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Electric field distribution and initial jet motion induced by spinneret configuration for molecular orientation in electrospun fibers

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ABSTRACT

Understanding the molecular orientation of electrospun fibers is a key challenge for tailoring fiber properties. The studies of electric field distribution, and the motion of the initial portion of the polymer jet, are of interest for clarifying molecular orientation in fibers during electrospinning. In this work, we study the impact of electric field distribution and the initial jet motion induced by two kinds of spinneret configurations, referred to as a needle configuration and a hole configuration, on molecular orientation in electrospun PEO fibers. Using FE-SEM, FTIR and WAXD techniques, the fiber diameter and molecular orientation of the fibers prepared with the needle electrospinning system and the hole electrospinning system are characterized. To explore jet stretching and chain orientation during the spinning process, electric field simulation and high-speed photography are performed to obtain the electric field characteristics and to measure the initial jet velocities for the needle and the hole systems. Our results reveal the higher electric field strength around the spinneret and the larger initial jet velocities, which depend on the spinneret configuration, result in the higher degree of molecular orientation in fibers.

1. Introduction

Electrospinning, which has now been established as an efficient technique for producing continuous nanofibers, is characterized by converting polymer solutions into nanofibers using an applied electric field. Typically, the process of electrospinning involves the presence of electrostatic charge to a polymer solution under a high-voltage supply. The induced surface charges cause the solution drop to distort into a cone shape. Above the critical level of voltage, a solution jet erupted from the cone travels to a collector, undergoing stretching and solidification due to the electric-driven drawing force and solvent evaporation. Such stretching not only is responsible for jet thinning but also affects the microstructure, including molecular orientation and crystallization behavior, within as-spun fibers [1]. Indeed, macroscopic morphology and internal microstructure of electrospun polymer fibers determine their improved mechanical and physical properties [2,3]. However, compared to the vast studies on controlling the macroscopic morphology of electrospun fibers, much less has been done on predicting and tailoring the microstructure of as-spun nanofibers.

It is well known that the orientation of polymer chains within fibers can affect the mechanical properties of the fibers [4,5]. Unfortunately, detailed studies on the evolution of chain orientation during electrospinning are limited. In particular, an explanation of the electric field for molecular orientation in electrospun fibers is still under study. The electrospinning process, in its simplest form, contains a spinneret and a collector as two electrodes to create the electric field under an applied voltage. Several researchers investigated the effect of collectors on molecular orientation within electrospun fibers, based either on mats or on single fibers [6–13]. Fenessey and Farris first proposed that a rotating mandrel collector operating at high rotation speeds can be used to induce increased molecular orientation of polyacrylonitrile fibers [6]. Based on this result, several researchers later used various types of rotating collectors to study molecular orientation of other polymer systems and arrived at the similar conclusions [9,10]. Pellerin and Kakade et al. reported that using air gap (created by two pieces of conductive plates) as a collector can induce an extremely high degree of molecular orientation of electrospun fibers [7,8]. In addition, molecular orientation in a single fiber has been analyzed using selected area electron diffraction patterns, revealing the difference between random-collected fibers and well-aligned fibers in the degree of molecular orientation [11,12]. Nevertheless, there is little evidence to show the impact of electric field distribution induced by spinnerets on molecular orientation in electrospun fibers. During spinning process, spinneret configurations play an important role in the electric field distribution,

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which can result in the degree of stretching of polymer chains. Our previous work explored an electrospinning system with a “hole configuration” spinneret [14]. We reported that the hole system can create an uniform electric field distribution that has a significant influence on fiber morphology in comparison with the conventional needle electrospinning system. Enough interest has been aroused to study the effect of the two kinds of spinnerets on molecular orientation in as-spun fibers.

Focusing on the electric fields created by the electrospinning system with the hole configuration spinneret (called “hole system” in this paper) and the conventional needle eletrospinning system (called “needle system” in this paper), we try to explore the role of electric field in the fiber stretching in diameter and molecular orientation during spinning process in this study. Conventional techniques used for studying molecular orientation require well-aligned fibers, and these results involve molecular orientation and fiber alignment. We used the most commonly used rotary drum and air gap collectors to align fibers to study molecular orientation in electrospun fibers in this paper. To exclude the effect of collecting way, in the same group of a comparative experiment, the collector and all the parameters used are maintained the same for both the systems except for the spinneret in which the polymer jet is formed. Field emission scanning electron microscopy (FE-SEM) is used to confirm macroscopic morphology of the resulting Polyethylene oxide (PEO) fibers. Polarized Fourier transform infrared spectroscopy (FTIR) and wide-angle X-ray diffraction (WAXD) are performed to determine molecular orientation in as-spun fibers. We apply electric field simulation and high-speed dynamic analysis of the initial portion of an electrospinning jet to explain the discrepancy of fiber diameter and molecular orientation of the electrospun fibers prepared by the two kinds of systems.

2. Experiments and simulation

2.1. Experimental materials

PEO, with an average molecular weight (M_w) of 600,000 g/mol, was purchased from Sigma-Aldrich, Inc., USA and used as received. A homogeneous PEO solution with 5 wt% concentration was prepared by dissolving PEO powder into distilled water followed by gently stirring for 5 h with an electric mixer (AM200, Shanghai Onlly, Inc., China) at 25 °C.

2.2. Experimental setup and processing conditions

Schematic illustration of the electrospinning system with a needle spinneret and a hole spinneret is displayed in Fig. 1. For the needle spinneret, a stainless steel needle with 0.5 mm inner diameter, 0.8 mm outer diameter and 25 mm length was used (Fig. 1a). As illustrated in Fig. 1b and c, the hole spinneret was composed of an aluminum material electrode and a plastic plate containing a circular hole of 0.5 mm diameter. The hole was drilled in the central location of the plastic plate made of polytetrafluoroethylene (PTFE), and a solution chamber was formed between the electrode and plastic plate.

To confirm the effect of spinneret configuration on orientation in as-spun fibers, two groups of comparative experiment were carried out, using rotary drum and air gap, respectively, to collect aligned fiber mats. For the air gap aligned fibers, the electrostatic attractive forces between the positive residual charges on the fibers and the negative charges induced on the surfaces of the gap edges, in concert with the repulsive forces between the deposited and the upcoming fibers, result in macroscopic alignment of the fibers [15]. The rotary drum made of a stainless steel cylinder with 24 cm length and 8 cm diameter kept the take-up velocity of 6 m/s (Fig. 1d). The air gap collector contained two aluminum plates of 15 cm length, 5 cm width and 0.5 cm thick, with a gap of 1 cm in between (Fig. 1e).

The PEO solution in a syringe was forced by a syringe pump (KDS 220, KD Scientific, Inc., USA) at a constant flow rate of 1 mL/h. A high voltage power supply (ES-60P 10 W/DDPM, Gamma High Voltage Research, USA) with an applied voltage of 20 kV was applied to the spinneret and collector. The distance between the spinneret outlet and drum collector was 20 cm. The experiments were carried out at the relative humid of 45% ± 5% at 25 °C.

2.3. Characterization

Morphology of the fiber mat was observed using a scanning electron microscope (SEM) (JSM-5600LV, Japan) at an accelerating voltage of 1.5 kV after gold coating. Then 500 fibers collected from the SEM images were used in calculating the average fiber diameter by Photoshop CS6 (Adobe System Inc., San Jose, CA, USA) software.

Molecular orientation was characterized by Fourier transform infrared (FTIR) and wide-angle X-ray diffraction (WAXD). Polarized FTIR spectra based on the transmission mode were carried out on a Thermo Nicolet 6700 at the room temperature. For each sample, a total of 64 scans were signal-average at a resolution of 1 cm^{-1} during spectrum acquisition.

WAXD measurements were recorded at the beam line BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China) with a wavelength of 0.124 nm [16]. The two-dimensional (2D) pattern was accumulated over periods of 50 s, which was then background corrected and normalized using the standard procedure. The sample-to-

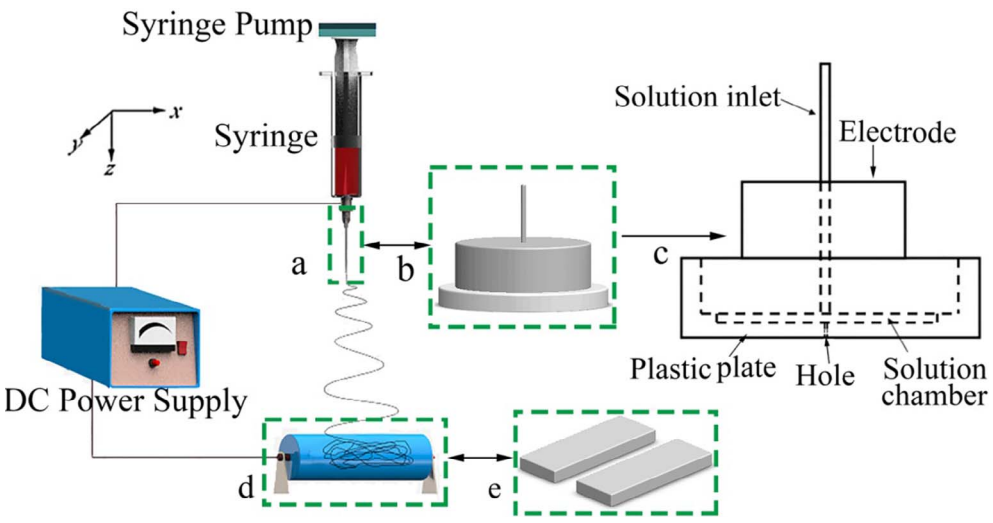

Fig. 1. A schematic of experimental setup: (a) needle spinneret, (b) hole spinneret, (c) the sketch of hole spinneret, (d) rotary drum, and (e) air gap.