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Drawing Suspended Polymer Micro/Nanofibers Using Glass Micropipettes

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ABSTRACT. This paper proposes a method for fabricating suspended micro/nanoscale polymer fibers continuously, in which polymeric micro/nanofibers are formed by drawing and solidification of a viscous liquid polymer solution which is pumped through a glass micropipette. By controlling the drawing parameters, this method is demonstrated to form networks of suspended fibers having amorphous internal structure and uniform diameters from micrometers down to sub-50 nm for different molecular weights of polystyrene dissolved in xylene.

KEYWORDS. Fiber drawing, polymer fibers, nanomanipulation, nanorheology.

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Fabrication of polymer fibers with diameters ranging from micron to nanometer scales has generated significant interest due to its potential impact in many applications such as nano-electronics[1] and optical sensors[2]. These applications require the fabrication of customized one (1D), two (2D) and three-dimensional (3D) network of nanofibers. This hierarchical approach first creates the individual components and then assembles them together into larger structures. The first step in such a manufacturing approach involves fabricating fibers. Recently, techniques such as self-assembly[3], drawing[4,5], template synthesis[6], and electrospinning[7,8] have been used to synthesize polymer fibers of micron and nanometer diameters. Of all the techniques, electrospinning is the most popular process that allows for the continuous production of fibers ranging from tens of nanometer to a few microns in diameter. The major challenges encountered in electrospinning are the uniformity of fiber diameter and random fiber alignment. Numerous schemes have been proposed[9,10] for aligning the electrospun fibers.

On the other hand, in the drawing process, suspended fibers are fabricated by contacting a previously deposited polymer solution droplet with a sharp probe tip such as a scanning tunneling microscope nanoprobe[5] and drawing it as a liquid fiber which is then solidified by rapid evaporation of the solvent due to the high surface area to volume ratio at reduced length scales. The drawn fiber is then connected to another previously deposited polymer solution droplet thus forming a suspended fiber. Here, the pre-deposition of droplets significantly limits the ability to extend this technique, especially in three dimensional configurations and hard to access spatial geometries. Furthermore, there is a finite time within which the fibers can be pulled as the viscosity of the droplet continuously increases with time due to solvent evaporation from the deposited droplet. The continual shrinkage in the volume of the polymer solution droplet affects the diameter of the fiber drawn and limits the continuous drawing of fibers.

To overcome the limitations of the aforementioned drawing process, a method based on drawing suspended fibers continuously using glass micropipettes is proposed in this paper. Here, the polymer solution is pumped continuously through the glass micropipette, which provides greater flexibility in drawing continuous fibers in any configuration. Moreover, this method offers increased flexibility in the

control of key parameters of drawing such as waiting time before drawing, the drawing speed and the drawn upon surface topography; thus, enabling repeatability and control on the dimensions of the fabricated fibers. For demonstrating the capabilities of this method, suspended polystyrene (PS) fibers are drawn. PS is selected as the polymer material since it is commercially available with wide range of molecular weights (M_w) and is well-characterized. In the experiments, M_w=900,000 gms/mol is typically used unless specified. PS (PolyChem) is dissolved in xylene 10% by weight to prepare the polymer solutions. Furthermore, glass micropipettes with few micrometers in tip diameter are pulled in a pipette puller (P-97, Sutter Instruments), and a micropump (BS-8000, Braintree Scientific) is used to pump the polymer solution inside the micropipette continuously at a constant flow rate of 15 μl/min. Finally, experiments are performed under ambient conditions.

The schematic in Fig. 1 depicts the basic steps of glass micropipette based drawing of polymer fibers. The pipette is fixed almost perpendicular to a given substrate which is moved by a motorized XYZ nanopositioner (VP25-XA, Newport). At first, the substrate is raised until it comes into contact with the polymer droplet at the end of the glass micropipette tip (Step A, Fig. 1). The substrate is selected to be solvophilic (having less than 30 degrees contact angle with the liquid polymer solution) to have a reliable droplet formation and adhesion. Next, the pipette is moved vertically with a constant speed and stopped at a constant height before laterally drawing a suspended fiber (Step B). Here, the waiting time after stopping, i.e. before drawing a fiber, offers control on the viscosity of the polymer solution. The stage is then subsequently moved along a predetermined XYZ trajectory with a constant speed, thus forming the solid polymer fiber by the evaporation of the solvent (Step C). After drawing the fiber, the substrate is brought in contact with the glass micropipette, thus forming a suspended fiber (Step D). Finally, the substrate is retracted quickly, which breaks the contact with the droplet (Step E) or it continues to draw other sequential fibers without breaking its contact.

Using the above process, suspended PS fibers in many different configurations are demonstrated. At first, to show the repeatability and continuity of the drawing process, an array of PS fibers is drawn

sequentially on a flat silicon substrate. Scanning electron microscope (SEM, Hitachi 2460N) image of the fibers is displayed in Fig. 2(a).

One of the most significant challenges of the fiber drawing process is to draw sub-100 nanometer fibers consistently. Using the proposed method, repeatedly less than 50 nm fibers were drawn and a sample PS nanofiber with diameter of approximately 37 nm is shown in Fig. 2(b). Here, M_w selection is a critical parameter for the strength of such nanofibers as low M_w sub-50 nm nanofibers break easily during SEM or transmission electron microscopy (TEM) imaging due to heating and electrical charge build up effects.

One of the key advantages of fabricating fibers using the proposed method is the versatility it offers in realizing different diameter fibers in the same process. Controlling the waiting time in Step B while the drawing speed is kept high enough at 2 mm/sec to form uniform fibers, different diameter fibers are demonstrated in the same process as displayed in Fig. 2(c). Here, a cross pattern is formed from two fibers which are around 100 nm and 1 μm diameters, respectively. To show the detailed effect of the waiting time in Step B, PS fibers are drawn repeatedly 40 times for a given waiting time and the average and standard deviation of the drawn fiber diameters around the fiber center are measured using SEM images. Results shown in Fig. 3 demonstrate that there is a direct monotonically increasing correlation with the waiting time and the fiber diameter. During waiting before drawing a fiber, the solvent evaporates constantly from the ejected volume and waiting for a longer period of time increases the viscosity of the solution which, in turn, leads to larger diameter fibers for the same drawing parameters.

Fiber networks are critical for wide range of ultra strong fabric manufacturing and micro/nano-device applications. Creating such networks on any flat or curved surface involves depositing fibers sequentially in layers, where each new layer is orthogonal at some desired orientation to the previously deposited layer. Such sample 2D fiber networks are demonstrated in Fig. 2(d) using the proposed method.

Polymer solutions undergoing high elongational flows can result in extension of the polymer chains. This can potentially impart an elongational order directed along the fiber axis. Previous studies have shown either no orientation[11] or high orientation[12] order along the fiber axis. Additionally, regions of low orientation and high orientation within the same fiber have also been reported[13]. To determine the internal structure of the drawn fibers, an approximately 75 nanometer diameter PS nanofiber (M_w=2,000,000 gms/mol) was drawn across fine copper grids for TEM imaging. The TEM imaging was carried out at 120 kV using a JEOL-120CX TEMSCAN. The TEM image and resulting diffraction pattern for the nanofiber are shown in Fig. 4. Diffraction pattern obtained across the length of the fiber suggests that it is uniformly amorphous. If a crystalline polymer instead of PS is drawn with the same method, highly oriented and ultra high strength polymer fibers could be formed which is a future work.

In conclusion, a method to fabricate controlled diameter suspended PS micro/nanometer scale fibers continuously is presented using glass micropipettes. Amorphous fibers with diameters down to 37 nm and lengths up to several millimeters, along with networks in one and two dimensional configurations have been fabricated. By controlling the waiting time before drawing, it is possible to control the diameter of the fabricated fibers. Though the method is currently serial, an array of pipettes would allow for parallel manufacturing of fiber arrays, involving different polymer blends and fiber dimensions. These suspended fibers can be used for fabricating ultra strong fabrics, biological scaffoldings, nanosensors, and polymer fibrillar adhesives[14].

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FIGURE CAPTIONS

FIG. 1. Schematic steps of the micropipette based suspended polymer fiber drawing method for a single fiber case: *Step A*: Raise the substrate until it comes into contact with the polymer droplet; *Step B*: Move the micropipette vertically with a constant speed and stop at a constant height; *Step C*: Move the stage along a predetermined trajectory with a constant speed while forming the solid polymer fiber by the evaporation of the solvent; *Step D*: Contact the substrate with the pipette to suspend the fiber; *Step E*: Break the fiber or continue to draw subsequent ones.

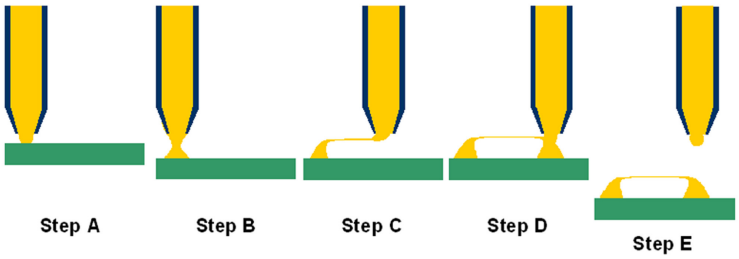

FIG. 2. SEM images of sample drawn suspended PS fibers: (a) continuously drawn array of fibers on a silicon substrate, (b) a 37 nm nanofiber (M_w=650,000 gms/mol), (c) a cross-pattern of two fibers showing the fiber diameter control in the same drawing process, and (d) 2D fiber network.

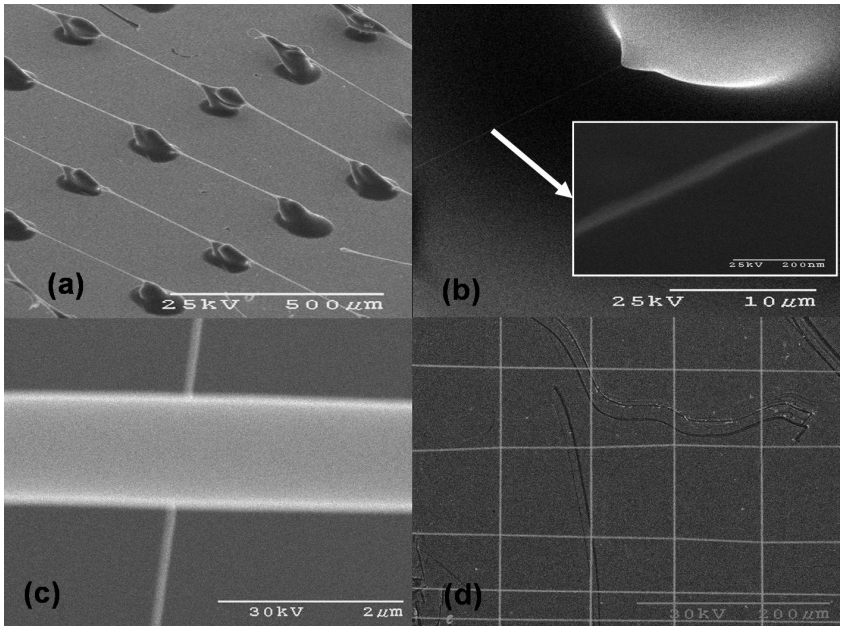

FIG. 3. The effect of waiting time in Step B in Fig. 1 on the PS fiber diameter.

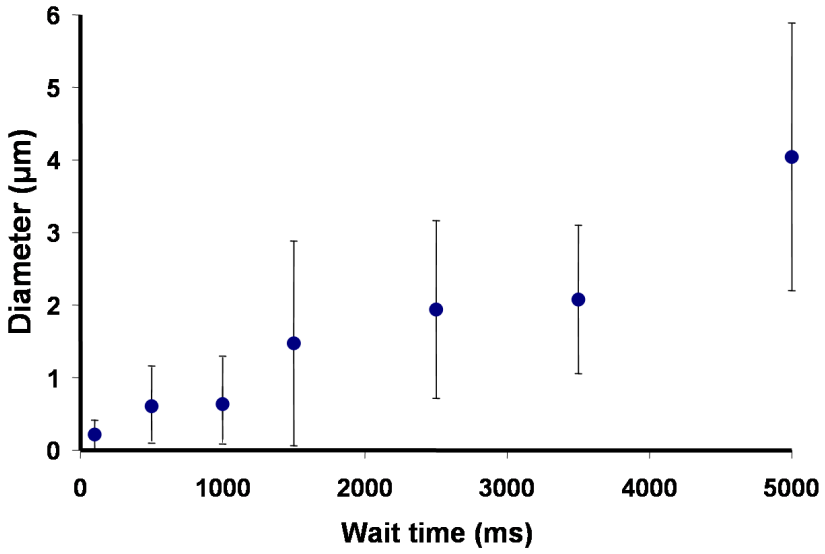

FIG. 4. TEM and diffraction images of a PS nanofiber with approximately 75 nm diameter (M_w=2,000,000 gms/mol).

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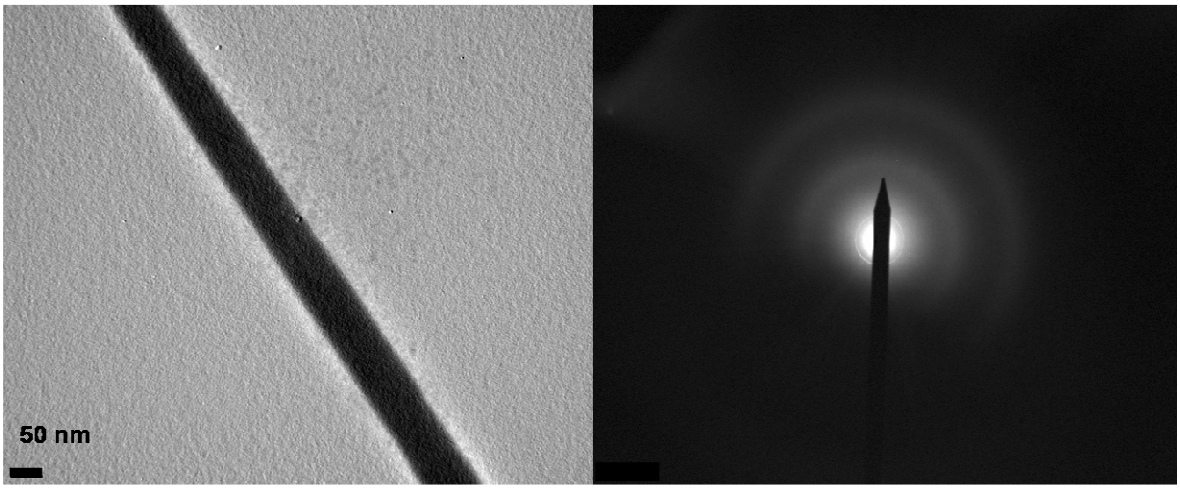

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