

Constant Rotational Rheological Behaviors of the PAN/DMSO/Nonsolvent Systems

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ABSTRACT: The constant rotational rheological behaviors of PAN/DMSO solutions with two kinds of nonsolvent (water and ethanol) have been investigated, respectively, using a cone-plate rheometer. From viscosity measurements, the flow behavior was described within the shear rate range $0.1\text{--}1000\text{ s}^{-1}$. The PAN solutions show shear thinning at high shear rates. The viscosities of the solutions decreased with the rising of the temperature at low shear rate. H_2O content has great influence on the viscosity of the

solutions, depending on the hydration of H_2O and PAN or desolvent effect, according to different H_2O content. The role of ethanol compared with H_2O was also researched and higher viscosity was found. Non-Newtonian index, structural viscosity index $\Delta\eta$, and flow activation energy of the PAN/DMSO/ H_2O systems were also studied. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 598–602, 2009

Key words: PAN precursor; viscosity; rheology; fibers

INTRODUCTION

PAN-based fibers have been found to be the most suitable precursors for producing high-performance carbon fibers (compared with pitch, rayon, etc.) generally because of its higher melting point and greater carbon yield (>50% of the original precursor mass).^{1–5} Conventional spinning processes for PAN fiber are wet spinning and dry-wet spinning, in which PAN or its copolymer is dissolved in a solvent such as dimethylformamide, dimethyl sulfoxide (DMSO), or dimethylacetamide to form a highly viscous solution.⁶ But, intrinsic disadvantages of these two methods greatly weaken the performance of final carbon fiber. Although dry-wet spinning increases the spinning speed and improves the fiber properties,⁶ such as reducing grooves in the axis direction and holes in the radial direction of the PAN precursors prepared using wet spinning, the deadly “skin-core” structure are still in existence. Gel spinning has been regarded as a promising

method for PAN fibers. Because of the fixation of the configuration of PAN chain and the spinning dope changed from solution to gel before the filament entering into coagulation bath, the “skin-core” structure resulted from mass transfer can be greatly inhibited. Also, it is found that the gel spinning provides fibers with a smaller number of defects in comparison with conventional spinning methods.^{7,8} In the PAN systems, the methods used to form a gel are adding nonsolvent to the solvent mixture and/or lowering processing temperature. A mixture of good solvent with a nonsolvent is used as the solvent mixture for PAN.⁹ The solvent mixture can be considered as a not-so-good solvent suitable to make PAN gel with the proper control of the nonsolvent amount.

Now, it has been popularly accepted that the quality of the high-performance carbon fibers depends mainly on the composition and quality of the precursor fibers.⁵ Rheological tests are effective means to study the structure, deformation, and properties of polymer solutions and gels as well as to prove that the solution is suitable for spinning and can be oriented easily, and to suggest better process conditions.¹⁰ The molecular structure of the solutions and gels can be deduced from their steady-state and dynamic rheological test results. In addition, the rheological behavior can be used to estimate the solution or gel's behavior in the extrusion tunnel, and to suggest better fiber spinning conditions for achieving better mechanical properties. It has been reported that flow behavior of polymer depends mainly on molecular characteristics, flow geometry,

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TABLE I
Content of PAN, DMSO, H₂O, and Ethanol in the PAN/DMSO/Nonsolvent Systems (wt %)

No.	PAN	DMSO	H ₂ O	Ethanol
1	23	77	0	0
2	23	75	2	0
3	23	73	4	0
4	23	73	0	4
5	20	76	0	4
6	20	80	0	0
7	20	79	1	0
8	20	78	2	0
9	20	76	4	0

and processing conditions, such as temperature, shear rate, or frequency.^{11–14}

In this article, the steady-state rheological tests of the PAN/DMSO/nonsolvent systems have been studied. The effect of PAN concentration, temperature, kind, and amount of nonsolvent are greatly influenced by the properties of the PAN solutions. The results can provide us the optimal component for PAN spinning and have great theoretic and practical signification.

EXPERIMENTAL

Materials

PAN material used in this work has a viscosity-average molecular weight $\overline{W}_\eta = 7.8 \times 10^4 \text{ g mol}^{-1}$. All the other reagents are of analytical grade, if not otherwise stated. DMSO was obtained from Boer Chemical (Shanghai) Co. Ltd. and ethanol from Changshu Yangyuan chemical plant. Deionization Water was used without further treatment.

Preparation of PAN/DMSO/nonsolvent solutions

All the experimental equipments and PAN materials were dried at 70°C for 3 h in advance to ensure desiccation. The solvent used for the experiments were mixtures of DMSO and nonsolvent, such as H₂O or ethanol, with weight fraction of DMSO = 73, 75, 76, and 77%. A given amount of PAN was first swelled statically in the mixed solvent at 55 °C for 4 h, and then stirred at 70°C for another 4 h to ensure that PAN dissolved evenly. The solutions were deaerated in a vacuum drying oven at 70°C for the removal of air bubbles and then kept at this temperature for 24 h before the rheological experiments. The weight percent (wt %) of each component is listed in Table I.

Rheological test

The constant rotational rheological measurements were conducted in a stress-controlled rheometer,

RS150L (HAAKE, Germany) using cone-plate geometry with the plate temperature controlled by a peltier unit. A sample cover provided with the instrument was used to minimize the change in sample composition by evaporation during the measurement. The steady shear measurements were carried out by a stepwise program of the shear rate ($\dot{\gamma}$) from 1000 to 0.1 s⁻¹. Before the test at each temperature, all the samples were kept at that temperature for a reasonable time to eliminate the effect of the thermal history. A new solution was chosen for each new test to avoid the memory effects. All the experiments were repeated three times and the mean result was used.

RESULTS AND DISCUSSION

Influence of temperature on the rheological behaviors of PAN/DMSO/H₂O

The flow curves of PAN solutions with 4% H₂O at different temperatures are shown in Figure 1. The concentrations of PAN are 20 and 23%, respectively. A steady-state shearing test can be used to explore the relationship between the apparent viscosity (η_a) and shear rate ($\dot{\gamma}$). It is obvious that temperature has much influence on the apparent viscosity of PAN systems under variational shear rate. As other spinning solutions, the PAN gel exhibits shear thinning at high shear rates,¹⁵ which is explained by shear alignment of the molecules as well as breaking of the entangled networks, which lead to decrease in the viscosity above a critical shear rate.¹⁶ Entanglement points exist between the molecules of PAN due to intermolecular van der Waals force. With the increase in the shear rate, some entanglements are destroyed, which results in the decrease in the

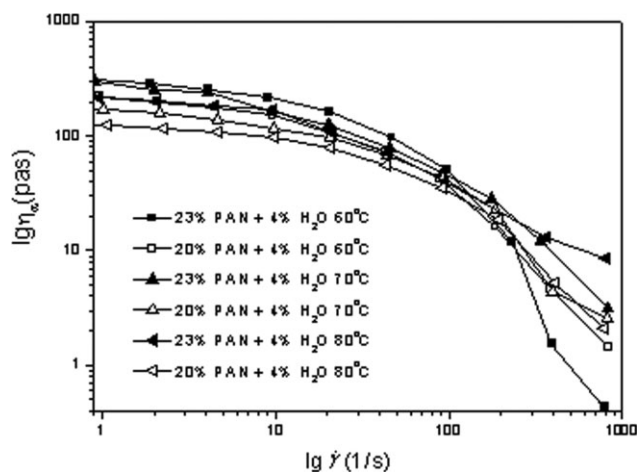


Figure 1 η_a as a function of $\dot{\gamma}$ for PAN solutions at 60, 70, and 80°C, respectively. The solid and hollow symbols represent the concentration of PAN are 23 and 20%. [H₂O] = 4%.

viscoelasticity. On the other hand, the molecule chains of the polymer are aligned in the direction of the flow by the shear force, and therefore the resistance to flow (the viscosity) is decreased.¹⁷ In addition, at the same shear rate, the η_a diminishes when temperatures change from 60 to 80°C. The intensity of molecule motion becomes stronger because of more energy provided to the PAN molecules with the rising of temperature. Entanglement can be broken and the viscoelasticity decreases due to the better fluidity. On the other hand, reducing the concentration of PAN can also make for the decline of viscoelasticity. The most probable reason is that the reduction in the number of macromolecular chains in the dilute solution makes the chains become more stretched.

Influence of H₂O content on the rheological behaviors of PAN/DMSO/H₂O

The role of nonsolvent has been widely researched.^{18,19} But, how the nonsolvent influencing the polymer solution is still not consistent. In this work, H₂O and ethanol were used as nonsolvent. The role of water was revealed by rheology using solutions containing different amount of H₂O. The viscosities of the solutions were examined under a shear-rate sweep, as seen in Figure 2. The PAN concentration is 23% and the H₂O content is 0, 2, and 4%, respectively. At low shear rate, the viscosity changes in the order of 0% > 4% > 2%. That is to say, when water concentration rises from 0 to 2%, the viscosity is decreased. While, when water concentration further increases to 4%, the viscosity reversely enhances a little. This phenomenon can be explained as follows^{20,21}: it is recognized that the pendant nitrile groups in PAN are partially intermolecularly coupled by attractive intermolecular inter-

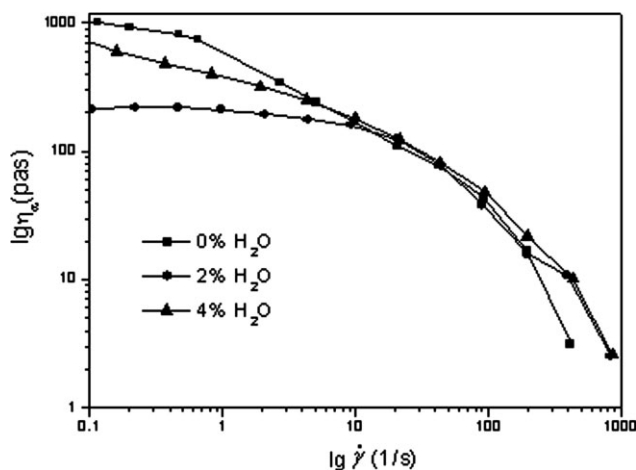


Figure 2 η as a function of $\dot{\gamma}$ for PAN solutions at 80°C. The content of H₂O is 0, 2, and 4%, respectively. [PAN] = 23%.

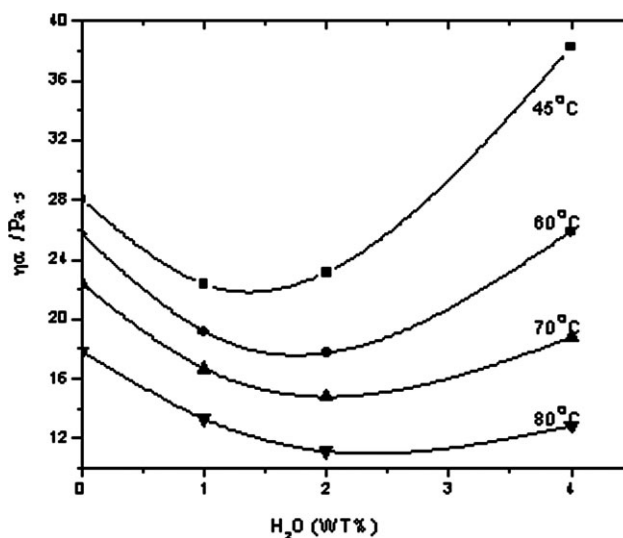


Figure 3 Relationship between H₂O content and temperature. The content of H₂O is 0, 1, 2, and 4%, respectively. [PAN] = 20%.

action. Water can interact with the lone pair orbital of nitrogen in a manner similar to hydrogen bonding, and therefore decouple the nitrile–nitrile association. Obviously, this hydration decreases intermolecular interactions, and therefore the PAN molecules are expected to move over each other more freely. So, the viscosity is reduced at first. On the other hand, further increasing of the water content beyond what is needed for hydrating the nitrile groups, and therefore water is believed to be more than affecting the hydration of the nitrile groups. Large amount of water molecules can rob DMSO molecular from the PAN–DMSO complex due to stronger interaction between DMSO and H₂O. Thus, some solvent is released and PAN aggregations occur, which induced the increase in viscosity. High water concentration helps to enhance the viscosity of the polymer solutions, even to form gels.

Relationship between H₂O content, temperature, and viscosity at constant shear rate was further verified using the 20% PAN solutions with H₂O content of 0, 1, 2, and 4%, respectively (Fig. 3). As in 23% PAN systems, the η reduces first, then increases with water contents enhance. Comparing the four curves, water content corresponding to the minimal η right shifts along with temperature rising. That is to say, the desolvent effect is more notable at lower temperature, which is because viscosity reducing resulted from molecular motion cannot compete with viscosity increasing induced by desolvent effect.²²

Influence of ethanol on the rheological behaviors of PAN/DMSO/ ethanol

The rheological properties of PAN solutions with 4% ethanol were investigated in regard to the role of

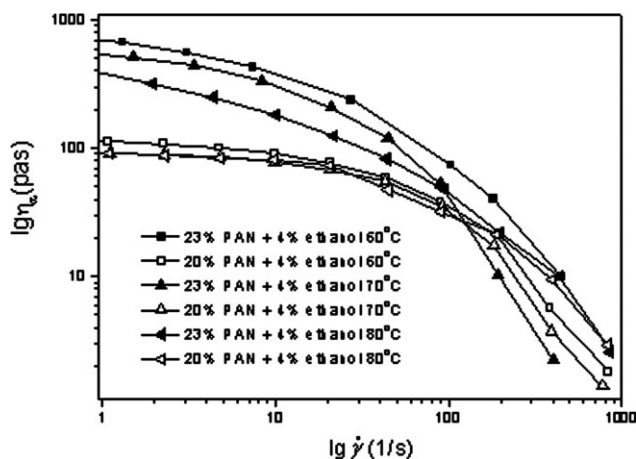


Figure 4 η as a function of $\dot{\gamma}$ for PAN solutions at 60, 70, and 80 °C, respectively. The solid and hollow symbols represent the concentration of PAN are 23 and 20%. [ethanol] = 4%.

ethanol in the PAN/DMSO/ethanol system, as seen in Figure 4. Compared with Figure 1, the PAN solutions with ethanol show some similar characters with added H₂O. With the increase in the shear rate, some entanglement points are destroyed, which results in the decrease in the viscosity. At the same shear rate, the η diminishes when temperature changes from 60 to 80 °C. As have been mentioned above, these phenomena are concerned with the destroying of the entanglement in PAN solutions. While, we have noted that the 23% PAN solutions with ethanol show higher viscosity than that with H₂O. The solubility parameter of PAN, DMSO, ethanol, and H₂O are 12.7–15.4, 13.4, 12.7, and 23.2, respectively. Closer the solubility parameter, better is the dissolution of the two materials. So, ethanol is a relatively good solvent compared with H₂O, which results in a higher viscosity.

Non-Newtonian index n and structural viscosity index $\Delta\eta$

For most polymers, non-Newtonian index n can be expressed as:

$$n = \frac{d \lg \tau}{d \lg \dot{\gamma}}$$

where τ is shear stress and $\dot{\gamma}$ is shear rate. n can be achieved through the slope of the $\lg \tau$ – $\lg \dot{\gamma}$ plot. For the PAN/DMSO/H₂O systems, the n values are listed in Table II.

As given in Table II, all the non-Newtonian indexes are below 1.0, which means all the spinning solutions are non-Newtonian flow although the H₂O content and temperature are different. With the increase in H₂O, n value is decreased. Adding H₂O

reduces the dissolution of PAN in DMSO and induces the entanglements between PAN molecules, which results in the worse flow fluidity, even gelation. In addition, with the increasing temperature, n value is enhanced. This is because more energy is provided with higher temperature and the relaxation of the macromolecular becomes faster, which make the orientation under shearing weaken.

Gel system has the characteristic structural viscosity. The viscosity of the gel will be enhanced along time. While, under shearing, viscosity decreases due to the destroying of the intrastructure. Structural viscosity index $\Delta\eta$ can be expressed as:

$$\Delta\eta_a = - \left(\frac{d \lg \eta_a}{d \dot{\gamma}^{1/2}} \right) \times 10^2$$

where η_a and $\dot{\gamma}$ are the apparent viscosity and shear rate, respectively. The calculated $\Delta\eta$ of the PAN/DMSO/H₂O systems are listed in Table II. As for “shearing thinning” flow, the spinning ability improves with lower $\Delta\eta$. Compared with n values in Table II, $\Delta\eta$ values show the opposite trend, which decrease with the increase in water and enhance with the temperature rising. When temperature increases, the interactions between PAN molecules weaken and the density of the cross-points reduces. Oppositely, adding water can enhance the PAN–PAN interactions and make the $\Delta\eta$ increase.

Flow activation energy E_η

Flow activation energy E_η is defined as the minimal energy for flow unit transiting to the “hole” nearby. E_η reflects not only the fluidity of the flow, but also the temperature sensitivity. Commonly, temperature has more greater influence on viscosity for bigger E_η values. Indeed, the temperature dependence of viscosity is satisfactorily described by the Andrade-Eyring equation $\eta(T) = A \exp(\frac{E_\eta}{RT})$, where A is the pre-exponential constant and E_η is the flow activation energy.²³ As given in Table III, at a constant

TABLE II
 n and $\Delta\eta$ of 23% Pan Solutions with Different Water Content at 60, 70, and 80 °C

H ₂ O (wt %)	T (°C)	n	$\Delta\eta$
0	60	0.60942	8.405
	70	0.7058	7.062
	80	0.76181	6.575
2	60	0.55167	8.935
	70	0.68568	7.589
	80	0.72421	6.989
4	60	0.51433	9.328
	70	0.64304	8.063
	80	0.685	7.528

TABLE III
 E_{η} of PAN/DMSO/H₂O Systems at Different
 Shear Rate (kJ mol⁻¹)

H ₂ O (wt %)	$\dot{\gamma}$ (s ⁻¹)			
	21	42	84	198
0	13.71131	9.05317	6.58957	4.68038
2	15.5564	12.32563	10.98336	8.15567
4	21.09974	15.70253	12.16842	10.18187

shear rate, E_{η} increases when H₂O content increases, which means the viscosity of the PAN solution with more H₂O has more sensitivity to temperature. While for a given solution, E_{η} reduces with the increase in shear rate, which is consistent with our results.

CONCLUSIONS

PAN/DMSO/nonsolvent systems have been investigated under constant rotational conditions using a rheological method.

- 1). PAN/DMSO/nonsolvent systems show “shearing thinning” properties. When temperature rises, the viscosities of the solutions decrease at low shear rate. Entanglements in the solution can be broken and the viscoelasticity decreases due to the better fluidity.
- 2). Adding nonsolvent can change the viscosity of the PAN solutions. Small amount of H₂O reduces the η , due to a similar hydrogen bonding formed between H₂O and PAN and therefore decouple the nitrile–nitrile association, which makes the PAN molecules move more freely. While, when H₂O increases further, η increases, which is attributed to desolvent effect.
- 3). The same trend of η is achieved using ethanol as the nonsolvent. But, the approximative solubility parameter of ethanol with PAN results in higher viscosity compared with H₂O.

- 4). Non-Newtonian index, structural viscosity index $\Delta\eta$ and flow activation energy were also been studied and the consistency with the experimental results were achieved.

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