European Polymer Journal 49 (2013) 3834–3845

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Parameter study and characterization for polyacrylonitrile nanofibers fabricated via centrifugal spinning process

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ARTICLE INFO

Article history:
Received 27 June 2013
Received in revised form 9 September 2013
Accepted 15 September 2013
Available online 25 September 2013

Keywords:
Nanofibers
Centrifugal spinning
Electrospinning
Polyacrylonitrile
Diameter
Crystallinity

ABSTRACT

Electrospinning is currently the most popular method for producing polymer nanofibers. However, the low production rate and safety concern limit the practical use of electrospinning as a cost-effective nanofiber fabrication approach. Herein, we present a novel and simple centrifugal spinning technology that extrudes nanofibers from polymer solutions by using a high-speed rotary and perforated spinneret. Polyacrylonitrile (PAN) nanofibers were prepared by selectively varying parameters that can affect solution intrinsic properties and operational conditions. The resultant PAN nanofibers were characterized by SEM, and XRD. The correlation between fiber morphology and processing conditions was established. Results demonstrated that the fiber morphology can be easily manipulated by controlling the spinning parameters and the centrifugal spinning process is a facile approach for fabricating polymer nanofibers in a large-scale and low-cost fashion.

1. Introduction

Being an important material class with fiber diameters ranging from less than 100 nm to 1000 nm, nanofibers are of great interests owing to their unique structure and properties. As a result of their high surface to volume ratio, extremely long fiber length, and superior mechanical strength, nanofibers can be potentially applied in fields such as filtration, medicine, textile, composite, and energy [1–5]. In the last decade, study on nanofiber production and applications becomes a hot topic in both academic and industrial world. The beneficial and practical applications of nanofibers also give rise to an urgent and insistent demand of producing high-quality nanofibers in a low-cost and large-scale fashion.

The state-of-the-art nanofiber production techniques include phase separation, template synthesis, self-assembly and electrospinning [6–9]. Except for the electrospinning technique, all the other abovementioned nanofiber production approaches have restricted applications due to the complexity of fiber fabrication procedures and limited material choices. Resulting from the simple working principle and relatively wide material choice, electrospinning is probably the most studied nanofiber production method by far. Although it is popular and versatile, electrospinning is not the ideal solution for producing nanofibers. First and foremost, the low production rate of electrospinning highly hampers its use for mass production of nanofibers. Moreover, electrospinning is sensitive to solution conductivity and environmental factors. Last but not least, the application of high-voltage electric field and the inevitable use of solvents lead to potentially increased production cost and safety concern. Thus, advanced technologies should be developed to overcome the disadvantages of electrospinning.

Aiming to eliminate the limitations encountered by the electrospinning process, researchers are sparing no effort to explore the possibility of producing nanofibers in simple, low-cost and large-scale ways. Recently, several studies demonstrated the successful fabrication of micro/nanofibers through centrifugal spinning of polymers, such as polyethylene oxide [10–12], polyvinylidene fluoride [13], polymethyl methacrylate [14], and polycaprolactone

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0014-3057/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2013.09.017

[15]. For example, Ellison's group reported that polybutylene terephthalate fibers centrifugally-spun from polymer melts showed high crystallinity and enhanced molecular orientation [16]. Ravandi and co-workers proposed an electro-centrifuge spinning system that synthesized nanofibers with enhanced quality, fineness and production rate [17]. Most other works associated with centrifugal spinning focused on the exploration of its potential applications and one of the most studied applications for centrifugally-spun nanofibers is probably tissue engineering. Parker and co-workers developed a rotary jet spinning device and applied the as-spun polylactic acid nanofibers in scaffold applications [18]. In another study, poly(L-lactic acid) fibrous tissue scaffolds with controlled nanoscale surface roughness were fabricated via the centrifugal jet spinning process [19]. Similarly, another research by Wang and co-workers implemented commercial cotton candy machine to prepare a fiber matrix of poly-lactic-co-glycolic acid and polystyrene, and its application in scaffold for cell culture was assessed [20]. Amalorpava Mary and co-workers also evaluated the possibility of using centrifugally-spun polycaprolactone and polyvinyl pyrrolidone nanofiber blends as drug delivery vehicle [21].

In this work, a centrifugal spinning system has been fabricated to facilitate the large-scale and low-cost production of fibers with diameters ranging from micro-scale to nano-scale (Fig. 1). The centrifugal spinning system consists of a spinneret, which is located in the center of the spinning platform and contains two small nozzles; several rod collectors, which are radially positioned in the outer perimeter; a DC motor, which is used to rotate the spinneret; and a speed controller, which is for adjusting the rotational speed of the spinneret. Two flexible air foils are placed below the spinneret to generate air turbulence and accommodate the fiber collection. This centrifugal spinning system is simple and is capable of eliminating the limitations of electrospinning process.

During centrifugal spinning, a polymer solution is fed into the spinneret, which is rotated at high speeds. When the rotational speed reaches a critical value, the centrifugal force overcomes the surface tension of the solution and ejects a liquid jet from each nozzle. The jet then undergoes a stretching process, accompanied by rapid evaporation of the solvent, and is eventually deposited on the rod collectors forming dried nanofibers. Since the centrifugal spinning process does not use high-voltage electric field, it alleviates the related safety concern. In addition, the high rotational speed allows fast and scalable fiber fabrication, which can dramatically improve the production rate by two to three orders of magnitude and reduce the production cost when compared with the electrospinning process. Moreover, the centrifugal spinning process enables the fabrication of nanofibers from polymer solutions with much higher concentrations than the electrospinning process, which also reduces the production cost by using less solvent.

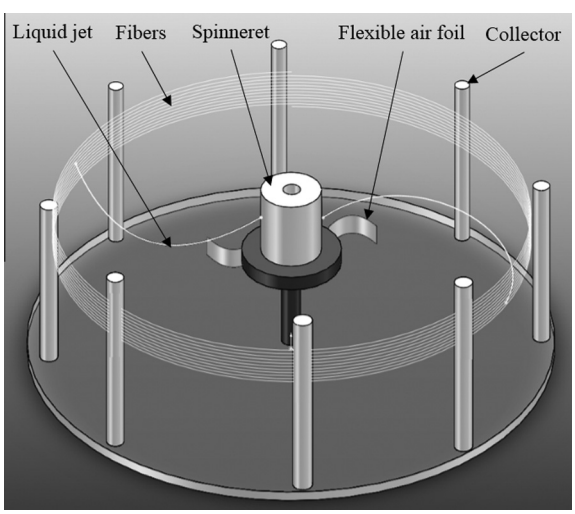

Fig. 1. Schematic of the centrifugal spinning system.

Polyacrylonitrile (PAN) is a well-known polymer with good stability and mechanical properties. PAN nanofibers can be potentially applied into multiple fields including tissue engineering, sensing, composites, battery separators, and precursors for producing carbon nanofibers [22–27]. Among the various applications, the most important role of PAN nanofibers is the precursor for producing carbon nanofibers due to its high carbon yield and flexibility for tailoring the structures of resultant carbon nanofibers [26]. Therefore, the mass production of high-quality PAN nanofibers is urgently demanded. In this study, we hypothesized the feasibility of producing PAN nanofibers with the newly-developed and facile centrifugal spinning system. In centrifugal spinning process, the morphology of nanofibers mainly depends on solution intrinsic properties and operational parameters. Hence, solution intrinsic properties including viscosity and surface tension were measured and critical polymer concentration for centrifugal spinning was determined. Operational parameters, such as rotational speed, nozzle diameter and nozzle-collector distance, were varied and their effects on the nanofiber morphology were evaluated. The morphology of resultant nanofibers was characterized using scanning electron microscopy (SEM); and the structural analysis was performed using X-ray diffraction (XRD). In order to fully understand this new process and take good control for the morphology of resultant products, the fundamental processing-structure correlations were studied and established.

2. Experimental

2.1. PAN solution preparation and property measurement

Polyacrylonitrile (PAN, homopolymer, Mw = 150,000) was purchased from Pfaltz & Bauer Inc. N, N-dimethylformamide (DMF, Aldrich) was selected as the solvent to dissolve PAN polymer. A series of PAN solutions with concentrations ranging from 0 (only solvent) to 15 wt.% were prepared by mechanically stirring at 60 °C for 24 h.

To understand the effects of solution intrinsic properties on the morphology of as-spun PAN nanofibers, the viscosities and surface tensions of PAN solutions were measured prior to centrifugal spinning. During the viscosity measurements, PAN solutions ranging from 0 to 15 wt.% were loaded into the viscometer (ATS Rheosystem) fitted