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Upward needleless electrospinning of multiple nanofibers

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Abstract

A new approach to electrospinning of polymer nanofibers is proposed. A two-layer system, with the lower layer being a ferromagnetic suspension and the upper layer a polymer solution, is subject to a normal magnetic field provided by a permanent magnet or a coil. As a result, steady vertical spikes of magnetic suspension perturbed the interlayer interface, as well as the free surface of the uppermost polymer layer. When a normal electric field is applied in addition to the system, the perturbations of the free surface become sites of jetting directed upward. Multiple electrified jets undergo strong stretching by the electric field and bending instability, solvent evaporates and solidified nanofibers deposit on the upper counter-electrode, as in an ordinary electrospinning process. However, the production rate is shown to be higher.

Keywords: Electrospinning; Polymer; Nanofibers

A normal magnetic field is known to have a destabilizing effect on planar free surfaces of magnetizable fluids [1,2]. As a result of its action, numerous sharp conical spikes stand vertically at the free surface of a horizontal shallow layer of magnetic fluid in a vessel. Moreover, if a normal electric field is applied in addition, the spikes could become origins of jets issued upwards [3,4]. Note that leaky dielectric fluids are also capable of upward jetting from the free surface in strong normal electric fields [5–8].

Electrospinning of polymer nanofibers, which is the main aim of the present work, attracted significant attention during the last several years as a simple and straightforward method of production of nanostructures, which are of interest in many applications [9–15]. These include filter media, composite materials, biomedical applications (tissue engineering, scaffolds, bandages, drug release systems), protective clothing, micro- and optoelectronic devices, photonic crystals and flexible photocells [10,13–15]. In electrospinning electric forces imposed by a capacitor-like electric field on a droplet of polymer solution result in jetting from its tip. The jet is unstable due to the bending instability which results in strong looping and stretching of the jet elements [11,12]. After the solvent evaporates, nanofibers with a diameter in the submicron range are deposited on the counter-electrode. At present, drops are typically suspended at the edge of a needle attached to a vessel filled with polymer solution, where supply to the droplet is sustained. Therefore a single jet is issued from a single needle, and to achieve a high production rate, one needs to use many needles. The latter is technologically inconvenient due to its complexity and high probability of clogging.

The main aim of the present work is to realize multiple upward jets from the free surface similar to that in magnetohydrodynamics, with polymer solutions. If such a goal could be achieved, electrospinning of multiple jets could be realized without any needles.

In Refs. [1–4] magnetic fluids were prepared by mixing magnetic powder in kerosene with oleic acid as a stabilizer. Using such fluids we were unable to initiate multiple jetting from the free surface of fluid layers under the action of the normal magnetic and electric fields similar to those reported in Refs. [3,4]. Moreover, the fluids were also incompatible with solutions of poly(ethylene oxide), PEO, in water–ethanol mixtures which were planned to be used for electrospinning. Therefore a different composition of magnetic fluids was used. Ferric–ferrous oxide black (F_3O_4, magnetite) of laboratory grade (Fisher Chemicals) was mixed with silicone oil (Fluka). Magnetite (4 g) was mixed with silicone oil (8 g) and magnetic fluid obtained was placed into a dish. A magnetic field was provided by a

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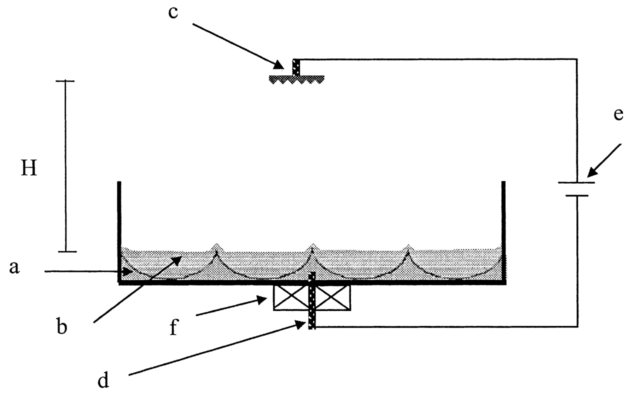

Fig. 1. Schematic drawing of the experimental setup. (a) Layer of magnetic liquid, (b) layer of polymer solution, (c) counter-electrode located at a distance H from the free surface of the polymer, (d) electrode submerged into magnetic fluid, (e) high voltage source, and (f) strong permanent magnet or electromagnet.

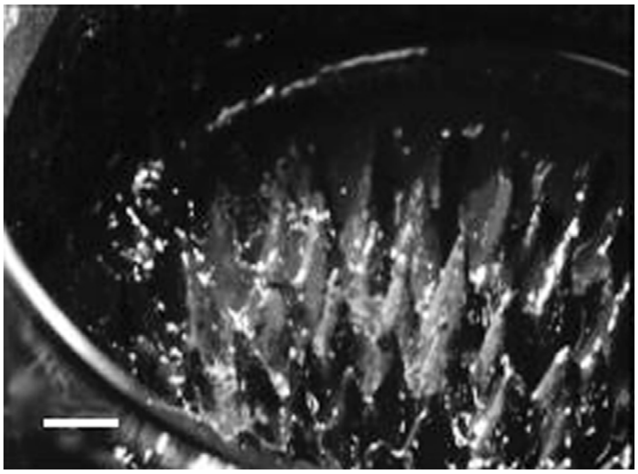

Fig. 2. A side view image of the spiking effect of a silicon oil-based magnetic fluid under the action of a permanent magnet. The bar is 10 mm.

permanent magnet with magnetic induction of 70 mT, or by a coil of magnetic induction of 50 mT. Under the action of the magnetic field numerous steady spikes could be generated at the free surface of the magnetic fluid.

A solution of 2% wt. of PEO (Aldrich, $M_w = 600,000$) in 40 wt.% aqueous ethyl alcohol was prepared. The PEO solution (12 ml) was carefully added above the magnetic fluid. The experiments were carried out in a device consisting of Pyrex crystallizing dish ($\phi 70 \times 18$ mm) fixed above a magnet (Fig. 1). An electrode was inserted through

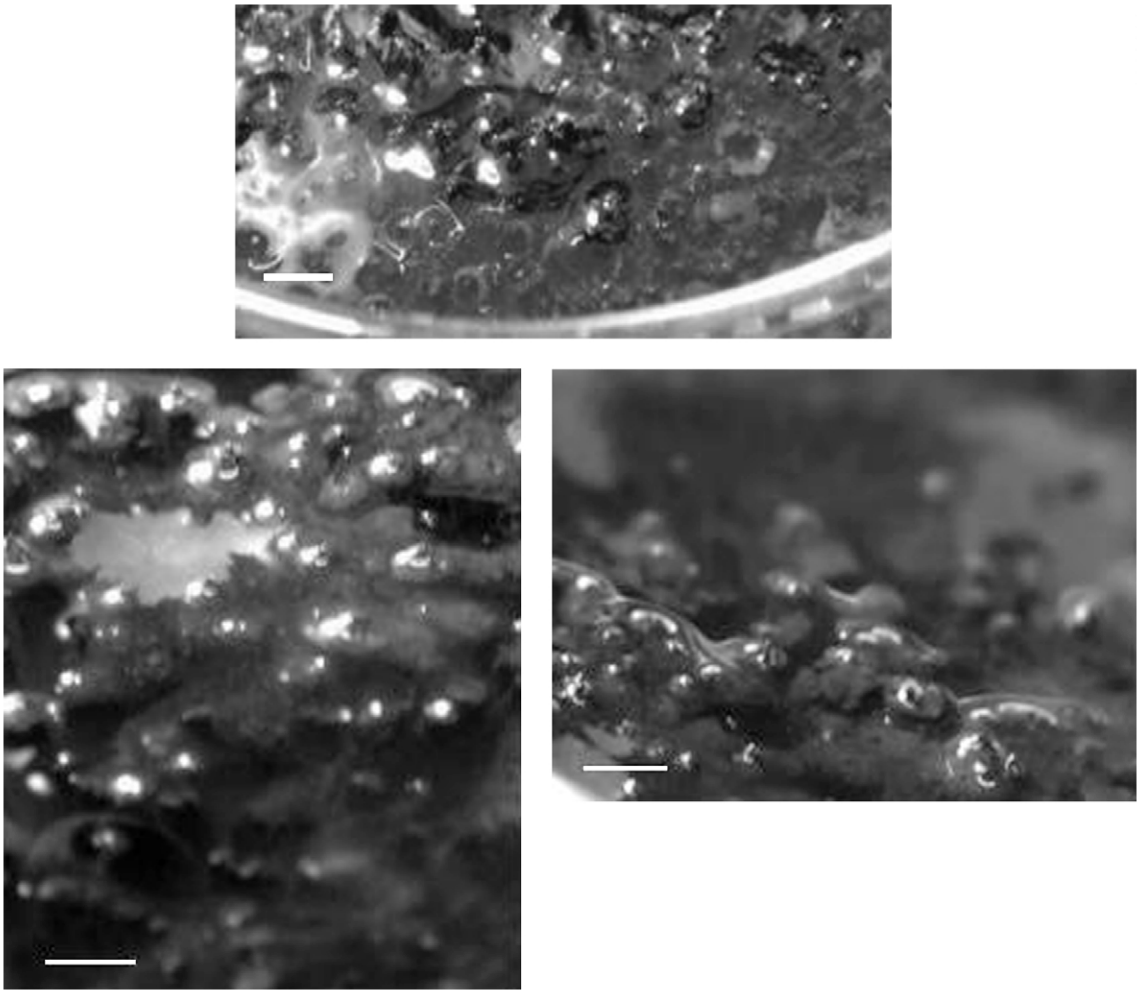

Fig. 3. Side view images of protruded parts of the polymer layer located above the magnetic fluid spikes. The bar size is 10 mm.

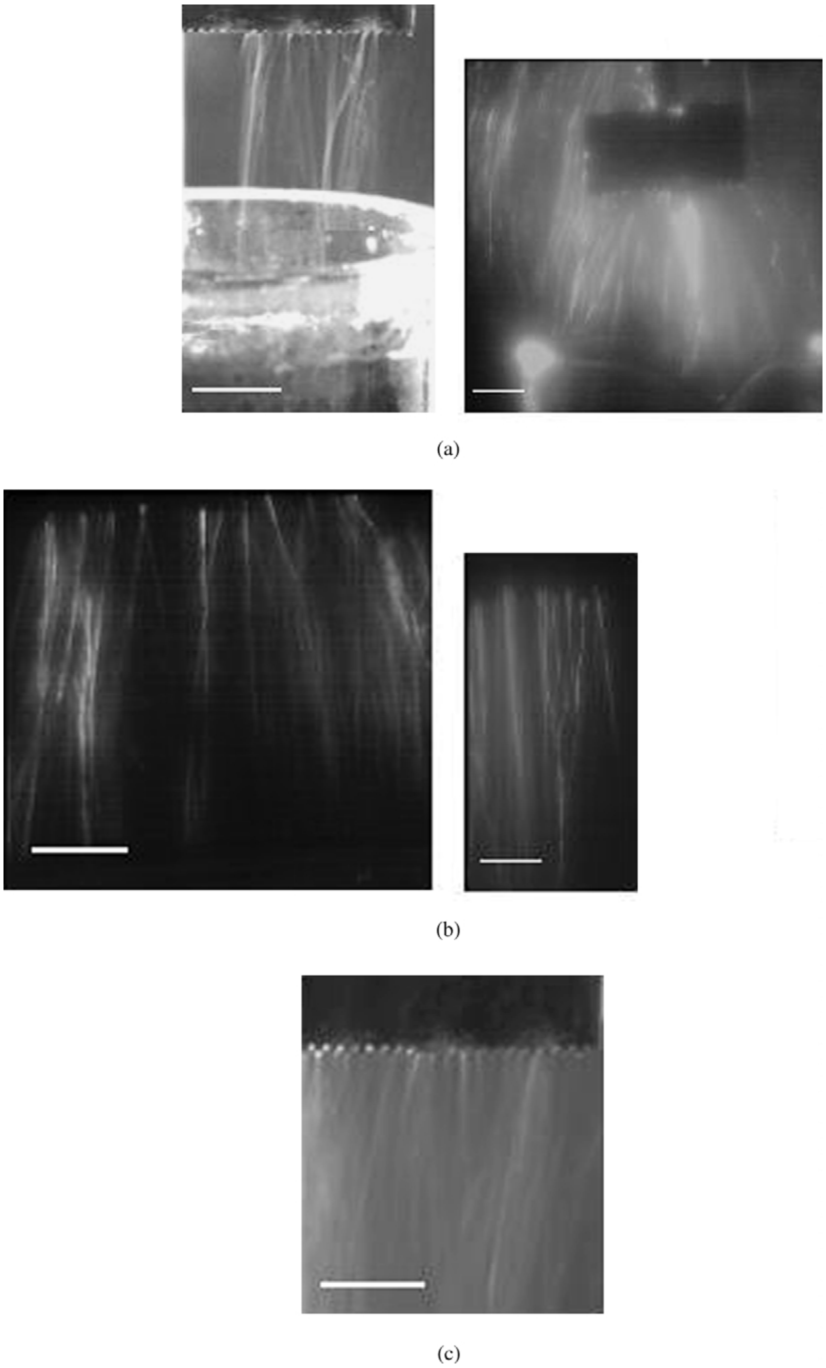

Fig. 4. Views of multiple jets attracted to a piece of a metal saw used as a counter-electrode. (a) Nanofibers are collected on the saw teeth and its upper edge, (b) close views of the metal saw and collected fibers, and (c) a still closer view of the ejected jets. Some of the jets display bending instability. The bar size is 10 mm.

the bottom of the dish and a counter-electrode placed over it. The distance H between the polymer solution layer and the counter-electrode could be adjusted.

Conical spikes due to the instability of the magnetic fluid layer in normal magnetic field are shown in Fig. 2 (there is no polymer above the magnetic fluid here and no electric field is applied). The magnitude of the perturbation forces is such that the peak height of the conical spikes can exceed their spacing. With the polymer layer added, the voltage at the electrode submerged in the polymer solution was gradually increased to 30 kV relative to the grounded upper counter-electrode located at a distance, $H = 10$ cm. This electrostatic field of the order of 10^5 V m^{-1} resulted in no visible changes. However, slightly above 30 kV some visible oscillations at the free surface of the polymer layer were detected, see Fig. 3. At 32 kV multiple jetting of the polymer solution began toward the grounded flat counter-electrode. The process, however, was not quasi-steady, and

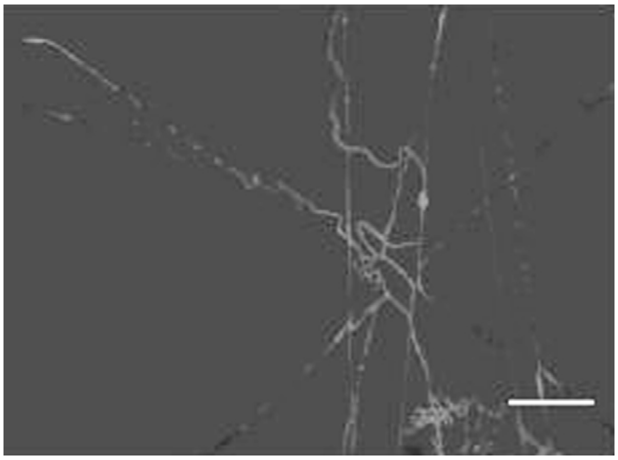

Fig. 5. Typical optical image of PEO-based collected nanofibers on a slide of glass. The bar size is 50 μm.

the number of vertical jets varied in time from 2 to about 70. To stabilize the process a grounded piece of metal saw with teeth oriented downward (toward the free surface) was used as a counter-electrode (see Fig. 4(a)). In this case the electrospinning process was quasi-steady with thousands upward jets recorded. Fibers collected on a slide of glass located underneath the metal saw electrode are shown in Fig. 5. The fiber diameters were measured using the optical instrument (Olympus BX51 optical system microscope) equipped with a blue filter. Hence, a resolution of the order of $\lambda/2\text{N.A.} \sim 200\,\text{nm}$ (Numerical Aperture) could be achieved. The generated signals were enhanced using image processing software (Olympus DP-Soft), and hence spatial and correlation details significantly smaller than the diffraction limit were revealed in the reconstructed pattern. Therefore, fibers, which vary by more than 100 nm, could be distinguished, albeit an accurate measurement was not guaranteed. Also, our results have often been compared/corroborated with SEM images of various nanofibers. The outcome of the measurements was that the diameters of the nanofibers electrospun in the present experiments were in the range between 200 and 800 nm.

The enhancement of the production rate in the present method can be estimated as follows. About 1000 jets were issued from the free surface of the polymer solution in the dish (the area of $\pi(3.5)^2 = 38.5\ \text{cm}^2$), which yields about 26 jets/cm^2. On the other hand, the calculations based on the model of Refs. [11,12] show that under comparable conditions 9 jets could be electrospun steadily from separate nozzles located with a pitch of 1 cm on a square of 4 cm^2. The latter yields 2.25 jets/cm^2. As a result, the production rate is expected to increase by a factor of 26/2.25, which is about 12, when the present method is used instead of separate nozzles. In addition, the present method eliminates the design problems related to multiple nozzles, as well as clogging.

To summarize, a new approach for mass production of nanofibers is presented. The approach is based on combination of normal magnetic and electric fields acting on a two-layer system. Nanofibers were electrospun from numerous cones located at the free surface of the upper layer, a polymer solution, punched by the lower layer, a magnetic fluid. It should be noted that jetting from the free surface of a polymer melt [8] (without magnetic fluid layer) could also be achieved, however, at much higher strengths of the electric filed of the order of $10^8\ \text{V m}^{-1}$. The present work shows that perturbing the free surface of polymer layer by ferromagnetic spikes leads to jetting at lower strengths of the electric field of the order of $10^5\ \text{V m}^{-1}$. The method leads to a 12-fold enhancement of the production rate of the elecrospinning process, as well as eliminates clogging problems.

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