The Influence of Sheath Solvent Compositions on the Diameters of Electrospun PCL/PTMC Nanofibers

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Abstract. The modified coaxial electrospinning, in which only organic solvents or their mixtures are utilized as sheath working fluids, is a useful way for manipulating nanofibers’ diameters. In this study, with a co-dissolving solution consisting of poly(ε-caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC) at a concentration of 12 wt% in a mixture of dichloromethane (DCM)/N,N-dimethylformamide (DMF) as the core fluid, a series of solvent mixtures with a varied compositions of them were exploited as the sheath fluids to control the sizes of electrospun PCL/PTMC nanofibers. The scanning electron microscopic results demonstrated that the nanofibers’ diameter (D) had a fine relationship with the DMF volume ratio (V_r) in the sheath fluids as D=162V_r-0.61 (R²=0.9922). This job opens a new way for conducting the modified coaxial processes and for adjusting the sizes of fibers intentionally.

Introduction

Electrospinning, together with electrospraying and e-jetting printing, are commonly termed as electrohydrodynamic atomization (EHDA) techniques, which are simple single-step “top-down” processes for nano fabrications [1-7]. Different with traditional methods, electro-static energy is directly exploited to remove organic solvents from the fluids for generating solid products during the EHDA processes [8-13]. These advanced processes are popular in many fields such as pharmaceutics, ceramics, energy and environments [14-19].

However, the intentional manipulation of nanofibers’ diameters is still one of the most intractable problems in electrospinning. Although many efforts have been paid to this goal, the results are far from being satisfied [20]. Even the aim of obtaining thinning nanofibers is often compromised by the detriment of nanofiber quality in a single fluid electrospinning process. New strategy that can produce high quality nanofibers stably and controllably is highly desired.

Coaxial electrospinning was initially applied in controlling secondary structures of nanofibers, later was expanded to the applications of encapsulating drugs or biological agents into the polymeric nanofibers [21,22]. During the coaxial process the sheath solution acts as a guide and surrounds the core material, and the viscosity of the sheath solution is required to overcome interfacial tension between the two solutions so enabling the formation of a compound Taylor cone and a constant jet. However, this traditional idea was broken by Yu. A modified process based on coaxial and triaxial electrospinning was reported, where only
solvent as used as a sheath fluid [23-26]. The new process has been demonstrated to be useful for stabilizing the electrospinning process and for manipulating the nanofibers’ diameters.

Materials and Methods

Materials
Poly(ε-caprolactone) (PCL, M_w ~ 80,000) and poly(trimethylene carbonate) (PTMC, M_w ~ 100,000) were provided by Minghe Functional Polymer Co., Ltd. (Qingdao, China). Dichloromethane (DCM) and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Preparations
A fixed blend ratio of PCL and PTMC (6:4, w/w) were dissolved in a mixture of DCM/DMF with a volume ratio of 70:30 (v:v) to prepare the core fluid at a concentration of 12 wt %. A series of mixture consisting of DCM and DMF with varied volume ratio were exploited as the sheath working fluids.

A ZGF60 kV/2 mA power supply (Wuhan Huatian Corp., Wuhan, China), two KDS100 syringe pumps (Cole-Parmer®, Vernon Hills, USA) and a cardboard wrapped with aluminum foil were utilized to set up the in-house electrospinning system. After some pre-experiments, the applied voltage and the spinneret-to-collector distance were fixed at 16 kV and 20 cm, respectively. The feeding rate of the sheath and core fluids were adjusted at 0.2 and 0.8 mL/h, respectively. Nanofibers prepared from a DCM/DMF volume ratio of 100/0, 80/20, 60/40, 40/60, 20/80 were denoted as F1, F2, F3, F4 and F5, respectively.

Characterizations

The morphology of the fibers was evaluated using a scanning electron microscope (SEM; FEI Quanta 200 FEG ESEM instrument). Each specimen was fixed with conductive double-sided carbon adhesive tape and were gold sputter-coated under a nitrogen atmosphere to render them electronically conductive. The average fiber diameter was determined by measuring their sizes in SEM images at more than 100 different places using the ImageJ software (National Institutes of Health, Bethesda, MD, USA).

Results and Discussion

The Modified Coaxial Processes

Shown in Fig. 1a is a schematic diagram of the coaxial system, which was composed of the typical four components, i.e. the two syringe pumps, the spinneret, the fiber collector and the high voltage power supply. The key component is the spinneret, which determines what types of electrospinning processes are carried out (Fig. 1b).
A digital picture of the electrospinning system is shown in Fig. 2a. The connections of the spinneret with working fluids and power supply are shown in Fig. 2b, in which the core fluid syringe was directly connected with the spinneret and the sheath fluid syringe was connected with the spinneret through a highly elastic silicon tubing. The high voltage was applied on the two fluids through an alligator clip.

An image of the real electrospinning process for preparing nanofibers F2 is shown in Fig. 2c. It was a typical process, starting from a Taylor cone, through which a straight fluid jet was emitted, and followed by a continuously enlarged bending and hipping loops. Its compound Taylor-cone was exhibited in Fig. 2d, in which an obvious image of half an core-shell structure. The working semi-vertical angle was 61°. It is a common sense that the semi-vertical angle $\theta$ reflects a balance between the electrical field ($E$) and the surface tension of working fluid ($\gamma$) in Fig. 2e, and its value should be at the range of 32° to 46° for a stable and robust electrospinning process [27]. In the present modified coaxial process, the value of $\theta$ was out of the range a lot, but the coaxial process was still stable and continuously. However, when the sheath mixture contained too much DMF, the coaxial process lost its stability to some extents. A typical enlarged image of the process for fabricating fibers F5 is exhibited Fig. 2f. It is obvious that the bending loops couldn’t be fully expand. This should have a close relationship with the physical property of solvent DMF, which has a high boiling point of 153 °C.
Morphology

The SEM images of the five kinds of nanofibers are exhibited in Fig. 3. All the nanofibers had the linear morphology without any spindles-on-a-string phenomena except nanofibers F5. Although nanofibers F5 (Fig. 3e) showed a smaller diameter than the others (Fig. 3a to 3d), these fibers had many spindles-on-a-string morphology. It should be the excessive DMF in the sheath mixture that resulted in these morphologies.

The Influence of Solvent-to-solvent Ratio in the Shell Fluid on the Electrospun Nanofibers

The average diameter and distribution of the prepared five types of nanofibers are shown in Fig. 4. As the volume ratio of DMF in the sheath mixture increased from 0% to 20%, 40%, 60% and 80%, their average diameters gradually decreased from 610 ± 150 nm, to 460 ± 110 nm, 270 ± 80 nm, 220 ± 50 nm, and 180 ± 50 nm for nanofiber F1 to F5, respectively. The more DMF in the sheath fluid, the more difficult it was exhausted during the electrospinning. Thus in turn, the longer time period the fluid jets were subjected to the electrical force drawing and the nanofibers with smaller diameters were generated.

To further disclose the above-mentioned trend and find the inner relationship between the nanofibers’ size and the sheath solvent compositions, both linear equation and exponential equation were exploited to fit the statistical data. The results were shown in Fig. 5a (linear equation) and 5b (exponential equation). The linear equation is \( D=557-530V_r \) with a correlation coefficient of \( R^2=0.9023 \), reflecting a poor linear relationship between them. However, the regressed exponential equation \( D=162V_r^{-0.61} \) gives a correlation coefficient value of \( R^2=0.9922 \), suggesting a fine relationship. Thus, the exponential equation was better than the linear one in reflecting the influence of sheath solvent compositions on the nanofibers’ diameters, and it could be effectively utilized to accurately predict the diameter of electrospun nanofibers.
Fig. 5 Different equations were exploited to fit the statistical data about diameters: (a) linear equation; (b) exponential equation.

Conclusions

A series of modified coaxial processes have been successfully carried out for preparing PCL/PTMC composite nanofibers. The solvent mixtures consisting of DMF and DCM and with a varied of compositions were exploited as the sheath fluids to control the sizes of electrospun nanoproducts. The SEM results demonstrated that the nanofibers’ diameter (D) had a quantitative relationship with the DMF volume ratio (V_r) in the sheath fluids as $D=162V_r^{-0.61}$ ($R^2=0.9922$). It can be concluded that the present job paved a new way for implementing the modified coaxial electrospinning processes and the diameters of resulted nanofibers.

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