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RAPID COMMUNICATION

A study on electrospinning of polyacrylonitrile nanofibers

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Abstract–Aligned and molecularly oriented Polyacrylonitrile (PAN) nanofibers were prepared using a non-conventional approach. Various take up velocity of rotating drum was examined for increasing of productivity, alignment and mechanical properties of nanofibers. Impressive techniques like Raman spectroscopy were utilized for characterization of nanofibers.

Key words: Electrospun Polyacrylonitrile (PAN) Nanofiber, Orientation, Characterization of Nanofibers

INTRODUCTION

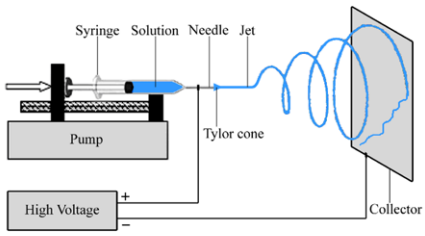
Electrospinning is a novel and efficient method by which fibers with diameters in nanometer scale, entitled as nanofibers, can be achieved. In the electrospinning process, a strong electric field is applied on a droplet of polymer solution (or melt) held by its surface tension at the tip of a syringe's needle (or a capillary tube). As a result, the pendent drop will become highly electrified and the induced charges are distributed over its surface. Increasing the intensity of the electric field, the surface of the liquid drop will be distorted to a conical shape known as the Taylor cone [1-4]. Once the electric field strength exceeds a threshold value, the repulsive electric force dominates the surface tension of the liquid and a stable jet emerges from the cone tip. The charged jet is then accelerated toward the target and rapidly thins and dries as a result of elongation and solvent evaporation. As the jet diameter decreases, the surface charge density increases and the resulting high repulsive forces split the jet into smaller jets. This phenomenon may occur several times, leading to many small jets. Ultimately, solidification is carried out and fibers are deposited on the surface of the collector as a randomly oriented nonwoven mat [5-7].

Fig. 1 shows a schematic illustration of conventional electrospinning setup and the setup used for this study.

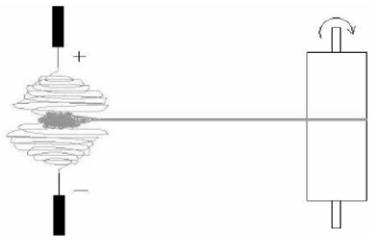
In this study, a simple and non-conventional electrospinning technique was employed for producing highly oriented Polyacrylonitrile (PAN) monofilament nanofibers. The electrospinning process was performed by using two needles in opposite positions and a rotating collector perpendicular to needle axis.

EXPERIMENTAL

The electrospinning apparatus consists of
- a high voltage power supply,
- two syringe pumps,
- two stainless steel needles (0.7 mm OD) and
- a rotating collector with variable surface speed which is controlled by an Inverter. In this setup, unlike the conventional technique, two needles were installed in opposite directions and polymer solutions were pumped to the needles by two syringe infusion pumps with the same feed rate.



(a) Conventional electrospinning technique



(b) Non-conventional electrospinning technique (present study)

Fig. 1. Schematic illustration of electrospinning setup: (a) Conventional, (b) Present study.

RESULTS AND DISCUSSION

1. Productivity

In this study, fibers were electrospun in the aligned form by using a simple and novel method which manufactures well-aligned polymer nanofibers with infinite length and over a large collector area [4]. The conditions pertinent to the minimum amount of rupture for nanofibers prepared at different concentrations are shown in Table 1.

PAN nanofibers prepared at 14 and 15 wt% concentrations have lower rupture, which can be due to high chain entanglement in these concentrations. Fig. 2 shows SEM images of PAN nanofibers electrospun in the obtained optimum conditions. The average diameter of nanofibers increased by increasing the solution concentration (Table 2).

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Table 1. The conditions obtained to generate nanofibers with minimum amount of rupture

Solution concentration (wt%)	Applied voltage (Kv)	Feed rate (mL/h)	Distance between two needles (cm)	Distance between needles and collector (cm)	Total number of rupture (at 15 miniutes)
13	10.5	0.293	13	20	12
14	11	0.293	13	20	6
15	11	0.293	15	20	6

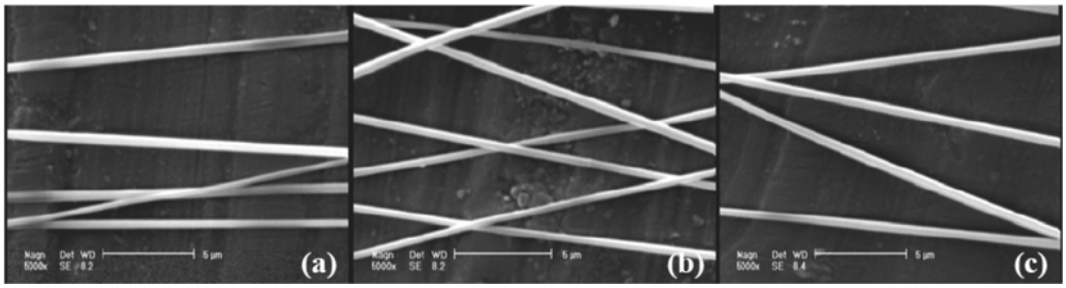

Fig. 2. SEM images of PAN nanofibers at concentrations of (a) 13 wt%; (b) 14 wt%; (c) 15 wt%.

Table 2. Average diameter of electrospun nanofibers at different solution concentrations

Diameter (nm) / Concentration	Average	Coefficient variation (CV%)	$\bar{x}$±sd (nm)
13 wt%	323.45	9.59	323.45±31.03
14 wt%	394.19	7.32	394.19±28.84
15 wt%	404.67	10.82	404.67±43.81

2. Alignment

The fiber alignment was analyzed by obtaining angular power spectrum (APS) of nanofibers collected at different take up speeds from 22.5 m/min to 67.7 m/min. The plot of normalized APS (ratio of intensity of the APS to the corresponding mean intensity of the Fourier power spectrum) versus angle was used for calculating the degree of alignment (Fig. 3). The alignment of the collected fibers is induced by the rotation of the target and improves as the surface velocity of the target is increased (Table 3).

3. Crystallization Index

The crystallization index (A1730/A2240) was calculated from FTIR spectra of PAN nanofibers collected at different take-up speeds from 22.5 m/min to 67.7 m/min in optimum conditions (Fig. 4).

4. Molecular Orientation

The molecular orientation of the nanofibers was examined by Raman Spectroscopy. Raman spectra were collected from bundles of fibers electrospun at 11 kV from 14 wt% PAN in DMF solutions collected onto a drum rotating with a surface velocity between 22.5 m/min and 67.7 m/min. The main differences among different molecular structures of PAN fibers usually arise in the region of 500-1,500 cm^{-1}, which is called the finger point region [9]. In this region, peaks over the ranges of 950-1,090 cm^{-1} and 1,100-1,480 cm^{-1} are common [9, 10], observed at Raman spectra of generated PAN nanofibers (Fig. 5).

Fig. 6 shows the Raman spectra of different samples of the nanofibers using VV configuration for different amounts of ψ. Raman spectra were obtained in two directions, parallel (ψ=0°) and vertical direction (ψ=90°) with respect to the polarization plane.

Trend in peak intensity observed for different sample shown in Fig. 7.

According to intensity ratios shown in Table 4, Raman spectra show a much stronger orientation effect in the sample c compared with the other spun nanofibers.

Table 4. The intensity ratios derived from Fig. 6 and Fig. 7 based on shown values of enhanced peak at 1,394 cm^{-1}.

The mathematical formulations of Raman intensity in VV and VH modes are represented by the following expressions [11,12]:

$$I^{VV}(\psi) \alpha \left(\cos^4\psi - \frac{6}{7}\cos^2\psi + \frac{3}{35}\right)\langle P_4(\cos\theta)\rangle + \left(\frac{6}{7}\cos^2\psi - \frac{2}{7}\right)\langle P_4(\cos\theta)\rangle + \frac{1}{5} \quad (1)$$

$$I^{VH}(\psi) \alpha \left(-\cos^4\psi + \cos^2\psi - \frac{4}{35}\right)\langle P_4(\cos\theta)\rangle + \frac{1}{21}\langle P_2(\cos\theta)\rangle + \frac{1}{15} \quad (2)$$

The orientation order parameters of <P2 ($\cos\theta$)> and <P4 ($\cos\theta$)> are, respectively, the average values of P2 ($\cos\theta$) and P4 ($\cos\theta$) for the SWNTs bulk product. The Pi($\cos\theta$) is the Legendre polynomial of degree i which is defined as P2($\cos\theta$)=(3 $\cos 2\ \theta - 1$)/2 and P4 ($\cos\theta$)=(35 $\cos 4\ \theta$−30 $\cos 2\ \theta$+3)/8 for the second and fourth degree, respectively. More specifically the <P2($\cos\theta$)> is known as the Herman orientation factor (f), which varies between values of 1 and 0 corresponding, respectively, to nanotubes fully oriented in the fiber

Table 3. The degree of alignment of the collected fibers

Take-up speed (m/min)	22.5	31.6	40.6	49.6	59.5	67.7
Degree of aligument (%)	24.59±3.97	34.4±5.29	32.72±7.65	29.48±5.97	37.53±5.26	29.43±7.04

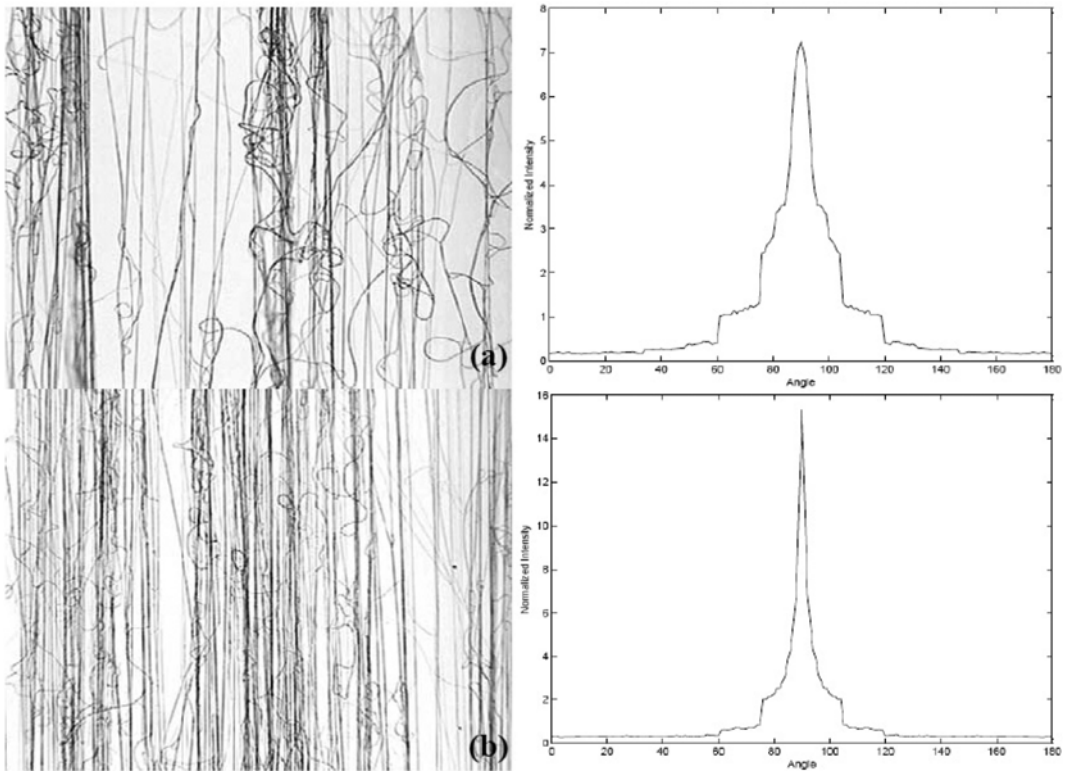

Fig. 3. Optical micrograph of electrospun PAN nanofibers with corresponding normalized APS at take-up speeds of (a) 22.5 m/min; (b) 59.5 m/min.

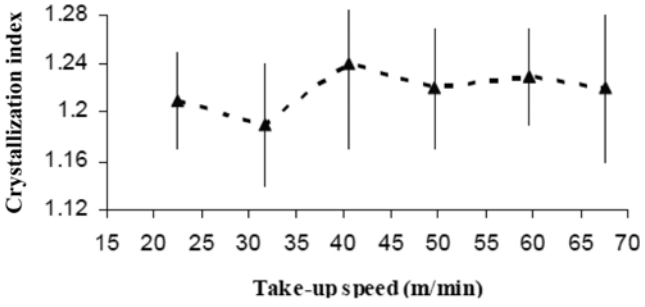

Fig. 4. Crystallization index of PAN nanofibers versus take up speed.

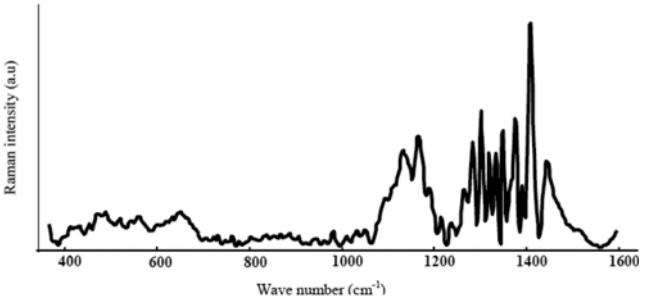

Fig. 5. Raman spectra of PAN nanofiber.

direction and randomly distributed [11].

$$f = \frac{3\langle \cos^2\theta \rangle - 1}{2} \tag{3}$$

The orientation factors can be determined by solving of following simultaneous algebraic equations given in (4) and (5). These equations are obtained from Eqs. (1) and (2) by dividing both sides of these equations and substitution of angles of 0 and 90 degrees for ψ.

$$\frac{I^{VV}_{G,RBM}(\psi=0)}{I^{VH}_{G,RBM}(\psi=0)} = -\frac{24\langle P_4(\cos\theta)\rangle + 60\langle P_2(\cos\theta)\rangle + 21}{12\langle P_4(\cos\theta)\rangle - 5\langle P_2(\cos\theta)\rangle - 7} \tag{4}$$

$$\frac{I^{VV}_{G,RBM}(\psi=90)}{I^{VH}_{G,RBM}(\psi=0)} = \frac{-9\langle P_4(\cos\theta)\rangle + 30\langle P_2(\cos\theta)\rangle - 21}{12\langle P_4(\cos\theta)\rangle - 5\langle P_2(\cos\theta)\rangle - 7} \tag{5}$$

The left-hand side terms of equations of (4) and (5) are the depolarization ratios that can be experimentally determined. As it can be seen, only the intensity at 0º and 90º is required to determine the <P2 ($\cos\theta$)> and <P4 ($\cos\theta$)> for uniaxially oriented nanofibers. Results calculated from Eqs. (4) and (5) for Herman orientation factor for different sample show a range between 0.20 and 0.25 at take up speeds of 67.7 m/min and 59.5 m/min, respectively (Fig. 8).

The maximum chain orientation parameter yield at speed of 59.5 m/min and further increase of it causes loss of molecular orientation, which corresponds to other studies [3]. It appears that applying high draw ratio at short time has no significant effect on molecular orientation. Comparing this result with orientation factors of 0.66 and 0.52, which have been observed for commercial wet-spun acrylic fibers and melt-spun acrylic fibers, respectively [13], it can be stated that electrospun PAN nanofibers have lower molecular orientation than commercial fibers.

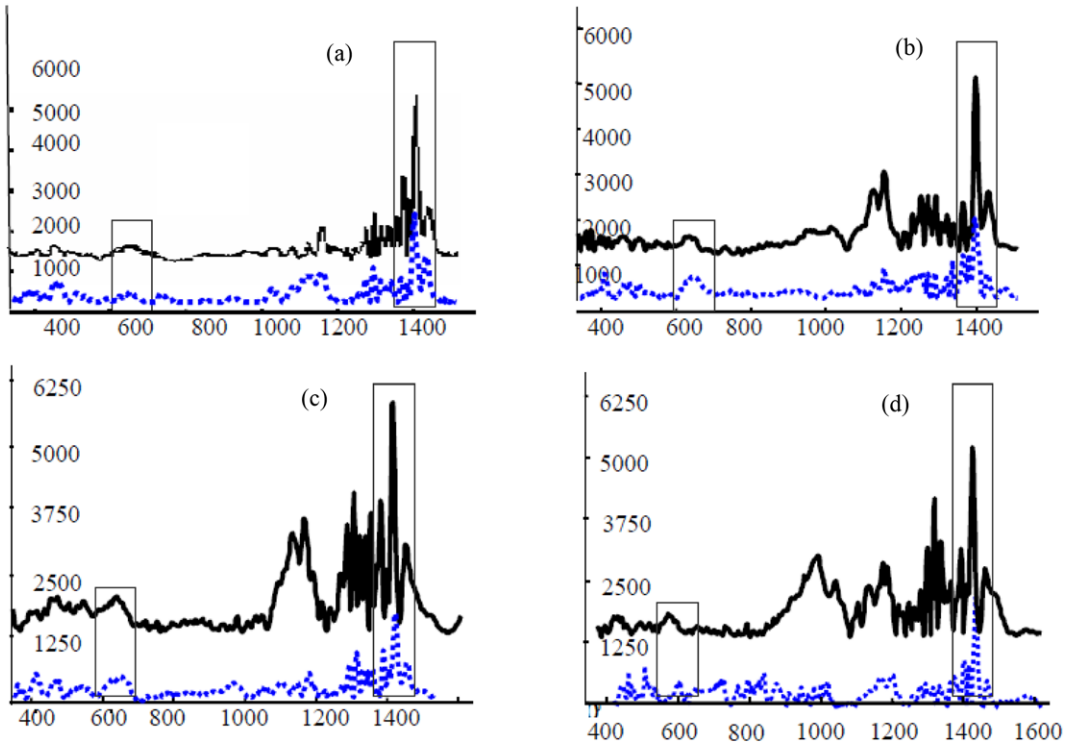

Fig. 6. The raman spectra under VV mode. (a) 22.5 m/min, (b) 49.6 m/min, (c) 59.5 m/min, (d) 67.7 m/min. From top to bottom, the angle between fiber axis and polarization plane is 0° and 90°.

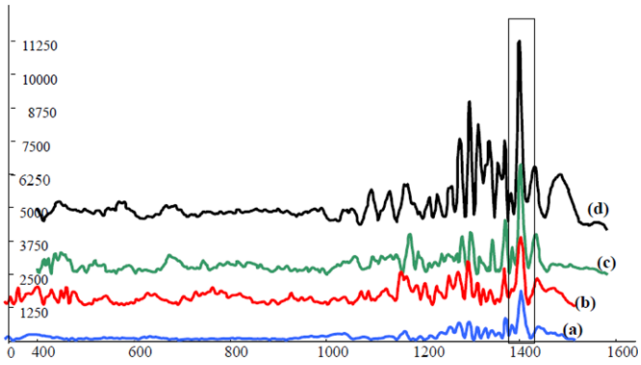

Fig. 7. The raman spectra under VH configuration at zero angle between fiber axis and polarization plane. (a) 225. m/min, (b) 49.6 m/min, (c) 59.5 m/min, (d) 67.7 m/min.

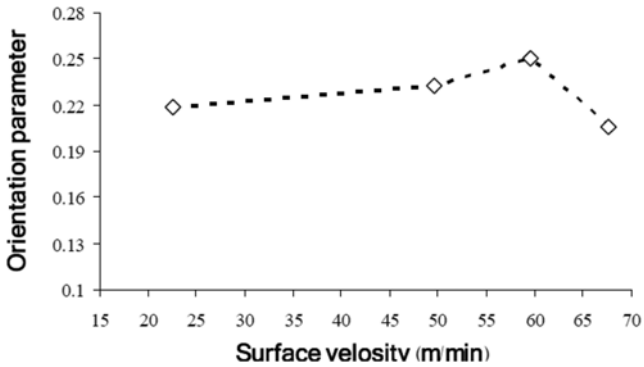

Fig. 8. Orientation parameter versus take up speed of rotating drum determined by raman spectroscopy.

Table 4. The intensity ratios derived from Fig. 6 and Fig. 7 based on shown values of enhanced peak at 1,394 cm^{-1}

Sample	I_{VV0}	I_{VV90}	I_{VH0}	I_{VV90}/I_{VH0}	I_{VV0}/I_{VB0}	I_{VV0}/I_{VV90}
A	4400	1900	1600	1.1875	2.75	2.31
B	3600	1500	2400	0.625	1.5	2.40
C	4000	1500	4277	035071	0.93523	2.67
D	3800	2200	6350	0.34646	0.59843	1.73

CONCLUSIONS

Electrospinning was carried out with a novel and modified method for production of Polyacrylonitrile (PAN) nanofibers using two needles which were placed from opposite directions and a rotating collector. The results showed that nanofibers collected by this method have satisfactory mechanical properties as a nanofiber. Raman spectroscopy was utilized as a new technique for analysis of molecular orientation. It was reasonably exhibited that the molecular chain orientation had an important and considerable effect on the mechanical properties of the generated nanofibers. In this study, the best alignment, molecular orientation and tensile strength were acquired for nanofibers prepared at a collection speed of 59.5 m/min. Also, it was demonstrated that this take up speed can be a good choice for collection and performance thermal treatment on PAN nanofibers.

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