Formation of Surface Morphology in Polyacrylonitrile (PAN) Fibers during Wet-Spinning

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ABSTRACT

The effects of concentration of dimethyl sulfoxide (DMSO) in the coagulation bath, draw ratio and extrusion speed on surface roughness of polyacrylonitrile (PAN) fibers prepared by wet spinning and dry-jet wet spinning were investigated. The surface roughness was much higher for PAN fibers produced by wet spinning than dry-jet wet spinning. The surface roughness of the fiber increased linearly with increasing concentration of DMSO in the coagulation bath. Higher roughness was observed at higher draw ratios during spinning. The surface roughness of the PAN fibers decreased initially until at 90m/h, then increased with further increases in extrusion speed. A mechanism for formation of PAN fiber surface morphology based on deformation of the soft skins of single fibers during solidification of PAN/DMSO solution caused by stress perpendicular to the fiber axis is proposed. The stress results from recovery of the aligned PAN macromolecules due to shear in the spinneret during extrusion.

Keywords: PAN fiber; Surface morphology; Wet spinning; Carbon fiber

INTRODUCTION

Polyacrylonitrile (PAN) fiber is the main precursor for production of high performance carbon fiber due to its high molecular orientation, high melting point, and high efficiency of carbon yield [1-3]. Solution spinning is a conventional approach for producing precursor fibers of commercial PAN-based carbon fibers. Wet spinning and dry-jet wet spinning are the two conventional processes to convert PAN solution into fibers. The surface of carbon fibers obtained by wet-spinning is characterized with micro-grooves along the fiber axis, while a smooth surface was observed for carbon fibers obtained by dry-jet wet spinning [4].

Surface morphology is important when carbon fibers are used as reinforcement in polymer based advanced composites. Interfacial adhesion between reinforcement and matrix is a key factor in determining the properties of the resultant composite because good interfacial adhesion results in effective stress transition. Many methods have been applied to modify the surface of carbon fibers to improve the interfacial sheer stress between carbon fibers and the matrix [5-11]. It was usually believed that chemical bonding was more important than physical bonding for carbon fiber composites. However, some researchers demonstrated that physical bonding could produce effective interfacial bonding between carbon fibers and the matrix. By employing air plasma to treat carbon fibers, Lu et al [12] concluded that mechanical interlocking had a dominant effect on the interfacial adhesion of composites. Song et al [13] investigated the effects of surface roughness on interfacial properties of carbon fiber/epoxy composites, and proved that the surface roughness of carbon fibers effectively overcame poor interfacial adhesion between carbon fibers and an organic matrix.

The surface morphology of carbon fibers is inherited from its precursor, and this is determined mainly by the spinning process used to produce the precursor fibers [14]. Efforts have been made to investigate the effects of various factors on the formation of surface morphology of PAN fibers or membranes [15-18]. Parameters studied include solvent type [1], coagulant composition, draw ratio [19], molecular weight [4] and spinning method [9]. By investigating the physical properties of PAN fibers fabricated using dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) as solvent, Mahmod et al [1] found that PAN fibers made using DMSO solvent exhibited a more circular shape

and smoother skin. In preparing PAN hollow fiber membranes, pores were found in the outer layer surface of the fiber at higher draw ratios due to the tension exerted on the fiber during coagulation [12]. However, there have been few studies concerning the combined effects of spinning parameters on surface morphology of PAN fibers, and the mechanism of the formation of surface morphology during spinning is still unclear. In this paper, PAN fibers were prepared from a PAN/DMSO solution via wet spinning and dry-jet wet spinning. The effects of DMSO concentration in the coagulation bath, draw ratio and extrusion speed on surface roughness are investigated. A mechanism for formation of surface morphology during spinning is proposed. By applying this mechanism, it is possible to control the surface morphology of carbon fibers.

EXPERIMENTAL

Raw Materials

Acrynitrile (AN), analytical reagent (AR), was purchased from Sinopharm, China, and distilled to remove inhibitor before polymerization. DMSO AR was purchased from Sinopharm, China. The PAN/DMSO spinning dope was prepared by solution polymerization using 2,2-azobisisobutyronitrile as an initiator with monomer concentration of 21% in volume and ratio of initiator to monomer of 0.25 mol percent. Polymerization was carried out at 60^{o}C for 20 hrs in a 5L polymerizer with a double ribbon agitator. The resulting PAN/DMSO solution was kept at 60^{o}C under vacuum and stirred for 4 hrs to remove the residual monomer. Since bubbles in the dope negatively affect the spinning process, the solution was further de-aired under vacuum at 60^{o}C for 8 hrs. The viscosity-average molecular weight of the obtained PAN was about 11.5*10^{4}.

Preparation of PAN Fibers

The PAN fibers were spun using a 0.1 k spinneret with hole diameter of 0.1 mm and 2:1 length to diameter ratio. The PAN/DMSO solution was extruded using a controlled volume pump to the spinneret and guided into a coagulation bath. The temperature of the PAN/DMSO dope was set at 60^{o}C. PAN fibers about 1 m in length (enough for characterization) were collected by a roller at the desired velocity and put into a 1 L acetone bath about for 2 hrs to set the surface morphology and remove residual DMSO. The fibers were dried under vacuum at 60^{o}C for 24 hrs. For wet spinning, the spinneret plate was submerged into the coagulation bath, while for dry-jet wet spinning; the spinneret was set above the coagulation bath with an air gap of 5 mm. Schematics of wet dry-jet wet spinning are shown in *Figure 1*. The diameter of fibers by both techniques was about 50 μm.

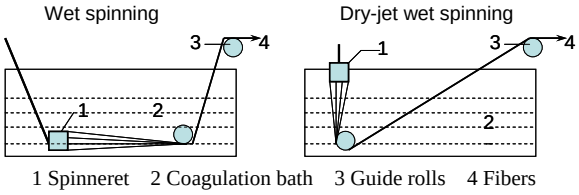

FIGURE 1. Schematic of wet spinning and dry-jet wet spinning.

Characterizations

The surface morphology of PAN fibers was observed using a scanning electron microscope (SEM) of SUPRA 55, SEISS, Germany. The fibers were vacuum coated with gold before examination. An atomic force microscope (AFM) (Nanoscope III, Digital Instruments, USA) was employed in a tapping mode to examine the surface roughness of the fibers. The scanning rate was 1 μm/s and the scanning scope was 2 μm X 2 μm. The surface roughness (Ra) of the fibers was obtained using the Nano Scope software of the instrument.

RESULTS AND DISCUSSION

Effect of Solvent Concentration in the Coagulation Bath

Figure 2 shows the cross section and surface of PAN fiber prepared by dry-jet wet spinning and wet spinning techniques. Rough surface morphology with grooves along the fiber axis was observed for the fibers produced by wet spinning, while the surfaces of the fibers obtained by dry-jet wet spinning are quite smooth. This implies that the difference in fiber surface morphology between the two spinning techniques is related to the 5 mm air gap in dry-jet wet spinning. To analyze the formation mechanism, the effects of DMSO concentration in coagulation, draw ratio and extrude speed on surface morphology for two spinning techniques were investigated and compared.

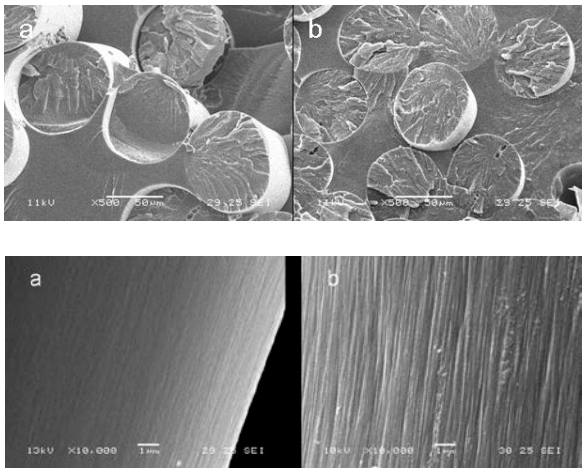

FIGURE 2. SEM images of PAN fiber obtained by dry-jet wet spinning (a) and wet spinning (b)

The transformation of PAN/DMSO solution to solid fibers involves a process of dual diffusion of solvent DMSO and precipitant H_2O during the spinning process. Driven by the difference in concentration, H_2O in the coagulation bath diffused into the polymer solution while DMSO in the fiber diffused into the coagulation bath. These two diffusion processes occurred at the same time to impart the final morphology to the surfaces of the fibers. The surface morphology of the fibers was mainly dependant on the rate of dual diffusion, which is controlled by the DMSO concentration of coagulation bath for given polymer solution at specific temperature. *Figure 3* shows AMF images of the fibers prepared by dry-jet wet-spinning at different DMSO concentrations in the coagulation bath. The fibers show a relatively smooth surface at low DMSO concentrations but became rougher with increasing concentration. The surface roughness (Ra) increased linearly with increasing DMSO concentration of the coagulation bath (*Figure 4*). Ra of the fibers obtained was about 2.8 nm at concentration of 16%, and was about 6.0 nm at concentration of 60 percent.

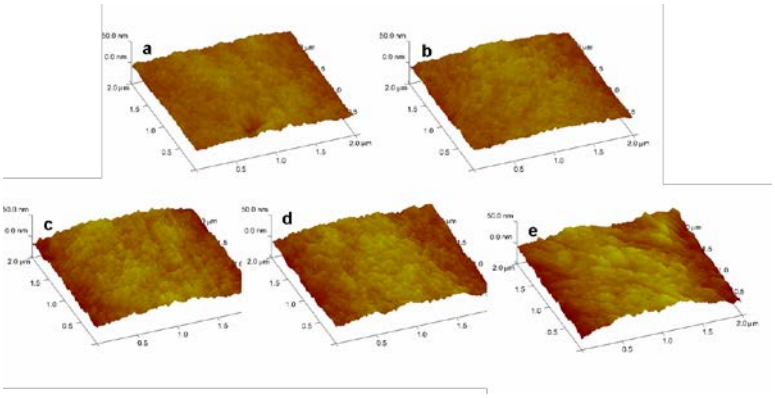

FIGURE 3. AFM images of surface for PAN fibers (DMSO concentration in the coagulation bath, a:16%, b:30%, c:40%, d:50%, e:60%).

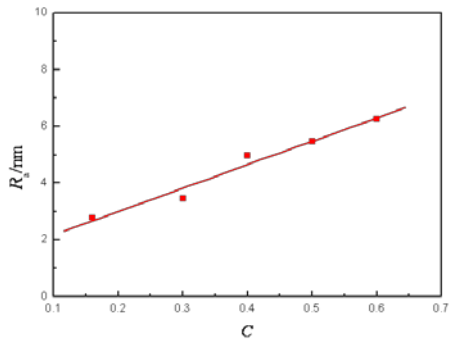

FIGURE 4. Surface roughness of PAN fibers at different DMSO concentrations.

Effect of Extrusion Speed

AMF images of the PAN fiber surface obtained at extrusion speeds of 30 to 150 m/h by dry-jet wet spinning and wet spinning are shown in *Figure 5*. Rougher surfaces were observed for fibers obtained by wet spinning than for those spun by dry-jet wet spinning method. The surface roughness (Ra) of the fibers decreased initially with increasing extrusion speed until 90 m/h, then increased with further increases in extrusion speed (*Figure 6*). The effect of extrusion speed on surface roughness was more significant for wet spinning. The Ra range of the fibers was between about 3 to 6 nm for dry-jet wet spinning, and was about 9 to 20 nm for wet-spinning.

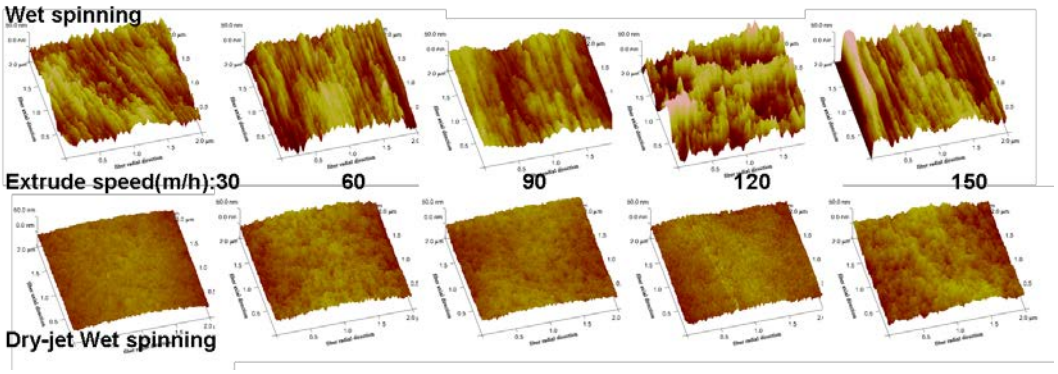

FIGURE 5. AFM images of PAN fiber at different extrude speed.

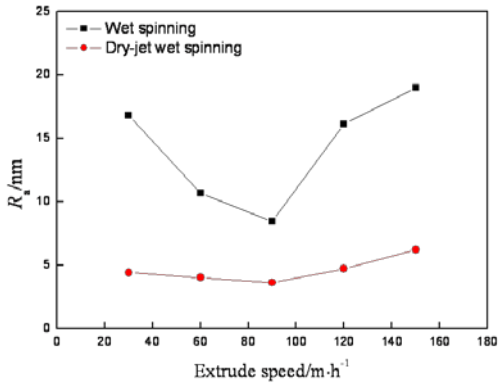

FIGURE 6. Effect of extrude speed on surface roughness.

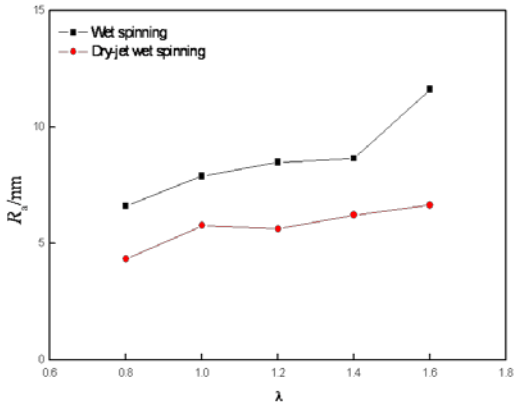

FIGURE 7. Effect of draw ratio on surface roughness of PAN fiber.

Effect of Draw Ratio

Figure 7 shows the change in surface roughness Ra with increasing draw ratios from 0.8 to 1.6 for fibers spun by wet-spinning and dry-jet wet spinning. Draw ratio λ was calculated by dividing the extrusion speed by the speed of the collecting roller. Ra increased steadily with increasing draw ratio for both spinning methods. The effect of draw ratio on surface roughness is more significant for wet spinning. The Ra value was generally about 1.5 times higher for fibers obtained by wet spinning than dry-jet wet spinning.

Mechanism Analysis

The formation of PAN fiber morphology can be attributed to two processes during wet spinning. When PAN/DMSO solution is extruded to the spinneret, PAN macromolecules become aligned due to the shear in the spinneret holes. This induced die swell when the solution left the spinneret. At the very instance when the PAN/DMSO solution contacted the coagulation bath, dual-interfusion of solvent DMSO and precipitant H_2O occurred between the PAN/DMSO solution and coagulation bath, and a soft solid skin was formed by PAN/DMSO solution in the core of the fiber. Recovery of the aligned PAN macromolecules in the core caused stresses perpendicular to the fiber axis, and some part of the soft skin deformed, resulting unsmooth fiber surfaces. As these two processes occurred continuously during spinning, formed along the fiber axis.

In the case of dry-jet wet spinning, as recovery of the macromolecules occurred in the air gap between the spinneret and the coagulation bath before solidification, little deformation at the perimeter of single fibers occurred and PAN fibers with smooth surfaces were obtained. More deformation occurred in softer skin of the single fiber with higher DMSO concentration of the coagulation bath, which resulted in higher surface roughness.

The surface roughness of the fibers increased with increasing draw ratio during spinning due to higher stress at higher draw ratios. With increasing extrusion speed, refreshing of the coagulation bath around the fibers became quicker, and solidification of PAN/DMSO solution became more rapid, resulting less deformation of the skin and lower surface roughness of the resulting fibers. However, increasing recovery of the aligned PAN macromolecules, which was induced by increasing shear stress at higher extrude speed, caused more deformation at the perimeter of the fibers, resulting in higher surface roughness of the fibers. Due to these two effects, the surface roughness of the PAN fibers decreased initially and then increased with further increasing extrusion speed.

CONCLUSION

1. The surface roughness was much higher for PAN fibers produced by wet spinning than dry-jet wet spinning. Ra values of the fibers increased linearly with increasing DMSO concentration in coagulation bath.
2. Higher roughness was observed at higher draw ratios during spinning. The surface roughness of the PAN fibers decreased initially, and then increased with further increases in extrusion speed.
3. A mechanism for formation of PAN fiber surface morphology based on deformation of the soft skins of single fibers during solidification of PAN/DMSO solution caused by stress perpendicular to the fiber axis is proposed. The stress results from recovery of the aligned PAN macromolecules due to shear in the spinneret during extrusion.

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