



Importance of viscosity parameters in electrospinning: Of monolithic and core–shell fibers

Sandeep Kumar Tiwari*, Subbu S. Venkatraman

School of Materials Science and Engineering, N4.1-1-30, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

ARTICLE INFO

Article history:

Received 1 April 2011

Received in revised form 10 November 2011

Accepted 2 February 2012

Available online 9 February 2012

Keywords:

Electrospinning

Viscosity

Overlap concentration

Entanglement concentration

$\eta_{\text{core}}/\eta_{\text{shell}}$

ABSTRACT

Electrospun polymeric fibers are attractive candidates in the development of scaffolds for the tissue engineering and for providing new systems for delivery of bioactive molecules. Co-axial fibers have emerged as an efficient tool to protect the core material from the adverse conditions of electrospinning process, to spin difficult-to-process fluids and to generate fibers with much more control of the delivery of encapsulated bioactive molecules. Currently, there is very little reported work on the optimization of the processing parameters of electrospinning, especially core–shell electrospinning. This study extends the understanding of the role of solution viscosity as a vital material parameter for electrospinning of fibers. The spinning solutions were characterized for viscosity and optical imaging of the compound Taylor cone for spinnability, and the fibers were imaged by Scanning Electron Microscopy (SEM). Our experimental results, using PLGA as the model polymer, confirm that the solution concentration be above the entanglement concentration (C_e) to obtain uniform beadless monolithic fibers; for core–shell fibers, the shell solution must fulfill the above criterion for spinnability and, further, the ratio of the viscosities of core and shell solutions ($\eta_{\text{core}}/\eta_{\text{shell}}$) has to be greater than a threshold value to get a stable compound Taylor cone and therefore to obtain uniform beadless core–shell fibers. Addition of surfactant led to reduction of the threshold $\eta_{\text{core}}/\eta_{\text{shell}}$ (from 0.55 to 0.18) for the PVA–PLGA system.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Electrospun nanofibers have drawn considerable attention in recent years by virtue of their unique properties and intriguing applications in a number of areas [1,2]. Electrospun nanofibers have led not only to a new approach in the development of scaffolds for the tissue engineering, but also to new systems for delivery of drugs and genes [3,4]. Polymeric nanofibers have proved to be attractive materials for a wide range of applications because of their unique properties, in particular their very high surface area to volume ratio, the possibility of surface functionalization, superior mechanical properties, and similarity in structural morphology to the fibrillar ECM (extracellular matrix) [5,6].

For controlled release of bioactives, including drugs and proteins, core–shell structures are a promising approach to obtain a constant rate of release, or the so-called “Zero-order” release kinetics. In addition, co-electrospinning only protects the bioactives in the core from the adverse conditions of electrospinning (e.g. high electric field, organic solvent, etc. which are encountered primarily by the shell material shielding the core) [7]. Liao et al. have studied core–shell fibers as a carrier for viral gene delivery and the encapsulated viruses could be

released in a porogen-assisted manner. The encapsulation was achieved by co-axial electrospinning, using virus dispersed in Minimum Essential Medium (MEM) with Bovine Serum Albumin as core. Poly(ϵ -caprolactone) with various concentrations of PEG or poly (ethylene glycol) as porogen was used as shell [8].

Dependence of electrospinning process on viscosity parameters has been reported for various polymer solutions. Some research groups have worked on relationship between concentration and viscosity of polymer solutions, which was predicted to be $\eta \sim C^{1.25}$ for semidilute unentangled and $C^{4.25-4.5}$ for semidilute entangled regime [9–11]. The chain overlap concentration (or the value of C^*) is dependent on molar mass, degree of branching of the polymer, as well as solvent power [9,12]. In this work we have studied the concentration–viscosity relationship and its implication in electrospinning of PLGA solutions (in mixed solvent of chloroform and N,N-dimethylformamide).

Co-electrospinning is also an efficient way to electrospin difficult-to-process fluids which themselves are not spinnable because of various reasons such poor solubility, restricted range of available molecular weights, rigid or compact molecular conformation (often encountered in proteins), low conductivity, etc. [13–16]. Electrospinning of cell suspensions has also been successfully done using co-electrospinning [17].

One of the most important requirements for electro-spinnability in core–shell spinning is the viscosity of the shell solution [14], as it guides the core solution to attain core–shell architecture. To act as a shell for

* Corresponding author. Tel.: +65 67904259; fax: +65 67909081.

E-mail address: sktiwari@ntu.edu.sg (S.K. Tiwari).

the fibers, the shell solution should be spinnable by itself. The viscosity should be high enough, in synergy with the electrostatic repulsion, to overcome the forces due to the surface tension.

The core solution must also possess a certain level of viscosity so as to be stretched continuously by the viscous drag. In the work done by Díaz et al. [18], the continuous core-shell structure could not be achieved as the core fluid (oil) underwent viscous break up at a rate faster than the solidification of the stretched shell solution, in spite of the small interfacial tension and high viscosity of the shell solution. The resulting fibers resembled strings of beads, containing pockets of the core material, distributed regularly along the fibers. The size distribution and bead-to-bead distance could, however, be manipulated by the processing conditions. Our work reported here describes an attempt to improve the understanding of this important criterion of core-shell electrospinning. This work, apart from emphasizing the importance of viscosity parameters for electrospinning, provides a starting point to optimize electrospinning parameters for new polymers.

Another critical parameter is the interfacial tension between the core and shell solutions, which should be as low as possible for the generation of a stable compound Taylor cone which leads to the core-shell fiber [14]. In the situation of high interfacial tension between the two fluids, the viscous force exerted by the shell on the core surface is unable to overcome the cohesive force and the spherical inner meniscus develops a small cusp leading to small droplets which are emitted cyclically (unsteady tip streaming). The presented work indicates the usefulness of surfactants in extending the range of solutions for co-axial electrospinning.

2. Materials and methods

2.1. Materials

PLGA80/20 (a copolymer of PLA and PGA in 80:20 ratio, MW 152 kDa) was purchased from Purac (Purac Far East Pte., Singapore). In this study, this copolymer will be referred as PLGA for the sake of simplicity as we have used only one type of PLGA. PVA (Polyvinyl Alcohol) (99 + % hydrolyzed; $M_w = 124\text{--}186$ kDa) was purchased from Aldrich Chemical, Milwaukee, WI, USA. As the organic solvent to dissolve PLGA, Chloroform (CHCl_3) and Dimethylformamide (N,N-dimethylformamide; $\text{C}_3\text{H}_7\text{NO}$) were purchased from TEDIA (Fairfield, OH, USA). As surfactant for core shell electrospinning, Triton® X-100 was purchased from Sigma-Aldrich (St. Louis, MO, USA) and was diluted to 1% before using.

2.2. Measurement of solution viscosities

The viscosities of the polymer solutions, used for electrospinning, were measured using Physica MCR501 Rheometer (Anton Paar® GmbH, Austria). The zero-shear viscosities were recorded in frequency sweep mode at room temperature (25 °C) using cone and plate geometry (diameter: 25 mm; gap: 0.047 mm). In order to prevent rapid evaporation the solvents (specially chloroform), a solvent trap was used around the sample during measurements.

2.3. Electrospinning of monolithic fibers

A combination of chloroform and DMF (N,N-dimethylformamide) was used as the organic solvent to dissolve PLGA (PLGA80/20, MW 152 kDa). Electrospinning was done in the NANON electrospinning apparatus supplied by MECC Co., Ltd. (Fukuoka, Japan). The operating voltage was set at 15 kV. The flow rate was maintained at 1 ml/h keeping the distance between the needle and collector as 14 cm. The needle's internal diameter was 0.4 mm. These parameters, reached after optimization with respect to voltage, collector distance and flow rates, were used for all the concentrations of PLGA. The needle diameter (0.4 mm) was suitable for using a range of flow rates (0.2–3 ml/h).

2.4. Scanning Electron Microscopy (SEM) imaging

Morphology of the fibers was characterized by Scanning Electron Microscopy (SEM, JEOL JSM 6360A). Samples were mounted on a metal holder using double sided tape and coated with gold using a sputter coater followed by observation at accelerating voltages of 15 kV.

2.5. Electrospinning of core-shell fibers

For generating core-shell fibers, a special spinneret was used which provided two inlets, one each for core and shell solutions. The nozzle of the spinneret was in the form of coaxially arranged capillaries where outer capillary supplied the shell solution while the inner needle supplied the core solution. The inner and outer diameters of the needle were 0.4 mm and 0.6 mm respectively. The inner diameter of the outer capillary was 2.4 mm. The shell solutions consisted of PLGA80/20 (in 80:20 mixture of Chloroform and DMF) while PVA solutions (in water) were used in core.

2.6. Imaging of electrospinning

Optical images of electrospinning process were taken by Nikon P90 camera (with 24× zoom). The zoomed photographs were used for analyzing the occurrence, shape and stability of the Taylor cones.

3. Results and discussions

3.1. Dependence of electrospinning on viscosity

Viscosity of a polymer solution is strongly influenced by its concentration, in general increasing with increase in concentration. There are four different concentration regimes for polymer solutions (in good solvents): (i) dilute, (ii) semidilute unentangled, (iii) semidilute entangled and (iv) concentrated. The transition between dilute to semidilute unentangled regime occurs at a concentration known as overlap concentration (C^*). At this concentration, the individual chains, which were separated by solvent molecules in the dilute regime, now begin to overlap with one another but still remain largely unentangled. As the concentration is further increased, the topological constraints induced by the larger occupied fraction of the available hydrodynamic volume in the solution, develop into chain entanglements. The fact that chain entanglement is crucial for fiber formation makes concentration, and consequently viscosity, a crucial parameter for electrospinning. The transition between semidilute unentangled to semidilute entangled regimes is known as entanglement concentration (C_e). It is believed that a concentration $\geq C_e$ is required before we get stable electrospinning, with production of uniform beadless fibers [11]. In general, at both transitions (C^* and C_e), there is a change in slope when solution viscosity is plotted against concentration (both in logarithmic scale). In this work, we explored a range of concentrations between the semidilute unentangled and semidilute entangled regimes. All the solution concentrations are expressed in % (w/v), i.e., percent weight (of the polymer) by volume (of the solvent).

Viscosities of various PLGA solutions in a mixed solvent containing chloroform and DMF (in 80:20 ratio) were measured and the solutions were checked for spinnability. The solution viscosities were plotted against solution concentration (both in logarithmic scale) to demonstrate the dependence of viscosity on concentration. As can be seen in Fig. 1, the zero-shear viscosity increase showed two different slopes of logarithmic linear relations, as expected for polymer solutions: a slope of 1.4 below 4%, and a slope of 4.34 above 4%. The dependence of viscosity of the PLGA solutions on their concentration was in agreement with the previous observations on other polymer solutions, which was predicted to be $\eta \sim C^{1.25}$ for semidilute unentangled and $C^{4.25\text{--}4.5}$ for semidilute entangled regime [9–11]. Uniform and beadless fibers were obtained at concentrations at and above 4% (Fig. 2). Above a

Download English Version:

<https://daneshyari.com/en/article/10614709>

Download Persian Version:

<https://daneshyari.com/article/10614709>

[Daneshyari.com](https://daneshyari.com)