

Morphology control of bi-component polymer nanofibers produced by gas jet process



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ABSTRACT

This study investigates morphology control of polymer nanofibers produced from solutions of two immiscible polymers in mutually miscible solvents by gas jet fiber (GJF) method. The morphology is controlled by selecting the solvents with a range of vapor pressure and solubility parameter to govern respectively the evaporation rates and the polymer-solvent affinity. Bi-component nanofibers with core-shell, bi-lobal, and interpenetrating network (IPN) morphology are produced by evaporation-induced phase separation of the polymers during spinning of homogeneous solutions of hydrophobic polyvinyl acetate (PVAc) and hydrophilic polyvinyl pyrrolidone (PVP) in two mutually miscible solvents. The tendency of phase-separation is inferred from the values of polymer-solvent mixture affinity. The results indicate that solvent pairs with closely matched vapor pressure yield IPN morphology, while solvents with large differences in vapor pressure produce core-shell morphology. Bi-lobal morphology is produced for solvent pairs with moderate differences in vapor pressure. In each case, nanofibers of smaller diameter are obtained when solvent pairs of lower vapor pressure are used.

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1. Introduction

Design of polymeric nanofibers is an active area of research due to the prospect of tailoring morphology and diameter selection to suit a host of applications in drug delivery systems, tissue engineering, and functional scaffolds [1–9]. Nanofibers are useful in removal of particulate pollutants, e.g., as filtration media for household and industrial installation [9–12] or can be used in manufacturing of protective clothing [9,13,14].

Nanofibers are usually produced by the methods of drawing [15], electrospinning [11,16–18], melt blowing [19–21], or solution blowing process [22–24] that also involves super-sonic gas jet [25,26]. In drawing, extruded strands of molten polymers are drawn into smaller diameter fibers, in electrospinning, an electrical field draws liquid drops into liquid jets, and in melt blowing a stream of high velocity hot air draws polymer melt into an ensemble of fibers. Medeiros et al. [22] used high pressure gas jet in a co-axial injection set up to blow core polymer solutions into nanofibers. These researchers observed multiple liquid jets emanating from the gas-liquid interfaces. Sinha et al. [27] applied

electric field to stabilize the liquid jets in co-axial solution blowing process. Detailed theoretical investigation of the mechanisms of fiber formation and solvent drying in solution blowing process was also reported [24,27–29]. Nylon 6 nanofibers of 20–50 nm diameter were produced in a process that combined electrospinning and super-sonic blowing process [26].

In the present work, the nanofibers were produced using an efficient method named Gas Jet Fiber (GJF) process [30–32], where the aerodynamic force is the only force responsible for liquid jet initiation from a delivery system and flapping and bending instability mechanisms lead to liquid jet attenuation [31]. In addition, in GJF process, the liquid jet meets the gas jet outside the nozzle system, e.g., on the surface of a pendent drop, at the tip of the nozzle, or on a flat surface as elaborated by Benavides et al. [30]. A liquid jet is initiated within tenth of a second after coming in contact with the gas jet. The polymer solidifies into fibers as the solvent evaporates rapidly [30,31]. The GJF process produces fluffy nanofibers from both polymer melts and solutions with different morphologies.

In the context of the different morphological forms reported in this paper, we discuss the steps that play significant role in fiber formation in the GJF process, namely stretching of the liquid jet, evaporation of the solvent, and fiber solidification due to phase separation of the polymers. Fig. 1 presents a schematic showing the

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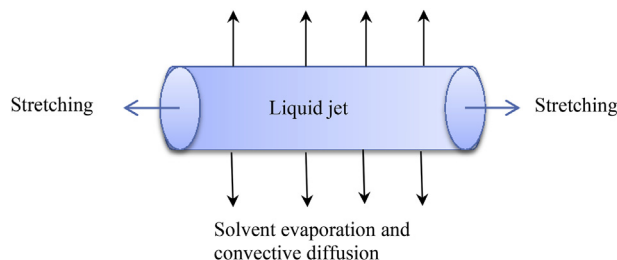
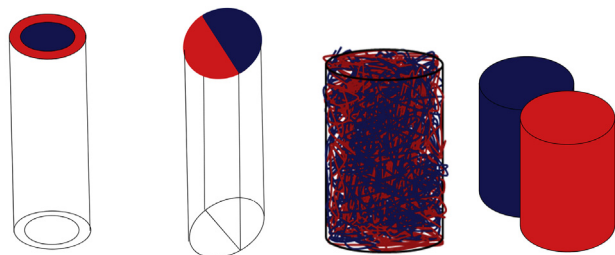


Fig. 1. Schematic showing simultaneous liquid jet stretching and solvent loss due to evaporation.

processes involved in fiber formation in GJF process. It is important to have a thorough understanding of the above three inter-related physical phenomena in order to design polymer nanofibers with unique morphological forms.

The diameter selection of the nanofibers is dependent on the stretching force of the gas jet and the viscosity of the liquid jet. Stretching continues until solvent evaporation leads to an increase of the viscosity to a level that further stretching is not possible. The present study focused on nanofibers derived from two immiscible polymers spun from a single homogeneous solution in two mutually miscible solvents. It is evident that nanofibers of multiple polymers provide scopes for design and optimization of useful properties in non-woven mats, e.g., by adjusting the amounts of the polymers and by tuning the organization of individual polymers in single fibers [33–43]. Single fibers containing one hydrophobic and one hydrophilic polymer are attractive in air purification, in removing moisture and hydrocarbon vapors, and in separation of hydrophobic and hydrophilic liquids [9,33,35]. The two polymers in bi-component nanofibers can be organized in various morphological forms, such as core–shell, bi-lobal, side-by-side, or interpenetrating network (IPN), as schematically presented in Fig. 2. In core–shell morphology, one polymer is encapsulated by the other (Fig. 2a). In bilobal morphology (Fig. 2b), the fiber cross section is composed of both the polymers with either a sharp or a diffused interphase. In IPN morphology (Fig. 2c), both polymers form domains of size less than 10 nm and are co-continuous. A topologically similar fiber to Fig. 2b is side-by-side fibers (shown in Fig. 2d) reported in electrospinning literature using adjacent two-nozzle electrospinning set up [44–48]. It is apparent that the area of contact between the polymers is higher for bi-lobal nanofibers than for side-by-side nanofibers.

Fabrication of core–shell [27,49–56] and side by side nanofibers (such as in Fig. 2d) [44,45,47,48,57] was reported in conjunction



(a) Core-shell (b) Bi-lobal (c) IPN (d) Side-by-side

Fig. 2. Schematic of anticipated fiber morphology from bi-component immiscible polymer systems. The two polymer are represented by red and blue colored domains in each case. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with the use of prototype co-axial and side-by-side nozzles. The techniques of template growth [58,59] and template synthesis [60,61] were also successful in fabrication of core–shell nanofibers. In the present work, an alternative method was developed for fabrication of bi-component nanofibers of different morphological forms via phase separation of the polymers induced by evaporation of the solvents during spinning.

In this case, the spinning solution was prepared by dissolving the polymers in a mixture of two mutually miscible solvents. Several factors were considered that influence the morphology development, e.g., by directly impacting the rate of diffusion of the solvents to the fiber–gas interfaces, solvent transport to the bulk gas, and phase separation of the polymers. These are gas flow rate, solvent vapor pressure, polymer concentration in the solution, solubility parameter, interfacial tension, and molecular weight of the polymers [1,62,63].

Many researchers claimed solvent evaporation rate as an important parameter in production of fibers with core–shell, side-by-side, or other morphological forms [62,63]. In this regard, a unique contribution of the present study is the production of nanofibers of core–shell, IPN, and bi-lobal morphologies from the same polymer pair by choosing selective mutually miscible solvent pairs. Solvents of different vapor pressure and solubility parameter were chosen to attain differences in evaporation rates of the solvents and the tendency of phase separation of the polymers. The pair of miscible solvents contained one good solvent for each polymer. Spinning of bi-component nanofibers with different morphologies using one homogenous solution has an additional advantage of better diameter control, e.g., by prolonging the stretching process when the solvents have low vapor pressure.

The concept of bi-component nanofibers of different morphologies was validated by producing fibers of polyvinylacetate (PVAc) and polyvinylpyrrolidone (PVP). PVAc is hydrophobic and PVP is hydrophilic in nature. In each case, the single fiber strands contained one hydrophilic and one hydrophobic polymer. The specific morphological forms were interpreted in terms of solubility parameter and vapor pressure of the solvents. Prediction of morphology using thorough quantitative analysis of the phase separation dynamics and coupled mass and momentum transport equations was not possible as the four-component experimental system that we investigated in this study is quite complex. First, the phase diagram of two polymers in solutions of two mutually miscible solvents is difficult to obtain experimentally. Existing literature also provided no guidance. Second, an exhaustive solution of coupled mass and momentum transfer equations is not possible at this point due to lack of precise knowledge of the dynamics of polymer phase separation in the liquid jet. On the other hand, the experimentally obtained two-component polymer fibers organized in core–shell, side-by-side, and IPN arrangements can be very useful in mitigating several technical challenges, such as to maintain a balance of burst vs. timed release of drugs in wound dressing materials or in high efficiency removal of water droplets from diesel fuel. In view of the above, we resorted to presenting the experimental findings in this paper using qualitative, first-order arguments based on the solubility parameter and the difference of vapor pressure of the two solvents.

2. Experimental section

2.1. Sample preparation

The polymer solutions were prepared at a fixed polymer concentration of 3 wt.% with PVP and PVAc content maintained at 1:1 wt./wt. ratio. The two solvents were used in 1:1 wt./wt. ratio from among the following pairs: methanol/ethyl acetate, 1-

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