Wet-spinning assembly of polyacrylonitrile/non-solvent reinforced fibers with improved structural order and mechanical properties

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Abstract
In this work, polyacrylonitrile (PAN) fibers with adding non-solvent (H₂O) have been prepared using wet spinning method. Tap-water has been applied as a coagulation bath and then it has diffused into PAN spinning solution which has led to a rapid PAN fiber solidification. All of synthesized fibers have been studied via field emission scanning electron microscope (FE-SEM) images, differential scanning calorimetry (DSC) analysis and X-ray diffraction (XRD) pattern. The cross-sectional morphologies of synthesized fibers show that presence of non-solvent in spinning solution reduces the number of micrometer channels and depth of the channels while increases number of finger channels. Also, XRD and DSC results presents that the PAN/H₂O fiber has a higher crystallinity and, in this sample, the polymer chains become less degraded as heat is. All of these findings indicate an enhancement in the structural order of PAN/H₂O fiber, which can ultimately improve the mechanical properties of them.

Keywords: Polyacrylonitrile fiber, Non-solvent, H₂O, Wet spinning

Introduction
Carbon fibers have enjoyed increasing use in a broad variety of high-tech applications, including material and devices for the energy, biomedical, electronics, and structural sectors.[1] The need for manufacturing industries to produce high-tech mechanical synthetic fibers, such as high module, high tensile, low density and low weight, has led to the production of carbon fibers.[2–4] Polyacrylonitrile (PAN) fibers are currently used as a preponderant precursor in the manufacture of high-performance carbon fibers because of their high strength, simpler fabrication process, high crystallinity, cheaper than other precursors like pitch, and the rate of pyrolysis as well as carbon yield and formability accessible.[5,6] The properties of carbon fibers are forcefully affected by the structure and physical properties of the precursor fibers. PAN contains highly polar nitrile groups, which hinder the alignment of the molecular chains during spinning; thus the fibers are not completely graphitized during the graphitization process, yielding fibers with moderate modulus and electrical conductivity.[3,7,8] The density of the current commercial PAN-based carbon fibers is in the range of 1.75–1.93 g/cm³.[2] As compared to metals and ceramics used in structural applications, carbon fiber composites have much higher specific strength and modulus. Recent commercial aircrafts such as the Boeing 787 Dreamliner and Airbus A350 that use substantial amounts of carbon fiber reinforced plastics (CFRP), demonstrate the importance of low-density materials in developing high-performance structures.[2,9]
To date, much research has been done on the functional evaluation of PAN fibers. Zhao et al. [5] have studied the morphology of PAN fibers using a phase separation technique at different temperatures and a concentration of terpolymer solution. With increasing the concentration of PAN terpolymer solutions as well as the quenching depth, the morphology of PAN fibers turns from large open channels to small bead-like structures, accompanying with a reduction of the porosity of PAN fibers. Arbab et al. [10] have investigated the effect of polymer and non-solvent concentrations in spinning solutions. They have observed that increasing the concentration of the polymer has resulted in a significant reduction in the total porosity. Weisenberger et al. [11] have worked on the effect of multiwall carbon nanotube (MWCNT) on the mechanical properties of the composite PAN fibers. They have found that when the volume fraction of MWCNT reaches 1.8%, the breaking stress, Young’s modulus, and yield stress of the composite fibers increases 31, 36, and 46%, respectively, compared with control PAN fiber. Kumar et al. [2] have prepared hollow carbon fibers with using PAN-based precursor fibers with islands-in-a-sea geometry. These fibers have possessed a tensile modulus of 209 N/tex, which is 60% higher than that of the commercial solid carbon fiber T300, as well as density of less than 1.2 g/cm³.

Based on the former literature, wet spinning method has counseled as an ideal strategy to form PAN fibers. [12] Wet-spinning is fascinating example of immersion precipitation, phase-separation, and various transport phenomena. At the moment the viscose polymeric solution is extruded into the coagulation bath, phase-separation begins due to solvent/non-solvent exchange and polymer chains cause as porous fibrils. [13,14] The as-spun fibers possess innumerable macro and nanovoids. [15] Therefore, in this study, non-solvent have been applied to modify PAN substrate to form PAN/Non-solvent fiber through wet spinning method. By analyzing XRD and DSC data, it has been found that the incorporation of water as a non-nonsolvent into PAN can improve mechanical and thermal properties.

**Experimental**

**Materials**

Poly(acrylonitrile-ran-methacrylate) (94 wt% of acrylonitrile monomer) has been provided by Polyaeryl Co. (Isfehan, Iran). Dimethylformamide (DMF, Merck Ltd.) and tap-water and distilled water have been used as solvent and non-solvent, respectively. Viscosity average molecular weight, Mv, of the acrylic copolymer has been measured by dilute solution viscometry of PAN/DMF solutions at 30°C. Number average molecular weight, Mn, weight average molecular weight, Mw, and molecular weight distribution, PDI, have been measured by gel permeation chromatography (GPC 150 C, Waters) at 30°C in DMF. The columns of GPC apparatus have been calibrated by polystyrene standard samples and DMF. The solvent has been injected into five columns with a flow rate of 0.5 mL/min. The detection type is modular differential refractive index and values of Mn = 36,000 g/mol, Mv = 70,000 g/mol, Mw = 116,000 g/mol, and PDI = 3.2 are obtained. The obtained values agreed well with the values provided by the supplier.

**Preparation of spinning solutions**

The spinning solutions have been prepared in two samples, the first sample without non-solvent (sample A) and the second sample with 4 vol.% non-solvent (sample B). Sample A has prepared by mixing 10 vol.% PAN powder and DMF and has swelled for 24 h at 45°C using a magnetic stirrer. Sample B has prepared by mixing 4 vol.% H2O and DMF and has stirred for 30 min using a magnetic stirrer at 25°C. Then, 10 vol.% Polyacrylonitrile powder has been swelled in resultant solution for 24 h using a magnetic stirrer at 45°C.
Wet-Spinning Route of Fibers

The spinning solutions of PAN or PAN/ H₂O have spun into fiber using a laboratorial wet spinning system as shown in Figure 1. The prepared spinning solutions have been extruded by a metering pump (pump constant = 0.5 cm³/rev.) at same shear rate (16000 1/sec), through a single-hole spinneret (diameter = 200 µm and L/D = 2) into a 1-m-long coagulation bath containing tap-water at 25°C. Finally, the spun fibers wound on a bobin.

Characterization

The cross-sectional morphology of PAN and PAN/ H₂O fibers have been measured using a field emission scanning electron microscope (FE-SEM) (MIRA3 TESCAN, Czech Republic). The fibers have freeze-fractured in liquid nitrogen. Finally, fractured surface has been coated with a thin layer of gold and has been scanned with FE-SEM. The powder X-ray diffraction (XRD) patterns has been obtained with a X Pertpro X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA). The correlation between the heat flow and the temperatures of the samples has been studied by using differential scanning calorimetry (DSC) to investigate cyclization reaction of the samples. DSC analysis has been performed on a Mettler Toledo Instruments and the temperature has been raised to 400°C at a rate of 10°C min⁻¹ in N₂ atmosphere. Single fiber mechanical properties (tensile strength, young's modulus) have been obtained using an Instron tensile machine (model 5565) according to the ASTM D 3379-75 standard. Randomly selected fibers have been centered and mounted straightly onto slotted paper frames with a 25 mm gauge length. The grip distance has been set at 50 mm and the setup has been clamped on the tensile machine.

Results and discussion

The morphology of synthesized fibers with different magnification using FE-SEM have been shown in Figure 2. From FE-SEM images. It is found that both fiber samples have almost a circular cross-section. It is worth mentioning that the circular cross-section is more preferred for manufacturing of carbon fibers than bean-like, or oval cross-sections.[16] All fibers have a dense center and finger-like channels in radial direction. As can be seen in Figure 2, when the non-solvent is added into the spinning solution, the number of micrometer channels and the depth of them decreased and the number of finger channels increased. These changes can be attributed to the decrease in thermodynamic affinity to the mass transfer between polyacrylonitrile and non-solvent. In FE-SEM images can be seen phase separation through polymer lean phase nucleation and growth in immersion precipitation process is one of the major practiced approaches toward void formation with controlled morphology. The phase separation in the practiced wet spinning process may be nominated as a complex solid-liquid phase separation through nonsolvent intrusion and polymer reach phase resistance against polymer lean phase growth.[10]
The XRD patterns of PAN and PAN/H₂O fibers have been presented in Figure 3, and the calculated samples d-spacing and crystallinity have been summarized in Table 1. The fiber crystallinity increases along with the adding H₂O (as non-solvent) content, because H₂O can enhance the crystallinity of fibers by inducing the alignment of polymer chains during the gelation process. The XRD spectrum of PAN has displayed a sharp intense peak at 17° and a weak diffraction peak at 28.5°. The first peak is corresponding to diffraction of the hexagonal lattice and the second weak peak relates to the second-order diffraction of the first peak. By adding of H₂O into the PAN fiber, the intensity of the diffraction peaks enhances and the crystallinity of fiber increases from 21.6% to 26.2%. This indicates an improvement in the graphitic order of the PAN/H₂O fiber and, ultimately, a rising in the mechanical properties of it.

![Figure 2. Representative SEM images of PAN fiber (A1, A2, A3) and PAN/H₂O fiber (B1, B2, B3)](image)

![Figure 3. XRD patterns of PAN fiber (sample A) and PAN/H₂O fiber (sample B)](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>d(Å)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (PAN)</td>
<td>5.13</td>
<td>21.6</td>
</tr>
<tr>
<td>B (PAN/H₂O)</td>
<td>5.12</td>
<td>26.2</td>
</tr>
</tbody>
</table>

![Table 1. XRD Data of samples fibers](image)
reactions occurred during this process, so the DSC exotherms of P(AN-MA) were attributed to the cyclization reactions. As shown in Figure 4, PAN fiber (sample A) has one sharp exothermic peak and the cyclization reactions are initiated through a free radical mechanism, causing a large amount of heat to be released at the same time, which results in the breakage of molecular chains and the defects in resultant carbon fiber. In this sample, the initiation temperature and the amount of released heat can be seen as 308.44 °C and 7.26 Wg⁻¹, respectively. However, in sample B, with addition of non-solvent into fiber, the initiation temperature observed at 297.55 °C, which is lower than sample A (about 10.89 °C). This decrease in initiation temperature leads to less energy and time saving as well as less damaged fiber structure. Also, significant reduction (59%) in the released heat (3.57 Wg⁻¹) for sample B (PAN/H₂O fiber) is obtained compared to sample A (7.26 Wg⁻¹). This decrease reflects the role of water in the PAN/H₂O fiber that leads the less destruction of polymer chains when heat releases. Finally, this thermal stability of polymer chains improves the mechanical properties and ordering of the fiber structure.

![Figure 4. DSC curves of PAN (sample A) and PAN/H₂O (sample B) fibers](image)

Conclusions
PAN/H₂O fibers have been successfully fabricated by wet-spinning method, which tap-water has been used as coagulation bath, achieving reinforced mechanical properties and order graphitic. It is found that presence of non-solvent (4 vol.% of H₂O) in fiber structure can express the optimal properties so that leads to enhancement in fiber crystallinity (from 21.6% to 26.2%) and fiber structural order. Also, the decrease of the released heat in the cyclic reaction of the stabilization phase leads to less destruction of structure and chains of polymer in the fiber compared with pure polymer sample. Finally, it can be clearly seen that the addition of water can be considered as a way to improve the order and mechanical properties of the fibers.
References


