

# Effect of the Solvent Type on the Formation and Physical Properties of Polyacrylonitrile Fibers via a Solvent-Free Coagulation Bath

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**ABSTRACT:** Polyacrylonitrile (PAN) fibers were fabricated via a dry-jet wet-spinning technique, and a solvent-free coagulation bath system was adopted. The effects of different types of dope solvent on the formation and physical properties of the PAN fibers were investigated. Dimethylformamide and dimethyl sulfoxide (DMSO) were selected as the solvents and were added to a spinning solution consisting of 18 wt % PAN. The PAN fibers were examined with field emission scanning electron microscopy, differential scanning calorimetry, and thermogravimetric analysis. The field emission scanning electron micrographs

revealed that the PAN fibers with the DMSO solvent exhibited a more circular shape and a smoother skin. The PAN fibers with the DMSO solvent had their glass-transition temperature ( $T_g$ ) at 121°C. This study indicated that the different types of dope solvent used in the dope preparation did not affect  $T_g$  of the PAN fibers because of the solvent-free coagulation bath system; however, they significantly affected the physical formation of the PAN fibers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2467–2472, 2011

**Key words:** electron microscopy; fibers; glass transition

## INTRODUCTION

Polyacrylonitrile (PAN) has been a superior precursor fiber worldwide for carbon fiber production since its discovery. This is primarily due to its well-known characteristics, including its high molecular orientation, high melting point, and high efficiency of carbon fibers; these characteristics are vital to carbon fiber production.<sup>1</sup> Also, the PAN structure does not liquefy or soften and permits a fast rate during pyrolysis and preserves its morphology.<sup>2</sup> An ideal precursor fiber should be easily converted into carbon fibers; it should give a high carbon yield and allow economic processing. PAN fibers fulfill these requirements. Various researchers believe that the properties of carbon fibers depend mainly on the quality of the precursor fibers. Several factors that affect the actual strength of PAN precursors are its chemical structure, molecular weight and molecular weight distribution, crystallinity and orientation, defects, and exterior conditions, such as temperature, tensile speed, and humidity.<sup>3</sup>

The first stage of fiber formation is the preparation of the spinning solution (dope). Solution spinning is a conventional approach and is usually used to produce precursor fibers for commercial PAN-based carbon fibers.<sup>4,5</sup> Normally, the dopes are prepared at a temperature that is higher than the extrusion temperature.<sup>6,7</sup> The factors that influence the thermodynamics of the spinning dope are the composition of the spinning dope, addition of nonsolvent, and temperature and concentration of the coagulation bath.<sup>8</sup> The solid content of the spinning solution can improve the mechanical properties of the precursor fiber, and the resulting carbon fiber always has an increased dope viscosity. This, however, is disadvantageous and dangerous for preparation and transportation.<sup>6</sup> Because of the drawbacks of a higher dope viscosity, it is crucial to obtain an optimum dope concentration that is suitable for spinning.

The selection of the solvent is essential in dope preparation. It is important to choose a solvent with a high purity and minimal water content. There are a few criteria for solvents that need to be considered seriously; these include a convenient boiling point, low heat evaporation, good heat stability, physiological inactivity, ease of recovery, chemical inertness to dissolve the polymer, and ability to form relatively high concentrated solutions of high-molecular-weight polymers at low viscosities. The most used solvents used for the preparation of spinning solutions are dimethyl sulfoxide (DMSO), dimethylformamide

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(DMF), and dimethylacetamide. Normally, DMSO is used in the wet-spinning process, whereas DMF can be implemented in both dry- and wet-spinning processes. As reported by Kobashi and Takao,<sup>9</sup> for wet-spinning processes, inorganic solvents are superior because they give coagulated gel fibers of better uniformity. Examples of inorganic solvents are sodium thiocyanates, zinc chloride, and nitric acid. However, nitric acid is unsuitable as a solvent because of its acidic features; it is corrosive and may cause damage to the system.

In addition to solvent type, additives also influence the formation of PAN precursor fibers. The addition of additives can enhance the solubility and thermal properties of PAN.<sup>10</sup> There are a few additives that have been used in dope preparation, such as acrylamide (AM), itaconic acid, and methylacrylate. In this research, AM was considered to be an additive for precursor fibers principally because of its effectiveness in promoting the stabilization process. Moreover, it is believed that AM can prevent excessive heat flow inside the fiber that could cause the fibers to melt.<sup>10,11</sup> Although the addition of additives will improve the quality of PAN fibers, there is an optimum amount of additive that is required to produce the best quality carbon fibers. An excessive amount of additive can cause a great weight loss, which then can reduce the mechanical properties of the carbon fibers.

Recently, a combination of wet- and dry-spinning methods showed that it could be used for the formation of precursor fibers, and this was in agreement with Baojun et al.,<sup>12</sup> who successfully produced high-performance Kelvar fibers by dry-jet wet spinning. In dry-jet wet spinning, the spinning dope is extruded through an air gap of less than 1 cm and into a coagulation bath.<sup>12,13</sup> A counterdiffusion occurs between the solvent and coagulant and causes the polymer to solidify. The advantages of dry-jet wet spinning are high-speed formation, high concentration of dope, and high degree of jet stretch with the ability to control the as-spun fibers structure by adjustment of the spinning bath parameters retained.<sup>12</sup> Furthermore, the air gap feature allows the extruded dope to cool to a certain extent before it reaches the coagulation bath and to relax the high stresses developed inside the spinneret.<sup>13</sup> Conventionally, the coagulation bath consists of a non-solvent and a solvent, where interaction among them affects the structure and morphology of the as-spun fibers. In addition, the coagulation bath temperature also plays a main role in the coagulation process. It is responsible for controlling the mass transfer and counterdiffusion of the solvent and nonsolvent in the coagulation bath.

Rahman et al.<sup>14</sup> and Ismail et al.<sup>15</sup> successfully fabricated PAN fibers in a solvent-free coagulation bath.

The fabrication process was implemented at a low residence time and at a moderate coagulation bath temperature. To further exploit the full potential of the proposed technique, therefore, the objective of this study was to investigate the effect of the solvent type on the formation and physical properties of PAN fibers via a solvent-free coagulation bath system.

## EXPERIMENTAL

### Material and dope preparation

PAN powder from Sigma-Aldrich (St. Louis, Missouri, United State), with a molecular weight of 150,000, was chosen as a precursor in this study. Two types of solvent, DMF and DMSO, were purchased from Merck (Germany). AM, obtained from Sigma-Aldrich, was used as an additive. Spinning dope solutions were prepared by the dissolution of finely powdered PAN and AM into DMF and DMSO solvents, respectively. The dope solutions, consisting of 18 wt % PAN, were continuously stirred at 80°C for 5 h until the mixtures became homogeneous. The solutions were then collected and stored glass bottles. Subsequently, the solutions were degassed with an ultrasonic bath to remove air bubbles.

### Fiber fabrication

The PAN fibers were fabricated with a dry-jet wet-spinning technique with a multihole spinneret (10 holes, 350  $\mu\text{m}$ ). Figure 1 illustrates the spinning machine used in this study. To extrude the dope from the reservoir into the spinneret, nitrogen gas was used to supply the pressure required. The air gap between the spinneret and the coagulation bath was kept at 0.5 cm. The coagulation bath was filled up with water and its temperature was maintained at 13°C with a cooling system. The details of the spinning settings and the conditions for PAN fiber production are presented in Table I.

### Characterization methods

The PAN fiber cross-sectional and surface morphologies were examined with a field emission scanning electron microscope (Zeiss Supra 35VP, Oberkochen, Germany). Before analysis, the samples were sputtered with gold with ion sputtering before they were viewed on the field emission scanning electron microscope, which had a potential of 10 kV under a magnification of 300 $\times$ . Thermal analysis was performed with differential scanning calorimetry (DSC; DSC 822<sup>e</sup> Mettler Toledo) and thermogravimetric analysis (TGA; SDTA851<sup>e</sup> Mettler Toledo) under a nitrogen flow at heating rate of 10°C/min from 50–300 and 50–1000°C, respectively. Each sample

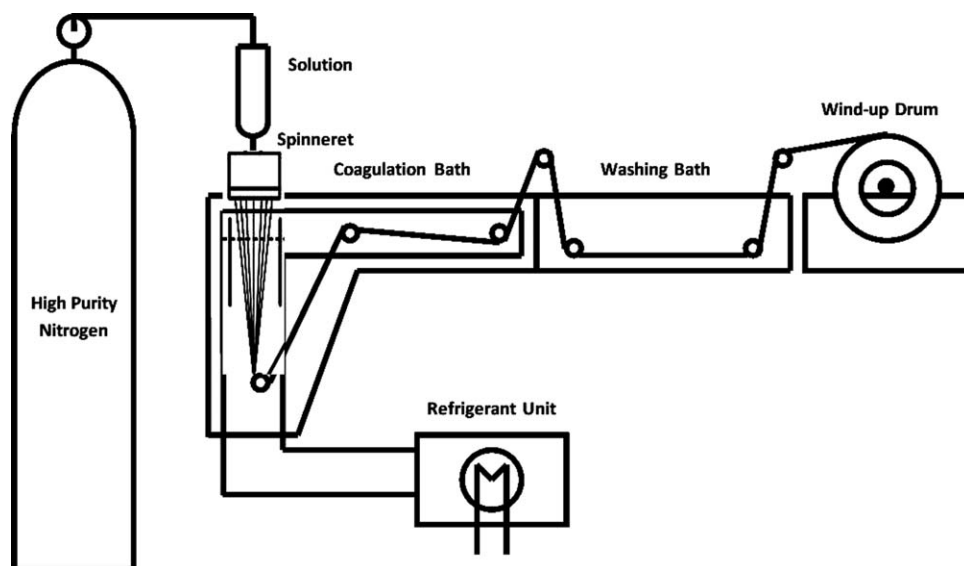


Figure 1 Schematic diagram of the dry-jet wet-spinning machine.

weighed about 4 mg for thermal analysis. DSC was carried out to determine the glass-transition temperature ( $T_g$ ), and TGA was conducted to determine the fiber weight loss when heat was applied.

## RESULTS AND DISCUSSION

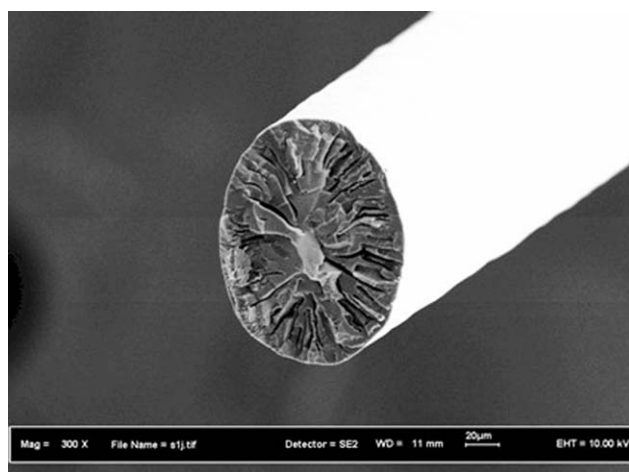
### Effect of the solvents on the morphology and structure of the PAN fibers

Figure 2 illustrates the cross sectional structures of the PAN fiber with the DMF [Fig. 2(a)] and DMSO [Fig. 2(b)] solvents, respectively. As shown in Figure 2(b), the PAN fibers prepared with DMSO as a solvent exhibited a better circular fiber shape compared to the PAN fibers prepared with the DMF solvent, shown in Figure 2(a). The difference in fiber formation shape might have been due to the high viscosity of the DMSO solvent, which contributed to the better formation of circular shape during the drawing process. These kinds of structures are believed to give uniformity of the stabilization rate during heat treatment. Generally, precursor fibers with a circular

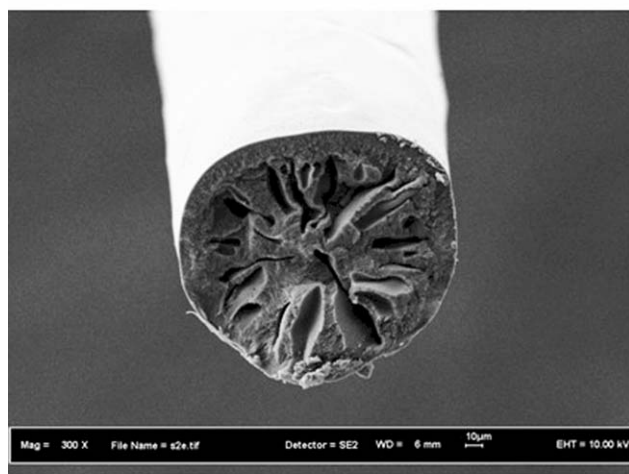
shape and symmetrical structure demonstrate a higher tensile strength.<sup>16</sup> Nevertheless, these PAN fibers structures also showed radial void formation. We observed that the voids were relatively bigger in the PAN fibers prepared with DMSO [Fig. 2(b)] compared to the PAN fibers prepared with DMF [Fig. 2(a)]. The high viscosity of the dope solution was the reason bigger voids appeared in the fibers prepared from the solvent of DMSO, and this affected the rate of solvent diffusion inside the nascent fiber. In this study, the rate of solvent diffusion in the PAN fibers with DMSO was faster in the solvent-free coagulation bath; this contributed to bigger voids and a lower rate of solvent diffusion in the PAN fibers prepared with DMF and contributed to smaller voids. The formation of radial voids was due to solvent diffusion out from the interior nascent fibers and the implementation of the solvent-free coagulation bath. The results indicate that the solvent played a significant role in affecting the fiber formation. Although the PAN fibers voids collapsed through heat treatment, it is significant to minimize

TABLE I  
Spinning Settings and Conditions of PAN Fibers

Spinning solution (dope)	PAN/AM/DMF	PAN/AM/DMSO
Polymer concentration	18 wt %	18 wt %
AM in polymer	2 wt %	2 wt %
Dope temperature	Ambient temperature	Ambient temperature
Spinneret diameter, number of holes	0.350 mm, 10 holes	0.350 mm, 10 holes
Air gap distance	0.5 cm	0.5 cm
Dope extrusion rate	0.013 cm <sup>3</sup> /s	0.010 cm <sup>3</sup> /s
Residence time	22 s	28 s
Coagulation bath composition	100% water	100% water
Coagulation temperature	13°C	13°C



(a)



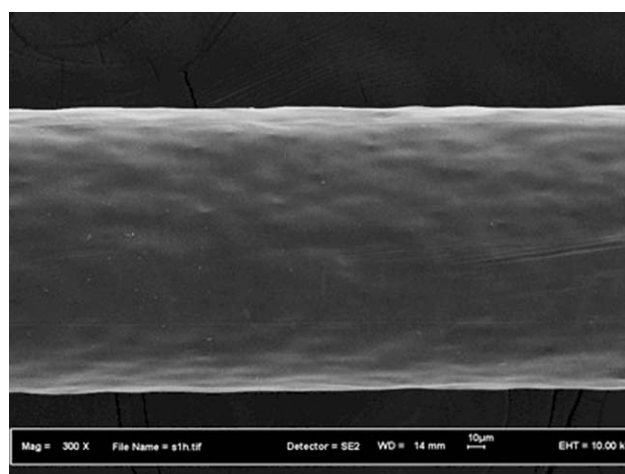
(b)

**Figure 2** Cross sectional structures of the (a) PAN fiber with DMF solvent and (b) PAN fiber with DMSO solvent.

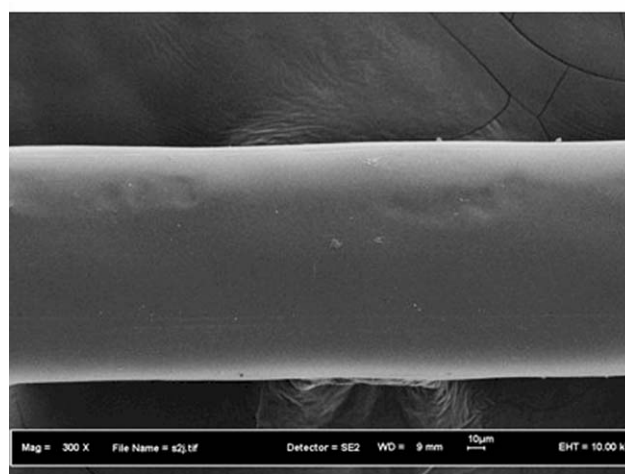
the amount and size of void formation, as voids would lower the mechanical properties of the PAN fibers. To minimize the void formation of the PAN fibers, it was important to select a dope solvent with an optimum dope viscosity.

Figure 3 shows micrographic images of the outer surface morphology of PAN fibers with the DMF [Fig. 3(a)] and DMSO [Fig. 3(b)] solvents, respectively. The PAN fibers fabricated with the DMF solvent, as shown in Figure 3(a), exhibited a rougher surface than those of the PAN fibers fabricated with the DMSO solvent, as demonstrated in Figure 3(b). According to Kruchinin et al.,<sup>17</sup> a coagulation bath with DMSO solvent resulted in the formation of fibers with a smoother surface. In contrast to this study, smoother surface fibers were also achieved with a solvent-free coagulation bath with dope preparation with DMSO solvent. Furthermore, the formation of a thin skin in both PAN fibers was observed. The thin-skin formation prevented the sol-

idification of the inner core; this led to fiber breakage by stretching during fiber spinning. The grooves appearing in the rough-surface PAN fibers with DMF [Fig. 3(a)] were expected to produce a bigger area on the surface of PAN fibers, and this would provide a benefit during heat treatment, whereby the grooves gave better area of adsorption throughout the oxidation stabilization treatment. On the other hand, PAN fibers with the DMSO solvent showed a smoother surface, and this may have provided a benefit by giving uniform adsorption throughout the heat treatment. On comparison of both advantages on the PAN fiber skin formation, it was better to have a uniform adsorption because it could result in uniform mechanical properties of the carbon fiber. These characters of the PAN fibers were significant, as carbon fibers are inherited from the precursor fibers. Therefore, it is important to achieve better precursor fibers, as this leads to high-quality carbon fibers. It is well-established that

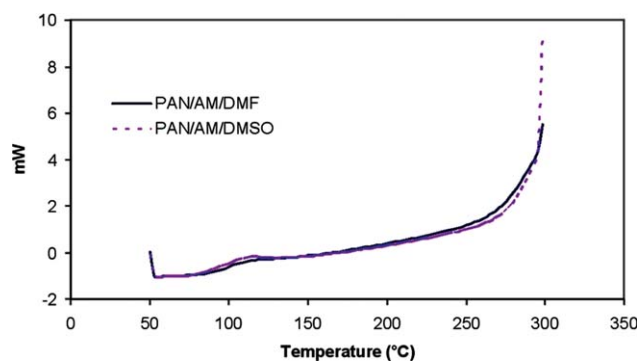


(a)



(b)

**Figure 3** Fiber surfaces of the (a) PAN fiber with DMF solvent and (b) PAN fiber with DMSO solvent.



**Figure 4** DSC curves of PAN fibers with different types of solvent. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

carbon fibers with high mechanical properties feature a round cross section and a smooth fiber surface.<sup>17</sup> However, the surface roughness of carbon fibers can improve the mechanical properties of composite materials reinforced with carbon fibers, as reported by Tsai and Lin.<sup>18</sup> This study showed that those physical characteristics of PAN fibers could be adapted for various applications of carbon fibers.

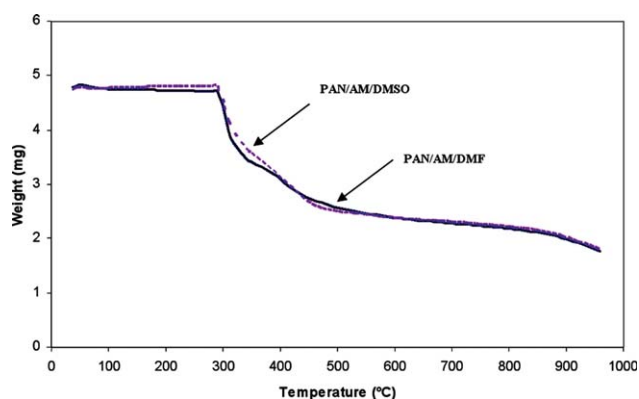
#### Effect of the solvents on the fiber glass transition

$T_g$  of PAN fibers with different types of dope solvent were determined by DSC. Typically,  $T_g$  values of PAN varied in the range of 52 to 180°C, and  $T_g$  for AM was approximately 84°C. This study revealed that value of  $T_g$  of PAN fibers with DMF solvent did not differ much compared to PAN fibers with DMSO solvent. Krigbaum and Tokita<sup>19</sup> found a  $T_g$  of 104°C for PAN in a DMF solution, and that value was lower than the  $T_g$  of the PAN fibers in the DMF solvent presented in this study. Figure 4 represents the DSC curves of PAN fibers with different types of solvent. PAN fibers with the DMF and DMSO solvents displayed  $T_g$  values of 118 and 121°C, respectively. In this study, the reason for the change in  $T_g$  was not the different types of dope solvent because the dope solvent was totally discharged during spinning in the solvent-free coagulation bath. The  $T_g$  values of the PAN fibers varied most probably because of the existence of AM as an additive; this was responsible for the change in  $T_g$  of the PAN fibers. AM might have incorporated with the PAN polymer and, thus, increased  $T_g$  of the PAN fibers. To calculate the percentage AM present, the  $T_g$  values for both types of PAN fibers were taken from DSC analysis and were then deposited into the Fox equation.<sup>20</sup> The percentages of AM present were 0.3 and 0.2 wt % for PAN fibers prepared with DMF and DMSO, respectively. When we compared both types of PAN fibers, a small difference in the weight percentage was observed. The reason

may have been the distribution of AM during dope preparation. In fiber view, especially during post-spinning modification, it was significant to proceed below  $T_g$  to prevent the fibrillar orientation from reverting back to the helical conformation. If the postspinning modification was conducted above  $T_g$ , it would have damaged the alignment of polymer chains and reduced the mechanical properties of the PAN fibers. Rosenbaum<sup>21</sup> claimed that modification below  $T_g$  was due to the straightening of twisted molecules against the intramolecular repulsion of adjacent dipoles, and the additional extension above  $T_g$  appeared to involve permanent relative displacement of fiber elements. Although the dope solvent did not influence the  $T_g$  remarkably, it was still important to determine the  $T_g$  of the PAN fibers to perform the postspinning modification.

#### Effect of the solvents on the fiber weight loss

Figure 5 shows thermograms of the PAN fibers with different types of dope solvent. These curves could be roughly divided into three stages according to the extent of weight loss. The PAN fibers with DMF solvent experienced a total weight loss of 62%, whereas the PAN fibers with DMSO solvent exhibited a 64% weight loss. At the first stage up to 250°C, both PAN fibers were observed to have a very small weight loss because of cyclization. On the basis of the TGA curves, the weight loss initiation temperature for both PAN fibers were approximately 291°C. During this step, the rate of weight loss was quite rapid; significant weight losses of about 30 and 31% for the PAN fibers with DMF and DMSO, respectively, were due to changes in the polymer bonds and the removal of volatile materials. This was in line with the work of Gupta et al.,<sup>5</sup> in which the weight loss was due to the dehydrogenation reactions, which minimized the chain scission reactions and led to the formation of volatile



**Figure 5** TGA curves of PAN fibers with different types of solvent. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

products, such as  $\text{NH}_3$  and  $\text{HCN}$ , and caused obvious weight loss.<sup>5</sup> A study by Tsai and Lin<sup>18</sup> explained that the weight loss curve was greater as CN groups were cyclized and decomposed rapidly. Initially, PAN fibers with the DMSO solvent showed approximately a 1% difference in the weight loss compared to the PAN fibers with the DMF solvent. The second stage of the thermogram curve showed that the PAN fibers with the DMSO solvent experienced a greater weight loss compared to the PAN fibers with the DMF solvent. The weight losses of the PAN fibers were about 17% with DMSO and about 14% with DMF. In the final stage, the rate of weight loss was observed to be steady and lower, and both PAN fibers fabricated from different types of dope solvent showed almost the same curves. The difference in the final weight loss between both PAN fibers was about 2%. This final weight loss represented noncarbon element elimination in the form of various gases.

### CONCLUSIONS

On the basis of the results obtained in this study, the following conclusions were drawn:

- PAN fibers were successfully fabricated in a solvent-free coagulation bath with a multihole spinneret. These results confirm that the solvent-free coagulation bath could be implemented to spin the PAN fibers when the spinning solution contained DMF or DMSO solvent, respectively.
- PAN fibers prepared from the DMSO solvent exhibited a better circular shape because of the high viscosity of the DMSO solvent, which contributed to the better formation of the circular shape during the drawing process and smoother skin formation compared to those in the PAN fibers prepared with DMF solvent.
- TGA and DSC curves for both PAN fibers with different types of dope solvent did not differ significantly. The  $T_g$  values for both PAN fibers showed slightly different values, and the increasing  $T_g$  might have been due to the presence of AM as an additive.

- The study indicated that different types of dope solvent did not affect the  $T_g$  of PAN fibers because of the implementation of the solvent-free coagulation bath, so it was significant to conduct the postmodification treatment below  $T_g$  of the PAN fibers.
- This study elucidated that different types of dope solvent significantly influenced the formation of the PAN fibers.

### References

1. Dong, X.-G.; Wang, C.-G.; Bai, Y.-J.; Cao, W.-W. *J Appl Polym Sci* 2007, 105, 1221.
2. Saufi, M. S.; Ismail, A. F. *Songklanakarin J Sci Tech* 24 2002, 24, 843.
3. Wang, Y.-X.; Wang, C.-G.; Wu, J.-W.; Jing, M. *J Appl Polym Sci* 2007, 106, 1787.
4. Edie, D. D. *Carbon* 1998, 36, 345.
5. Gupta, A.; Harrison, I. R. *Carbon* 1996, 34, 1427.
6. Ying, L.; Hou, C.; Qun, W. *J Appl Polym Sci* 2007, 103, 2320.
7. Hou, C.; Ying, L.; Wang, C.-G. *J Appl Polym Sci* 2004, 93, 2622.
8. Dong, R.; Keuser, M.; Zeng, X.; Zhao, J.; Zhang, Y.; Wu, C.; Pan, D. *J Polym Sci* 2008, 46, 1997.
9. Kobashi, T.; Takao, S. U.S. Pat. 4,659,529 (1987).
10. Abdul Rahman, M. Thesis, Universiti Teknologi Malaysia, 2006.
11. Wangxi, Z.; Jie, L.; Gang, W. *Carbon* 2003, 41, 2805.
12. Baojun, Q.; Ding, P.; Zhenqiou, W. *J Adv Polym Tech* 1986, 6, 509.
13. Bajaj, P.; Sreekumar, T. V.; Sen, K. *J Appl Polym Sci* 2002, 86, 773.
14. Rahman, M. A.; Ismail, A. F.; Mustafa, A. *J Mater Sci Eng A* 2007, 448, 275.
15. Ismail, A. F.; Rahman, M. A.; Mustafa, A.; Matsuura, T. *J Mater Sci Eng A* 2008, 485, 251.
16. Sedghi, A.; Farsani, R. E.; Shokuhfar, A. *J Mater Process Tech* 2008, 198, 60.
17. Kruchinin, N. P.; Spirova, T. A.; Medvedev, V. A.; Serkov, A. T.; Radishevskii, M. B.; Volodin, V. I.; Prokhorov, V. A.; Krutova, I. N.; Egorova, R. V.; Grekhova, E. V. *Plenum: New York*, 1991; p 19.
18. Tsai, J.-S.; Lin, C.-H. *J Appl Polym Sci* 1991, 42, 3045.
19. Krigbaum, W. R.; Tokita, N. *J Polym Sci* 1960, 43, 467.
20. An, L.-H.; He, D.-Y.; Jing, J.-K.; Wang, Z.-G.; Yu, D.-H.; Jiang, B.-Z.; Jiang, Z.-H.; Ma, R.-T. *Eur Polym J* 1997, 33, 1523.
21. Rosenbaum, S. *J Appl Polym Sci* 1965, 9, 2071.