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# PAN monofilament in nanoscale: a novel approach

*M. Sadrjahani,[1] S.A.Hoseini,[1] V. Mottaghitalab,[2*] A.K.Haghi[2]*

[1]Textile engineering faculty, Isfahan university of technology, POBOX 84156, Isfahan, I.R. Iran; fax: +98(311) 3912444; e-mail: hoseinir@cc.iut.ac.ir
[2*]Textile Engineering Department, Faculty of Engineering, POBOX 3756, University of Guilan, Rasht, I.R.Iran; fax: +98(131)6690271; e-mail: motaghitalab@guilan.ac.ir

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***Abstract:*** A novel electrospinning setup was employed for producing aligned polyacrylonitrile (PAN) monofilament in nanoscale. Unlike conventional method, the PAN monofilaments is collected using a rotating drum with various linear speed from bulk of nanofibers. it originates from two syringe infusion pumps contain 14wt% PAN/DMF solution which passes through two separate high voltage electric field. Various collecting drum speed were examined to clarify its effect on degree of alignment, internal structure and mechanical properties. Image process technique used to illustrate the best degree of alignment for nano-monofilament collected at take up velocity of 59.5 m/min. The amount of Crystallization Index (C.I) and orientation parameter calculated respectively from FTIR spectra and Raman spectra also supports the results demonstrated by image processing techniques. The ultimate strength and elastic modulus of nano-monofilament bundles increase with increase of take up velocity. They approach respectively to a maximum of 73.7 MPa and 4.2 GPa at take up velocity of 59.5 m/min. Results acquired by differential scanning calorimetry (DSC) show no significant effect on glass transition temperature with increasing take up velocity. However, minimum value of evolved heat caused by chemical reaction was obtained at surface speed of 59.5 m/min.

## Introduction

The emergence of various applications for nanofibers is stimulated from their outstanding properties such as very small diameters, huge surface area per mass ratio and high porosity along with small pore size. Moreover, the high degree of orientation and flexibility beside superior mechanical properties are extremely important for diverse applications [1, 2, 3]. Electrospinning is a sophisticated technique that relies on electrostatic forces to produce fibers in the nano to micron range from polymer solutions. In a typical process, an electrical potential is applied between droplet of a polymer solution held at the end of a capillary tube and a grounded target. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution is ejected. The jet extends through spiraling loops, as the loops increase in diameter the jet grows longer and thinner until it solidifies or collects on the target [3]. Due to initial instability of the jet, fibers are often collected as randomly oriented structures in the form of nonwoven mats, where the stationary target is used as a collector. These nanofibers are acceptable only for some applications such as filters, wound dressings, tissue scaffolds and drug delivery [4]. Aligned nanofibers are another form of collected nanofibers that can be obtained by using rotating collector or parallel plates [1, 2]. Recent studies have shown that aligned nanofibers have better molecular orientation and as a result

improved mechanical properties than randomly oriented nanofibers [3, 5, 6]. These nanofibers can be used in applications such as composite reinforcement and device manufacture [4]. Moreover, the aligned nanofibers are better suited for thermal or drawing treatment (the methods of collecting aligned nanofibers can be utilized for preparing of carbon nanofibers from electrospun PAN nanofibers precursor) [7]. Recently, PAN nanofibers have attracted a lot of interest as a precursor of carbon nanofibers. Zussman et al. have demonstrated the use of a wheel-like bobbin as the collector to position and align individual PAN nanofibers into parallel arrays. Herman's orientation factor of 0.34 for nanofibers obtained at collection speed of 5 m/s. [5]. In this study, aligned and molecularly oriented PAN nanofibers were prepared using a novel technique using two needle with opposite voltage and a rotating drum for applying take-up mechanism. The electrospinning process was optimized for increasing of productivity and improving the mechanical properties through controlling internal structure of the generated fibers.

## Results and discussion

Figure 1 shows the SEM images of PAN nanofibers prepared at different concentration. The generated monofilament has uniform shape and bead free structure. As expected, the average diameter of nanofibers increased by increasing solution concentration (Table 1).

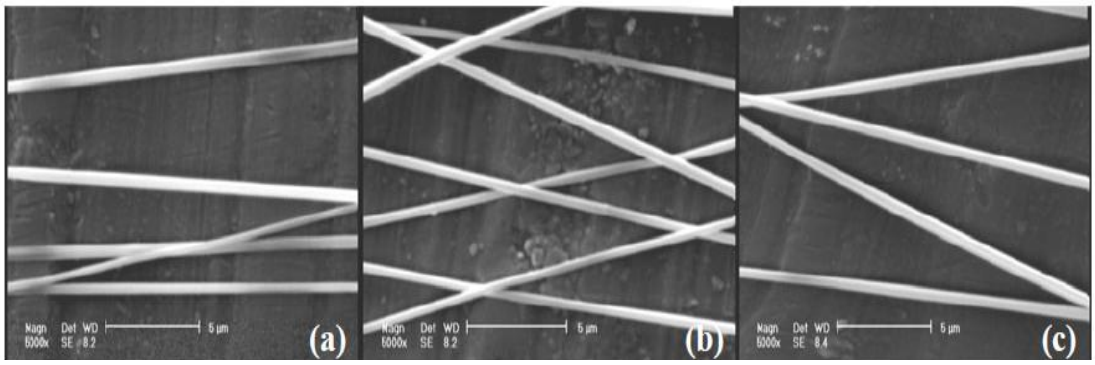


**Fig. 1.** SEM images of PAN monofilament at PAN/DMF concentrations of (a) 13 %w/w (b)14 %w/w (c) 15 % w/w.

This is presumably because of the greater solution resistance at higher viscosity against stretching resulting from applied charges on the jet [2]. The prepared nano-monofilaments at 14%w/w concentration shows higher uniformity as a consequence of lower coefficient of variation (CV%) of diameter compared to other concentrations. Therefore the 14 wt% concentration was chosen as a optimum concentration for producing PAN nanofibers when other electrospinning parameters kept constant.

Alignment analysis of nanofibers collected at different take up speeds from 22.5 m/min to 67.7 m/min was carried out using angular power spectrum (APS) based on micrographs captured by Optical microscope. Acquired image was processed using MATLAB software to produce angular power spectrum as square of Fourier power spectrum. APS is a plot of how much the orientation varies from point to point on the web of nanofibers versus the angular frequency (the x-axis variable). Furthermore, 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 degree of alignment (Fig. 2).

**Tab.1.** Average diameter of electrospun nano-monofilament at different concentration.

| ***PAN/DMF (% w/w)*** | ***Diameter*** | | |
|---|---|---|---|
| | $\overline{X}\,(nm)$ | **CV%** | $\overline{X} + sd(nm)$ |
| 13 | 323.45 | 9.59 | 323.45±31.03 |
| 14 | 394.19 | 7.32 | 394.19±28.84 |
| 15 | 404.67 | 10.82 | 404.67±43.81 |

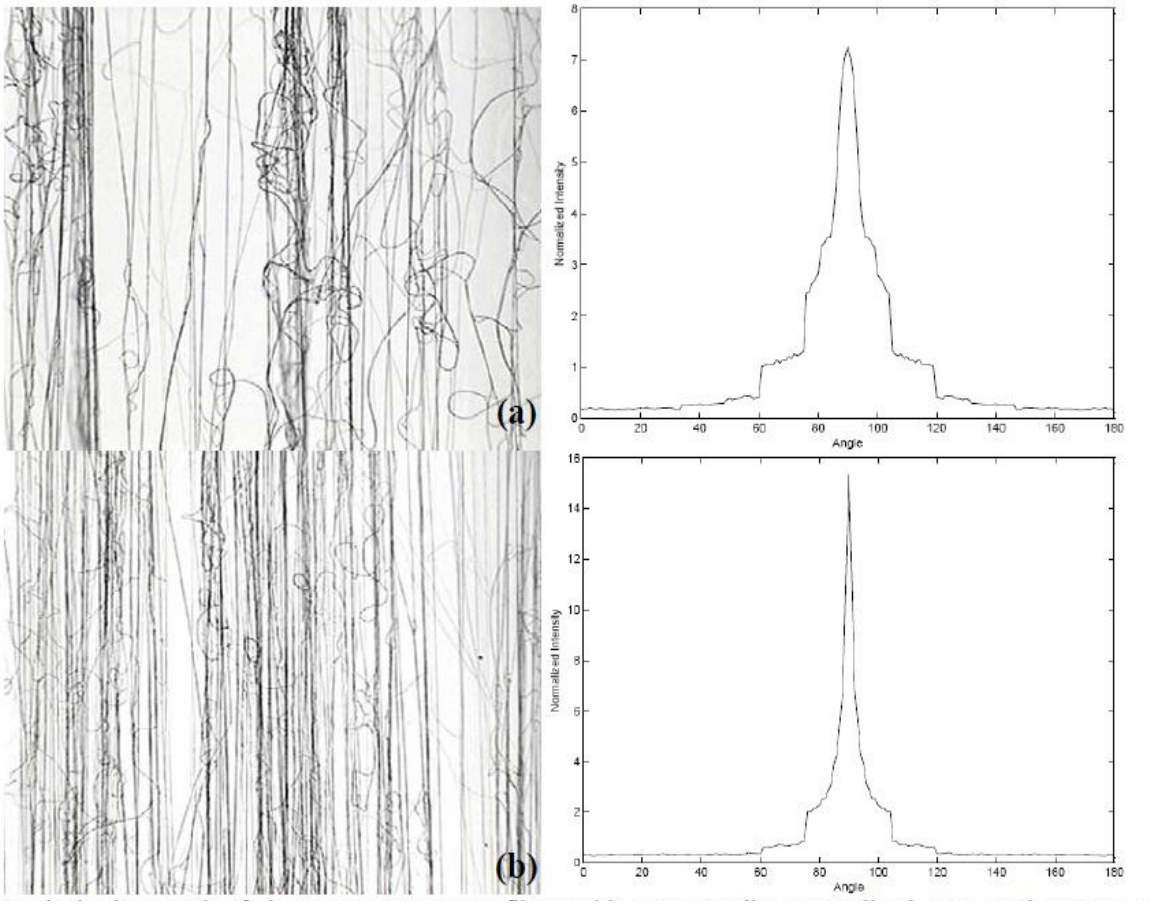


**Fig. 2.** Optical micrograph of electrospun PAN nano-monofilament with corresponding normalized APS at take –up speed of(a)22.5 m/min(b) 59.5 m/min.

**Tab. 2.** The effect of take-up velocity on degree of alignment.

| ***Take-up speed(m/min)*** | *22.5* | *31.6* | *40.6* | *49.6* | *59.5* | *67.7* |
|---|---|---|---|---|---|---|
| **Degree of alignment (%)** | 24.6 | 34.4 | 32.7 | 29.5 | 37.5 | 29.4 |

Disorientation of nanofibers generates a broad spectrum around 90°which reflect directly low degree of alignment. The ratio of peak area at $90^{o}$±3 $^{o}$ to total area of APS plot was utilized to calculate the density of aligned nanofibers. Table 2 shows

the influence of linear take up speed of rotating collector on degree of alignment of nanofibers. (The higher the take up speed, the more aligned nanofiber is collected. As the rotation speed increases, the effective draw (difference between surface velocity of drum and final velocity of fiber) is increased resulting in better alignment of the collected fiber and less deviation between the fiber and rotation direction. However the positive impact of linear take up velocity on degree of alignment pass a maximum of 37.5% at 59.5 m/min and trend of data inverses after this collection speed. Decreasing of degree of alignment after specific take up speed presumably is due to insufficient time for arrangement of molecular chains in drawing mechanism. Although drawing mechanism inherently uncoil the molecular chain to reach higher orientation but after an optimum take up speed the breaking force acting on molecular chain starts to build up. At early stage, the decreasing of nanofiber alignment can be observed due to partial segregation of polymer chain and reforming of coiled structure. Meanwhile, if take up speed is to be continued, the complete fracture occurs in nanofiber structure.

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 constant electrospinning condition. The obtained results (Figure 3) and ANOVA statistic analysis over acquired data show an infinitesimal increase in crystallization index while surface take up speed increases.

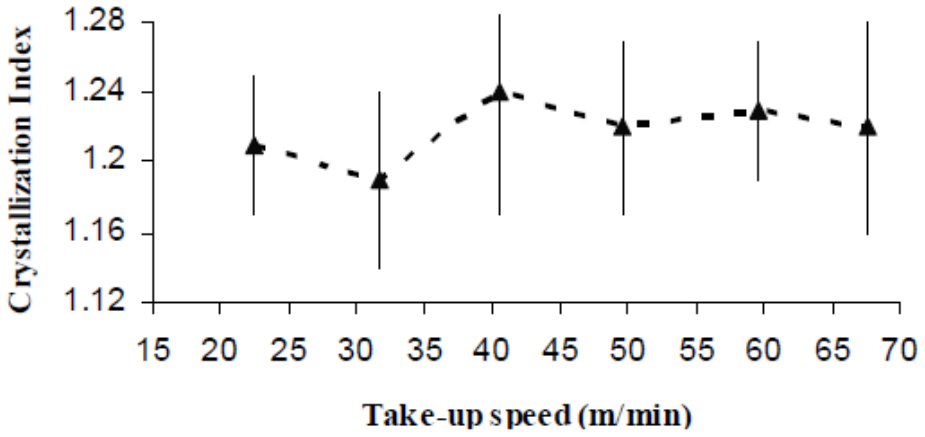


**Fig. 3.** Crystallization index of PAN nano-monofilament versus take-up speed.

The molecular orientation of the nanofibers was examined using Raman Spectroscopy to support data given for degree of alignment. 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 difference among different molecular structures of PAN fibers usually arise in the region of 500-1500 cm-1 [9]. In this region, the peaks over the ranges of 950-1090 cm-1 and 1100-1480 cm-1 are common [9,10], be observed at Raman spectra of generated PAN nanofibers (Figure 4).

Figure 5 shows the Raman spectra of nanofiber samples collected at different take up speed under VV configuration at ψ= 0º (parallel) and 90º(Vertical) versus polarization plane. Four samples with symbols A, B, C and D were prepared using condition given in Table 1 for 14 wt % polymer solution and various rotating drum

speeds. Raman spectra of PAN nanofibers usually arise in the region of 500-1500 $cm^{-1}$ which is commonly can be seen as Raman finger print of PAN microfiber [8].

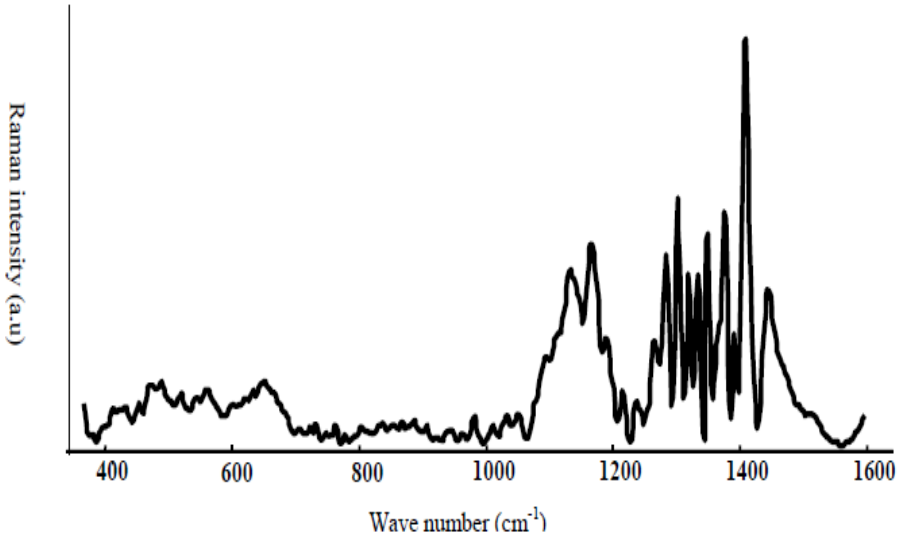


**Fig. 4.** The Raman spectra of PAN monofilament.

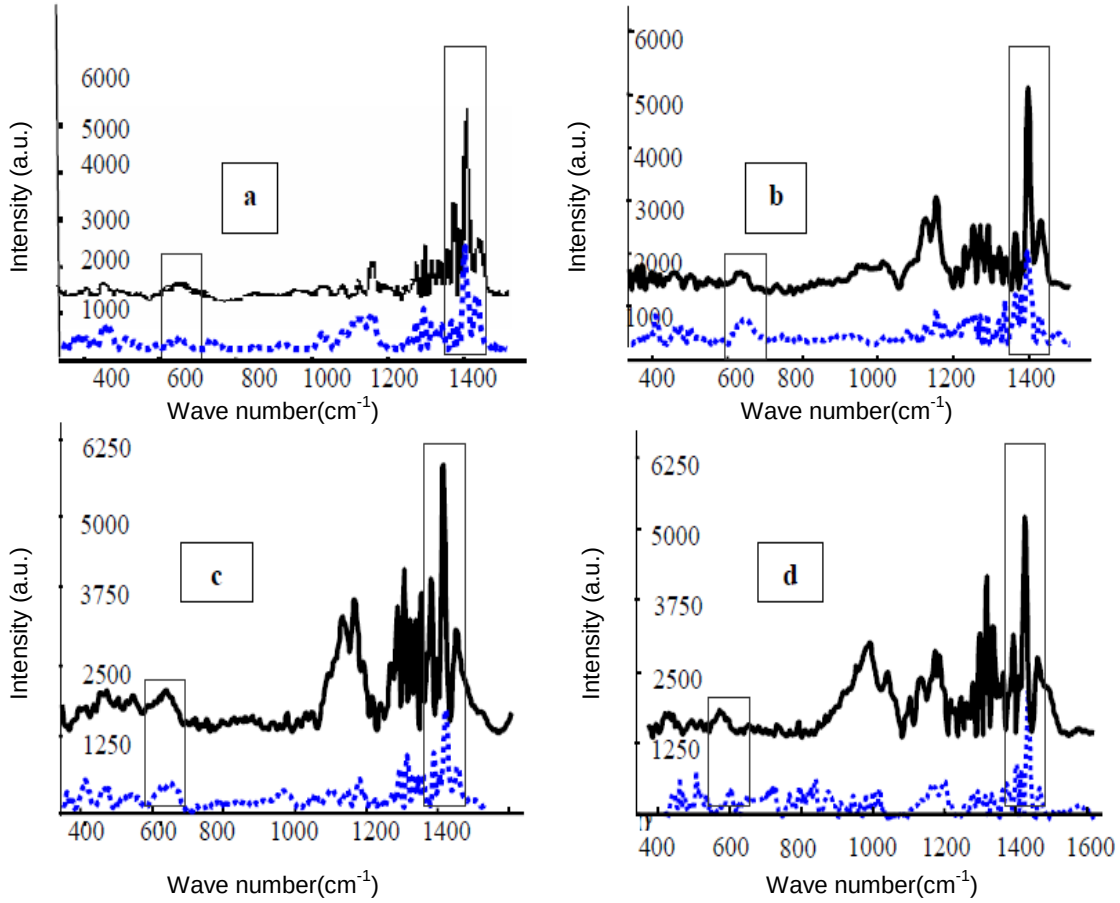


**Fig. 5.** The Raman spectra under VV mode,(a) 22.5 m/min(b) 49.6 m/min(c) 59.5 m/min(d) 67.7m/min. the angle between fiber axis and polarization plane for filled curve and dashed curve is 0 ° and 90 °, respectively.

According to intensity ratios shown in Table 3, Raman spectra show a much stronger orientation effect in the sample (C) compared to other spun nano-monofilament. It is clear that the higher take up speed is mostly responsible for the orientation of molecular chain in the fiber direction. The orientation parameter of <P2 (cosθ)> as the average values of Legendre polynomial P2 (cosθ) for the bulk product can be calculated based on Raman intensity ratios in VV and VH modes given in Table 3 [11].

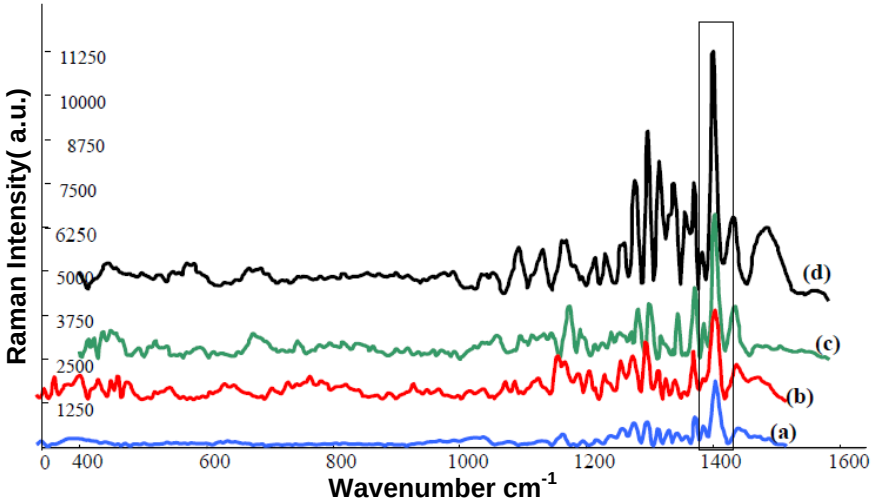


**Fig. 6.** The Raman spectra under VH configuration at zero angle between fiber axis and polarization plane(a) 22.5 m/min(b) 49.6 m/min(c) 59.5 m/min (d) 67.7 m/min

Compared to Peak enhanced in 600 $cm^{-1}$ with constant intensity in different polarization angle, the intensity at 1394 $cm^{-1}$ monotonically decreases with increasing of ψ. The intensity dependence of peak enhanced in 1394 $cm^{-1}$ to the angle between fiber and polarization plane can be considered as powerful tool for determination of nanofibers orientation.

**Tab. 3.** The intensity ratios of enhanced peak at 1394 $cm^{-1}$ using VV and VH configuration.

| *Sample* | *Rotating drum speed (m/min)* | $I_{VV0}$ | $I_{VV90}$ | $I_{VH0}$ | $I_{VV90}/I_{VH0}$ | $I_{VV0}/I_{VH0}$ | $I_{VV0}/I_{VV90}$ |
|---|---|---|---|---|---|---|---|
| A | 22.5 | 4400 | 1900 | 1600 | 1.19 | 2.75 | 2.31 |
| B | 49.6 | 3600 | 1500 | 2400 | 0.63 | 1.50 | 2.40 |
| C | 59.5 | 4000 | 1500 | 4277 | 0.35 | 0.93 | 2.67 |
| D | 67.7 | 3800 | 2200 | 6350 | 0.35 | 0.60 | 1.73 |

Other peaks that enhanced between 1394 $cm^{-1}$ and 600$cm^{-1}$ did not decrease significantly, except the peak enhanced at 1190 $cm^{-1}$. Similar to VV configuration, the

peak intensity observed for different sample in VH configuration at ψ=0 characterized to specify the degree of molecular orientation. It is worth noting that trend in peak intensity observed for different sample shown in Figure 6 in VH configuration can also be attributed to different orientation magnitude. When the nanofibers were examined using the VH configuration, the intensity dependence of enhanced peak at 1394 cm-1 on ψ showed a different trend for different sample that cannot be directly correlated to degree of orientation. The higher intensity obtained for sample D, however the intensity value decreases for samples C, B and A, respectively as shown in Figure 6.

Herman orientation factor for different sample shows a range between 0.20 and 0.25 at take up speeds of 67.7 m/min and 59.5 m/min, respectively (Figure7). In general, based on the data of orientation factor for different sample, it can be clearly stated that the increase of surface velocity of collector has a quite positive impact on molecular orientation of PAN nanofibers. The maximum chain orientation parameter yield at speed of 59.5 m/min and further increase in collecting speed causes loss of molecular orientation which is in good agreement with other studies [3]. Regarding to constant distance between the needles and the collector , this phenomenon is likely to arise from decreasing of drawing time with increasing take up speed . Therefore, there is not sufficient time for arranging molecular chains in drawing direction. Electrospun PAN nano-monofilament shows lower molecular orientation compared to commercial fibers with orientation factor of 0.66 and 0.52 respectively for wet-spun and melt-spun acrylic fibers [13].

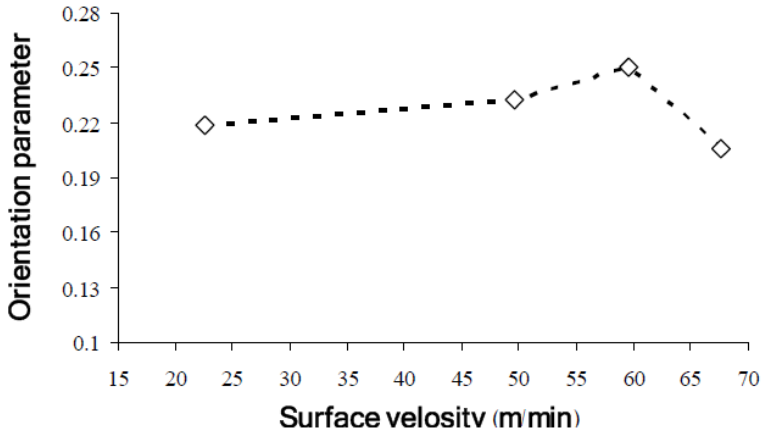


**Fig. 7.** Orientation parameter versus take up speed of rotating drum determined by polarized Raman spectroscopy.

The average linear density of the bundles was 176 dens. The stress-strain behavior of the bundles was examined and the modulus, ultimate strength, and elongation at the break were measured as a function of take up speed. The initial modulus and ultimate strength increase gradually with take up speed from 1.3 GPa (12.31 g/den) and 61.7 MPa (0.577 g/den) at a surface velocity of 22.5 m/min to 4.2 GPa (39.43 g/den) and 73.7 MPa (0.694 g/den) with a liner velocity of 59.5 m/min, respectively. The modulus and ultimate strength of the bundles decreased with take up speed greater than 59.5 m/min (Figure 8).On the contrary, the elongation at break decreases from 23.3% to 8.4% with increasing take up speed from 22.5 m/min to 67.7 m/min, respectively.

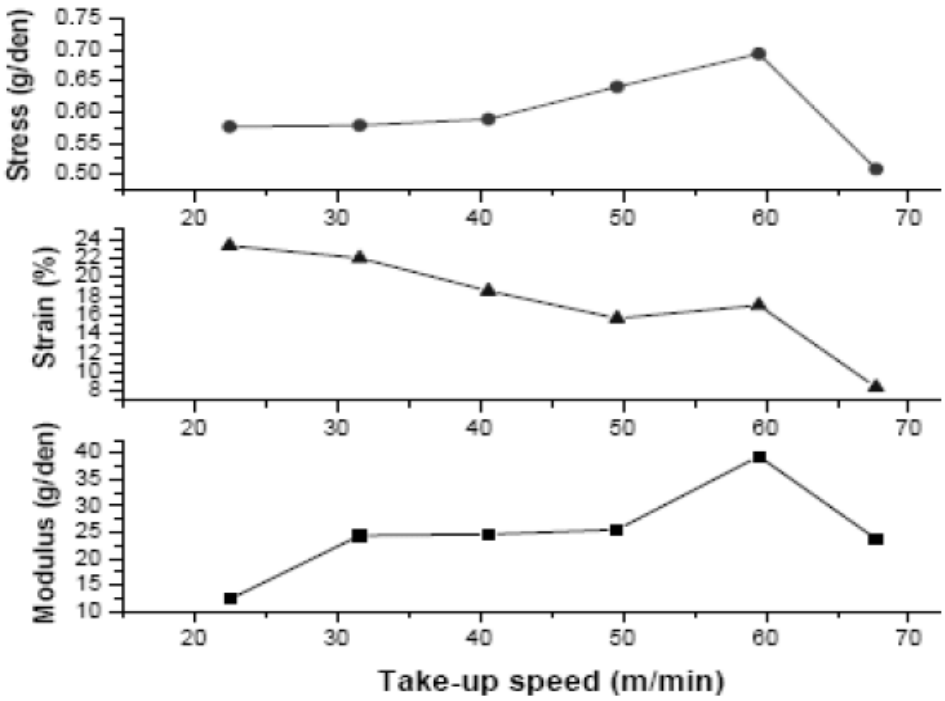


**Fig. 8.** Stress, strain and elastic modulus of PAN nano-monofilament versus take up speed.

Figure 9-a, b show the variation of stress versus degree of alignment and molecular orientation parameters, respectively. Degree of alignment determines the number of fibers subjected in tension direction and increases stress of bundles of fiber. The positive and low correlation factor of 0.53 (acquired by SAS statistic software) between stress and alignment demonstrates their direct and also weak correlation. On the other hand, the positive and high correlation factor of 0.99 is direct consequence of linear and good correlation between stress and molecular orientation parameter.

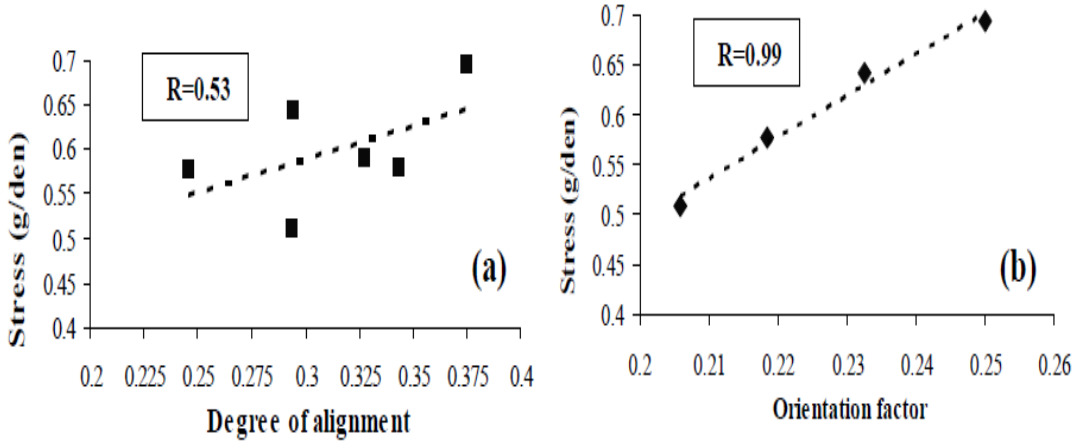


**Fig. 9.** The stress of PAN nano-monofilament versus (a) Degree of alignment (b) molecular orientation parameter.

Figure 10 shows the typical results of differential scanning calorimetry (DSC) for monofilament samples collected by takeup speed 59.5 m/min. In the mean time the gathered data from DSC curves of PAN all samples with take-up velocity between 22.5 m/min and 67.7 m/min are summarized in Table 4.

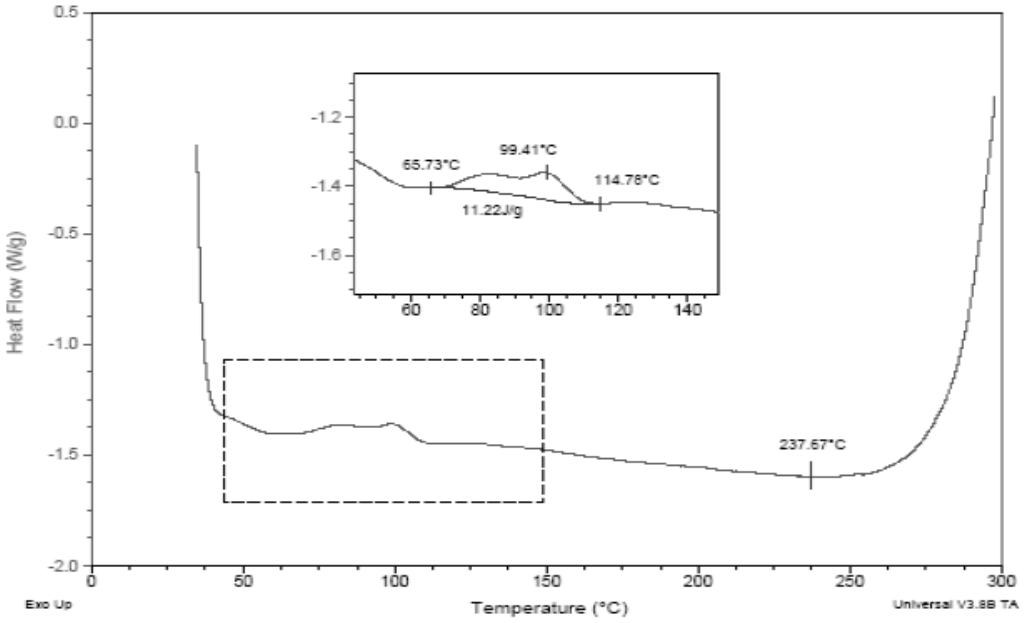


**Fig. 10.** Typical DSC curve of PAN nano-monofilament (takeup speed of 59.5 m/min).

The glass transition temperature ($T_g$) has no substantial change with increasing take up speed and approximately is equal to 100 $^oC$. An exothermic peak present in DSC curve presumably can be attributed to dehydrogenation and cyclization reactions [14, 15, 16]. These chemical reactions must be conducted for a slow heat release. The molecular orientation loses while fast heat release occurs [14, 15]. The minimum rate of heat release observed for samples collected at speed of 67.7 m/min and 59.5 m/min. Therefore, it can be stated that.

**Tab. 4.** Thermal properties of PAN nano-monofilament collected at different take-up speed

| *Take up speed(m/min)* | *22.5* | *31.6* | *40.6* | *49.6* | *59.5* | *67.7* |
|---|---|---|---|---|---|---|
| Tg(°C) | 100.9 | 101.5 | 102 | 100.6 | 99.4 | 100.5 |
| ΔH/Δt(J/g.s) | 0.258 | 0.415 | 0.524 | 0.342 | 0.242 | 0.205 |

Moreover, nanofibers with better initial molecular orientation must be employed to prevent fiber shrinkage during thermal treatment. It is probably originated from strain relaxation acquired by stretching during spinning over $T_g$ temperature. The chemical reaction at higher temperature also possibly reduces chain molecular orientation and subsequently mechanical properties [14, 15].

## Experimental part

Industrial polyacrylonitrile (PAN) was provided by Iran Polyacryle and dimethylformamide (DMF) was purchased from Merck. The weight and number average molecular weight of PAN were respectively 100000 g/mol and 70000 g/mol. All solutions of PAN in DMF were prepared under constant mixing by magnetic mixer at room temperature.

The electrospinning apparatus consist 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 (Figure 11). In this setup unlike the conventional technique, two needles were installed in opposite direction and polymer solutions were pumped to needles by two syringe infusion pumps with same feed rate. The flow rate of solutions to the needle tip was maintained so that a pendant drop remains during electrospinning. The horizontal distance between the needles and the collector was several centimeters. When high voltages were applied to the needles with opposite voltage, jets were ejected simultaneously. Then the jets with opposite charges attracted each other, stuck together and a cluster of fibers formed. For collecting aligned nanofibers, the cluster of fibers formed between the two needles was towed manually to the drum is rotated from 0 to 3000 rpm.

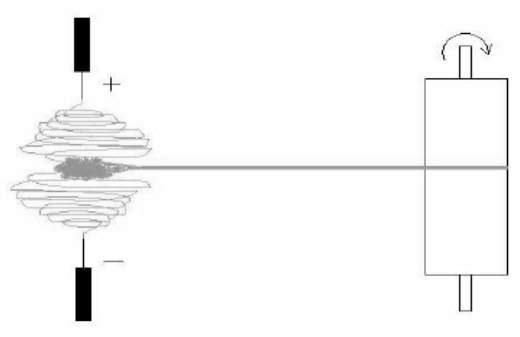


**Fig. 11.** Schematic electrospinning setup for collection of continues aligned nano-monofilament

The gemotrical specification of Electrospun nanofibers were studied using scanning electron microscopy (SEM) and optical microscopy. Samples were mounted onto SEM plates; sputter coated with gold, and examined using a Philips XL-30 electron microscope to determine fiber diameters. A Motic optical microscope was also used to capture images for alignment analysis. Fibers alignment was analyzed using image processing technique by Fourier power spectrum method as a function of take up speed. All images used in the process were obtained using the Motic optical microscopy at a resolution of 640×480 pixels in 1000× magnifications. The number of captured images was 30 at each of take up speeds.

Dried, electrospun fiber bundles were examined using a Bomen MB-Series100 infrared spectrometer (FTIR) to measure crystallization index of PAN nanofibers as a function of collection speed. FTIR spectra were recorded over the range of 400-4000 $cm^{-1}$ with 21scans/min. The crystallization index (A1730/A2240) for PAN fibers was acquired by rationing the absorbance peak areas of nitrile (2240 $cm^{-1}$) and carbonyl (1730 $cm^{-1}$) groups. The relation between degree of crystallinity and A1730/A2240 is indirect (i.e. the larger A1730/A2240, the less crystalline fibers are) [8].

Raman spectroscopy was used for the survey of molecular orientation variability with take up speed. Raman spectra were obtained with the Thermo Nicolt Raman spectrometer model Almega Dispersive 5555. The spectra were collected with backscattering mode, using the 532 nm line of a Helium/Neon laser. The nominal power of the laser was 30 mW. A Gaussian/Lorentzian fitting function was used to obtain band position and intensity. The incident laser beam was focused onto the specimen surface through a 100 × objective lens, forming a laser spot of approximately 1 μm in diameter, using a capture time of 50 s. The analysis of PAN nanofiber orientation using polarised Raman spectroscopy was carried out based on a coordination system defined in Figure 12. The nanofiber axis is defined as Z and molecular chain are oriented at angle θ° with respect to the Z axis. The nanofiber is mounted on the stage of the Raman microscope such that the incident laser comes in along the x' axis. The angle between the polarization plane and the nanofiber axis is ψ. The orientation studies were performed when fibers were at ψ = 0° and ψ = 90° to the plane of polarization of the incident laser. At each angle, the enhanced spectra at VV and VH configuration collected. In the VV configuration, the polarised laser and the analyzer are parallel to each other; and in the VH configuration, the polarized laser and the analyzer are perpendicular to each other.

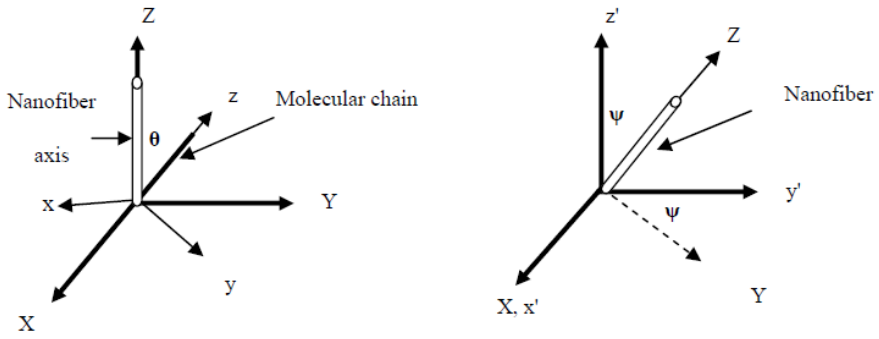


**Fig. 12.** Demonstration of molecular chain coordination(XYZ coordinates) and the nanofiber arrangement in reference frame of the Raman stage(x´y´z´).

The mechanical properties of bundles of aligned PAN nan-monofilament was examined using the Zwick 1446-60 with a crosshead speed of 60 mm/min and gauge length of 25 mm under standard conditions. All samples were included in standard container during 24 h under temperature of 25 $^{o}$C and relative humidity of 65% before being tested. The initial modulus, stress and strain of samples were determined.

DSC curves of electrospun fibers were obtained using a DSC 2010V4/4E by heating from 30 to 300 $^{o}$C at a heating rate of 10 $^{o}$C /min. The effect of take up speed on the $T_g$ temperature and evolved heat per time was examined.

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