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Electric-magnetic field-induced aligned electrospun poly (ethylene oxide) (PEO) nanofibers

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Abstract In this work, we report our attempt on the production of well-aligned nanofibers of poly (ethylene oxide) (PEO) by the introduction of magnetic field in the electric field by placing a cylindrical magnet within the electric field. Well-aligned nanofibers were obtained on top of the magnet. No particular structure could be associated with the other sides of the magnet. The aligned nanofibers were characterized by a host of characterization techniques such as optical and scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The diameter of the PEO nanofibers ranged between 500 and 1000 nm.

Introduction

Most recently, there has been a renewed interest in electrospinning, a process that uses repulsive electrostatic forces to produce nanofibers from polymeric solutions or melts. Nanofibers with their large surface area to volume ratio have a great potential to improve current technology as they find application in several new areas [1]. Nanofibers have a wide variety of applications ranging from protective clothing, nano-electronics [2, 3] to nanocatalysis, tissue scaffolds [2, 4, 5], capacitors [6], filtration [7] and wound dressing [8]. For many of these applications, preferred and ordered orientations of the nanofibers are indispensable for optimal performance. As reported by Teo and Ramakrishna [1], one potential application for the highly aligned nanofiber is in gas sensors where the fibers are required to be placed across conducting electrodes. They further reported that the alignment and orientation of the fibers could facilitate the transfer of electrical signals across the electrodes. In addition, it has been established by MacDiarmid et al. [9] and Ishii et al. [10] that well-aligned and preferred ordered structures of conducting polymers are often essential for optimizing the performance of electrical devices. In their efforts to control the stability of the electrospun fiber by magnetic field, Wu et al. [11] reported dramatic reduction in the radius of the whipping circle. Despite the fact that the simple and highly versatile technique of electrospinning has been known for several decades, controlled deposition of aligned fibers still poses a big challenge in this area of research [12–16] due to bending instability in the polymer jet trajectory. Hence, several modifications to this technique have been proposed to realize the preferred orientation of electrospun fibers. For example, recent works [17–19] have reported novel electrospinning process for the production of uniaxially aligned submicron fibers. Wang et al. [20] have succeeded in the fabrication of magnetic ferrite nanofibers by magnetic-field-assisted electrospinning coupled with oxygen plasma treatment. They were able to produce large and flexible magnetic hybrid membranes of aligned Fe_3O_4/PVP composite nanofibers. Of late, in the same vein, Xu [21] developed a mathematical model of the electrospinning process under multi-field such as electric field, magnetic

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field, vibrational force and air drag to control the physical characters of the nanofibers. Moreover, Yang et al. [22] employed a technique called magnetic electrospinning where magnetized fibers were stretched into parallel fibers over large areas in a magnetic field to produce well-aligned nanofibers and multilayer grids. Of recent, Yarin and Zussman [23] proposed a novel approach to electrospinning of polymer nanofibers. It involved upward needleless electrospinning of multiple nanofibers where a two-layer system (with the lower layer being a ferromagnetic suspension and the upper layer a polymer solution) was subjected to a magnetic field provided by a permanent magnet or coil on application of a normal electric field to the system. Besides, Teo and Ramakrishna [1] have given a catalogue of different electrospinning set-ups to obtain various fibrous assemblies. The uniaxial alignment method has been used to suspend single fibers across insulating gaps, thereby facilitating property measurements [10, 24, 25]. However, up to date, reported works on electric-magnetic field-induced preferred orientation of nanofibers are limited in the open literature. Hence, in this contribution we attempt the production of aligned poly (ethylene oxide) (PEO) nanofibers in the simultaneous presence of both electric and magnetic fields. The PEO was so chosen due to its ease of solubility in water and convenience of electrospinning.

Experimental

Materials

PEO with an average molecular weight of 3×10^5 (g/mol) was obtained from Sigma–Aldrich Batch # 08314JD and used without further purification while deionized water was used as solvent. PEO (7 wt%) solution was prepared in deionized water at room temperature and gently stirred for about 24 h to enhance a speedy dissolution and homogeneity before use.

Electrospinning set-up

The modified electrospinning set-up used is shown in Fig. 1. The solution obtained was loaded into pasteur pipette held horizontally and fitted over a positive electrode lead connected to a high voltage power supply that can generate DC voltages up to 25 kV. A copper wire was inserted into the pasteur pipette to act as the electrode for charging the polymer solution. Grounded aluminum foil stuck on a perspex board was placed 15 cm away from the pipette tip. Electrospinning was carried out in air at applied voltages that ranged from 5 to 15 kV. The modified version of our electrospinning set-up includes a cylindrical magnet placed vertically in front of the grounded aluminium foil. On top, sides and front of the magnet were placed silicon wafer

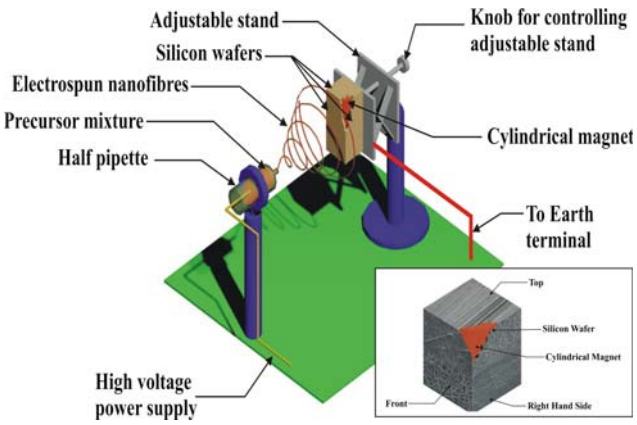

Fig. 1 Modified schematic drawing of single-nozzle electrospinning set-up used in this work. Inset shows the schematic drawing showing the different microstructures observed on the different sides of the magnet

substrates for the collection of the nanofibers formed at varied times for characterization after solvent evaporation. The whole set-up was enclosed in order to minimize the effect of air currents on the trajectory of the electrospun jet.

Characterization

Ultraviolet–visible (UV–VIS) spectra were recorded on a Varian 500 UV-Vis/NIR spectrophotometer. Fourier transform infrared (FTIR) spectra were obtained using a Perkin Elmer Pragon 1000PC FTIR spectrometer. The supermolecular structure which describes the configuration of the macromolecules in the nanofibers was characterized by wide-angle X-ray diffraction (WAXD). The X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å). Optical microscopy was performed on the electrospun fibers using a polarized optical compound microscope Nikon Eclipsen 90i/80i to ascertain the presence of fibers before electron microscopy. For higher magnifications and detailed morphology of the fibers, samples were mounted onto scanning electron microscope (SEM) plates; sputter coated with carbon and examined using a Leo-StereoScan 440 scanning electron microscope. Atomic force microscopy (AFM) measurements were carried out with a Nanoscope III Digital Instrument in tapping mode in air with etched Si probe.

Results and discussion

Scanning electron microscopy

Figure 2 shows the scanning electron micrographs of the PEO solution under different electrospinning conditions.

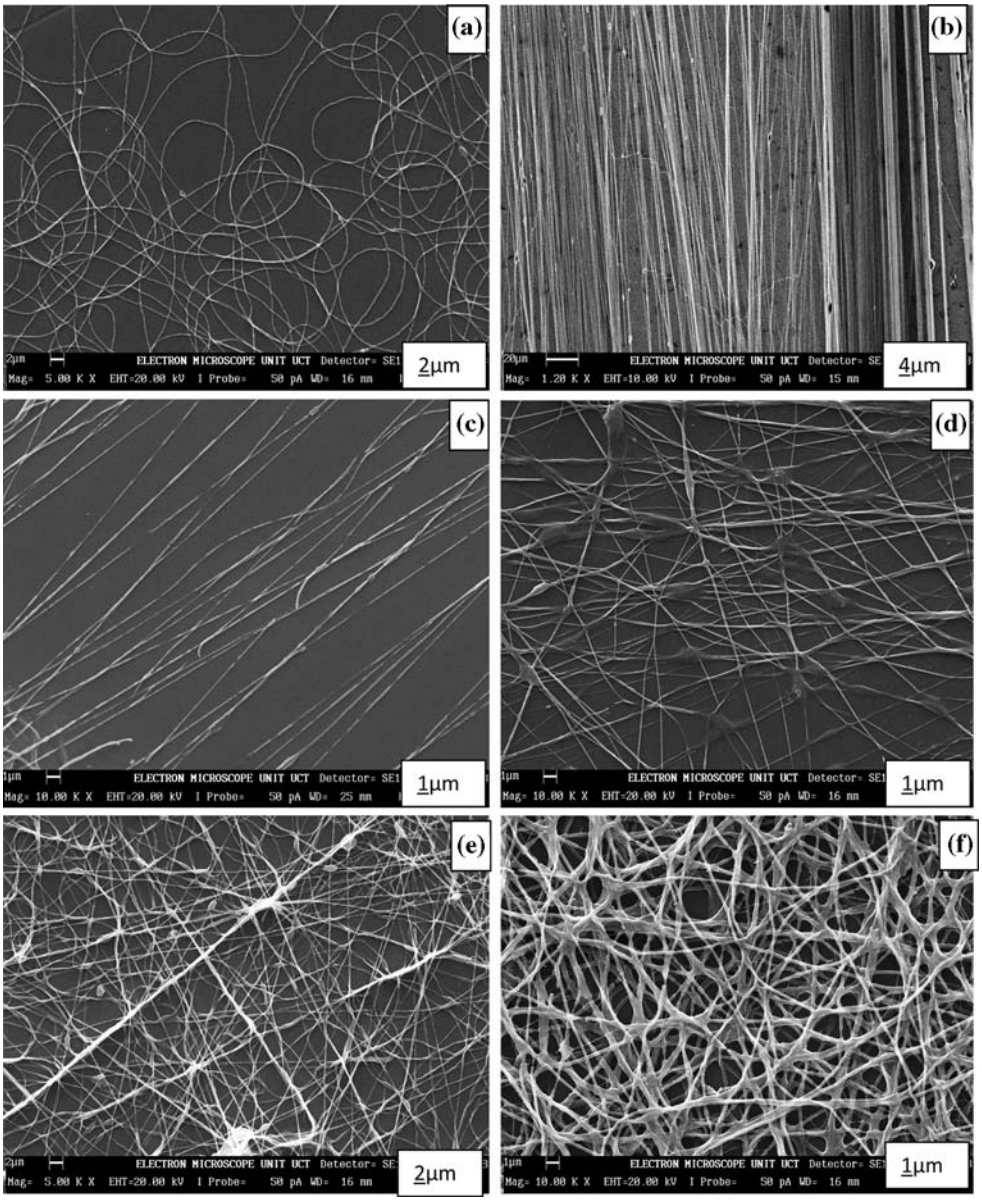

Fig. 2 **a** SEM images of pure PEO fibers electrospun in the absence of magnetic field. **b**, **c** Well-aligned nanofibers observed on top of the magnet. **d** Scanning electron micrographs observed on the sides of the magnet. **e**, **f** Scanning electron micrographs observed in the front of the magnet showing diverse microstructures

The introduction of the magnetic field in the electric field generated an avalanche of varied and complex microstructures which we shall attempt to explain. Figure 2a shows the scanning electron micrograph of PEO nanofibers electrospun in the absence of magnetic field. The fibers are randomly oriented and there exist many curvatures along the axis of fibers, which might be attributed to the asynchronous deposition of different parts of the electrospun fiber because of its own instabilities, such as whipping or non-axisymmetric instability [15]. The major contributing factor to random orientation of fibers is bending instability which is chiefly due to repulsive electrostatic forces brought about by the induced surface charges. The bending becomes more pronounced when the fiber diameter decreases. A sheet of PEO nanofibers fabricated by our method with the silicon wafer substrate placed on top of the cylindrical magnet is shown in the scanning electron micrographs of Fig. 2b and c. It can be seen that the fibers are well-aligned and well- oriented with their diameter ranging between 500 and 1000 nm. It should be noted that the aligned fibers in their overall morphology are bead- and junction-free and that no such well-aligned fibers were obtained from the other sides of the enclosed cylindrical magnet. For example, on the right side of the magnet, a

variety of microstructure was observed. It was made up of beads and necklaces as depicted by the scanning electron micrograph of Fig. 2d. On the silicon wafer substrate placed in front of the magnet were obtained randomly oriented web-like fibers with minimal number of beads as shown in Fig. 2e and f. According to preliminary reports from Wu et al. [11] on stability of electrospun fiber by the application of magnetic field, the current in the polymeric jet produced a centripetal force leading to the shrinking of the radius of the whipping circle, thereby resulting in the enormous improvement in the stability condition. In effect, the electromagnetic field profile between the tip of the pipette and the grounded collector has a noticeable influence on the electrospinning jet which can be controlled to produce aligned or patterned fibers. It is known that the magnetic field does not point along the direction of the source of the field; instead, it points in a perpendicular direction. In addition, the magnetic force acts in a direction that is perpendicular to the direction of the field. This could probably explain the well-aligned nanofibers observed on the silicon wafer substrate placed on top of the cylindrical magnet as the charged electrospinning jet passed through the field. This is in agreement with the work of Sundaray et al. [13] which reported that fibers were formed even with small applied voltage and concluded that it was the field which was primarily responsible for fiber formation. It should also be stated in this present work that no particular structure could be associated with the other sides of the enclosed magnet (except the top side; Fig. 1 inset) as the microstructures obtained were complex and difficult to correlate with the electric-magnetic field.

Fiber surface morphology

The surface morphology of the aligned fibers was investigated by atomic force microscopy (AFM). The surface topographical image obtained for the aligned fibers of PEO is shown in Fig. 3. It can be seen from the AFM images that the electrospun fibers are pore-free, homogeneous, smooth and uniform with cylindrical structure with diameters in the range of 400–800 nm. Besides, an accurate measurement of the electrospun fiber diameter with AFM requires a rather precise procedure as enumerated by Demir et al. [26] since the fibers appear larger than their actual diameter because of AFM tip geometry [27]. The AFM was also used to characterize the surface roughness of the fibers. The one-dimensional (1-D) surface roughness average which gives a general information on the surface texture and random orientation of the nanofibers along the fiber length, ($Ra_{1\text{-}D}$), of the AFM image, using Nanoscope software, is 62 nm as

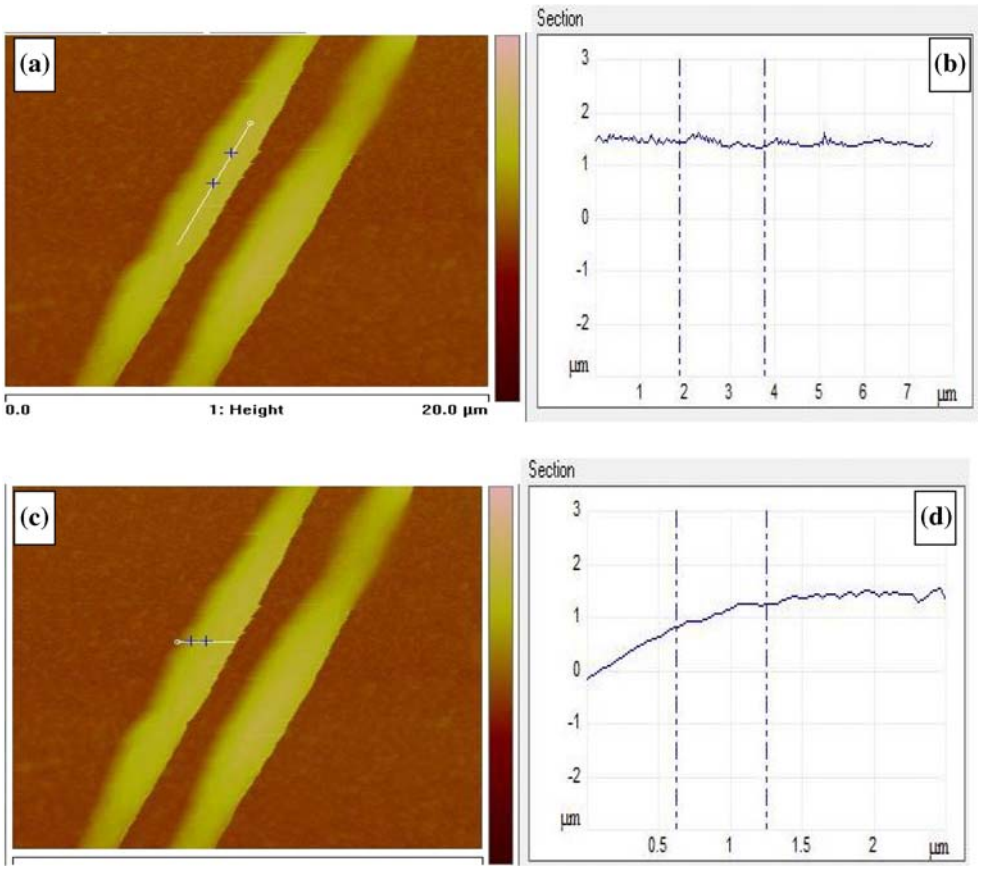

Fig. 3 AFM images of the well-aligned PEO nanofibers

shown in Fig. 3a and b while the 1-D surface roughness average value across the diameter of the fiber is 205 nm (Fig. 3c, d). The options of plane fit and flatten filters available in the Nanoscope software were employed to subtract the contribution from the cylindrical curvature of the electrospun nanofibers. Since the roughness measured by the AFM depends on the size of the area selected, in this report, the area used varied between 40 and 150 μm^2. Slight improvement of the surface roughness of the aligned fibers could be noticed compared to non-aligned fibers but this could not be entirely associated with the alignment of the fibers. It could also partly be due to other preparation conditions such as the electric-magnetic field, the viscosity of the solution, the nozzle-to-collector distance and many other parameters.

FTIR analysis

The molecular interactions within the PEO nanofibers were determined from the FTIR spectra of the PEO nanofibers as shown in Fig. 4. The figure shows the FTIR spectra obtained on the PEO nanofibers for different deposition times. No significant difference could be seen in the spectra obtained at different deposition times. It is known that PEO is one of such polymers with hydrophilic oxygen atom and hydrophobic ethylene group aligned alternatively. The FTIR spectra of PEO nanofibers (Fig. 4) show a strong band near 2900 cm^{-1} attributed to the symmetric and asymmetric C–H stretching modes. The bands at about 1456 and 1350 cm^{-1} are attributed to the vibrations of $–CH_2–$ group and the bands at about 1102 and 962 cm^{-1} are assigned to the asymmetric stretching vibration of the C–O group [28]. Furthermore, the intensity of the vibration bands of $–CH_2–$ group is close to that of the C–O group, which indicates as reported by Sui et al. [28] that the weight of extended oxygen atom is small and the PEO molecule exhibits a zigzag configuration. It should be noted that no significant changes were observed in the FTIR spectra of both the well-aligned and randomly oriented nanofibers.

XRD

XRD studies were performed on the pure PEO powder and PEO nanofibers as shown in Fig. 5. From the figure, for pure PEO powder, the diffraction peaks at $2\theta = 19.35°$ and 22.55° correspond to the PEO crystalline phase. This is in agreement with the report of Yan et al. [29]. From the peaks corresponding to the PEO nanofibers, it can be seen that the PEO powder has become semi-crystalline. The semi-crystallinity of the PEO nanofibers could probably be attributed to the molecular interactions between the water molecule (the solvent for PEO) and the oxygen atoms on the PEO chain during the preparation of the PEO solution.

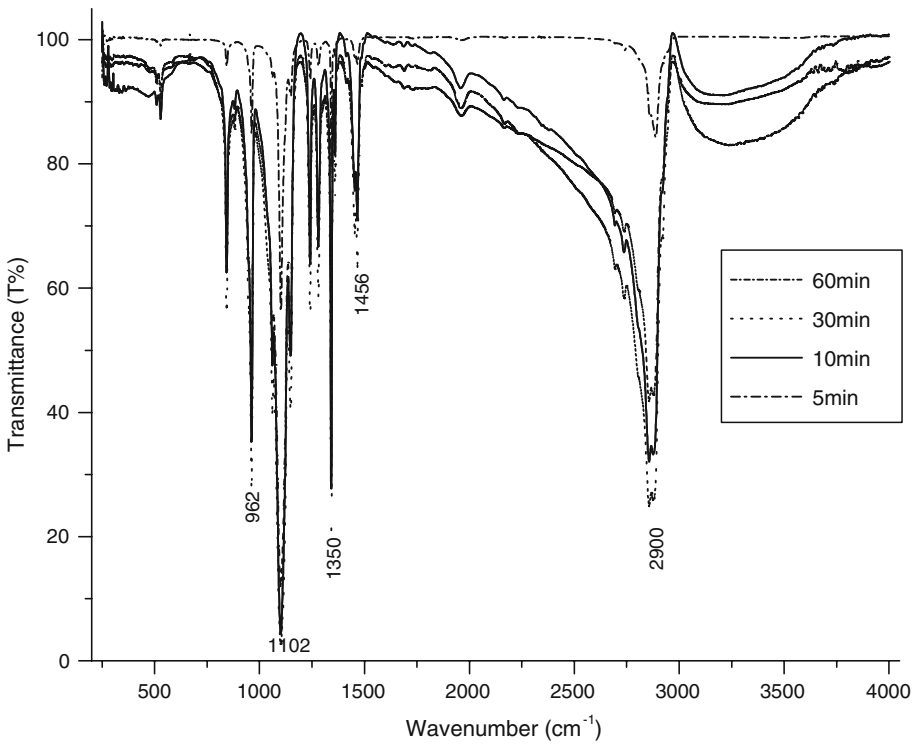

Fig. 4 FTIR spectra of the well-aligned PEO nanofibers obtained at different times of collection

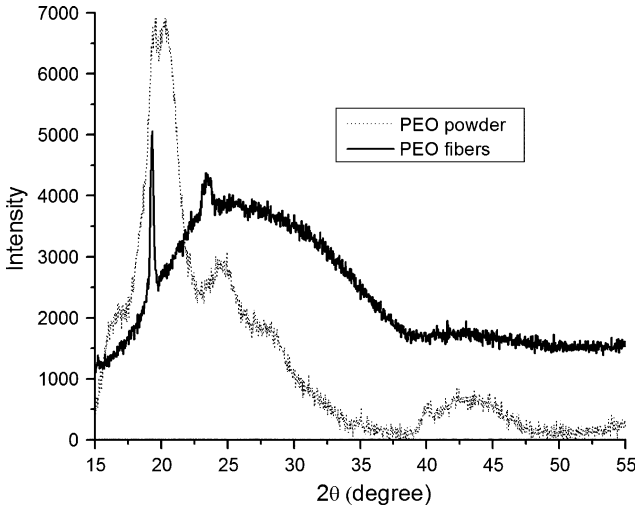

Fig. 5 XRD patterns of pure PEO powder and PEO nanofibers

Conclusion

The simple and versatile technique of electrospinning has been modified by the introduction of magnetic field within the electric field to prepare well-aligned PEO nanofibers with diameter ranging between 500 and 1000 nm as observed in the SEM and AFM. Well-aligned nanofibers were only observed on a particular side (top) of the magnet within the electric-magnetic field while the other sides presented diverse microstructures. Slight improvement of the surface roughness of the aligned fibers could be noticed compared to non-aligned fibers. No significant changes were observed in the FTIR spectra of both the well-aligned and randomly oriented nanofibers. Alignment of nanofibers of other polymers is anticipated by this modified electrospinning set-up in our further works.

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