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Influence of solvent characteristics in triaxial electrospun fiber formation

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ABSTRACT

Triaxial electrospinning is a novel method for fabrication of multilayered nano and microsize fibers with desirable features for particular applications. Since the effect of solvent volatilities in each layer and relative polymer molecular weights on uniform encapsulation of the core polymer process is not well understood, we evaluated (i) the role of solvent volatilities, and (ii) molecular weights using cellulose acetate (CA, 30 kDa), polycaprolactone (PCL, 45 kDa and 80 kDa), mineral oil, and polyvinyl alcohol (PVA, 30 kDa and 100 kDa). Different solvent mixtures were evaluated based on the boiling points determined using a simulator. Inner mineral oil was selectively removed to form Hollow fibers. Analysis of chemical compositions using FT-IR and DSC revealed the presence of each component. 24-h viability of human umbilical vein endothelial cells indicated the formed fibers were not toxic. Scanning electron micrographs indicated the formation of triaxial structured fiber of outer hydrophobic PCL/CA/Hollow, PCL/PVA/Hollow and outer hydrophilic CA/PCL/Hollow fibers. Tensile tests (both wet and dry) revealed that PCL/CA/Hollow fibers had increased stiffness and load carrying capacity than CA/PCL/Hollow fibers. Successful fiber formation was dependent on ensuring that the outer shell formed first i.e., the relative solvent volatility of encapsulating core polymer to lower than that of the shell polymer.

1. Introduction

Electrospinning is a versatile polymer processing technique in which sub-micron polymer particles, fibers or interconnected porous fiber meshes can be produced using an electrostatically driven jet of polymer solution [1–3]. A high voltage is applied to polymer solution using two electrodes: one connected to the nozzle ejecting the polymer solution and the other connected to a conductive collector. When the charge build-up at the nozzle (near 15 kV), droplet deforms into a conical structure referred to as Taylor cone. Increasing the electrical force above the surface tension of the polymer solution, breaks the Taylor cone and polymer jet ejects from the apex of the Taylor cone. This jet deviates in a course of violent whipping from bending instabilities brought about by repulsive charges existing along the jet length. The jet is stretched and solvent is evaporated, resulting in the thinning of the fiber [4]. Important properties inherent to electrospun fibers include high surface area per volume ratio, porous structure, highly ordered structure, high rate of adsorption and high strength to weight characteristics [5–7]. However, there is a growing interest in modifying the solid fibers to impart necessary morphological, biological, and mechanical properties [8–10]. For example, formation of co-continuous fibers of cellulose acetate (CA) with polyurethane improved the mechanical properties of CA [11].

While the electrospinning setup itself is relatively uncomplicated, the variables concerned in producing a nano and micro sized fiber with relative uniformity are numerous [12]. Process parameters such as applied voltage could significantly affect the shape and size of the droplet at the tip of spinneret from which the jet is generate. The optimum range of applied voltage varies with the type of polymer solution from 5 to 25 kV. Solution flow rate influences the size, porosity and geometry of fibers. Increasing the flow rate to high value causes wet and incomplete drying because of decreased time for solvent evaporation. A minimum flow rate is required to replace the lost of the polymer solution from the jet being ejected from the Taylor cone at the tip of the spinneret. Changes in polymer concentration affects both viscosity and surface tension of the solution, which determine solution electrospinnability. Solution viscosity controls the polymer chain entanglement when polymer jet travels from spinneret to collector.

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Exceeding the solution viscosity limit could cause blocking and disruption of solution flow.

In the past two decades many changes have been made in the basic principles of electrospinning process [13]. New spinnerets consisting of coaxial capillaries allow fiber generation with improved control over fiber properties to control the release kinetics of embedded drugs [14–20]. Fibers with unique structure and functions can be formed such as (i) altered surface (hydrophobic and hydrophilic), and (ii) multilayered structure. These structures are useful for delivering bactericidal chemicals to abate bacterial fouling in filtration applications. Also, natural and synthetic heterogeneous structure can be prepared with desirable properties of synthetic polymer function providing mechanical properties while natural polymer promoting cellular attachment and growth in tissue engineering [21–24]. Due to these unique properties, electrospun coaxial and or multilayered structures have been widely studied [25–31]. However, there is limited understanding of governing conditions necessary to electrospin triaxial fibers.

Many have evaluated the effects of type of solvent and solvent content (phase separation and fast solvent evaporation) on the solid fiber diameter, shape, surface morphology, mechanical properties and crystallinity [4,11,32–34]. These studies are extended to some composite fibers and or blended polymers in single-phase process. However, the effect of solvent volatility and relative polymer molecular weights on uniform encapsulation of the core polymer in coaxial and or triaxial electrospinning process is not well understood. Selection of solvents with appropriate boiling point for each layer in coaxial and or triaxial electrospinning is critical as rapid solvent evaporation from the jet surfaces could cause instabilities in fiber formation.

In this study, we investigated the effect of type of solvent, solvent volatilities and polymer MW on uniform triaxial fiber formation. We utilized combinations of polycaprolactone (PCL), cellulose acetate (CA), polyvinyl alcohol (PVA), and mineral oil. PCL is non-toxic, biocompatible and biodegradable synthetic polyester. PCL has gained much attention due to its low melting point (60 °C) elastomeric properties. It has been studied to form many medical devices or scaffolds for tissue regeneration of in vivo and in vitro cell culture using serum added media [35]. To alter the hydrophobic characteristics of the surface, PCL has been blended with many natural polymers and also has been extensively evaluated in core-sheath structures [32]. CA fibers have good thermal stability, biodegradability and chemical resistance [11,34,36]. CA fibers are proposed for tissue engineering, and drug delivery [37]. PVA is a biodegradable and biocompatible polymer explored in various biomedical applications [38]. Mineral oil was used as an inner core layer due to ease of spinning with CA solution [39] and selective extraction with octane forming the hollow structure.

Different solvent mixtures were analyzed based on their boiling points, estimated using a process simulator. Solution viscosities were evaluated at various shear rates. Obtained fibers were analyzed by scanning electron microscopy and fiber sizes were characterized using digital micrographs. Differential scanning calorimetry (DSC) and FTIR were performed to determine components in the triaxial fibers. Tensile tests (both wet and dry) were assessed to determine the use of different layers. 24-h viability of human umbilical vein endothelial cells was evaluated. These results show that triaxial fibers can be formed with different features such as hydrophobicity, hydrophobicity, and mechanical strength. Upon formation of the fiber, outer sheath can be extracted, exposing the desired inner sheath allowing fibers of polymers that cannot electrospun in their own. Understanding the mechanism of coaxial and triaxial jet formation will assist in fabrication of uniform fibers with controlled features.

2. Experimental

2.1. Materials

Cellulose acetate (CA) M_n = 30,000 GPC, octane 99%, acetone 99.9%, 1–2 dioxin, Polycaprolactones (PCL 80 kDa, M_n = 80,000), polyvinyl alcohol (PVA 100 kDa, M_n = 80,000–120,000 and PVA 30 kDa, M_n = 30,000) 99% hydrolyzed were purchased from Sigma–Aldrich (St. Louis, MO). Mineral oil 99.9% was from Rexall (Goodlettsville, TN). Polycaprolactone (PCL 45 kDa, M_w = 43,000–50,000) was obtained from Polysciences (Warrington, PA). All other chemicals were used as received without further purification.

All polymer solutions were freshly prepared by stirring for 24 h. CA was dissolved at 14 wt% in room temperature using a mixture of acetone and dioxin (2:1 v/v) (Table 1). PCL spinning solution at 20% mass concentration was prepared at room temperature in a mixture of chloroform and methanol (9:1 v/v) or other solvent mixtures. PVA was dissolved in distilled water under heating at 80 °C and after the solution was cooled, other solvents were added. The polymer solutions were then transferred into a 10 mL plastic syringe fitted with 10 cm long plastic tubing and connected to the electrospinning setup.

2.1.1. Electrospinning setup

The electrospinning setup (Fig. 1) consisted of two syringe pumps (74,900 series, Cole-Parmer Instrument Company, Vernon Hills, IL) for the sheath and core solutions to be pumped independently, 10 mL syringe (Luer-Lok Tip; Becton Dickinson and Company, Franklin Lakes, NJ), custom-built spinneret, high voltage power supply (ES30P-5W/DAM, Gamma high Voltage Research, Ormond Beach, FL), earth grounding, and a collection mandrel. The triaxial spinneret consisted of three concentric needles; inner core needle had an inner diameter of 0.58 mm, the intermediate needle had an inner diameter of 2.1 mm, and the outer sheath needle had an inner diameter of 3 mm.

The spinning solutions were loaded into a 10 mL syringe via 30 cm long PTFE tubing (Sigma Aldrich, St. Louis, MO) connecting the syringe to the spinneret. Solutions were pumped to the spinneret at controlled feed rate. The core fluid (mineral oil) was pumped to the core spinneret at varied flow rate ranging from 0.01 to 1 mL/h. The intermediate and outer sheath solutions were pumped to the spinneret at flow rates ranging from 0.1 to 2 mL/h. The spinning distance (distance from spinneret to ground collector) was set at 8 cm. A 17 kV voltage was applied between the needle and the conductive collector. All experiments were

Table 1
Summary of conditions and polymers evaluated.

Outer sheath	Intermediate	Inner FR	Outer FR	Observation
14%CA (dio/ace) 1:2	20%PCL (chl/me) 9:1	0.01–10	0.1–2	No fiber formation
14%CA (dio/ace) 1:2	20% PCL (acc/chl/me) 4:5.4:6	0.5	2	Uniform fibers
20%PCL (chl/me) 9:1	14%CA (dio/acc) 1:2	0.5	2	Uniform fibers
20%PCL (chl/me) 9:1	10%PVA (water)	0.1	3	Uniform fibers
10% PVA (water)	20%PCL (acc/chl/me) 4:5.4:6	0.01–2	0.1–3	Dripping
14%CA (dio/acc) 1:2	10%PVA (water)	0.01–10	0.01–2	Dripping

All polymer compositions are based on wt%. Chloroform (chl), Methanol (me), Dioxan (dio), Acetic acid (acc), Acetone (ace), Dimethyformmade (Dime), Distill water (water). FR = Flow rate.