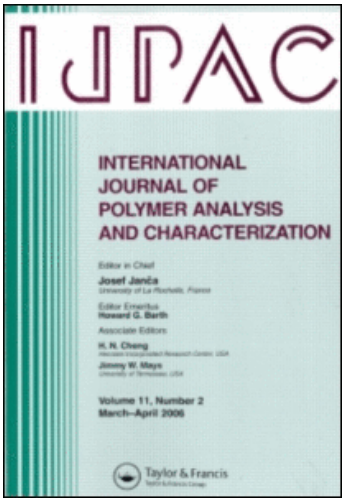

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A Novel Method for Investigating the Structural Uniformity of Polyacrylonitrile Nascent Fibers

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Abstract: A new method for studying structural uniformity of polyacrylonitrile (PAN) nascent fibers is presented. The difference between external and internal structures of nascent fibers could be accessed by measuring radial direction solubility ($r_0 - r_n$). Scopephoto and microscopy were employed as tools to observe the cross section and surface of nascent fibers at any DMSO/H_2O dissolution time. The dissolution velocity ratio (exterior/interior) of nascent fibers was considered as a convenient means to study structural uniformity. The results showed that homogeneous nascent fibers were achieved at higher temperature when the coagulation bath concentration was set at 70 wt.%.

Keywords: Dissolution velocity ratio; PAN nascent fibers; Radial direction solubility; Scopephoto; Structural uniformity

INTRODUCTION

Polyacrylonitrile-based carbon fiber (PANCF) is one of the most promising synthetic fibers, and it has been widely used not only in

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high-tech fields such as aviation, missiles, and spaceflight, but also in civil applications. The properties of the final carbon fibers are determined by the quality of precursor fibers.[1,2] Hence, to obtain good quality carbon fibers, the precursor fibers must exhibit high-quality parameters. Good quality precursor fibers require not only reasonable chemical composition, but also given physical characteristics, such as a smooth surface, few lacunas, homogeneous structure, and so on.[3] The cross section of nascent fibers is fixed when leaving the coagulation bath, and the congregate structure and lacunas of nascent fibers will be inherited by precursor fibers and carbon fibers. On the basis of the above-mentioned analysis, coagulation is a very important step for fiber forming during the wet-spinning process.

During wet-spinning, fiber forming is a double-diffusion process; the diffusion first takes place around the surface, and the surface pellicle forms, which baffles the diffusion into the core of the fibers, so the fibers are heterogeneous. The exterior is compact, but the interior looses even the existing core/shell structure.[4] Hence, the external and internal dissolution velocities of nascent fibers in dimethyl sulfoxide (DMSO) are different.

Many studies have been carried out to investigate the structure of PAN nascent fibers. Scanning electron microscopy (SEM) is often used to observe their cross section and surface morphology.[4–8] X-ray diffraction (XRD) is an important method to study solid-state structures and has been widely used in characterizing the physical structure of nascent fibers.[4,8,9] In addition, transmission electron microscopy (TEM),[10] high-resolution TEM,[11] atomic force microscopy,[12] and mercury intrusion porosimetry (MIP)[13] have been also applied to characterize the fine structures of fibers. Moreover, the dissolution method was used to determine the precursor fiber structure uniformity[14] and preoxidation extent.[15] However, few studies have been focused on studying quantitatively the difference between external and internal structure of PAN nascent fibers.

In this article, we present a convenient and effective way to investigate the structure uniformity of nascent fibers. A microscope (Alphaphot 2 SY 2, Nikon) and Scopephoto (LY-WN 300, Hangzhou Scopetek Opto-Eletric Co., Ltd.) were employed to observe the cross section and surface variation as a function of time.

EXPERIMENTAL SECTION

Preparation of PAN Nascent Fibers

PAN copolymer was polymerized with acrylonitrile, itaconic acid, and methyl acrylate in dimethyl sulfoxide (DMSO) using 2,2′-azobisisobutyronitrile

(AIBN) as initiator under an inert atmosphere of nitrogen at 65°C for 18 h. The polymerization solution consisting of 17.72% copolymer was deaerated under 80°C, filtered, and then pumped to a DMSO/H_2O coagulation bath system. The nascent fibers were obtained by varying coagulation bath temperatures when other factors were constant.

Dissolution of Nascent Fibers

PAN nascent fibers were cut into 10 cm long pieces, detached to a single fiber, and put into a DMSO/H_2O solution consisting of 98 wt.% DMSO at 20°C for different dissolution times. Then the remaining fibers were taken out as quickly as possible and immersed in 70 wt.%, 50 wt.%, and 30 wt.% DMSO/H_2O solution for one minute. Thus, various samples were obtained.

Measurements

The cross section and surface of nascent fibers were examined by Scopephoto and a microscope at different DMSO/H_2O dissolution times. Scopephoto is image disposal software that connect a microscope to a computer to observe fibers.

To examine the linear density (a measure of the nascent fibers' mass per unit of length), bulk density, and mass of the samples, they were watered thoroughly by an ultrasonic cleaner and then dried in a vacuum oven. The linear density was noted as L and bulk density was noted as ρ. The mass of original nascent fibers was noted as w_0, and w_1, $w_2 \ldots w_n$ along with dissolution time.

The radius of fibers was determined quantitatively according to a formula as follows:

$$r_0 = \sqrt{\frac{L}{\pi\rho}} \tag{1}$$

The r_n of fibers under different dissolution times was expressed as follows on the assumption that the linear density and bulk density were constant:

$$r_n = \sqrt{\frac{w_n L}{w_0 \pi\rho}} \tag{2}$$

A series of radial direction solubilities ($r_0 - r_n$) was accessed easily. Then we obtained a plot, in which the X-axis refers to dissolution time of nascent fibers and the Y-axis refers to the radial direction solubility.

With the exterior radius defined as $r_0 - r_n = 0 \sim 25\%$ and the interior radius as $r_0 - r_n > 40\%$, the exterior and interior radii must adopt four plots by adjusting the dissolution time. Using the least squares method, the slopes of exterior and interior radii were adopted as dissolution velocity. If the dissolution velocity ratio (exterior radius/interior radius) was much closer to 1, the nascent fibers were more homogeneous in the radial direction. In addition, the radii of the fibers were more similar at different positions, and the fibers were found to be more homogeneous in the circular direction.

RESULTS AND DISCUSSION

In order to test the applicability of this new method, the coagulation bath conditions were designed as follows: the bath concentration was set at 70 wt.%, the stretch ratio was 0.9, and the temperatures were 30° and 50°C. Figure 1 shows the cross section and surface morphology of different dissolution time fibers, for which the bath temperature was 30°C. The cross section shape of the original fibers was circular (Figure 1(a)), the surface contained some residual liquid (Figure 1(b)) owing to the lower diffusion rate, and the dissolution of fibers was irregular according to the irregular radii changes under different dissolution

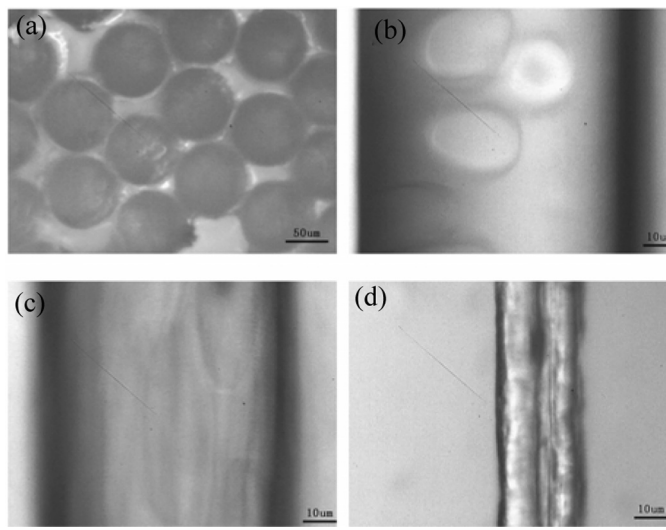

Figure 1. Cross section and surface of nascent fibers spun at 70 wt.%, 30°C $DMSO/H_2O$ coagulation bath under different dissolution times: (a) cross section, 0 min; (b) surface, 0 min; (c) surface, 5 min; (d) surface, 15 min.

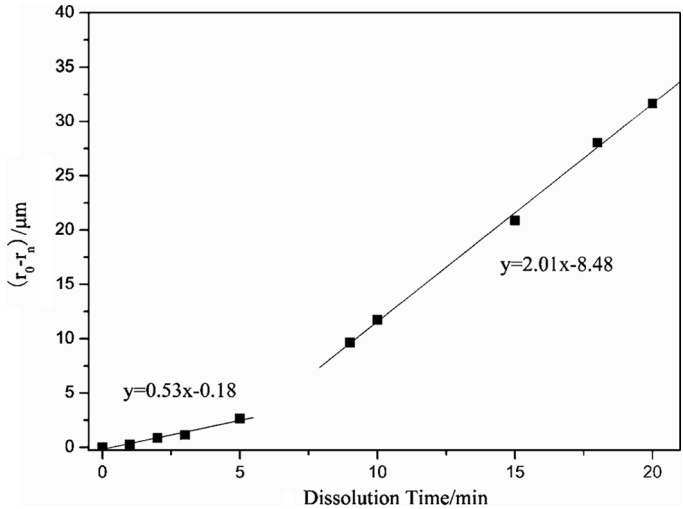

Figure 2. Dissolution velocity of nascent fibers spun at 70 wt.%, 30°C $DMSO/H_2O$ coagulation bath.

times (Figures 1(c) and 1(d)). Moreover, the dissolution velocity ratio was 0.26 according to Figure 2, which proved that the nascent fibers were heterogeneous in the radial direction.

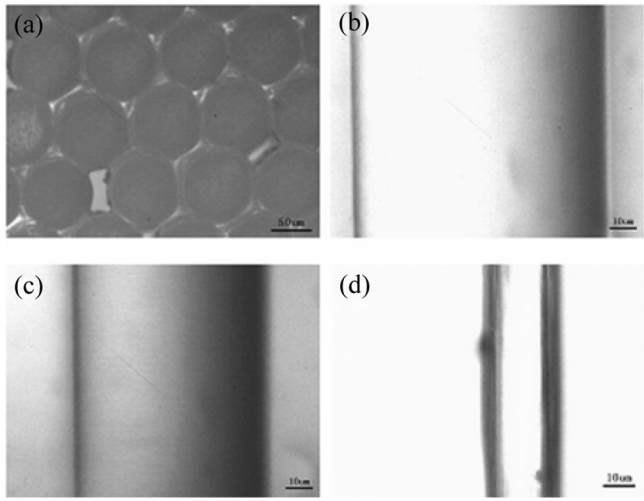

Figure 3. Cross section and surface of nascent fibers spun at 70 wt.%, 50°C $DMSO/H_2O$ coagulation bath under different dissolution times: (a) cross section, 0 min; (b) surface, 0 min; (c) surface, 5 min; (d) surface, 15 min.

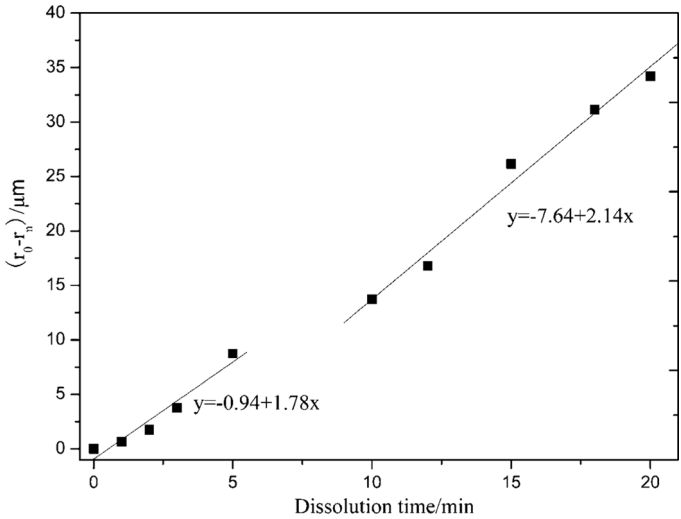

Figure 4. Dissolution velocity of nascent fibers spun at 70 wt.%, 50°C $DMSO/H_2O$ coagulation bath.

Figure 3 shows the cross section and surface morphology of different dissolution time fibers, in which the bath temperature was 50°C. The cross section shape was circular, the dissolution of fibers was homogeneous in the circular direction as shown in Figure 3, and the dissolution velocity ratio was 0.83 according to Figure 4. On the basis of this analysis, the nascent fibers became more homogeneous when spun in higher bath temperature whereas the others were constant.

The phenomenon can be explained in terms of fiber structure: at lower temperature and higher concentration, the outer side of the nascent fibers was compact, and the inner one coagulated inadequately. However, with an increase of temperature, the coagulation accelerated, the pellicle was deeper, the diffusion was more homogeneous,[4] and the nascent fibers became more uniform.

CONCLUSIONS

A novel and effective method to study the difference between external and internal structures of PAN nascent fibers was described. The uniformity of nascent fibers, including in the radial and circular directions, was determined by this method. The results showed that more homogeneous nascent fibers could be achieved at higher temperature

when the coagulation bath concentration was set at 70 wt.%, and the stretch ratio was 0.9.

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