Differentsurfactantsareintroducedtostudythediameterandmorphologytransformationcharacteristicsofelectrospunnanofiber.


1. Introduction

Ultrafinepolymericnanofibers havewideapplication in the fields ofmicro/nanosystem and flexibleelectronics. At present, quick and low costfabrication are the main aspects for the development and industrial application of ultrafine polymeric nanofibers, whichhaveattractedalot of attentionsinrecentyears[1, 2]. As a unique and simple nano/micromanufacturingtechnology, electrospinning does not requir stencil-plate, photo etching, or ultra clean chamber. Nanofiberdiameter ranges from severananometers to severalmicrometers[3]can beelectrospun at normal pressure and temperature. Electrospinningalsohavesgood materials compatibilitythat meetsthe development demands ofpolymeric, flexible, and bio-nano/microsystem. By now, hundreds of materials havebeen electrospun into nanofibers throughelectrospinning[4, 5], suchas polymer, glass, metal, and protein. Electrospun nanofiber has extremely highsurface area and outstandingmechanical andphysical properties,whichare suitableforawide range application fields, suchasadrug delivery[6, 7], sensing materials[8, 9], catalyze template[10], and ion battery membrane[11, 12]. Decreasingthediameter and promotingtheuniformityofelectrospun nanofiberson thekey roles for theirindustrial application.

During the electrospinningprocess, the highvoltageis appliedto stretchviscoelastic solution into the cone shape namedas“Taylor Cone.” Whenthe electricalfield forcetheccovers the surfacetension,a jet is ejectedfrom the cone tip. Thedrathrepulsion force that stemstheaccumulatedcharges imports disturbancesinto theejectionand motionprocess ofpolymer jet. The instability motionis theimportant facorto stretchand thinthe chargedjet[13]. Attributedto thebendingand whippinginstability, electrospinning nanofiber depositedrandomly on collectoras nonwoven.

Themorphology of electrospun nanofibers is an important factor to investigatethetherochemistrybehaviors ofcharged jet in theejection process. Withtheinadequatestretchingof liquidjet, thereares usual beadedstructures appearingalong
the electrospun nanofiber. The beaded structures stem from the competition surface tension of liquid jet [14], in which the solution viscosity, surface tension, and net charges are the main influencing factors [15]. Repulsion force among electrospinning jets increases with the increase of charge density and provided an effective way to increase the uniformity and decrease the diameter of electrospun nanofiber. The surfactants have been introduced to decrease the surface tension and increase the net charge density. As such, Lin et al. [16] used cationic surfactants to increase the jet charge density; then instability motion can be enhanced and the beaded nanofibers were also overcome; Jia and Qin [17] used surfactants to change the surface tension of electrospinning solution; then the thermal performance and inner structure of nanofibers can be adjusted. The influences of surfactants on the diameter and morphology should be studied further to promote its application.

In this work, different surfactants were introduced to decrease the nanofiber diameter and prevent the formation of beaded structures in electrospun nanofiber. The surfactants would increase the net charge density and enlarge the repulsion force among charged jets. Then, the instability motion was also enhanced by the charge repulsion force. The transformation characteristics of nanofiber diameter and morphology were studied.

2. Experiments Details

2.1. Experiment Setup. The electrospinning setup based on conventional pole-type nozzle configuration was built up in this work. The high voltage source (DW-P403-1AC, Tianjing Dongwen High Voltage Power Supply Plant, China) was used to provide electrical field between steel nozzle spinneret (inner diameter was 323 μm and outer diameter was 500 μm, Shanghai Kindly Enterprise Development Group, China) and aluminum paper collector (thickness 0.04 mm, Zhongshan Sinon Daily Products Co., Ltd., China). The anode of the high voltage source was connected to the steel nozzle spinneret, and the cathode was connected to the grounded collector. The precision syringe pump (Harvard II Pico Plus, USA) was used to transfer polymer solution from syringe to spinneret.

2.2. Electrospinning Solution. Polyvinylidene fluoride (PVDF, average molecular weight = 141,000 g/mol, DuPont, USA) solution was used as electrospinning solution. PVDF powder was added to the mixed blends of acetone (Sinopharm Chemical Reagent Co. Ltd., China) and N, N-dimethylformamide (DMF, Sinopharm Chemical Reagent Co. Ltd., China). The weight ratio of acetone to DMF in the blending solvent was 2:3. The PVDF concentration in the solution was 12 wt%.

Anionic surfactant sodium dodecyl sulfate (SDS), non-ionic surfactants Triton X-100, and cationic surfactants hexadecyl trimethyl ammonium bromide (HTAB) were added to the PVDF solution to investigate the effect of surfactants on the diameter and morphology of electrospun nanofiber, respectively. All of these three surfactants were purchased from Sinopharm Chemical Reagent Co., Ltd. China, which were used without any further purification. The surfactant concentrations in the PVDF solution were 3.5 × 10⁻³ mol/L, 1.75 × 10⁻² mol/L, and 3.5 × 10⁻² mol/L, respectively.

2.3. Electrospinning Process. In the experiment, the PVDF solution was transferred to the nozzle spinneret by the precision syringe pump at a flow rate of 200 μL/hr. High voltage of 13 kV was applied at the nozzle spinneret, and the distance between spinneret to collector was 15 cm. The electrospun nanofibers were observed and measured by a SEM (LEO 1530 field emission scanning electron microscope). Before the observation of SEM, the samples were sputter-coated with a gold layer of about 10 nm thickness.

3. Results and Discussion

3.1. Solution Characteristics. Firstly, the characteristics of polymer solution with surfactants were tested. The viscosity of PVDF solution was 153 mPa-s, which was the same as the polymer solution without surfactant. Surfactants can increase the free charges in polymer solution and conductivity of solution. The conductivity of polymer solution increased from 138 μs/cm to 860 μs/cm, as SDS surfactant concentration increased from 3.5 × 10⁻³ mol/L to 3.5 × 10⁻² mol/L. And the conductivity of polymer solution increased from 167 μs/cm to 1104 μs/cm, as HTAB surfactant concentration increased from 3.5 × 10⁻³ mol/L to 3.5 × 10⁻² mol/L. The relationship between conductivity of polymer solution and surfactant concentration was shown in Figure 1. But the Triton X-100 did not change the conductivity, since the Triton X-100 was nonionic surfactant and did not increase the free charges in polymer solution. Figure 1 showed that the conductivity did not increase with the surfactant concentration. The conductivity of PVDF solution with Triton X-100 was 9 μs/cm, which was the same as the polymer solution without surfactant.

3.2. Beaded Nanofiber without Surfactants. Then, PVDF solution without surfactants was used as electrospinning solution. Due to the fast evaporation of solvent, the charged jets cannot be stretched adequately into fine and uniform ones. Liquid jet would be shrank into beaded structure by the surface tension, as shown in Figure 2. The beaded nanofibers with a diameter range from 30 nm to 170 nm, and the average diameter was 67.02 nm. The standard deviation of electrospinning nanofiber was 31.62 nm. Attributed to the large surface tension and small stretching ratio, the electrospinning nanofiber had large diameter distribution. The beaded structure on the electrospinning nanofibrous web also had large diameter distribution, which ranged from 422 nm to 6.28 μm. And the average diameter of beaded structure was 2.06 μm. The diameter distribution range of nanofiber electrospun from PVDF solution without surfactant was shown in Figure 3. Decreasing the surface tension and solution viscosity provided a good way to overcome the beaded structure. On the other hand, increasing the net charge density and electrical field forced applied on the charged jet would also promote the stretching and uniformity of charged jet.
The diameter and morphology of electrospun nanofiber was observed and measured by SEM. The average diameter was calculated from more than 50 data points in 10 samples.

3.3. Uniform Nanofiber with Surfactants. And then, the effects of surfactant on the diameter and morphology were investigated by adding the surfactants to the polymer solution. The nanofibers electrospun form PVDF solution with surfactants of SDS, Triton X-100, and HTAB were shown in Figures 4–6, respectively. With the increase of surfactant concentration, both the conductivity of polymer solution and the net charge density of electrospinning jet can be increased [18]. The electrical field force applied on the charged jet increased with the increase of net charge density, which also enhanced the instability whipping and spiral motion of charged jets. The instability motion of charged jet was an important role to promote the stretching process of electrospinning jet, decrease the diameter of liquid jet, and prevent the formation of beaded structures in the nanofibers [19]. Therefore, higher surfactant concentration in polymer solution leaded to less beaded structures and more uniform nanofiber. Figures 4–6 showed that the surfactants played a good factor to prevent the formation of beaded structure and increase the uniformity of electrospun nanofiber.

Then, the effects of surfactant concentration on the nanofiber diameter and distribution were studied. The relationships between nanofiber diameter and surfactant concentration in solution were shown in Figure 7. With the help of surfactant, the average nanofiber diameter was less than 65 nm. As surfactant concentration in polymer solution

Figure 1: The relationship between solution conductivity and surfactant concentration in the solution.

Figure 2: Beaded PVDF nanofiber electrospun from PVDF solution without surfactants. (a) Electrospun beaded PVDF nanofiber. (b) Close view of beaded nanofiber with magnification of 22,000x.
The diameter distribution range of nanofiber gained from PVDF solution without surfactant.

Figure 4: Electrospun nanofiber gained from PVDF solution with anionic surfactants of SDS. The concentration of SDS in the solution is (a) $3.5 \times 10^{-3}$ mol/L, (b) $1.75 \times 10^{-2}$ mol/L, and (c) $3.5 \times 10^{-2}$ mol/L.

Figure 5: Electrospun nanofiber gained from PVDF solution with nonionic surfactants of Triton X-100. The concentration of Triton X-100 in the solution is (a) $3.5 \times 10^{-3}$ mol/L, (b) $1.75 \times 10^{-2}$ mol/L, and (c) $3.5 \times 10^{-2}$ mol/L.

increased from $3.5 \times 10^{-3}$ mol/L to $3.5 \times 10^{-2}$ mol/L, the diameter of PVDF nanofiber with SDS decreased from 51.68 nm to 39.89 nm, the diameter of PVDF nanofiber with Triton X-100 decreased from 63.91 nm to 40.62 nm, and the diameter of PVDF nanofiber with HTAB decreased from 60.19 nm to 41.61 nm. Figures 8–10 showed the diameter distribution range of nanofiber electrospun from PVDF solution with surfactant. The diameter of nanofiber ranged from 30 nm to 70 nm. The surfactant concentration in solution was $3.5 \times 10^{-3}$ mol/L in Figure 8. The surfactant concentration in
Figure 6: Electrospun nanofiber gained from PVDF solution with cationic surfactants of HTAB. The concentration of HTAB in the solution is (a) $3.5 \times 10^{-3}$ mol/L, (b) $1.75 \times 10^{-2}$ mol/L, and (c) $3.5 \times 10^{-2}$ mol/L.

Figure 7: The relationship between nanofiber diameter and surfactant concentration in the solution: (a) SDS, (b) Triton X-100, and (c) HTAB.
solution was $1.75 \times 10^{-2}$ mol/L in Figure 9. The surfactant concentration in solution was $3.5 \times 10^{-2}$ mol/L in Figure 10. Both of nanofiber diameter and diameter distribution range decreased with the increase of surfactant concentration.

Different surfactants had played different roles in the rheology behaviors of charged jet. The nanofibers gained from PVDF solution with anionic surfactant SDS were shown in Figure 4. There were the least beaded structures in Figure 4(b), when surfactant concentration of SDS was $1.75 \times 10^{-2}$ mol/L. When surfactant concentration of solution was $3.5 \times 10^{-2}$ mol/L, nanofibers electrospun from PVDF solution had large beaded structure, as shown in Figure 4(c). Then, the diameter of beaded structure in Figure 4(c) was larger than that in Figures 4(a) and 4(b). The nanofibers gained from PVDF solution with nonionic surfactant of Triton X-100 were shown in Figure 5. Large surfactant concentration led to less beaded structures and smaller diameter. The nanofibers gained from PVDF solution with surfactant of HTAB in Figure 6 had less and smaller beaded structures than that in Figures 4 and 5. The relationship in Figure 7 showed that the nanofiber with the surfactant of SDS had the smallest diameter, attributed to larger charge repulsion force among liquid jets.

In this work, the anode of the high voltage source was connected to the steel nozzle spinneret. When injected from the spinneret, the liquid jet also carried away the positive charge accumulated on the spinneret. The cationic surfactant of HTAB would play a good way to provide excess positive charge to the liquid jet during the injection process. On the other hand, polymer solution with HTAB had the highest
Figure 9: The diameter distribution of nanofiber gained from PVDF solution with surfactants: (a) SDS: average diameter is 40.71 nm and standard deviation is 10.02 nm; (b) Triton X-100: average diameter is 56.51 nm and standard deviation is 22.95 nm; (c) HTAB: average diameter is 45.55 nm and standard deviation is 15.15 nm. The surfactant concentration in solution was $1.75 \times 10^{-2}$ mol/L.

4. Conclusion

Different surfactants were introduced to investigate the rheology behaviors of charged jet electrospun from PVDF solution. With the help of surfactants, net charge density in electrospinning jet was increased to enhance the charge repulsion force and the instability motion of charged jet. Charged jets can be stretched adequately into finer and uniform ones by the larger electrical field force. With the help of surfactants, electrospinning nanofiber with average diameter less than 65 nm can be fabricated, which was finer than nanofiber electrospun from PVDF solution without surfactant. The nanofiber diameter and diameter distribution range decreased with the increase of surfactant concentration in solution. Attributed to the larger net charge density, the cationic surfactant of HTAB would provide a great way to prevent forming beaded structures.

The effects of surfactant on the transform characteristics of nanofiber diameter and morphology were studied, which would provide a good way to promote the industrial application of polymeric nanofibers.
Figure 10: The diameter distribution of nanofiber gained from PVDF solution with surfactants: (a) SDS: average diameter is 39.89 nm and standard deviation is 9.99 nm; (b) Triton X-100: average diameter is 40.62 nm and standard deviation is 10.24 nm; (c) HTAB: average diameter is 41.61 nm and standard deviation is 12.88 nm. The surfactant concentration in solution was $3.5 \times 10^{-2}$ mol/L.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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