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Evolution of core–shell structure: From emulsions to ultrafine emulsion electrospun fibers

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ABSTRACT

Due to the relative ease for fabricating fibers with a core–shell structure, emulsion electrospinning has been investigated intensively for making nanofibrous delivery vehicles for local and sustained release of biomolecules such as growth factors. In this investigation, water-in-oil (w/o) emulsions consisting of deionized (DI) water or phosphate buffer saline (PBS), poly(lactic-*co*-glycolic acid) (PLGA) solution and a surfactant were electrospun into fibers for studying the evolution of core–shell structures in emulsion electrospun fibers. Optical microscopy, high speed imaging, fluorescence microscopy and transmission electron microscopy were employed to examine the morphology of the water phase in fibers at different locations of the jet (or fiber) trajectory during emulsion electrospinning. The results indicated that the water phase in emulsion jets underwent multi-level stretching and breakup. When the jet (or fiber) diameter was large (i.e., for the jet near the Taylor cone), the water phase within the jet (or fiber) exhibited a discrete morphology whereas in ultrafine fibers collected beyond certain distance from the Taylor cone, a mostly continuous water phase core was formed. The Rayleigh/capillary instability determined the breakup point of the deformed water phase. When the water phase in emulsions for electrospinning was changed from DI water to PBS, it changed from a continuous state to a discontinuous state in electrospun nanofibers.

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1. Introduction

Electrospinning is a versatile technique for producing ultrafine fibers and hence has attracted great attention in recent years for its applications in several industries including biomedical engineering [1]. This is a simple technology involving the use of a polymer solution reservoir, a high-voltage power supply and a fiber collection device [2]. Using the electrospinning principle, the basic electrospinning method can be developed into other electrospinning technologies such as emulsion electrospinning. Electrospinning can be used to make nanofibrous scaffolds for tissue regeneration [3]. Electrospun nanofibers with core–shell structures are also excellent delivery vehicles for biomolecules, providing their controlled and sustained release [4,5]. Two methods can produce core–shell structured fibers: emulsion electrospinning, and co-axial electrospinning. In emulsion electrospinning, water-in-oil (w/o) emulsions consisting of a water phase (normally, an aqueous solution), an immiscible oil phase (mainly a polymer/organic solvent solution) and a surfactant are generally used. To fabricate core–shell structured fibers with targeted characteristics such as fiber diameter, core-diameter-to-fiber-diameter ratio and core continuity, a good understanding of the evolution of the core–shell structure from the initial w/o emulsions to final electrospun fibers is highly important. However, the structural evolutions have been rarely investigated and reported. Xu et al. made core–shell structured poly(ethylene oxide)/poly(ε-caprolactone) (PEO/PCL) electrospun fibers and speculated that the core–shell formation may be attributed to the deformation of the water phase, solvent evaporation and stretching induced de-emulsification [6]. Yarin reported co-electrospinning of core–shell structured micro- or nanofibers from a single nozzle, using poly(methyl methacrylate)/dimethyl formamide (PMMA/DMF) and polyacrylonitrile/dimethyl formamide (PAN/DMF) polymer solutions as the core and shell sources for fibers, respectively [7]. In their study, only simple cases which yielded core–shell structured fibers with a long, continuous core were discussed. Furthermore, the jetting process is important not only for electrospinning but also for other electrohydrodynamic related techniques [8,9]. Therefore, in the current investigation, w/o emulsions composed of deionized (DI) water or phosphate buffer saline (PBS), poly(lactic-*co*-glycolic acid) (PLGA)/chloroform solution and a surfactant were electrospun into core–shell structured fibers. To study the morphological evolution of the water phase in the emulsion Taylor cone (due to the electrostatic force), microfluidic experiments were conducted

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and the evolution of the water phase within emulsions subjected to an applied electric field was recorded using a high speed camera. In the actual emulsion electrospinning process, at different locations of the jet trajectory, samples were collected for analyzing their structures using different microscopies including transmission electron microscopy (TEM). The effect of the water phase in emulsions on the fiber structure was also studied.

2. Experimental

DI water (pH 7.0) or PBS (pH 7.2) was used to form the fiber core. Span 80 (a surfactant) and fluorescein isothiocyanate isomer I (FITC) were Sigma-Aldrich products. PLGA (LA:GA = 50:50; inherent viscosity: 0.6–0.8 dL/g; medical grade) was purchased from Lakeshore Biomaterials Ltd., USA. Chloroform (AR grade) was supplied by Uni-Chem Co., Korea. A standard electrospinning setup [4] was used for conducting emulsion electrospinning experiments.

For emulsion electrospinning, 1 g of PLGA and 50 μl of Span 80 were dissolved in 10 ml chloroform, forming a PLGA solution (10% w/v). 1 ml of DI water (or PBS) containing FITC (0.1% w/v) was then added to the PLGA solution dropwise, followed by ultra-sonication (Bransonic Digital Sonifier S-450D, New York, U.S.A.; 3 min, 50% of full amplitude) to form a w/o emulsion. The emulsion was transferred to a 5 ml syringe, which had a stainless steel needle (inner diameter: 0.8 mm), and then subjected to an applied voltage (15 kV). The distance between the needle and fiber collector (a flat plate) was 10 cm and the solution feeding rate was maintained at 1.27 ml/h.

To study the evolution of fiber core in an emulsion Taylor cone pendent on the needle tip, microfluidic experiments were designed and conducted. In a typical experiment, an emulsion was slowly pumped into a glass capillary tube (inner diameter: 400 μm) which was subjected to an electric field (field strength: 1.5 kV/cm) (Fig. 1a). When the emulsion entered the electric field, shape changes of the water phase including stretching, breaking and coalescence were observed through an optical microscope (Nikon Eclipse TE2000-U inverted microscope, Japan) and recorded by a high speed CCD camera at 100 fps.

To investigate the core–shell structure evolution in emulsion jets, fibers with different diameters were collected by using cover slides with TEM copper grids at different locations of the emulsion jet path between the stainless steel needle and fiber collector (Fig. 1b). A fluorescence microscope (Nikon Eclipse TE2000-U inverted microscope, Japan) and a TEM (Philips EM208s, the Netherlands) were used to examine the fiber samples collected.

3. Results and discussion

In the current investigation, w/o emulsions consisting of DI water (or PBS) and PLGA solution were used as model emulsions. After emulsion formation, the water phase (DI water or PBS) in emulsions were spherical droplets (diameter: 5–20 μm) which were randomly dispersed in the oil phase (the PLGA solution) (Fig. 2a). To investigate the core–shell structure evolution, the morphology of the water phase in emulsions before emulsion ejection from the needle and in electrospun fibers with a gradually reduced fiber diameter was observed using microfluidic experiments and emulsion electrospinning experiments, respectively. In electrospinning, when a positive high voltage is applied to the conductive needle, a static electric field between the needle tip and fiber collector is present immediately. Therefore, emulsions pumped to the needle tip from a Taylor cone due to the balanced electrostatic force and emulsion surface tension. To simulate this, microfluidics experiments were conducted. It can be seen from Fig. 2b that, under the applied electric field, deformed water droplets were parallel arrays in the electric field direction, appearing like pearl chains. The formation of pearl chain-like water phase could be partially explained by dielectrophoresis [10,11]. Due to the presence of the highest electric field at the w/o interface, water droplets were drawn towards each other, forming a pearl chain-like water phase. Subsequently, some large water droplets changed their elliptical shape into columnar shape due to the electric force, followed by the breakup of water columns, resulting in a string of water droplets with smaller diameters (Fig. 2c). The breakup of deformed water droplets was because some droplets were too large to survive the above-critical electric force, which could be explained by Rayleigh/capillary instability. The columnar water phase or deformed "mother droplets" became unstable and

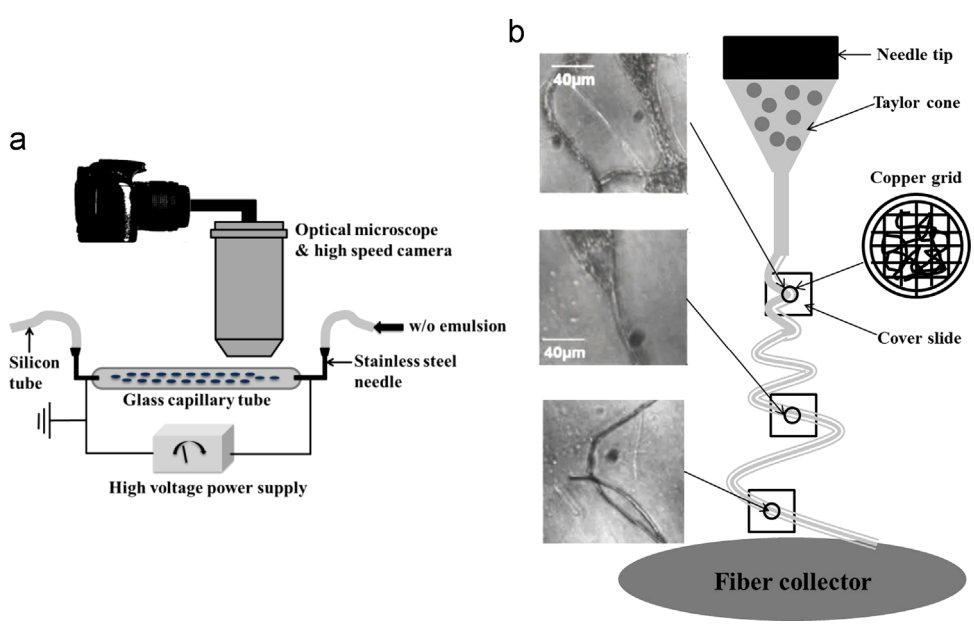

Fig. 1. Experimental setup for investigating the evolution of core–shell structure of emulsion electrospun fibers: (a) microfluidics experiments to observe morphological evolution of the water phase in an emulsion Taylor cone; (b) collection of emulsion electrospun fiber samples at different locations of the emulsion jet path.

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