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# The Influence of Sheath Solvent's Flow Rate on the Quality of Electrospun Ethyl Cellulose Nanofibers

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## ABSTRACT

The present research investigates the influence of sheath solvent's flow rate on the quality of electrospun ethyl cellulose (EC) nanofibers using a modified coaxial process. With 24 w/v % EC in ethanol as electrospinnable core fluid and ethanol as sheath fluid, EC nanofibers generated under different sheath flow rates were generated from the modified processes. FESEM observations demonstrate that the modified process is effective in preventing the clogging of spinneret for a smooth electrospinning. The key for the modified coaxial process is the reasonable selection of a sheath flow rate matching the drawing process of core EC fluid during the electrpospinning. The EC nanofibers' diameters ($D$, nm) could be manipulated through the sheath-to-core flow rate ratio ($f$) as $D = 819\text{-}1651f$ ($R$= 0.9754) within a suitable range of 0 to 0.25. The present paper provides useful data for the implementation of the modified coaxial process controllably to obtain polymer nanofibers with high quality.

**Keywords:** Coaxial Electrospinning; Nanofibers; Ethyl Cellulose; Sheath Fluids; Flow rate

## 1. Introduction

Ethylcellulose (EC) is a derivative of cellulose in which a defined percentage of the hydroxyl groups of the repeating glucose units are substituted with ethyl ether groups. It fulfills all the requirements of major pharmacopoeias (USP, EP, and JP) and food regulations. EC is an inert, hydrophobic polymer and is essentially tasteless, odorless, colorless, non-caloric, and physiologically inert. It has long been used as solvent-based tablet and pellet coating, tablet binder, to prepare microcapsules and microspheres, and both as film and matrix-forming material for sustained- release dosage forms [1]. Most recently, EC was selected as the drug carrier and polymer matrix to generate composite fibers and microparticles to achieve sustained-release profiles [1,2].

All the above-mentioned EC-based functional nanomaterials were generated using a single fluid electrohydrodynamic atomization process (including electrospinning, electrospraying and e-jetting printing), which is a popular procedure for producing nanofibers or microparticles due to ease of implementation and cost-effectiveness, and the unique properties and versatile applications of the resultant products [1-3]. Although electrospinning is simple and straightforward, the mechanism of fiber formation involves complex electro-fluid-mechanical issues and there are many factors that can affect the fiber diameters and morphology. Controlled production of electrospun nanofibers with uniform diameter and structure remains a challenge [4,5]. To ensure a successful electrospinning process, the chain-entanglement density in the working solution must be high enough to prevent the capillary breakup and also to subdue Rayleigh instability. However, high concentration polymer solutions often result in clogging of the spinneret and failure of the electrospinning process. Thus polymers often have narrow windows of electrospinnable solution concentrations, and the objective of obtaining finer structures (such as by lowering polymer concentration, by adding salt or surfactant, and by manipulating the electrospinning parameters) is often limited and compromised by sacrificing the fiber uniformity [6,7].

Clogging is a critical but common problem experienced during the traditional single fluid electrospinning, especially when a high-volatility solvent is used to prepare a polymer solution. With zein as model, Kanjanapongkul [8,9] reported that clogging would occur even when the zein concentration in its ethanol aqueous solutions (85 wt %) decreased from an electrospinning level to electrospraying level (< 18 wt %), 16 wt % and 10 wt % zein solutions were also tested. It was found that clogging was still observed in both cases. They have put forward a method to prevent clogging simply by providing an additional solvent through another syringe pump onto the surface of the droplet at the needle tip. But this

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method is difficult for precise control of the process, because the additional solvent was put on the needle tip simply by gravity.

Coaxial electrospinning, in which a concentric spinneret can accommodate two different liquids, is regarded as one of the most significant breakthroughs in this area [10,11]. It has been applied broadly in controlling secondary structures of nanofibers, encapsulating drugs or biological agents into the polymer nanofibers, preparing nanofibers from materials that lack filament-forming properties, enclosing functional liquids within the fiber matrix, manipulating the size of self-assembled nanoparticles, and preparing ultrafine fibers from concentrated polymer solutions. It is a common sense that the sheath fluids must have enough viscosity to overcome the interfacial tension between the two solutions through “viscous dragging” and “contact friction” for a successful coaxial electrospinning process [11]. However, our group have broken this concept and developed a modified coaxial electrospinning process, in which only organic solvent was used as sheath fluid. This opens a new way for manipulating the additional solvent to accompany the electrospinnable fluids in a core-sheath and controllable way, and thus should provide new possibility in controlling the nanofiber-forming process and also the nanofibers’ quality.

## 2. Experimental

### 2.1. Materials

EC (6 mPa·s to 9 mPa·s) was obtained from Aladdin Chemistry Co., Ltd (Shanghai, China). Methylene blue and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals used were analytical grade.

### 2.2. Coaxial Electrospinning

The core solutions were prepared by dissolving 24 g EC, 3 g KET and 2 mg methylene blue in 100 mL ethanol. The sheath solvent was pure ethanol. Two syringe pumps (KDS100 and KDS200, Cole-Parmer, IL, USA) and a high-voltage power supply (ZGF 60kV/2 mA, Shanghai Sute Corp., Shanghai, China) were used for coaxial electrospinning. All electrospinning processes were carried out under ambient conditions (21℃ ± 2℃ with a relative humidity 64% ± 6%). A homemade concentric spinneret was used to conduct the coaxial electrospinning processes. A stainless steel capillary with an inner diameter of 0.3 mm was used to conduct the single fluid electrospinning.

The electrospinning process was recorded using a digital video recorder (PowerShot A490, Canon, Tokyo, Japan). For optimization, the applied voltage was fixed at 14 kV, and the fibers were collected on an aluminum foil at a distance of 20 cm. All other parameters are listed in **Table 1**.

### 2.3. Characterization

The surface morphologies of electrospun fibers were assessed using a JSM-5600LV scanning electron microscope (SEM, Japan Electron Optics Laboratory Co. Ltd.). Prior to the examination, the samples were gold sputter-coated under argon atmosphere to render them electrically conductive. The pictures were then taken at an excitation voltage of 3 kV. The average fiber diameter was determined by measuring diameters of fibers at over 100 different locations from the same SEM images using Image J software (National Institutes of Health, USA).

## 3. Results and Discussion

A schematic diagram of the modified coaxial electrospinning process with solvent as sheath fluid is shown in **Figure 1(a)**. A homemade concentric spinneret was used to carry out the modified process (**Figure 1(b)**). The critical voltage applied to a fluid to initiate Taylor cone formation and the straight thinning jet (Vc) have a close relationship with the diameter of sheath part of the concentric spinneret [12].

$$V_c \sim \sqrt{\frac{\gamma d^2}{\varepsilon R}}$$

Where Vc is the critical voltage for a jet emanating from the meniscus tip, d is the electrode separation, ε is the permittivity, γ is the surface tension, and R is the principal curvature of the liquid meniscus. A small

**Table 1. Parameters of EC nanofibers and their preparation.**

| No. | Flow rate (ml/h) | | $R_s$[a] | Morphology[b] | Diameter (μm) |
|---|---|---|---|---|---|
| | Sheath | Core | | | |
| F1 | Single fluid spinning | | | Line | 0.42±0.18 |
| F2 | 0.1 | 0.9 | 0.11 | Line | 0.34±0.15 |
| F3 | 0.2 | 0.8 | 0.25 | Line | 0.23±0.14 |
| F4 | 0.3 | 0.7 | 0.43 | Mixed | -- |

[a] $R_{sc}$ Sheath-to-core flow rate ratio; [b] In this column, “Line” morphology refers to that nanofibers have few beads or spindles on them; “Mixed” morphology refers to that there are beads/spindles on the nanofibes.

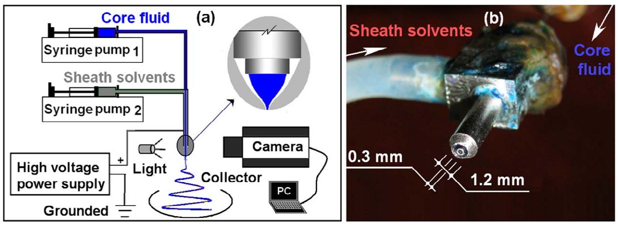

**Figure 1. The modified coaxial electrospinning: (a) Schematic diagram of the modified process; (b) The homemade concentric spinneret.**

diameter of the spinneret's orifice means a small R, and thus a small Vc to imitate the coaxial electrospinning process. The homemade spinneret here has an out and inner diameter of 1.2 and 0.3 mm respectively (**Figure 1(b)**), facilitating the coaxial electrospinning process. In addition, the inner capillary is a little project out the sur-face of the out capillary, which should help to make the sheath ethanol well surround the core EC solutions.

When a single fluid electrospinning of the EC solutions was conducted using a stainless steel capillary, the spin-neret was clogged from time to time, as shown in **Figure 2(a)**. Manual remove of semi-solid substance hung on the nozzle of the spinneret was needed to keep the electro-spinning process go on. The fast evaporation of ethanol on the surface of fluid jet led to the formation of a highly viscous semi-solid substance, which clung to the nozzle of spinneret and thus retarded the electrospinning process.

When the modified coaxial electrospinning was carried out to prepare the EC nanofibers, two syringe pumps were used to drive the sheath and core fluids independently. An alligator clip was used to connect the inner stainless steel capillary with the high voltage supply (**Figure 2(b)**). With ethanol as sheath fluid and under a sheath-to-core flow rate ratio of 0.25, the arrangement produced a typical fluid jet trajectory, in which a Taylor cone followed by a straight fluid jet and a bending and whipping instability region (**Figure 2(c)**). The compound Taylor cone is clear to be composed of two parts with the sheath solvent well surrounding the core polymer solutions, indicating by the methylene blue in **Figure 2(d)**.

The coaxial electrospinning process could be car-ried out without any clogging phenomena and go on smoothly for finishing the electrospinning of the whole EC solution in the syringe. Solvent evaporation and vis-cosity of the solution have been noted to have strong impacts on clogging. High volatility of a solvent accelerates solvent evaporation, thus increases the likelihood of clogging. This is because applied electric field cannot overcome the viscous drag force. If the viscosity is too high, it is possible that, the higher the solution viscosity is the applied electrical force would not be adequate to overcome the viscous drag force at the droplet-air inter-face, leading to clogging at the spinneret. When sheath ethanol was exploited to surround the core EC solution during the electrospinning, the sheath ethanol can effectively prevent the fast evaporation of the ethanol from the surface of the core EC solutions, retarding the formation of "skin" surface to smooth the electrospinning of EC solutions.

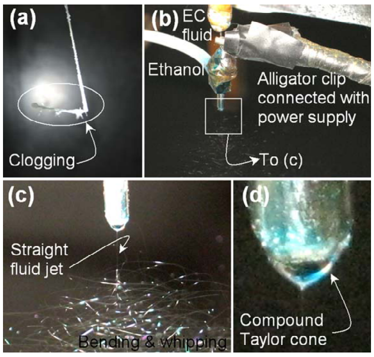

**Figure 2. Observations of the modified coaxial electrospinning and a single fluid process: (a) a typical clogging of the single fluid electrospinning; (b) a digital picture shows the connection of the concentric spinneret with the syringe pump and the power supply; (c) a typical coaxial electrospinning process with ethanol as sheath fluid and under a sheath-to-core flow rate ratio of 0.25 (taken under a magnification of 12×); (d) the compound Taylor cone.**

Nanofibers obtained from the single fluid electrospinning and the modified coaxial electrospinning are showed in **Figure 3**, and the nanofibers' diameter distributions are given in **Figure 4**. All the nanofibers have linear morphology, except F4 which has a typical beads-on-a-string morphology resulted from the excessive sheath solutions (**Figure 3(d)**).

Nanofibers F1 obtained from the single fluid electrospinning are showed in **Figure 3(a)**, and the nanofibers had an average diameter of 860 ± 230 nm (**Figure 4(a)**). Besides a larger diameter, nanofibers F1 also have a wide distribution of diameters. As the flow rate of sheath ethanol was increased from 0.1 to 0.2 mL/h, the resultant nanofibers F2 andF3 were progressively narrower (**Figures 3(b)** to **(c)** and **Figures 4(b)** to **(c)**), with

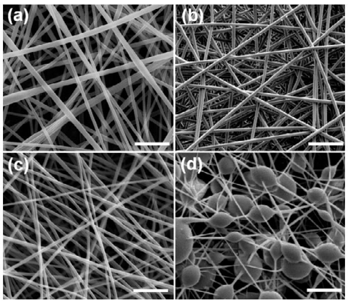

**Figure 3. FESEM images of EC nanofibers: (a) F1; (b) F2; (c) F3; (d) F4, the scale bar represents 5 μm.**

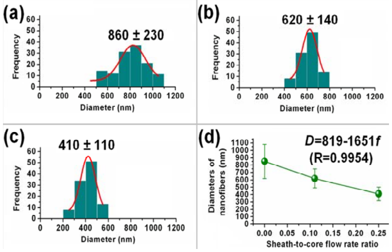

**Figure 4. Nanofiber diameters' distributions: (a) F1; (b) F2; (c) F3. The relationships between the EC nanofibers' diameter and the sheath-to-core flow rate ratio.**

a diameter of 620 ± 140 nm, 410 ± 110 nm, respectively. Moreover, all had diameters smaller than F1 fibers (**Figure 4(a)**) prepared from the single fluid EC solution using a traditional single fluid electrospinning process. Both the nanofibers had good structural uniformity and a relatively small diameter distribution, suggesting a finer quality of the EC nanofibers. A linear relationship between the sheath-to-core flow rate ratio (f) and the resultant nano-fibers' average diameters (D, nm) was found (**Figure 4(d)**) within a suitable range. The regressed equation is D = 819-1651f, with a correlation coefficient of 0.9754. The results suggest that the diameters of uniform nanofibers can be tailored through manipulating the sheath flow rates over a suitable range through the modified coaxial electrospinning.

Throughout the modified coaxial electrospinning, the sheath solvent would exert the following influences on the process: 1) facilitating the formation of Taylor cone due to lower solvent surface tensions; 2) surrounding the straight thinning jet of the core electrospinnable EC solutions that retards the fast evaporation of the core solvent, while the sheath solvent itself outwardly evaporates to the open air; 3) following the core fluid to enter the instability region. The primary reason for the sheath solvent to thin the nanofibers should be the retarding effect on the evaporation of solvents from the surface of the core spinning polymer solutions prematurely (**Figure 5**), and in turn to retain the core jet in a fluid state thus allowing it to be subjected to electrical drawing for a longer period in the instability region. This should be the reason that the modified coaxial electrospinning process could generate thinner EC nanofibers than the single fluid electrospinning. The single fluid electrospinning process is very sensitive to the environmental changes, in particular for spinning liquid systems prepared from volatile organic solvents such as ethanol. The present modified process provided a stable and robust core- sheath interface for the core EC solutions to be drawn in the electrical field, keeping from the disturbances of environmental changes. Thus the modified coaxial process could produce EC nanofibers with more uniform diameter distributions.

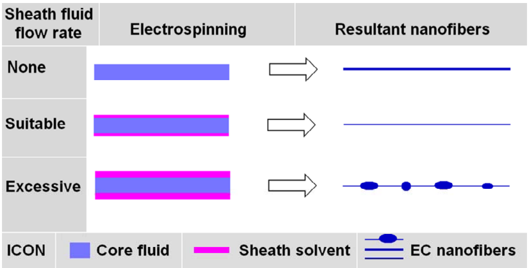

**Figure 5. The proposed mechanisms of sheath solvent on the formation of EC nanofibers using the modified coaxial electrospinning.**

However, when an excess sheath flow was used, such as the case of nanofibers F4, the surrounding solvent remained with the core fluid for a relatively long time period and would break up into separate segments along the core EC jets due to lack of viscoelasticity (**Figure 5**). It is postulated that the divided sheath solvent might mix with the core fluid locally to form sections of the fluid jet with different local polymer concentrations, which in turn would result in nanofibers with beads-on-a-string structure, as showed in **Figure 3(d)**.

## 4. Conclusions

A modified coaxial electrospinning process, in which only pure ethanol was used as sheath fluid, has been successfully developed to produce EC nanofibers with high quality. It was evident from FESEM observa-tions that the modified coaxial electrospinning process is an effective method for preparing high quality nanofibers in terms of nanofibers' diameter and distribution, struc-tural uniformity. The key for the modified coaxial proc-ess is that the reasonable selection of the sheath flow rate, which must well match the drawing process of core EC fluid during the electrpospinning. The EC nanofibers' diameters (D, nm) could be manipulated through the sheath-to-core flow rate ratio (f) as D = 819-1651f (R= 0.9754) within a suitable range of 0 to 0.25. The mechanisms of the sheath solvent influence on the formation of EC nanofibers are discussed. Sheath solvents can act as a useful tool, permitting core electrospun fluid jets subjected a longer period of electrical drawing while having little influence on the entanglement of the core spinning solutions. They can also render the spinning process more stable by transferring the air-spinning-solution interfaces to solvent-spinning-solution interfaces and thus avoiding any negative influence of environment on the core fluids. The present report provides a simple method for implementation of the modified coaxial process to smooth the electrospinning and obtain polymer nanofibers with high quality.

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