Polym. Bull. (2009) 62:657–666
DOI 10.1007/s00289-009-0043-1

ORIGINAL PAPER

# Effect of dope extrusion rate on the formation and characterization of polyacrylonitrile nascent fibers during wet-spinning

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Received: 23 October 2008 / Revised: 18 December 2008 / Accepted: 18 January 2009 /
Published online: 25 January 2009


**Abstract** Polyacrylonitrile nascent fibers were prepared via the wet-spinning technique and a dimethyl sulphoxide/$H_2O$ coagulation bath system was adopted. The objective of this study was to investigate the influence of dope extrusion rates on formation and characterization of nascent fibers. Nine different dope extrusion rates were adopted when other technique parameters were kept steady. The surface morphology of nascent fibers was observed by field emission scanning electron microscopy. The results showed that the dope extrusion rates played significant effects on the cross-section structure, surface morphology, degree of crystallization, and sound velocity of the nascent fibers. With an increase of dope extrusion rate, the surface roughness increased, and the sound velocity had a point of inflexion. Moreover, the degree of crystallization had a maximum when the dope extrusion rate was 5.92 m/min.

**Keywords** Dope extrusion rate · Polyacrylonitrile nascent fibers · Shear rate · Surface morphology · Wet-spinning

## Introduction

Polyacrylonitrile (PAN) based carbon fibers have been widely used for spaceflight as well as civilian fields owing to a series of excellent properties [1, 2]. The properties of

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the final carbon fibers are determined by the quality of precursor fibers [3]. Moreover, the coalesced structure and lacunas of nascent fibers will be inherited by the precursor fibers and carbon fibers. In other words, the spinning conditions in which the nascent fibers formed have a critical effect on the properties of PAN fibers [4].

During the past years, many studies have been carried out to investigate the effect of forming conditions on the structure and properties of PAN nascent fibers during wet-spinning. Knudsen [4], Takahashi et al. [5] and other researchers [6–9] studied the coagulation bath conditions, including dope solids, bath concentration, bath temperature, and drawing on the structure and properties of nascent fibers. And the effect of molecular orientation induced rheologically on fiber properties was well investigated by Paul [10]. Moreover, much attention has been gradually paid to the effect of dope extrusion rate on morphology and properties of nascent fibers because of wide application of PAN fibers.

Recently, many researches in the field of PAN fibers have been focused on the development of an industrial material. However, it should be noted that there are many difficulties in developing the industrial material in the spinning process of commercial fibers due to the problems of the spinning process, such as spinnability, rheological and diffusion phenomena [11]. Of course, spinning speed or dope extrusion rate should be taken into account for commercial fibers. The aim of this work was to achieve a complete understanding of the dope extrusion rate affecting formation and characterization of nascent fibers. Fibers were spun at various dope extrusion rates ranging from 0.43 to 7.32 m/min and hence at different levels of shear. The effect of dope extrusion rate on formation and characterization of nascent fibers was investigated in our work, providing a reliable and scientific data for industrial production of PAN fibers.

## Experimental

### Materials

Acrylonitrile (AN): Asahi Kasei, Japan.
Itaconic acid (IA): Acros Organics, NJ, USA.
Methyl acrylate (MA): Tianjin FuChen Chemical Reagent Factory, Tianjin, China.
2, 2′-Azodiisobutyronitrile (AIBN): Shanghai No. 4 Reagent & H. V. Chemical Co., Ltd, Shanghai, China.
Dimethyl sulphoxide (DMSO): ARKEMA, France.

### Preparation of PAN nascent fibers

Polyacrylonitrile copolymer was polymerized with AN, IA [AN: IA = (99:1)] in DMSO using AIBN as initiator under an inert atmosphere of nitrogen at 65 °C for 18 h. The polymerization solution containing 19% copolymer was deaerated by a vacuum pump at 80 °C, filtered, and then spun into a DMSO/$H_2O$ coagulation bath

**Table 1** Spinning parameters and coagulation bath conditions

| Process parameters/spinning conditions | Value |
|---|---|
| 1. Spinning temperature (°C) | 50 |
| 2. Spinneret diameter (μm) | 70 |
| 3. Stretch radio | 0.6 |
| 4. Coagulation bath temperature (°C) | 50 |
| 5. Coagulation bath length (m) | 0.8 |
| 6. Coagulation bath flux (l/h) | 400 |

**Table 2** Corresponding apparent shear rates spun with different dope extrusion rates

| Dope extrusion rate (m/min) | Apparent shear rates ($s^{-1}$) |
|---|---|
| 0.43 | 409.5 |
| 0.61 | 581.0 |
| 1.24 | 1,181.0 |
| 1.71 | 1,628.6 |
| 2.70 | 2,571.4 |
| 3.94 | 3,752.3 |
| 5.09 | 4,847.6 |
| 5.92 | 5,638.1 |
| 7.32 | 6,971.4 |

system. The nascent fibers were obtained by varying the dope extrusion rate holding other factors constant; the parameters and spinning conditions are listed in Table 1. Besides, Table 2 presents corresponding apparent shear rates spun with different dope extrusion rates.

Observation of the cross-section shape and measurement of the nascent fibers' diameter

The cross-section shape of the nascent fibers was examined in an optical microscope (Nikon Alphaphot-2 YS2, Japan) with the image transfer software-Scopephoto (LY-WN 300, Hangzhou Scopetek Opto-Eletric Co., Ltd). The objective lens' and ocular lens' magnifications were 40× except Fig. 1a (10×), and 25×, respectively. The samples were obtained by cross-sectioning.

Observation of nascent fibers' surface morphology

The surface morphology of the nascent fibers was examined by a field emission scanning electron microscopy (FESEM) (JSM-6700F, JEOL Ltd) with 1 nm point-to-point resolution operating with a 10-kV accelerating voltage under vacuum condition. For this purpose, the specimens were first frozen in liquid nitrogen to preserve the structure of the nascent fibers and sputtered with Au before FESEM observation.

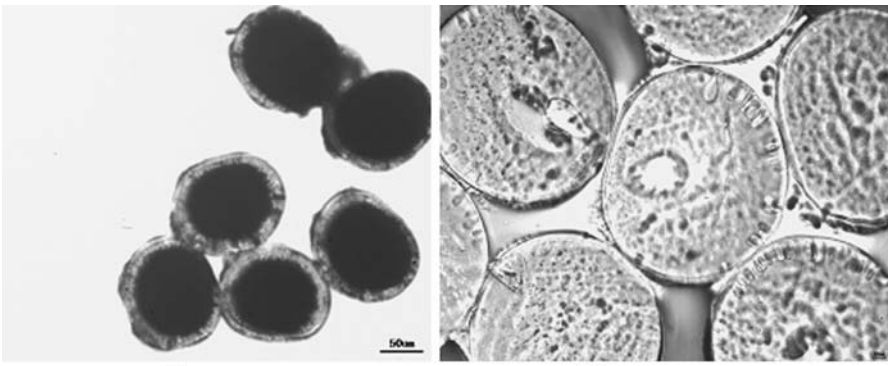


**Fig. 1** Optical microscope photographs of the nascent fibers' cross-section (wet) under different dope extrusion rates

### Measurement of degree of crystallization

Degree of crystallization and crystal sizes of the nascent fibers were conducted on an X-ray diffractometer (Rigaku D/max-RA), with Ni filter, Cu K$\alpha$ radiation, tube voltage of 40 kV, and 100 mA current; the scanned range $2\theta$ was 5°–40°.

The degree of crystallization $C = S_c/S_t \times 100\% = S_c/(S_c + S_a) \times 100\%$. $S_t$ is the total peak area, $S_a$ is the amorphous peak area, and $S_c$ is the crystalline peak area [2].

### Measurement of sound velocity

The sound velocimeter is a very convenient and applicable instrument for measuring overall orientation degree of PAN fibers [12]. The sound propagation velocity of fibers with a certain stress was measured by a sound velocimeter (MC68VZ328, Institute of Chemistry of CAS, China).

## Results and discussion

### Effect of dope extrusion rate on the cross-section shape and diameter of the nascent fibers

In order to understand the influence of dope extrusion rate on the cross-section structure, the samples spun from coagulation bath were sliced directly when the samples were still wet and the cross-section of nascent fibers is shown in Fig. 1. Figure 2 also presents the optical microscope photographs of nascent fibers' cross-section when the samples were washed with acetone to remove the residual DMSO and water. It can be found that all of the cross-section shapes were circular and obvious core/shell structure existed especially when they were wet. It is interesting that the exterior of nascent fibers had good light transmission as shown in Fig. 1a

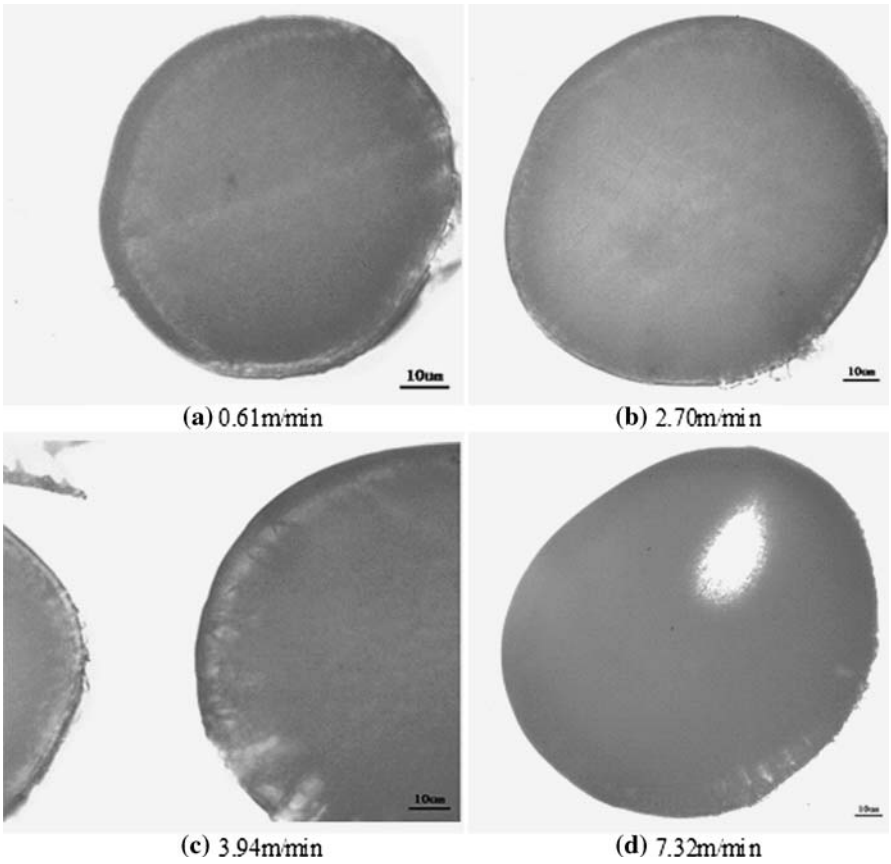


**Fig. 2** Optical microscope photographs of the nascent fibers' cross-section (dry) under different dope extrusion rates

owing to the shearing. Moreover, with the increase of dope extrusion rate, the core/shell structure became more obvious, even big voids emerged in the inner part of the nascent fibers (Figs. 1b, 2d). It is suggested that with the increase of dope extrusion rate, "the jet swelling effect"—"Barus effect" became bigger, the molecular of the surface was oriented by the shearing and the compactness enhanced accordingly [13]. Meanwhile, the "Barus effect" caused the increase of the fiber' framework, and baffled the inner double diffusion which caused the insufficient coagulation of the inner part.

Figure 3 presents average diameter of the nascent fibers under different dope extrusion rates. The average diameter of nascent fibers increased with the increasing of the dope extrusion rate because of "Barus effect". However, the increasing speed of average diameter decreased, which was consistent with Fig. 4. These two pictures can be explained that the spinning dope exhibited "shear-thinning" behavior [14], and there was some polymer relaxation during swelling process especially at higher extrusion rate.

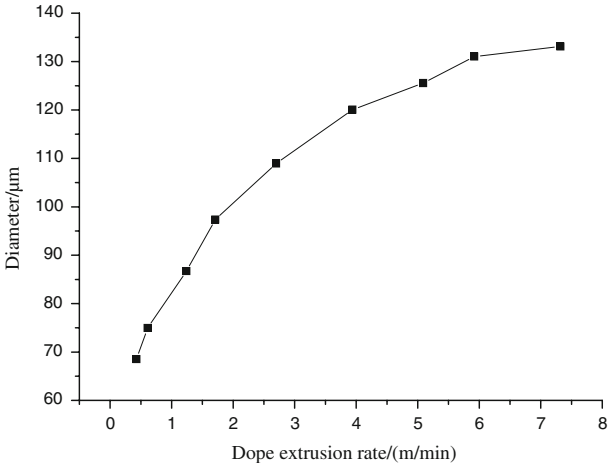


**Fig. 3** Average diameters of the nascent fibers under different dope extrusion rates

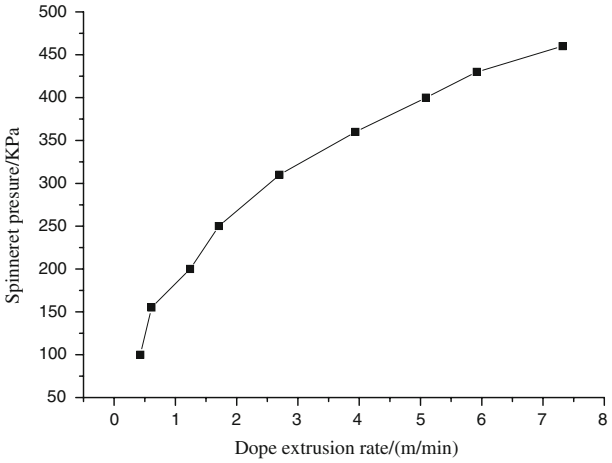


**Fig. 4** Spinneret pressure under different dope extrusion rates

## Effect of dope extrusion rate on the nascent fibers' surface morphology

Figure 5 shows the FESEM of the nascent fibers' surface morphology as a function of dope extrusion rate, in which Fig. 5e, f are the magnified images of Fig. 5a, d. It can be found that the surfaces of the nascent fibers spun at lower dope extrusion rates (Fig. 5a, b, e) were smoother than the ones spun at higher dope extrusion rates (Fig. 5c, d, f). There were some depressions on the surface of the nascent fibers (Fig. 5a) caused by the liquid–liquid demixing process [15]. As the dope extrusion rate increased, the grooves appeared (Fig. 5b) and became more irregular when the dope extrusion rate was added up to 2.7 m/min (Fig. 5c). Moreover, when the dope extrusion rate was too high, there were large spherical or massive depressions,

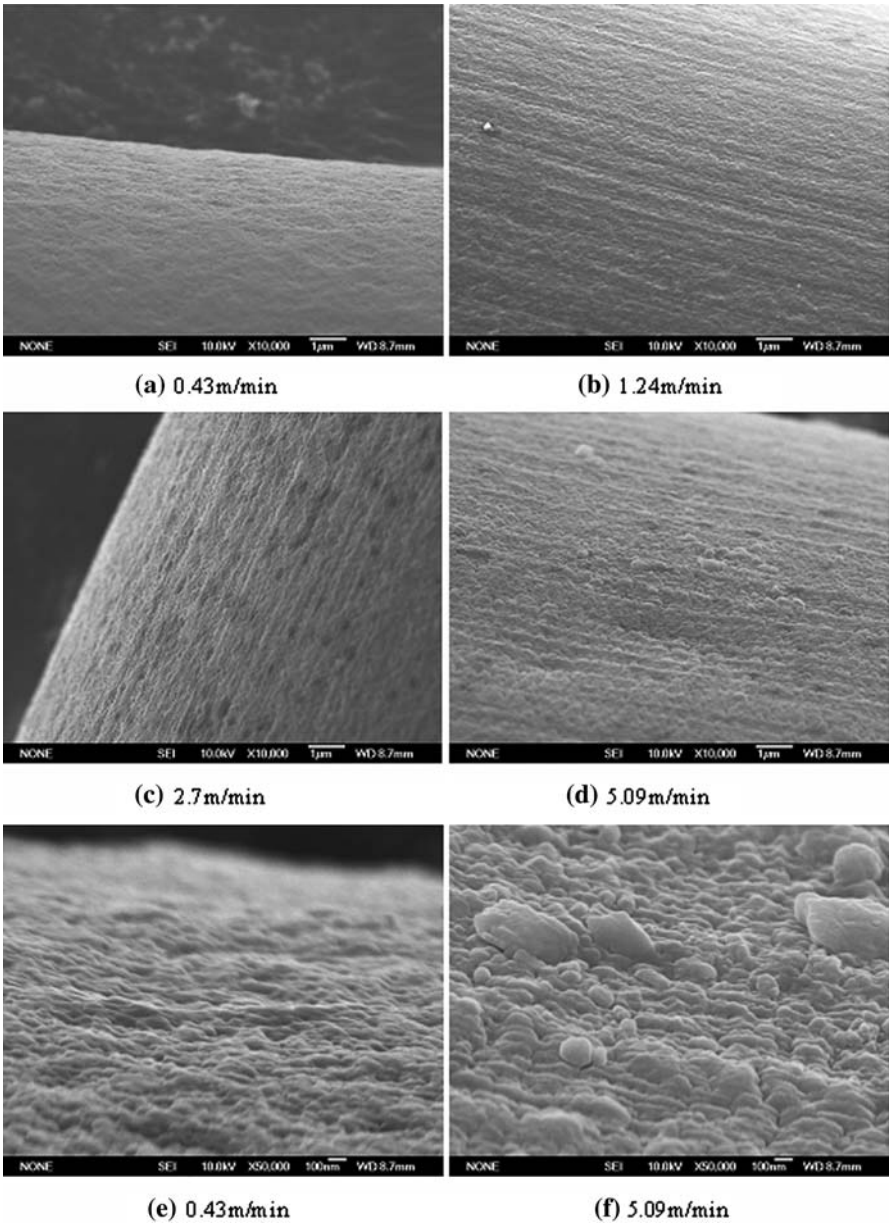


**Fig. 5** FESEM of the nascent fibers' surface morphology under different dope extrusion rates

which exhibited "filament breakage" [16]. That is to say, higher dope extrusion rate can increase the shear rate which induces the molecular orientation, but it also accompanied with surface defects and core/shell structure. At higher dope extrusion rate, the shear effect played a decisive role in the forming of fiber' surface, and

polymer relaxation phenomena caused core/shell structure. Hence, in practical production, enhancing the productivity should consider the structure and properties of fibers.

## Effect of dope extrusion rate on the degree of crystallization

The WXRD intensity profiles of the nascent fibers spun with different dope extrusion rates are shown in Fig. 6. The crystallization of the nascent fibers was very small, with PAN having only lateral order, and a significant amount of amorphous phase existed around $2\theta = 25.5°$ [17]. The diffraction peak was found to gradually enhance as the nascent fibers was spun with elevated dope extrusion rate. WAXD provides the crystallization fraction developed in the fibers by resolving the diffraction peak from the total scattering curve. Table 3 also presents the degree of crystallization of the nascent fibers under different dope extrusion rates. The apparent increase of fiber crystallization spun at the high dope extrusion rate was attributed to the enhanced shear-induced nucleation [18, 19], which promoted the chain ordering process to take place. However, when the dope extrusion rate wais

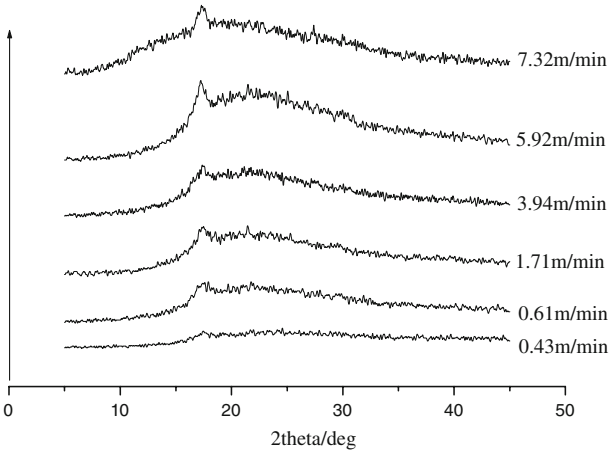


**Fig. 6** WXRD intensity profiles of the nascent fibers spun with different dope extrusion rates

**Table 3** Degree of crystallization of the nascent fibers under different dope extrusion rates

| Dope extrusion rate (m/min) | Degree of crystallization (%) |
|---|---|
| 0.43 | 15.3 |
| 0.61 | 17.9 |
| 1.71 | 23.3 |
| 3.94 | 25.8 |
| 5.92 | 28.5 |
| 7.32 | 19.7 |

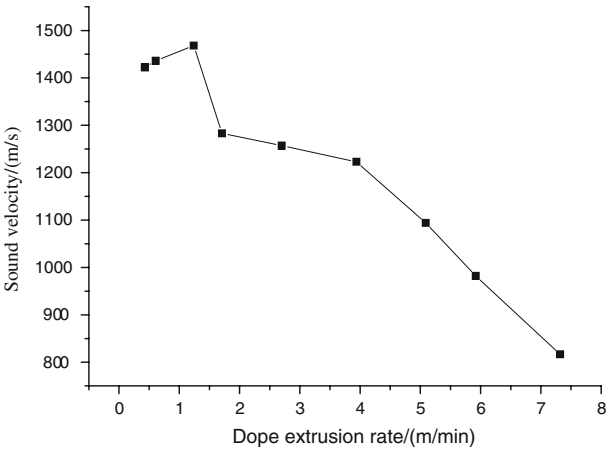


**Fig. 7** Sound velocities of the nascent fibers under different dope extrusion rates

too high (7.32 m/min), the crystallization decreased associated with the increase of peak width owing to the inner insufficient coagulation and relaxation phenomena as discussed before.

Effect of dope extrusion rate on the sound velocity of the nascent fibers

The effect of dope extrusion rates on the sound velocity of the nascent fibers is shown in Fig. 7. At lower dope extrusion rate, the sound velocity of the nascent fibers increased with the increase of dope extrusion rate. This can be attributed to increasing the dope extrusion rate (shear rate) which induces the molecular orientation. However, an abrupt reduction of the nascent fibers' sound velocity was observed at the higher dope extrusion rates. This can be explained that at high dope extrusion rate, the deformation of the nascent fibers and "shear thinning" resulted in the stress relaxation of the molecular chain, so that the sound velocity decreased.

## Conclusion

The effect of dope extrusion rate on the formation and properties of PAN nascent fibers was presented in this work. According to the experimental results, the spinning dope exhibited obvious "shear thinning" behavior. Enhancing dope extrusion rate can increase the shear rate which induces the crystallization, but it also causes more surface defects and even insufficient coagulation of the inner part. With the increase of dope extrusion rate, the nascent fibers' surface became rougher, but the sound velocity had a maximum. The fibers' properties and extrusion rate are both important for practical production, and increasing the dope extrusion rate should consider the fibers' properties meeting the qualification.

**Acknowledgments** This work was financially supported by National High-Tech Research and National Basic Research Program of China (2006CB605304) and National Natural Science Foundation of China (50604025).

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