Macromolecules
NOTE

Macromolecules **2010**, *43*, 10743–10746 **10743**
DOI: 10.1021/ma1024363

Electrospinning of Concentrated Polymer Solutions

Deng-Guang Yu,*,† Christopher J. Branford-White,‡ Nicholas P. Chatterton,‡ Kenneth White,‡ Li-Min Zhu,*,† Xia-Xia Shen,† and Wei Nie†

†*College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China, and* ‡*Institute for Health Research and Policy, London Metropolitan University, London N7 8DB, U.K.*

Received October 25, 2010; Revised Manuscript Received November 17, 2010

Introduction

Polymer concentration is one of the most important parameters that influence the electrospinnability of polymer solutions and the properties of the resultant fibers.[1,2] The range of polymer concentration in a given solvent that allows successful electrospinning which produces high-quality fibers is usually narrow.[3−5] Fiber formation requires the presence of sufficient chain-entanglement density in the working solution to prevent capillary breakup and Rayleigh instability, and much work has focused on the lower concentration limit of filament-forming polymer in a given solvent needed to prepare uniform nanofibers using a single fluid electrospinning process.[6,7] Little attention has focused on characterizing the upper concentration limit of a given polymer solution that would allow smooth electrospinning, nor on the possibility of smooth electrospinning with polymer solutions normally unspinnable due to high polymer concentrations. This may be because (1) it is not possible to spin concentrated polymer solutions when the viscosity is so high that the solvent will have evaporated before the formation of a stable jet, thereby clogging the flow and preventing continuous electrospinning, and (2) the main trend of electrospun fiber production is toward thinner fibers, while a solution with high polymer concentration always means fibers having relatively big diameters. This is because the presence of more material in the jet and the increase in viscoelastic force due to high polymer concentration would lead to an increase in fiber size.[8,9]

However, the capability of preparing fibers from concentrated polymer solutions may broaden the electrospinning process and its applications. For example, it may (1) extend the range of electrospinnable concentrations of polymer solutions, (2) improve the productivity of the electrospinning process important in any potential commercialization of the procedure, and (3) allow preparation of ultrafine fibers with diameters between several micrometers and 50 μm and thus fill the gap in size between electrospun fiber products (often smaller than several micrometers) and traditional wet/dry/melt spinning fiber products (often $\geqslant$30 μm). Such fibers may find good applications in biomedical fields, such as improving cell penetration effects of fiber-based scaffolds.[10,11] It may also (4) facilitate the coaxial electrospinning processes involving encapsulation of functional ingredients, through eliminating concerns about sheath viscosity, which is regarded as a key factor in traditional coaxial electrospinning process. In conventional coaxial electrospinning, the sheath solution acts as a guide to the core material and must impart enough shearing stress to overcome the interfacial tension between the two solutions via "viscous dragging" and "contact friction",[12,13] and thus high viscosity of the sheath solution (which depends on the polymer concentration for a given solution) would be desirable for a successful process.

*Corresponding author: Tel +86-21-67792751; Fax +86-21-67792655; e-mail lzhu@dhu.edu.cn, ydg017@dhu.edu.cn.

On the other hand, the need for fiber materials with advanced functions and diverse structures has recently led to the development of new and modified electrospinning processes, including specialized nozzle systems, auxiliary apparatus, guiding electrodes, and functionalized target electrodes.[14] Among them, coaxial electrospinning[15−17] was regarded as one of the most useful breakthroughs in this field. Utilizing a concentric spinneret, coaxial electrospinning has been successfully used to produce core−sheath nanofibers, hollow nanofibers, fibers containing microencapsulated compounds, and internal microscopic periodic structures in nanofibers and has enabled template spinning of nonelectrospinnable solid and liquid materials.[8,12,13,18−21] In all these studies, the sheath fluid inevitably has good electrospinnability, and the core solution can have either poor or good electrospinnability.

In this Note, we report a modified coaxial electrospinning process, in which an unspinnable concentrated polymer solution acted as a guide and a pure solvent was used as sheath fluid to facilitate the process and thin the fibers. Polyvinylpyrrolidone and Eudragit L100 are used as model polymers to demonstrate the modified process.

Experimental Section

The detailed protocols about the modified coaxial electrospinning process will be discussed later. Polyvinylpyrrolidone K60 (PVP, $\overline{M}_w$ = 360 000) was purchased from Shanghai Yunhong Pharmaceutical Aids and Technology Co., Ltd., Shanghai, China. Eudragit L100 (E-L100, $\overline{M}_w$ = 135 000), which is a methacrylic acid copolymer and has been widely used for preparing colon-targeted drug delivery systems in pharmaceutics, was supplied by Rohm GmbH&Co. KG (Darmstadt, Germany). Analytic grade anhydrous ethanol and *N*,*N*-dimethylacetamide (DMAc) were obtained from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

A 35% w/v concentrated PVP solution prepared in anhydrous ethanol was used as core fluid at a fixed flow rate of 1.0 mL/h. The sheath fluid, DMAc, was used at flow rates 0.1, 0.2, 0.5, and 1.0 mL/h. A fixed voltage of 10 kV was applied, and the fibers were collected on an aluminum foil plate at a distance of 28 cm. The electrospinning process was recorded using a digital video recorder (maximum magnification of ×16, Canon, Japan).

27% and 30% w/v solutions of E-L100 were prepared in anhydrous ethanol. The 27% w/v solution was electrospun using a single fluid process. The 30% w/v solution was electrospun using the modified coaxial electrospinning process and was used as core fluid at a fixed flow rate of 1.0 mL/h. The sheath solvent flow rate was fixed at 0.5 mL/h. Ethanol, DMAc, and a 70:30 volume ratio mixture were used as sheath fluids. A fixed voltage of 8 kV was applied, and the fibers were collected on the aluminum foil plate at a distance of 25 cm.

The surface morphologies of fibers were assessed using a JSM-5600LV scanning electron microscope (SEM, Japan Electron

Published on Web 11/29/2010

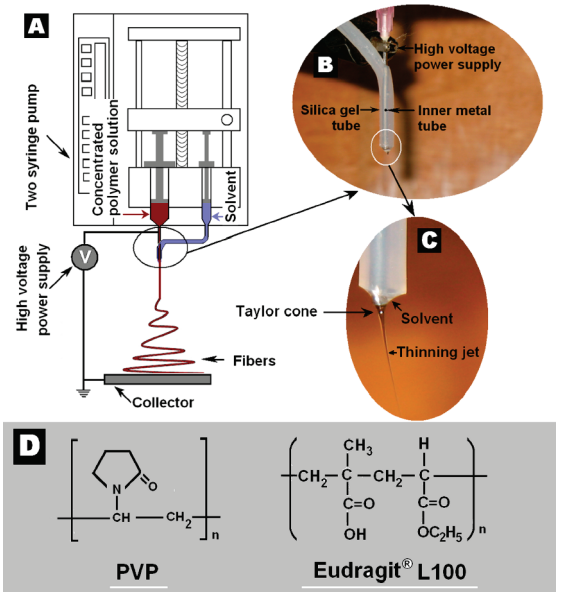

Figure 1. Modified coaxial electrospinning process. (A) Schematic diagram of the electrospinning with surrounding solvent. (B) A stainless steel capillary metal-hub needle (connected with the high-voltage supply) was inserted into silica tubing to form the concentric spinneret. (C) The Taylor cone and the thinning jet formed from 35% (w/v) PVP solution in ethanol as core fluid (1.0 mL/h) and DMAc as sheath solvent (0.1 mL/h) under 10 kV and a collection distance of 28 cm. (D) The structural formulas of PVP and E-L100.

Optics Laboratory Co. Ltd.). Prior to examination, samples were gold sputter-coated under argon to render them electrically conductive, and electron micrographs were then taken at an excitation voltage of 10 kV. The average fiber diameter was determined by measuring diameters of fibers at over 100 points from SEM images using Image J software (National Institutes of Health).

Results and Discussion

Modified Coaxial Electrospinning Process. A schematic diagram of the modified coaxial electrospinning apparatus with surrounding solvent is shown in Figure 1A. A stainless steel capillary metal-hub needle (with an inner diameter of 1 mm and outer diameter of 1.32 mm) was inserted into silica tubing (outer and inner diameters of 4 and 2 mm, respectively) to form the concentric spinneret (Figure 1B). A crocodile clip was used to connect the inner stainless steel capillary with the high-voltage supply (ZGF 60 kV/2 mA, Shanghai Sute Corp., China). A double syringe pump (KDS200, Cole-Parmer) was used for driving the concentrated polymer solutions and the surrounding solvent synchronously. The flow rate of the surrounding solvent can be manipulated by varying the volume of the syringe. Two single syringe pumps (KDS100, Cole-Parmer) may work similarly as a substitute for the double syringe pump. Both PVP and E L-100 have a good solubility in ethanol and DMAc.[22−24] Their structural formulas are shown in Figure 1D.

It was not possible to electrospin a concentrated solution of 35% (w/v) PVP into fibers using a conventional single fluid electrospinning process. A key factor is the fast evaporation of ethanol from the concentrated PVP solution, resulting in a solid skin and in turn clogging the spinning head. Although PVP solutions in pure DMAc have no electrospinnability, when DMAc was pumped as sheath fluid to surround the concentrated PVP solution and a voltage of 10 kV was supplied, a stable and compound Taylor cone and straight thinning jet were formed (Figure 1C).

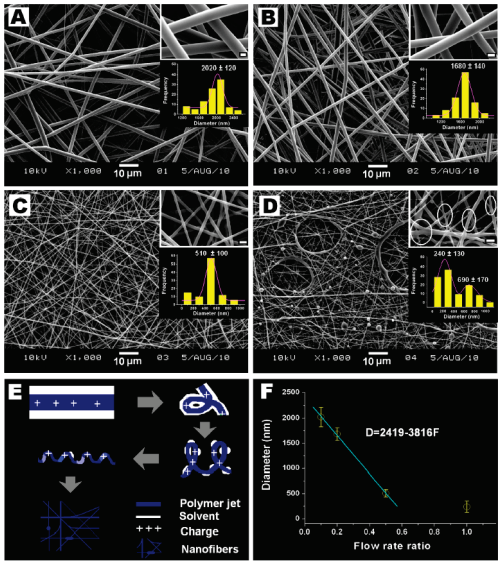

Figure 2. PVP fibers prepared from concentrated solutions using a modified coaxial electrospinning process. (A) to (D) are SEM images of PVP fibers produced by different ratios of sheath:core fluid (DMAc:PVP solution) flow rate: (A) 0.1:1, (B) 0.2:1, (C) 0.5:1, and (D) 1:1. The upper inset of each picture is an SEM image of fiber surface morphology under a higher magnification; the scale bar represents 1 μm. The lower inset shows the statistical distribution of fiber diameters. The white ellipses in the inset of (D) indicate the rebonding of "wet" thin fibers. (E) The mechanism of excessive DMAc influence on fiber formation during the modified electrospinning process. (F) The linear relationship between the PVP fiber diameter and the sheath:core fluid flow rate ratio.

During the coaxial electrospinning process the sheath solvent DMAc possibly plays the following roles: (1) lubricating the spinning head to avoid the polymer clinging to it, (2) retarding the fast evaporation of ethanol from the viscous PVP solution, and (3) retaining the fluid jet under the electrical drawing force for a longer period. The single fluid electrospinning shares characteristics of both electrospraying and the conventional solution dry spinning, where the spinning polymer solution contacts the atmosphere directly. In the coaxial process presented here, the formation of the Taylor cone and the thinning of the straight jet would take place in a liquid environment. Consequently, by using a sheath solvent, in this case DMAc, it was possible to prevent the fast loss of ethanol at the Taylor cone−air and jet−air interfaces and hence avoid the formation of a gel-like skin and resultant clogging of the spinning head.

Influence of Sheath Solvent Flow Rates. Besides avoiding the clogging of the spinning head and the formation of a semisolid "skin" on the thinning jet prematurely, electrospinning with sheath solvent could be used to modulate the PVP fiber diameter by controlling the flow rate of the sheath DMAc solvent. This results in the formation of high-quality fibers that possess smaller diameter, smoother surface morphology, and structural uniformity.

Figure 2 shows SEM images of fibers collected at different flows rates of DMAc. From Figure 2A−D, each picture has two insets. The upper inset relates to fiber surface morphologies taken at larger magnification, and the lower inset is a statistical distribution of fiber diameters. Fibers shown in Figure 2A−C all have a smooth surface and became thinner as the ratio of the flow rate of DMAc to PVP solution increased. For example, increasing the flow rate ratio from 0.1:1 to 0.2:1 to 0.5:1 reduced the average diameter from 2020 to 1680 to 510 nm, respectively. Since the sheath DMAc prevented the evaporation of ethanol, the greater the flow rate of DMAc, the longer the jet is retained in a fluid state. In turn, the jet would be subjected to a longer

drawing process under the electrical field so resulting in thinner fibers.

When the ratio further increased to 1:1, the collected fibers exhibited significant changes in morphology (Figure 2D). Fibers exhibited a range of structures that included a combination of thin, thick, and branched fibers. Beads-on-a-string, spindle-on-string, and circular and large joint points of fibers were also noted. Overall the fibers had two distinct diameter distribution peaks, and the larger diameter fibers have occurred as a result of rebonding of the "wet" thin fibers, as indicated by the branching of fibers in the white ellipses in the inset of Figure 2D. All these phenomena could arise due to excessive DMAc sheath solvent that promotes a mixed set of fiber forms.

In the instability region, often a succession of three or more smaller diameter bending instabilities would be present before the jet solidified by evaporation of the solvent, during which the jet path continues in a manner of three-dimensional coils.[25,26] Shown in Figure 2E, when an excessive DMAc was taken as sheath fluid, it would follow the core fluid to go deeper into the second, the third bending coils, and even the finally collected fibers. During the fast elongation process of the former bending coils, the core polymer solutions could be drawn evenly and continuously due to their viscoelasticity, whereas the sheath solvent could not follow the core fluid path due to lack of viscoelasticity and would be disassociated into separate parts along the core fluid. As a result, the jet consisted of varying polymer concentrations due to local mixing of DMAc with the core fluid in the later bending coils. Combined with rebonding of "wet" fibers on the collector, fibers with a broader diameter distribution and multiple morphologies were inevitable.

Within a suitable range, the diameters of fibers made from the concentrated PVP solution can be tailored simply through adjusting the sheath solvent flow rate using the modified coaxial electrospinning. Figure 2F shows that there is a linear relationship between the PVP fiber diameter and the ratio of sheath: core flow rate and this covers the range 0.1−0.5. The regression equation is $D = 2419 - 3816F$ with a correlation coefficient of 0.9996, where D denotes the fiber diameter and F denotes the flow rate ratio.

Influence of Different Sheath Solvent. The above experiments demonstrate that fibers could be made from a concentrated PVP solution using a modified coaxial electrospinning process with DMAc as sheath fluid. The diameter of the PVP fiber can be modulated in a controlled manner. The following experiments demonstrate that E-L100 fibers can be produced from a 30% w/v concentrated solution in ethanol using the modified coaxial electrospinning process and investigate the influence of different sheath solvents on fiber quality.

Pornsopone et al. had reported that only 10−20% w/v E-L100 solutions in ethanol could be successfully electrospun into fibers.[24] We attempted to electrospin a 27% w/v E-L100 solution using a single fluid electrospinning process, which could only be performed by manually removing the clogging gel clumps that formed on the spinning head from time to time. Examples of the resultant fibers are shown in Figure 3A. Fiber diameters of 3220 ± 1550 nm were noted, and there was a wide distribution range. There are many wrinkles on the fiber surface, and this could be attributed to the rapid evaporation of ethanol from the jet surface, which would make the outer surface of the fluid jet "dry" much faster than its inner core and hence prematurely form a solid skin. When the jet deposited on the fiber collector, the inner core was not completely dried as the evaporation of the residual ethanol continued and the fibers shrunk to form the furrows as denoted on the surface morphology.

When ethanol, DMAc, or a 70:30 v/v mixture was used as sheath solvent at a flow rate of 0.5 mL/h, all the electrospinning processes of the concentrated E-L100 solutions could be

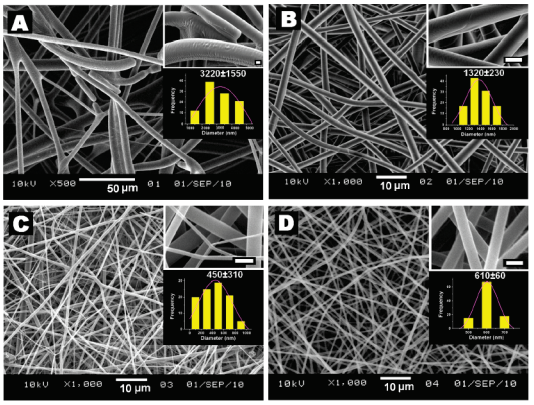

Figure 3. SEM images of fibers prepared from 30% (w/v) E-L100 solutions in anhydrous ethanol. (A) Fibers prepared using a single fluid electrospinning process with manual removal of the clogging material. (B) to (D) show fibers prepared using the modified coaxial electrospinning process with sheath solvents (B) ethanol, (C) DMAc, and (D) a 70:30 volume ratio mixture of ethanol and DMAc. The upper inset of each picture shows SEM images of fiber surface morphologies under higher magnification; the scale bar represents 1 μm. The lower inset shows the statistical distribution of fiber diameters.

effectively carried out. The resultant fibers (Figure 3B) had a diameter of 1320 ± 230 nm, and some fissures on their surface was evident, indicating that the jet surface was still drying faster than the jet core due to the high vapor pressure of ethanol.

Fibers prepared using DMAc as sheath solvent had a smooth surface and very small diameter of 450 ± 310 nm but a wide diameter distribution (Figure 3C). DMAc has a much higher boiling point (166 °C) than ethanol (78 °C), which means that DMAc surrounded the concentrated polymer jet for a longer time and went deeper into the instability regions than ethanol. Thus, on one hand, DMAc favored the further thinning of the fibers and meanwhile stopped the core jet from forming semisolid "skin" to promote the exhaustion of inner solvent. This in turn produced collected fibers dry enough to prevent any shrinking, and hence they had a smooth surface. On the other hand, the persistence of DMAc with the core jet would yield fiber sections with different polymer concentrations and subsequently fibers with a variety of diameters.

When a mixture of ethanol and DMAc with a volume ratio of 70:30 was used as sheath solvent, E-L100 fiber quality was improved a lot in terms of structural uniformity and fiber size distribution (Figure 3D). The mixture of ethanol and DMAc appears to remain surrounding the core polymer solution for an optimal length of time and is longer when ethanol is used but shorter than DMAc. This suggests that the mixed solvents can influence the jet enabling enough drawing under electrical forces to result in thinner fibers, whereas did not allow the mixing of the core E-L100 solution with sheath solvents to take place and hence resulted in a more uniform fiber structure. Evidently the suitable selection of sheath fluid solvents is a critical factor to consider in order to produce high-quality fibers by a coaxial electrospinning process. The first and foremost consideration is the length of time the surrounding solvent remains on the core fluid, which has a direct relationship with the solvents' boiling points. Beside boiling points of the sheath solvents, other properties that influence fiber quality include the solvent conductivity, the solubility of core polymer in the solvent, and whether the solvent is protic or aprotic. All these factors and their influence on the formation of the Taylor cone and on jet thinning in a liquid environment still need to be addressed.

Conclusions

This study represents an initial effort to electrospin ultrafine fibers from concentrated polymer solutions that would normally be unspinnable. A modified coaxial electrospinning process, with pure solvent as sheath fluid to surround the core polymer solution, was carried out to achieve this goal. PVP fibers from a 35% w/v solution in ethanol have been prepared using the modified process, and the fiber diameter could be manipulated by adjusting the sheath solvent (DMAc) flow rate. E-L100 fibers from a 30% w/v solution in ethanol have been produced with different types of sheath solvents. The highest quality fibers, with a smooth surface, small diameter, and uniform structure, were obtained when a mixture of ethanol and DMAc was used as sheath fluid. The type of sheath solvent and the sheath/core solvent flow rate ratio are two critical factors that determine the quality of fiber produced. The modified coaxial electrospinning process described provides an alternative option to increase the range of nanofibers that can be obtained by the electrospinning and broadens further the potential applications of nanofibers.

Acknowledgment. We thank the financial support from China Postdoctoral Science Foundation (No. 200902195) and the UK-CHINA Joint Laboratory for Therapeutic Textiles.

References and Notes

(1) Casper, C. L.; Stephens, J. S.; Tassi, N. G.; Chase, D. B.; Rabolt, J. F. *Macromolecules* **2004**, *37*, 573–578.
(2) Rutledge, G. C.; Fridrikh, S. V. *Adv. Drug Delivery Rev.* **2007**, *59*, 1384–1391.
(3) Gupta, P.; Elkins, C.; Long, T. E.; Wilkes, G. L. *Polymer* **2005**, *46*, 4799–810.
(4) Lee, K. H.; Kim, H. Y.; Bang, H. J.; Jung, Y. H.; Lee, S. G. *Polymer* **2003**, *44*, 4029–4034.
(5) Cengiz, F.; Dao, T. A.; Jirsak, O. *Polym. Eng. Sci.* **2010**, DOI 10.1002/pen.21599.
(6) Wang, C.; Chien, H. S.; Hsu, C. H.; Wang, Y. C.; Wang, C. T.; Lu, H. A. *Macromolecules* **2007**, *40*, 7973–7983.
(7) Reneker, D. H.; Yarin, A. L.; Fong, H.; Koombhongse, S. *J. Appl. Phys.* **2000**, *87*, 4531–4547.
(8) Moghe, A. K.; Gupta, B. S. *Polym. Rev.* **2008**, *48* (2), 353–377.
(9) Theron, S. A.; Zussman, E.; Yarin, A. L. *Polymer* **2004**, *45*, 2017–2030.
(10) Zhang, Y. Z.; Su, B.; Ramakrishna, S.; Lim, C. T. *Biomacromolecules* **2008**, *9*, 136–141.
(11) Badami, A. S.; Kreke, M. R.; Thompson, M. S.; Riffle, J. S.; Goldstein, A. S. *Biomaterials* **2006**, *27*, 596–606.
(12) Yu, J. H.; Fridrikh, S. V.; Rutledge, G. C. *Adv. Mater.* **2004**, *16*, 1562–1566.
(13) Díaz, J. E.; Barrero, A.; Márquez, M.; Loscertales, I. G. *Adv. Funct. Mater.* **2006**, *16*, 2110–2116.
(14) Park, S.; Park, K.; Yoon, H.; Son, J. G.; Min, T.; Kim, G. H. *Polym. Int.* **2007**, *56*, 1361–1366.
(15) Wang, M.; Yu, J. H.; Kaplan, D. L.; Rutledge, G. C. *Macromolecules* **2006**, *39*, 1102–1107.
(16) Wang, C.; Yan, K. W.; Lin, Y. D.; Hsieh, P. C. H. *Macromolecules* **2010**, *43*, 6389–6397.
(17) Zhang, J. F.; Yang, D. Z.; Xu, F.; Zhang, Z. P.; Yin, R. X.; Nie, J. *Macromolecules* **2009**, *42*, 5278–5284.
(18) Wu, X. M.; Branford-White, C.; Yu, D. G.; Chatterton, N. P.; Zhu, L. M. *Colloids Surf., B* **2011**, *82*, 247–252.
(19) Lu, X.; Wang, C; Wei, Y. *Small* **2009**, *21*, 2349.
(20) Chen, H.; Wang, N.; Di, J.; Zhao, Y.; Song, Y.; Jiang, L. *Langmuir* **2010**, *26*, 11291.
(21) Ma, M.; Krikorian, V.; Yu, J. H.; Thomas, E. L.; Rutledge, G. C. *Nano Lett.* **2006**, *6*, 2969–2972.
(22) Yu, D. G.; Gao, L. D.; White, K.; Branford-White, C.; Lu, W. Y.; Zhu, L. M. *Pharm. Res.* **2010**, *27*, 2466–2477.
(23) Yu, D. G.; Yang, J. M.; Branford-White, C.; Lu, P.; Zhang, L.; Zhu, L. M. *Int. J. Pharm.* **2010**, *400*, 158–164.
(24) Pornsopone, V.; Supaphol, P.; Rangkupan, R.; Tantayanon, S. *Polym. Eng. Sci.* **2005**, *45*, 1073–1080.
(25) Yarin, A. L.; Koombhongse, S.; Reneker, D. H. *J. Appl. Phys.* **2001**, *89*, 3018.
(26) Reneker, D. H.; Yarin, A. L. *Polymer* **2008**, *49*, 2387–2425.