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# A Theoretical Rod Model for Investigating the Polyacrylonitrile Copolymer Coagulation Process

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A theoretical rod model for investigating the polyacrylonitrile (PAN) copolymer coagulation process was presented in this work. The mass transfer rate and coagulation rate under different coagulation conditions were obtained using this method. An optical microscope with image transfer software was employed to observe the coagulation boundary of the filament. The results showed that the coagulation rate decreased continuously with the increase of bath concentration. However, with the increase of the bath concentration, the mass transfer rate decreased at the beginning of the coagulation, and as the $t^{1/2}$ increased, the weight loss was greater when the bath concentration was higher. Moreover, the coagulation rate and mass transfer rate increased with the increase of the coagulation temperature, and the coagulation was most moderate when the bath temperature was 50°C.

**Keywords:** Theoretical model, filament, mass transfer rate, coagulation rate, polyacrylonitrile

## 1 Introduction

PAN based carbon fibers have been widely used for spaceflight as well as civilian fields owing to a series of excellent properties (1, 2). Coagulation as the first step takes a critical effect on the structure and properties of PAN carbon fibers, and has been investigated by many researchers (3–9). The morphological characteristics of the filament, such as the cross-sectional shape, surface morphology and pores, are greatly influenced by the coagulation conditions.

The mass transfer rate, coagulation rate and diffusion rate are considered as the most important factors in the coagulation process. However, it's difficult to observe the boundary movement as well as mass transfer during the coagulation of dope solution owing to micron sized fibers. Generally, the rod model was used to simulate the coagulation process, which can extend the time scale, mass-transfer rates and boundary movement rates into measurable regions. The determination of diffusion coefficients in PAN formation was calculated by Crank equation by Chen et al. (10–12). Modeling techniques were found by Baojun et al. (13), Paul (14) and Liu et al. (15) to understand diffusion process. Besides, a new model was proposed by In Chul Um et al. (16) to investigate the coagulation phenomena of silk fibroin filaments. However, the study of the visible boundary movement and real-time transfer rate of PAN copolymer is lacking. In our work, a magnified filament which is called rod model was used to investigate the PAN coagulation process, providing a reliable, scientific method for producing high quality PAN fibers.

## 2 Experimental

### 2.1 Preparation

PAN copolymer was polymerized with acrylonitrile (AN), and itaconic acid (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.

To investigate the different coagulation process, a DMSO/$H_2O$ coagulation bath system was adopted, five bath DMSO concentrations (0, 30, 43, 61, 70, 73wt%) and four coagulation bath temperatures (25, 30, 40, 50, 60°C) were designed holding other factors constant.

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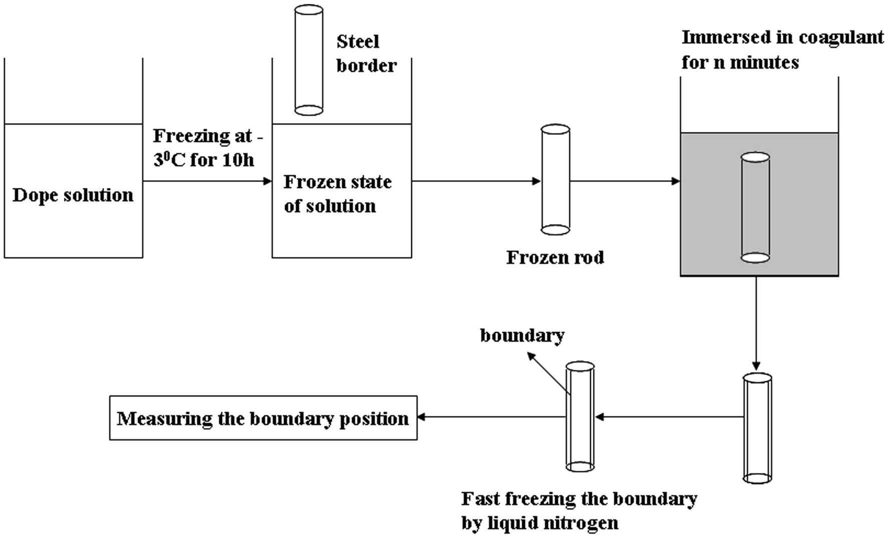


**Fig. 1.** Procedure for measuring the boundary movement and mass transfer rate of the rod model of PAN copolymer dope solution.

## 2.2 Measurement

The cross-section (boundary position) of the gained rod was examined using an optical microscope (Nikon Alphaphot-2 YS2, Japan) with the image transfer software.

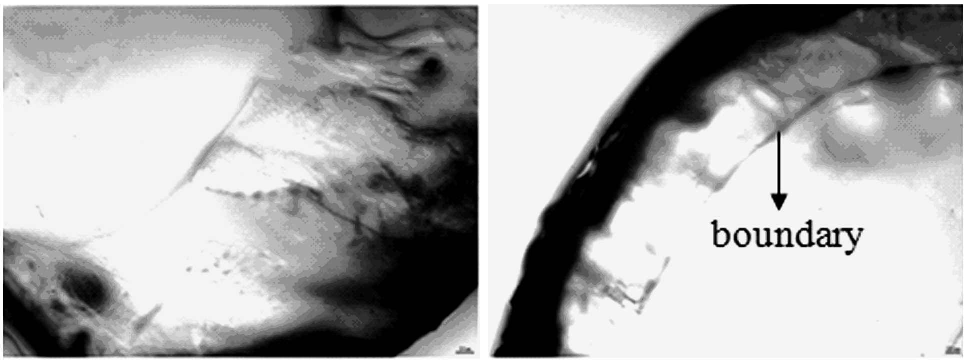
To measure the coagulation rate difference of the PAN filament in various coagulation conditions, a procedure was proposed using a rod of PAN filament, as shown in Figure 1. The PAN dope solution was chilled for 10 h at −3°C. A frozen rod can be prepared by pushing a steel borer (8 × 1 mm) into the frozen solution. After the rod was immersed in various coagulants for a certain time to solidify the surface of the rod, it was moved into liquid nitrogen to fast freeze it and then, the movement of the coagulation boundary in the rod model was measured by optical microscopy with image transfer software. The coagulation rate was calculated from the movement of the coagulation boundary against the square root of time (16).

The rod model of PAN filament used in the measurement of the coagulation rate difference was also used for measuring the mass transfer rate. The rod was immersed in various coagulants for a certain time to solidify the surface of the rod, only the surface of the rod was solidified, and its inner part remained as solution. The rod model was immersed in a coagulation bath and the weight change of the rod was measured, with time using an analytical balance. The mass transfer rate difference could be calculated from the ratio of the weight loss to the square root of time (16).

## 3 Results and Discussion

### 3.1 Effect of Coagulation Bath Concentration on the Coagulation Rate and Mass Transfer Rate of the Rod

Figure 2 shows the examples of the optical microscope photographs of boundary position of PAN copolymer rod immersed in a different bath DMSO concentration at 25°C for different coagulation time. It is found that a very distinct moving boundary can be observed by the optical microscope. One side of the boundary was a



(a) (b)

**Fig. 2.** Examples of boundary position of PAN copolymer rod immersed into different bath DMSO concentration at 25°C for different coagulation time: (a) 43 wt%, 10 min; (b) 61 wt%, 10 min.

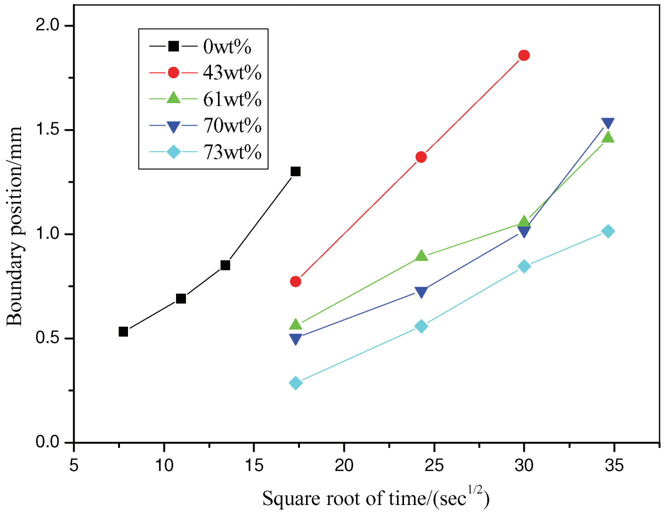


**Fig. 3.** Coagulation rate of PAN copolymer rod under different bath concentrations.

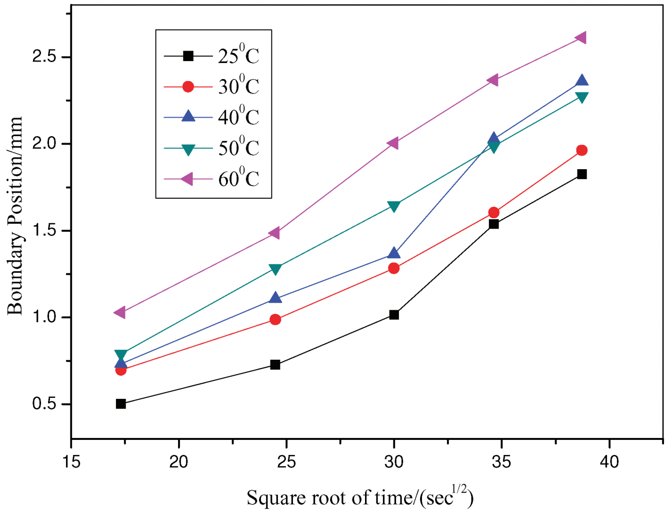


**Fig. 5.** Coagulation rate of PAN copolymer rod under different bath temperatures.

hard-coagulated copolymer, while the other side was the soft original dope. The boundary began at the sample surface and moves inward with coagulation time, and a linear relationship between the boundary movement and the square root of time was obtained as shown in Figure 3. At lower DMSO bath concentration, the boundary moved too fast. It exceeded the detection ranges of the Microscope and image transfer software, so the short time was just adopted. It can be seen that as the bath DMSO concentration increased, the slope of the boundary position against the square root of time ($x/t^{1/2}$), which was regarded as the coagulation rate, decreased. This can be explained in that the concentration gradient of DMSO ($H_2O$) became smaller with the increase of bath DMSO concentration (17), and this resulted in the decrease of coagulation rates.

Figure 4 shows the slope of weight loss curve ([Mo-M (t)]/Mo) against the square root of time immersed in different bath concentrations. In this figure, the linear regression was not adopted. It is found that with the increase of the bath DMSO concentration, the mass transfer rate decreased at the beginning of the coagulation, however, as the $t^{1/2}$ increased, the weight loss was greater when the bath concentration was higher. It can be explained that coagulating in lower bath concentration, the coagulation of the surface was very rapid (Figs. 3 and 4) that it solidified and restricted further coagulation from deeper within. That is

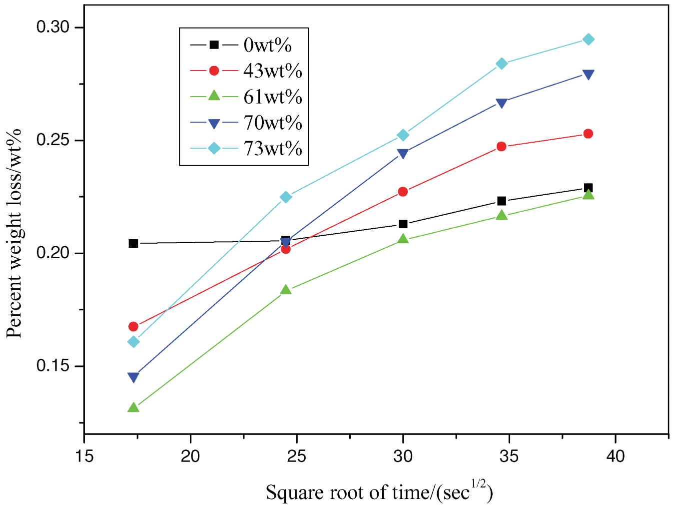


**Fig. 4.** Rate of weight loss of PAN copolymer rod under different bath concentrations.

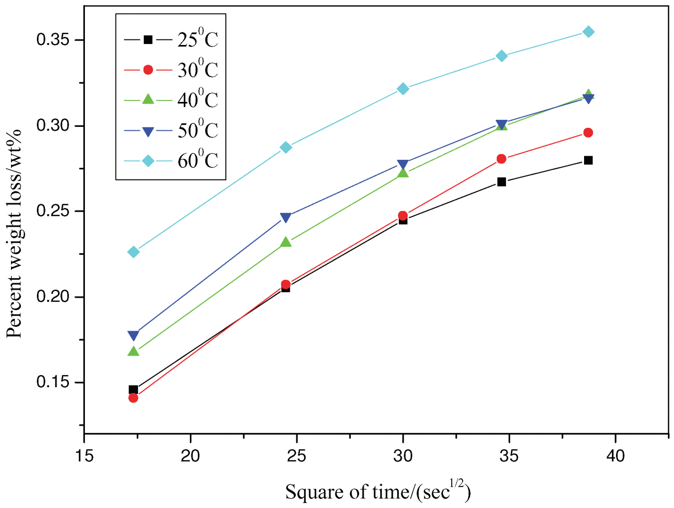


**Fig. 6.** Rate of weight loss of PAN copolymer rod under different bath temperatures.

to say, the inner part would obey the instantaneous phase separation (18, 19). With the increase of bath DMSO concentration, the concentration gradient between the rod and bath became smaller; the coagulation rate and diffusion rate were more moderate, and the coagulation was a nucleation and growth process (18, 19). The double diffusion was moderate and the inner mass transfer rate was consistent with the outer.

### 3.2 Effect of Coagulation Bath Temperature on the Coagulation Rate, Mass Transfer Rate and Surface Morphology of the Rod

Figure 5 shows the slope of boundary position curve against the square root of time immersed in different bath temperatures when the bath DMSO concentration was 70 wt%. It is found that with the increase of the temperature, the boundary moved more quickly towards to inner of the rod owing to the higher diffusion coefficient at higher temperature (12). From the picture, it also can be seen that the boundary moved more uniform with a good linear relationship when the bath temperature was 50°C, which was consistent with our practical experimental data as discussed in another paper (20).

Figure 6 show the slope of weight loss curve ([Mo-M (t)]/Mo) against the square root of time immersed in different bath temperatures. As the bath temperature enhanced, the mass transfer rate increased continuously. Moreover, the mass transfer rate at $70^0$C was much quicker than that at 60°C, that is to say, temperature played a very important role in the mass transfer when the bath concentration was high-70 wt%. Higher coagulation temperature increases the exchange of the solvent and non-solvent (Fig. 6), the molecular motion becomes more quickly, the phase separation accelerates accordingly, which is harmful to the forming of nascent fibers (21).

## 4 Conclusions

In this present work, the coagulation process of PAN copolymer was investigated by the rod model, which proved to be an effective method to calculate the coagulation rate and mass transfer rate. Furthermore, the boundary position of the rod can be observed obviously by the microscope with the image transfer software. With the increase of the bath concentration, the coagulation rate and mass transfer rate decreased, while the coagulation rate and mass transfer rate increased continuously as the bath temperature increased. Moreover, the coagulation rate and mass transfer rate were most moderate when the bath temperature was 50°C.

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