORGANICS. Dimethylsulfoxide

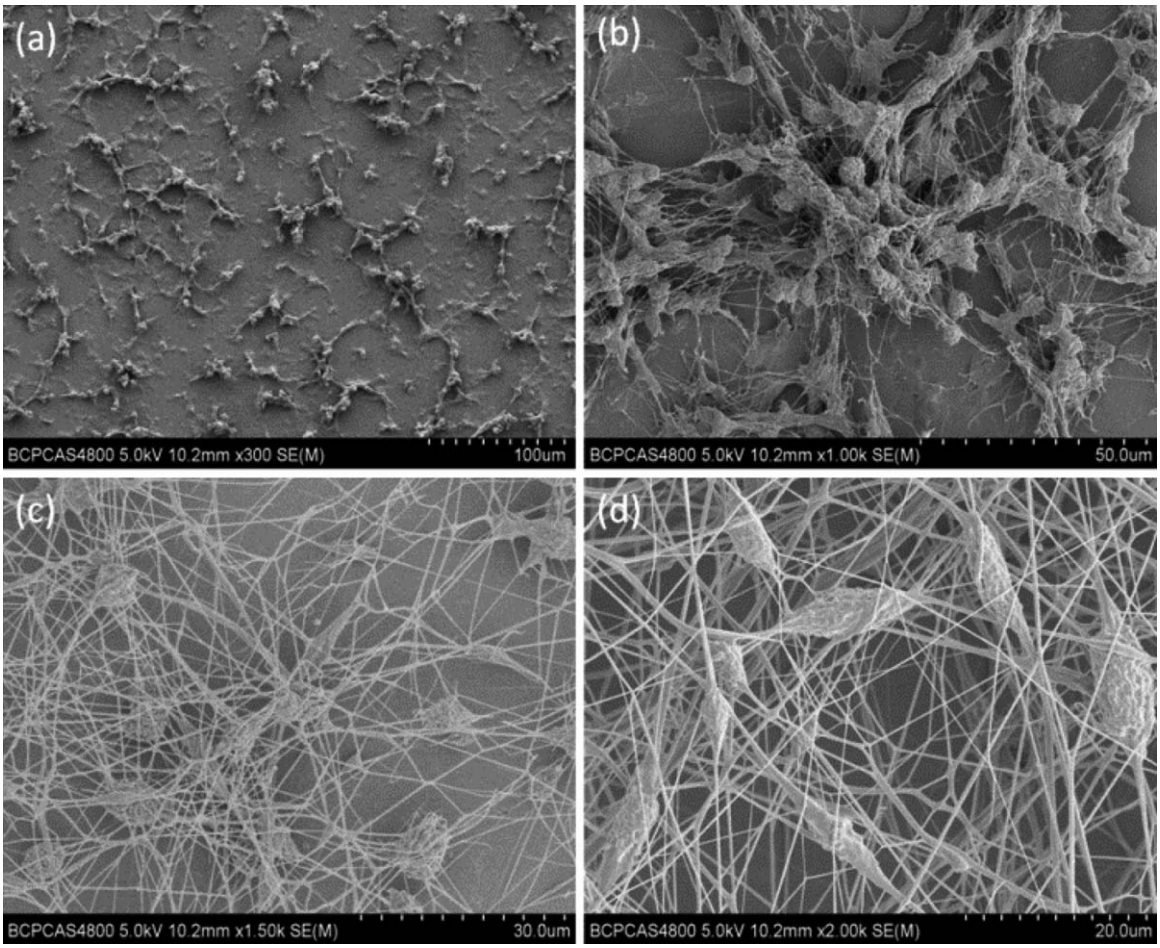

Figure 2. SEM micrographs of CTA discrete beads and beaded fibers obtained from DMSO (a: 4 wt %, b: 6 wt %, c: 8 wt %, d: 10 wt %).

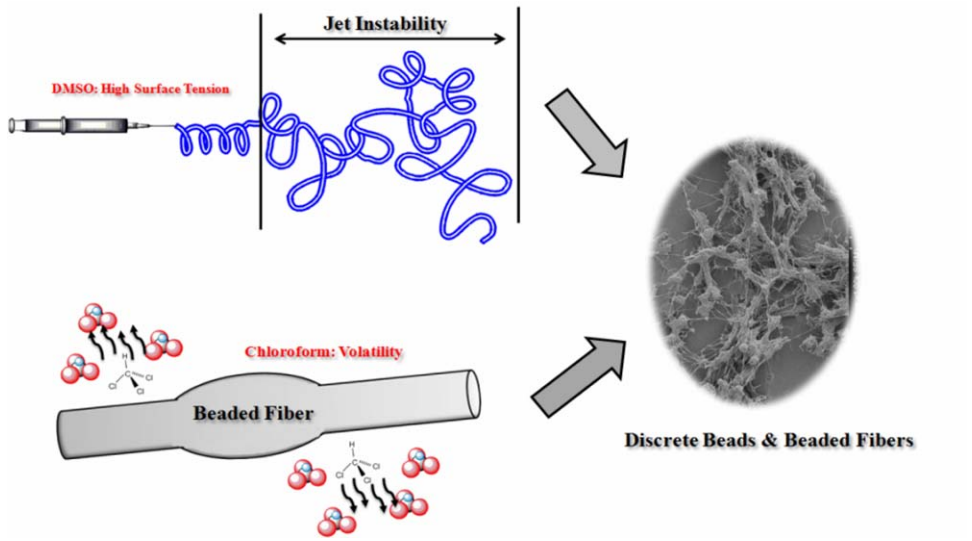

Figure 3. Schematic representation of the possible mechanism of the formation of CTA discrete beads and beaded fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(DMSO) was supplied from Tianjin chemical reagent factory. Chloroform was provided from Beijing chemical works. These chemicals were used as received.

Preparation and Characterization of CTA Solution

The concentration of 4, 6, 8, 10 wt % CTA solutions were dissolved in DMSO or a mixed solvent of DMSO/chloroform with different volume ratio (1 : 1, 3 : 2, 2 : 1, 3 : 1, 5 : 1, 7 : 1), respectively. The viscosity, conductivity, and surface tension of all the solutions were measured by the use of a Brookfield DV-I programmable rheometer, DDSJ-318 conductivity meter, and a CSC Scientific tensiometer, respectively. All these measurements of solution property were carried out at 28°C.

Electrospinning of CTA Solution

The experimental setup used for electrospinning process of this study is schematically shown in Figure 1. This apparatus consists of a static square collector, a high-voltage generator (BGG + 6-373), and a syringe pump (TS2-60 Longer Pump). The CTA solution was flowing through a stainless needle of 0.84 mm inner diameter. The electrospinning parameters as follows: voltage potential, 18–20 kV; tip-to-collector distance, 15 cm; flow rate of the solution through the syringe, 1 mL/h. All electrospinnings were carried out at room temperature.

Morphological Observation

The morphology of CTA nanofibrous mat was examined using a FE-scanning electron microscopy (HITACHI S4800) after gold coating. Diameters of the as-spun smooth or beaded fibers were measured manually from selected SEM images using Image pro-plus analysis software, with an average value for each sample being calculated from at least 200 measurements. For beaded fibers, only the sections of the fibers between beads were measured.

RESULTS AND DISCUSSION

Electrospinning of CTA from DMSO or Chloroform

Solvent choice and polymer concentration are important parameters that influence the formation of electrospun fibers. As a dissolving agent for cellulose triacetate, dimethylsulfoxide (DMSO) can be used to decrease the surface tension, viscosity, and entanglement density of the network and increase the conductivity of the spinning dope, thus contributing to a continuous jet.[24] On the other hand, chloroform is chosen over other possible organic solvents because of its higher dielectric constant and high volatility.

In order to investigate the electro-spinnability and formation of CTA nanofibers in single-solvent system, DMSO, and chloroform were selected as solvents for dissolving CTA powder. DMSO and chloroform dissolved CTA forming a transparent solution, respectively. However, discrete beads were obtained on the screen collector when CTA solutions in these solvents were electrospun. Figure 2 displays that electrospinning of the 4, 6, 8, and 10 wt % CTA solutions in DMSO resulted in the formation of beads and beads that were connected by extremely fine fibrous strings. When the concentration of CTA solution was increased to 6 wt %, beaded fibers were obtained. The number of beaded fibers was decreased when the concentration of solution increased to 8 wt %. A further increasing in the CTA concentration up to 10 wt % resulted in a slight decrease in the number of beaded fibers. However, at the solution concentrations of 8 and 10 wt % the average diameter of beaded fibers obtained were approximately 2.78 and 4.07 μm, respectively. In the same way as for DMSO, electrospinning of CTA solution in chloroform produced discrete beads only (results not shown).

This phenomenon is caused probably by a couple of reasons: first, the electrospun beaded fibers is related to high surface tension, which could cause the occurrence of jet instability in electrospinning. Several researches stated that the formation of these beaded fibers is due to the capillary breakup of the spinning jet by surface tension.[25,26] DMSO, which posses a higher value of surface tension than other common solvents for spinning dope, is easy to cause disturbances and unstable jet. Chloroform, which is more volatile than DMSO, evaporates too fast

Table I. Conductivity, Shear Viscosity, and Surface Tension of CTA Solutions in DMSO, DMSO/Chloroform Co-solvent System, and Its Electrospinnability

Sample	CTA concentration (wt %)	Ratio of DMSO/chloroform (v/v)	Conductivity (μs/cm)	Shear viscosity (Pa s)	Surface tension (dyn/cm2)	Spinnability	Average diameters of CTA fiber (μm)
CTA solution in DMSO	4	/	48.2	0.46	47.8	+	–
	6	/	49.7	1.98	52.6	+	–
	8	/	48.8	7.47	52.8	++	–
	10	/	47.6	11.72	55.7	++	–
CTA solution in DMSO/chloroform	4	1 : 1	29.5	0.61	42.8	+++	0.41 ± 0.11
	6	1 : 1	28.8	2.94	44.1	+++	0.56 ± 0.16
	8	1 : 1	26.8	11.28	47.6	+++	1.11 ± 0.25
	10	1 : 1	26.7	35.78	51.8	+++	1.30 ± 0.33
8 wt % CTA solution in DMSO/chloroform	/	3 : 2	30.5	11.48	48.5	+++	0.77 ± 0.19
	/	2 : 1	33.2	10.97	49.6	+++	0.68 ± 0.19
	/	3 : 1	34.9	10.50	49.8	+++	0.44 ± 0.14
	/	5 : 1	42.7	10.30	52.8	+++	0.26 ± 0.07
	/	7 : 1	42	9.93	52.7	++	0.19 ± 0.09

+++: stable jet and continuous process; ++: some disturbances; +: spraying; –: results could not obtained.

so that the charged droplets cannot elongate completely to form fibers in electrospinning. A tentative schematic representation of the process is given in Figure 3, but further investigation is necessary for more details of its mechanism.

Electrospinning of CTA from DMSO–Chloroform Co-solvent System

Because electrospinning of 4, 6, 8, and 10 wt % CTA solutions in the individual solvents DMSO and chloroform produced discrete beads and beaded fibers, both of the solvents were mixed and the mixture was used to dissolve CTA powder, at a fixed volume ratio of 1 : 1 (v/v), to prepare the spinning solutions. After complete dissolution of the CTA powder, the resulting solutions were measured for their shear viscosity, conductivity, and surface tension, as summarized in Table I. Evidently, the addition of chloroform caused the surface tension of the CTA solutions to decrease obviously, possible because of the lower surface tension of chloroform in comparison with that of DMSO. The observed slight changes in both shear viscosity and conductivity was unexpected. There are probably several reasons: (1) the solubility of CTA in DMSO is different with in chloroform; (2) the dielectric constant of chloroform is lower than DMSO.

The SEM images of 4, 6, 8, and 10 wt % CTA fibers from solvent composition of 1 : 1 DMSO/chloroform were presented in Figure 4. It can be obviously seen from these pictures that the presence of chloroform significantly improved the spinnability of CTA and yielded uniform fibers. However, at 4 wt % CTA mat with a combination of smooth and beaded fibers was obtained. At such low viscosities, the viscoelastic force (a result of the low degree of chain entanglements) was not enough to counter the stretching forces from electrostatic. Overstretching of the charged jet, as a result of these forces, resulted in partial breakup of the jet and, as a result of the surface tension, beads were formed on some of the fibers. When the concentration of these solutions was varied between 6 and 10 wt %, electrospinning of the solutions resulted in the formation of smooth fibers only, a result of the high viscoelastic force that could counter the stretching forces, thus completely preventing partial breakup of the jet. On the basis of the SEM images shown in Figure 4, the diameters of the as-spun fibers increased regularly with increasing solution concentration. Specifically, the mean diameters of the resulting fibers increased from 0.41 μm when the concentration was 4 wt % to 1.3 μm when the concentration was 10 wt %. All these observations at higher concentrations led to fiber having a random orientation. Furthermore, a broad diameter distribution of CTA fibers was obtained when the concentration was 10 wt %. In order to reduce fiber diameter and diameter distribution of ultrafine CTA mats, an optimum solution concentration of 8 wt % was used for further studies.

Optimization of Fiber Diameter and Distribution of Ultrafine CTA Fiber

In order to improve the fiber diameter and size distribution of the ultrafine CTA nanofiber mats, CTA solutions at a fixed concentration of 8 wt % were prepared in 1 : 1, 2 : 3, 2 : 1, 3 : 1, 5 : 1, 7 : 1 (v/v) DMSO/chloroform co-solvent system. Some of the properties, such as conductivity, viscosity, surface tension of the CTA solutions are listed in Table I. It is clearly that the conductivity of the CTA solutions increased as the DMSO content was increased up to 82.5%. In addition, the shear viscosity of CTA solutions was obviously decreased when the volume ratio

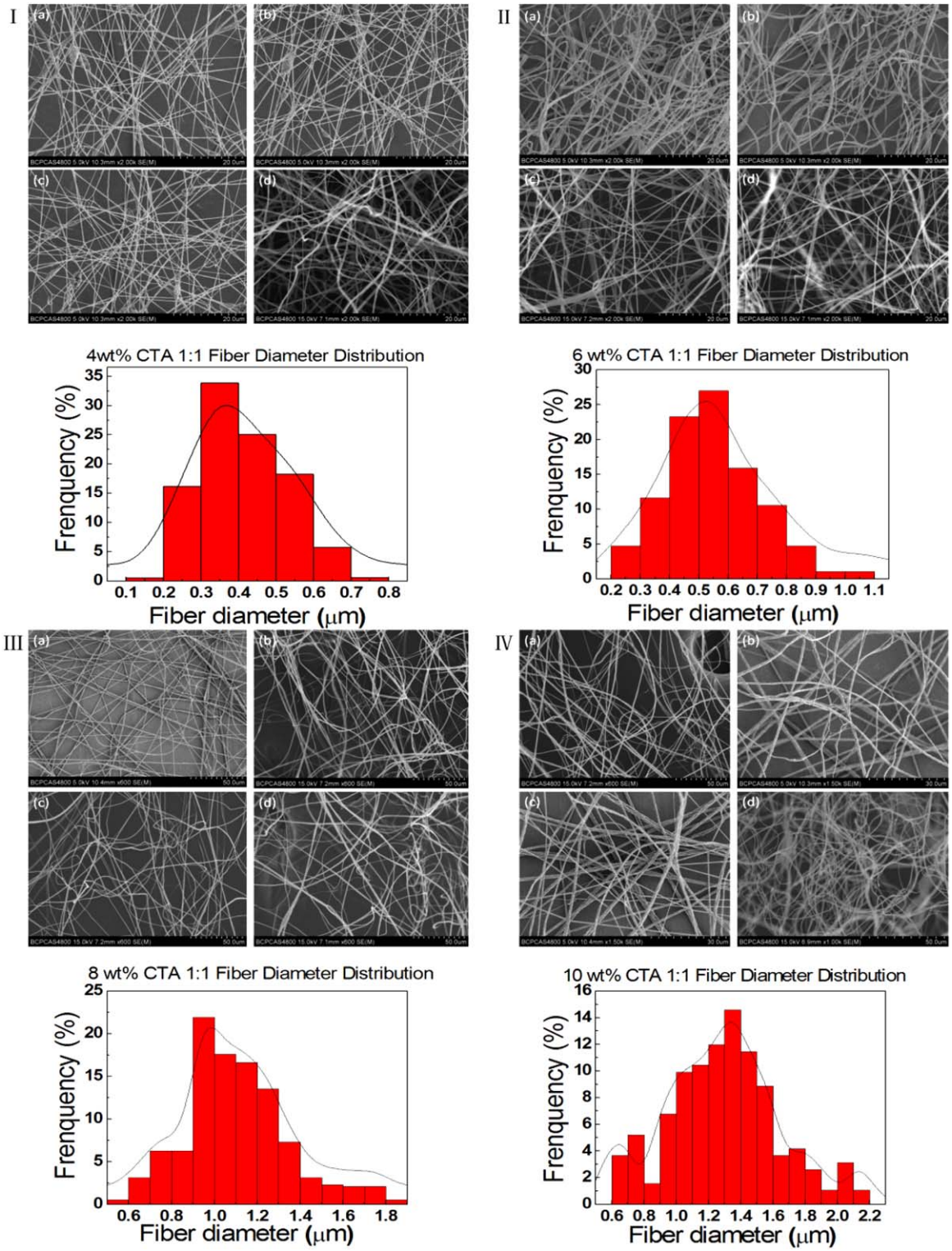

Figure 4. Selected SEM micrographs of as-spun nanofibers from (I) 4, (II) 6, (III) 8, and (IV) 10 wt % CTA solutions in 1 : 1(v/v) DMSO–chloroform. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of DMSO/chloroform increased to 7 : 1. But the surface tension of spinning solutions shows little change. As previous mentioned, this phenomenon is attributed to different properties of DMSO and chloroform.

Selected SEM images of electrospinning of 8 wt % CTA solution in 1 : 1, 3 : 2, 2 : 1, 3 : 1, 5 : 1, 7 : 1 (v/v) DMSO/chloroform co-solvent system were shown in Figure 5. It was found that CTA fibers can be continuously electrospun using different

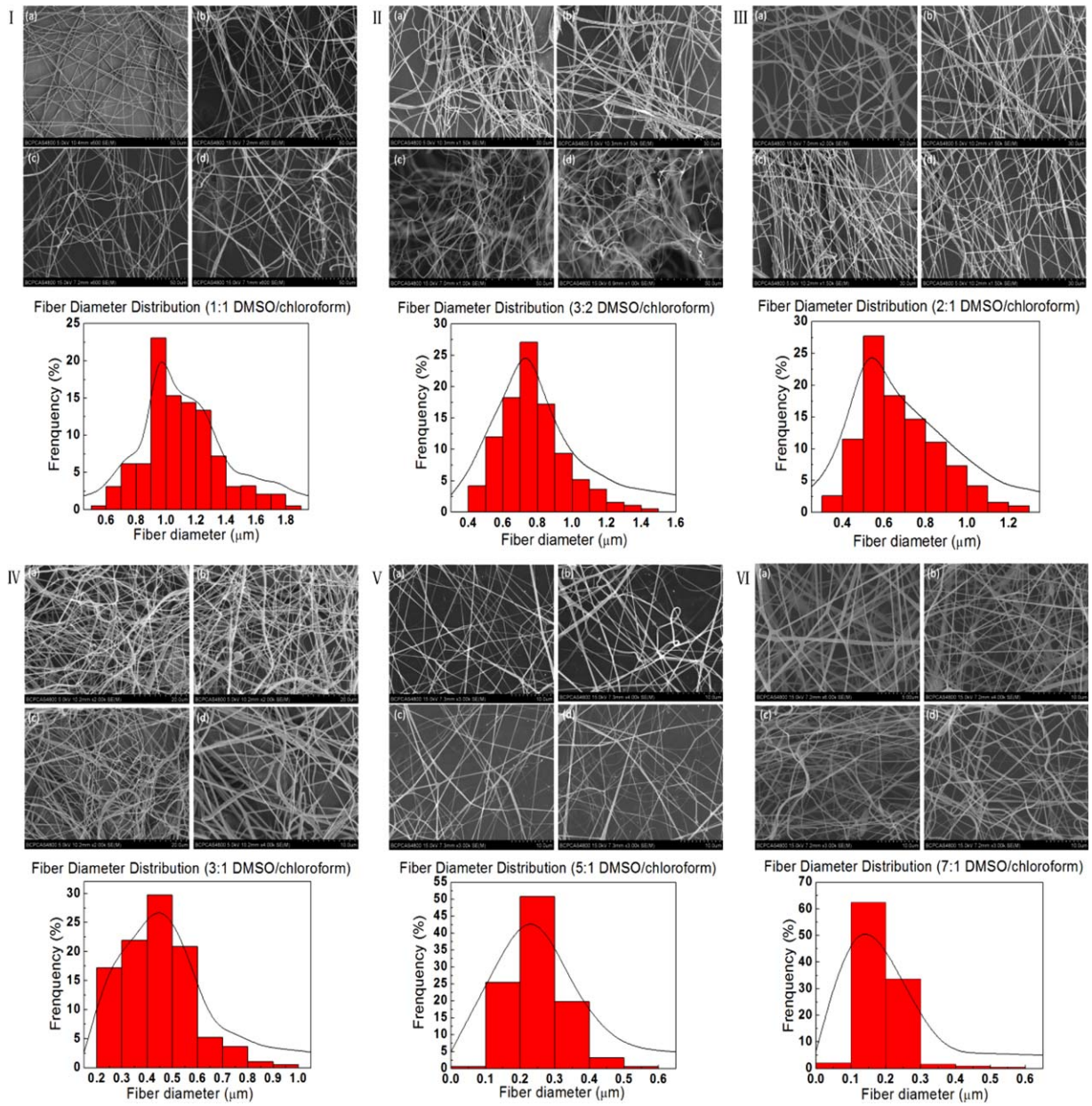

Figure 5. Selected SEM micrographs of as-spun nanofibers from 8 wt % CTA solutions in (I) 1 : 1, (II) 3 : 2, (III) 2 : 1, (IV) 3 : 1, (V) 5 : 1, and (VI) 7 : 1 (v/v) DMSO–chloroform. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

volume ratio of a mixed DMSO/chloroform solvent. The reason is probably that DMSO had been used as co-solvent to lower the viscosity, increase the conductivity, and to lower the surface tension of CTA solution (Table I). Repulsive forces are generated by applying a high voltage into CTA solution. As the electric field exceeds a critical value where electrostatic repulsion force of surface charges overcome surface tension, a charged jet of the solution is ejected from the tip of the Taylor cone. As the charged jet accelerates toward regions of lower potential, the chloroform, which has a comparatively high vapor pressure (195 mmHg at 25°C), rapidly evaporates while the entanglements of the polymer chains prevent the jet from breaking up. This results in the deposition of long and uniform fibers as a nonwoven structure.

The average fiber diameter of electrospun CTA mats was characterized quantitatively by image analysis of scanning electron microscope based on at least $n = 200$ fibers per sample (4 of SEM graphs represent a sample). Figure 5 shows fiber diameter distribution of CTA electrospun in different volume ratio of DMSO/chloroform. It is clearly seen that the fiber diameters in the range 98 nm to 1.81 μm were obtained by varying the volume ratio of DMSO/chloroform. The narrow fiber diameter distribution of CTA was obtained when the volume ratio of DMSO/chloroform reaches 7 : 1, the average diameter of the fibers obtained were in the range 0.13–0.58 μm [Figure 5 (VI)]. Some of disturbances and unstable jet, however, are occurred along with reduction of chloroform content in mixed solvents. So, a volume ratio of 5 : 1 in DMSO/chloroform co-solvent is beneficial for preparing ultrafine CTA nanofiber.

As mentioned, the data of Table I shows that the conductivity of the CTA solutions increased with increasing the content of DMSO and this caused the diameters of as-spun fibers to decrease. While the distribution of fiber diameter become more uniform with increasing DMSO content. It is illustrated that the increase in conductivity causes the jet to travel closer to the aluminum foil and increase Coulombic stretching force. So, the volume ratio of DMSO/chloroform is responsible for the diameter distribution of CTA fiber.

CONCLUSIONS

In this work, the electrospinning of cellulose triacetate in a new co-solvent system of DMSO/chloroform was investigated for the first time. It was found that only a combination of discrete beads and beaded fibers of CTA mats were obtained from DMSO or chloroform, but long uniform and continuous CTA nanofiber mats were electrospun in a mixed-solvent of DMSO/chloroform. Some properties (conductivity, shear viscosity, surface tension) of CTA solution for electrospinning were measured, it was indicated that DMSO had been used as co-solvent to lower the viscosity, increase the conductivity, and to lower the surface tension of CTA solution. Chloroform as a volatile solvent, which can be improve the formation of nanofiber in electrospinning. Electrospinning of 8 wt % CTA solutions in 1 : 1, 3 : 2, 2 : 1, 3 : 1, 5 : 1, 7 : 1 (v/v) DMSO/chloroform co-solvent system produced long and smooth nanofibers with diameters in the range of 98 nm–1.81 μm. The average diameters of the obtained fibers were found to decrease and their distributions were narrowed with increasing the DMSO content in the mixed solvent. When DMSO–chloroform 5 : 1 (v/v) is used as the electrospinning solvent system for 8 wt % CTA solution, smooth filaments without beads and fiber diameters of about 260 nm could be fabricated.

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