The Formation of Polyacrylonitrile Nascent Fibers in Wet-Spinning Process

Juan Chen,[1] He-Yi Ge,[1] Xing-Guang Dong,[2] Cheng-Guo Wang[2]

[1]*College of Materials Science and Engineering, University of Jinan, Jinan 250022, People's Republic of China*
[2]*Carbon Fiber Engineering Research Center of Shandong Province, College of Materials Science and Engineering, Shandong University, Jinan 250061, People's Republic of China*

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ABSTRACT: The formation of polyacrylonitrile (PAN) nascent fibers in wet-spinning process was studied by $KMnO_4$ back titration method and scanning electron microscopy (SEM). It has been found that the rate of DMSO diffusion was rapid at the beginning of coagulation then decreased and reached balance at 24 s. With coagulation time increase, the nascent fibers became denser and had fewer inner defects gradually, but transverse stripes appeared on the surface at 24 s, and got deeper. The main defects of nascent fibers included transverse stripes, impurity, fish tail, inner microvoids etc. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 692–696, 2007

Key words: PAN; coagulation bath; nascent fiber; structure

INTRODUCTION

Carbon fibers are widely applied due to their high performance. It has been established that the properties of carbon fibers are mainly determined by the microstructure of the precursor fibers because of the structural inheritance.[1–3] PAN precursor fibers are the most successful and promising precursors for making high performance carbon fibers. The structure of PAN precursor fibers has substantial influence on the development of stabilized fibers and carbon fibers.[4–6] In wet-spinning process, a viscous polymer solution is extruded through small holes of a spinneret immersed in a liquid bath. Mutual-diffusion between the freshly formed fluid filament and the bath cause the solidification of polymer. This process is called coagulation, which is the fundamental process governing the fiber structure in wet spinning. Early studies were just empirical attempts to correlate the actual spinning variables with the final properties of the fibers.[7–9] The mechanism of nascent fibers structure has been studied in our early work,[10] where the counter diffusion of solvent and nonsolvent from nascent fiber in PAN-DMSO-H_2O system have been simulated. In this work, the formation process of nascent fibers and the formation mechanism of defects in PAN wet-spinning were studied.

Correspondence to: Dr. J. Chen (chen2000juan@163.com).

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EXPERIMENTAL

Wet spinning

The PAN solution made by solution polymerization[11] was used as spinning dope after removal of excess solvent and uncreated monomers. Then, the dope was deaerated, filtered, followed by pumping through a spinneret (1000 holes, 0.06 mm/hole, $L/D = 1.2$) to a coagulation bath. After a definite time, the coagulated nascent spinning filaments were obtained. The schematic of coagulation bath is shown in Figure 1.

A H_2O/DMSO mixture was used as the coagulation bath. PAN concentration in the polymer solution was 20%, DMSO concentration in the coagulation bath was 65 wt %, the coagulation bath temperature was 50°C, and jet stretch ratio was 0%.

Jet stretch ratio is defined as the ratio of the linear take-up rate at which protofibers are taken out of the coagulation bath to the linear rate at which spinning dope is extruded through the spinneret holes. According to this, the jet stretch ratio can be expressed as:

$$\varphi = \frac{v_1 - v_2}{v_2},$$

where φ is the jet stretch ratio, v_1 is the linear velocity of the filament at the take-up roller, v_2 is the linear velocity of the spinning dope in the spinneret hole.

Characterization

The weight of solvent in filaments was measured by the following method. The bath solution smeared on

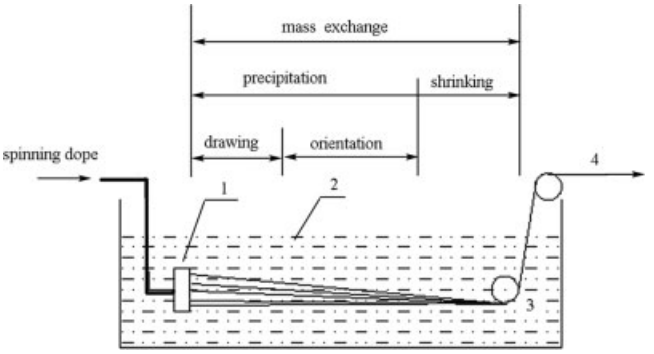

Figure 1 Schematic sketch of experimental spinning apparatus:1, spinneret; 2, coagulation bath; 3, guide roller; 4, nascent fibers.

the filament surface was carefully removed by moisture absorption paper, and filament was dipped in water and boiled for 1 h to extract the solvent from the filament sufficiently. The solvent concentration in water was measured by $KMnO_4$ back titration method.[12]

The titre (the linear density of fibers) of a filament and the mechanical properties of precursor fibers were measured by a XD-1 fiber fineness machine and a XQ-1 fiber tensile strength machine.

Density was measured at 25°C by the use of density gradient column method in a mixture of *n*-heptane and carbon tetrachloride with a gradient from 1.00 to 1.60 g/cm.[3]

A JSM-6700 scanning electron microscope (SEM) operated at 3 kV was used to obtain SEM images. The nascent fiber specimen was embed in epoxy and ruptured in liquid nitrogen for the observation of cross-sectional microstructure. A tow of nascent fiber (about 200–300 filaments) was adhered on the specimen desk to be observed the surface. And the cross-sectional microstructure of broken single fiber was examined.

RESULS AND DISCUSSION

The formation process of nascent fibers in coagulation bath

The mechanical properties of nascent fibers

The mechanical properties of nascent fibers of different coagulation time are shown in Table I. It can be seen that the tensile strength and the density increase with coagulation time increase, but the titer gradually decreases.

In wet-spinning process, the filaments shrink in vertical direction due to the swelling of spinning dope near the spinneret.[13] Although the jet stretch ratio was 0%, the filaments still bore spinning tension in the coagulation process. The spinning tension led to orientation of solid skin in filaments so that the tensile strength was gradually increasing. Meanwhile, fibers became denser and finer under the spinning tension.

Cross-sectional profile

The cross-sectional profiles of nascent fiber at different coagulation time are illustrated in Figure 2. In the coagulation process, the filaments get denser and finer gradually from P1 to P6. The skin-core structure in nascent fiber P1 is obvious. Its core region is loose with voids, whereas the outside region is more compact and denser. The diameter of P4 is thinner than P1, and the skin-core structure is not clear. The diameter of P6 is thinnest and the cross-sectional structure is more homogeneous than that of P4. The result accords with the trend of mechanical properties in Table I. According to boundary moving model put forward by Paul,[14] as the streamlet coagulating, the surface of filament coagulates firstly and forms a layer of skin. The interface between the coagulated and noncoagulated layers is obvious and moves to core region with mutual-diffusion process. This interface is called moving boundary. When the coagulation time was 6 s, the mutual-diffusion occurred on the surface of the streamlets firstly and formed a layer of skin and the inner of filament was true solution of polymer. As a result, the skin and the core had different densities. Table I indicates that DMSO concentration in filaments changed rapidly at the beginning (0–12 s) then became tempered and kept constants after 24 s. The decrease of DMSO concentration reflects the mutual-diffusional rate.[10] The trend of concentration change illustrates that the mutual-diffusion reached balance at 24 s. Therefore, the moving boundary reached the core region when filaments coagulated after 24 s, which resulted in the homogeneous cross-sectional profile (P4). Then filaments shrank under spinning tension until they left the coagulation bath (P6). The cross-sectional structure was densest and the diameter was finest.

TABLE I
The Mechanical Properties of PAN Nascent Fibers

Sample	Coagulation time (s)	Strength ($cN \cdot dtex^{-1}$)	Titer (dtex)	Density ($g \cdot cm^{-3}$)	DMSO residues (wt %)
P1	6	0.52	8.00	1.160	70.26
P2	12	0.54	7.99	1.162	60.92
P3	18	0.55	7.97	1.165	54.15
P4	24	0.57	7.96	1.167	51.16
P5	30	0.58	7.93	1.169	51.01
P6	36	0.58	7.92	1.169	50.99

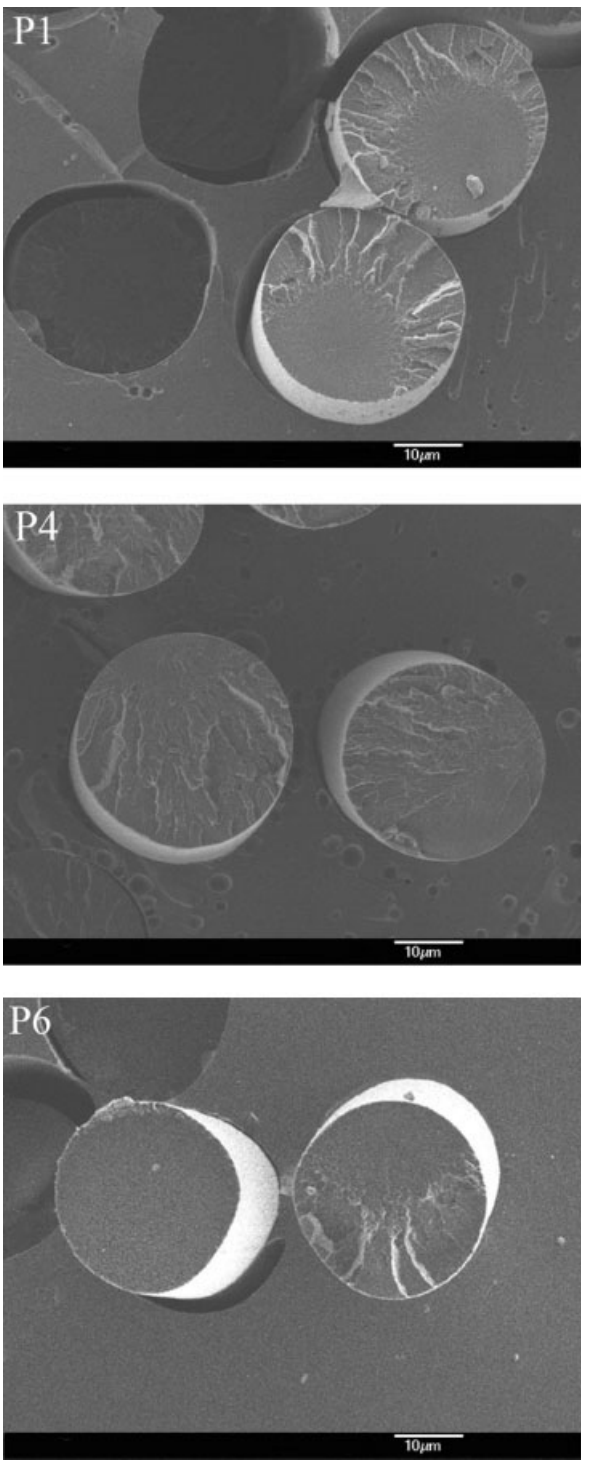

Figure 2 SEM photographs of nascent fibers cross-section.

Vertical surface microstructure

Figure 3 shows the vertical surface profile of nascent fiber at different coagulation time. It can be clearly seen that the diameter of fiber decreases from P1 to P6. There were transverse stripes appearing on the surface of fiber when coagulation time reached 24 s (P4). When the fiber left the coagulation bath (P6), the transverse stripes were getting deeper and developed into grooves. The endured load of polymer is mainly undertaken by its molecular chains. During coagulation process, the spinning tension leads to orientation of solid polymer in filaments so that the tensile strength is increased. When the stretch

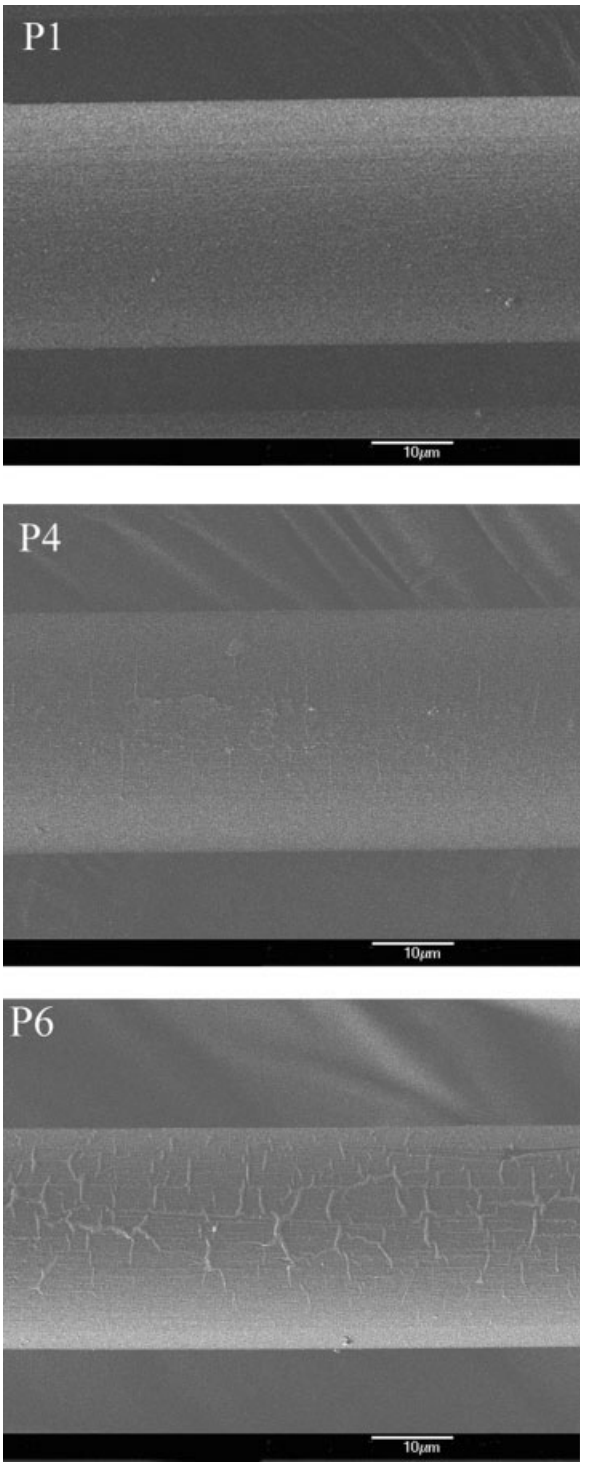

Figure 3 SEM photographs of nascent fibers vertical surface.

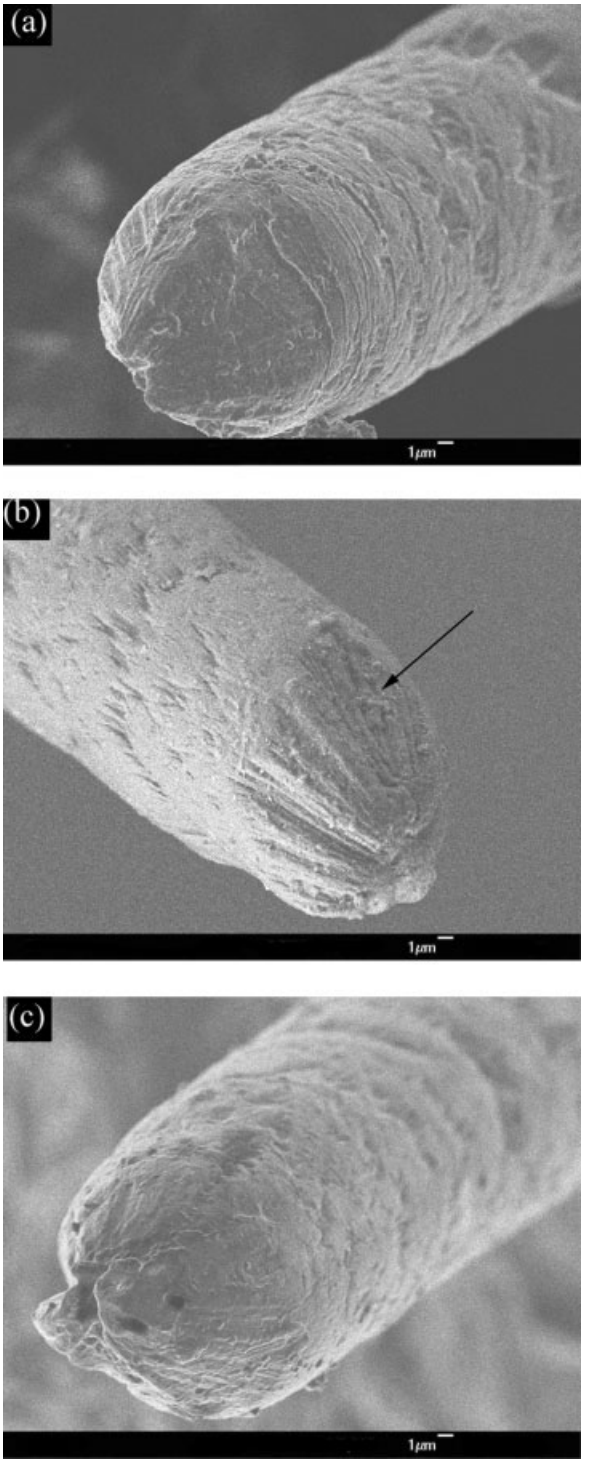

Figure 4 SEM photographs of single nascent fiber.

exceeds the critical value, the polymer molecular chains would rupture, which results in transverse stripes on the filament surface. The nascent fibers with transverse stripes would break easily in follow-up processes and decrease tensile strength of precursor fibers. Therefore, to avoid rupturing nascent fibers, zero stretch ($\varphi = 0$) or apparent minus stretch ($\varphi < 0$) is always used in the coagulation process. According to Wang et al.,[15] the minus stretch is commonly controlled within 30–60%.

Formation of defects

To study the formation of defects, P6 nascent fibers were adopted. The microstructure of single nascent fiber ruptured by strength testing instrument at a speed 10 mm/min was observed by SEM as shown in Figure 4. Their mechanical properties are listed in Table II.

Figure 4 illustrates that the cross-section of nascent fibers presents a step-like shape taper, the diameter of fiber decreases and transverse stripes become deeper until fracture. This proves that the formation of transverse stripes is caused by the overlarge spinning tension. From Figure 4(a), it is found that there are no obvious defects in cross section. As a result the tensile strength of (a) is highest as shown in Table II. The obvious surface defect at the broken point in Figure 4(b) (indicated by arrow) is a fish tail defect, which leads to the lowest tensile strength (0.50 $cN \cdot dtex^{-1}$) of (b). There are many microvoids and even two big voids (about 1 μm) in the core region of fiber cross-section of (c), which led to stress concentration and the fracture. The tensile strength of (c) is lower than (a). Therefore, fibers with more defects have lower mechanical properties.

Surface defects

Besides the transverse stripe, there are other surface defects observed on nascent fibers as shown in Figure 5. There is impurity adhering on surface of nascent fiber caused by unclean coagulation bath or guide roller [Fig. 5(a)]. A part of impurities can be eliminated during water-washing process, but some will be left on fibers until carbonization process. Light fish tail [Fig. 5(b)] and severe fish tail [Fig. 5(c)] are due to rough guide roller, which may scratch the surface of fibers. The fibers with fish tail are easily broken during drawing in spinning, stabilization or carbonization process due to stress concentration. Therefore, spotless environment and polished equipment are essential to obtain high performance precursor fibers.

TABLE II
The Mechanical Properties of PAN Single Nascent Fibers

Sample	Strength ($cN \cdot dtex^{-1}$)	Elongation (%)
a	0.58	106
b	0.50	118
c	0.54	105

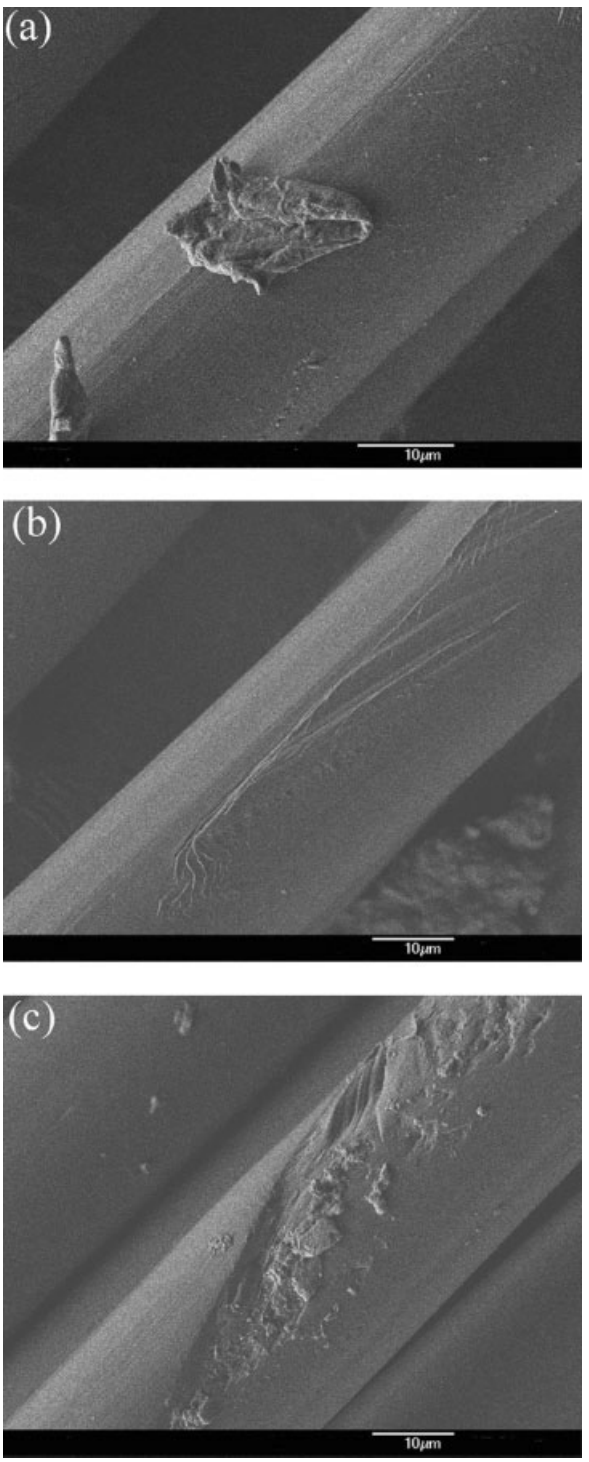

Figure 5 SEM photographs of nascent fibers vertical surface with defects.

Inner defects

Microviods are the main inner defects that cause the decline of fiber tensile strength as shown in Figure 4(c). The formation of microviods was mainly ascribed to the different rate of mutual-diffusion from the skin to the core. The mutual-diffusion occurred on the surface of the nascent fiber firstly and formed a layer of skin. The thin skin cumbered mutual-diffusion process. As a result, the skin and the core had different structure and densities. The skin region is compact and well oriented, whereas the core region is loose and has some voids.

The quality of precursor fibers is a key factor in the resultant carbon fibers. Inner defects of precursor fibers will pass down to the carbon fibers. There are many reports[6,9,16] about the relation between inner microviods of nascent fibers and coagulation conditions. Dry-jet wet spinning technique can availably lessen microviods. Furthermore, properly debasing coagulation bath temperature and concentration can lead to lower porosity.

CONCLUSION

The formation process and main defects of nascent fibers in PAN wet-spinning have been studied by SEM. The nascent fiber became denser and finer gradually during coagulation process. The cross-sectional profile of fiber was homogeneous when the mutual-diffusion reached balance and became denser during later shrinking process. The transverse stripes on the surface of fiber got deeper gradually under spinning tension. The main defects of nascent fibers included transverse stripes, impurity, fish tail, inner microvoids, etc. To attenuate defects and obtain high performance PAN precursor fiber and the resultant carbon fiber, it is essential to improve the lustration of circumstance and the precision of spinning equipment as well as modulate the technological parameter of spinning for controlling mutual-diffusion process.

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