Viscoelastic Behavior of Polyacrylonitrile/Dimethyl Sulfoxide Concentrated Solution with Water

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ABSTRACT: The spinnability and polydispersity of polyacrylonitrile/dimethyl sulfoxide (PAN/DMSO)/H_2O spinning solutions with conventional PAN molecular weight and comparative high PAN concentration have been investigated using a cone-plate rheometer. It is observed from the measurements that, the viscosities of the solutions decreased with the rising of shear rate, and then stabilized to almost the same value, regardless of the PAN concentration. The chain orientation in the fiber formed under constant shear rate cannot be changed considerably even after long relaxation of more than 900s. For dynamic experiments, a steady increase of both G' and G'' with escalating oscillation frequency was seen for all samples. Higher viscous-elastic modulus at higher H_2O content was found, too. It is also concluded from the log G' − log G'' plot and the gel point that the PAN/DMSO/H_2O system with regular PAN molecular weight behaves very close to a mono-disperse system, thus very suitable for gel spinning and for preparation of high performance PAN precursor fiber. © 2009 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 47: 1437–1442, 2009

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INTRODUCTION

Polyacrylonitrile (PAN)-based precursor fibers are widely known for producing high performance carbon fibers (compared to pitch, rayon, etc.) mainly because of its higher melting point and greater carbon yield (>50% of the original precursor mass).[1–5] Conventional spinning processes for PAN precursor fiber include wet and dry-wet spinning,[6,7] both with inherent disadvantages of uneven skin and core structure due to the phase separation process in the coagulation bath, hence greatly weakening the performance of the carbon

fiber. To avoid this skin and core disparity, gel spinning is introduced by doping nonsolvent into the PAN spinning solution and/or using a low processing temperature.[8,9] Thus, the spinning solutions would change from a sol state to a gel state before the filament enters into the coagulation bath. Owing to the reduced mobility of the PAN chains, the evenness of the fiber structure resulted from mass transfer can be greatly improved, leading to eventually high performance carbon fibers.[10]

The structure, viscous flow and other properties of the spinning dope can be examined through its rheological behavior.[11–16] Such rheological behavior can also be used to predict the extrusion performance of the spinning solution. So, rheology results can be used to prove whether the solution

is suitable for spinning and to find better process conditions.[17]

PAN gel spinning with ultra high molecular weight and low concentration PAN has been studied.[18] However, PAN with high molecular weight is difficult to dissolve to form a homogeneous solution, and the low PAN concentration is adverse to the mechanical properties of the fibers. In our early articles,[19,20] the gelation process of PAN/dimethyl sulfoxide (DMSO) solutions (20 and 23%) with or without water have been studied according to Winter and Chambon theory through dynamic methods. The gelation temperature, gel time, and the critical values of relaxation exponent n were obtained by measuring the dynamic parameters (G', G'', tan δ, and η^*) based on the Winter and Chambon theory. Although, in this article, solutions with regular molecular weight and comparatively high concentration PAN were proposed. The static and dynamic rheological behaviors of the PAN/DMSO solutions with H_2O as the nonsolvent were investigated using a cone-plate rheometer. The relationships between the viscosity and shear rate, the chain orientation, the effects of temperature and H_2O content on both G' and G'' were studied. The homogeneity and polydispersity of the system and their effects were also discussed.

EXPERIMENTAL

Materials

PAN copolymers (acrylonitrile: itaconic acid = 98:2 by weight) were provided by Shanghai Institute of Synthetic Fiber with a viscosity-average molecular weight about 7.8×10^4 g mol^{-1}. Analytical grade DMSO was obtained from Boer chemical (Shanghai) Co. Ltd. Deionization water was used as nonsolvent without further treatment.

Preparation of PAN/DMSO/H_2O Solutions

All the experimental equipment and PAN materials were predried at 70 °C for 3 h for desiccation. The solvent used for the experiments was mixture of DMSO and the nonsolvent, H_2O. A given amount of PAN was first swelled statically in the mixed solvent at 55 °C for 4 h, and stirred at 70 °C for another 4 h to ensure PAN dissolved evenly. The solutions were then deaerated in a vacuum drying oven at 70 °C for the removal of air bubbles and subsequently kept at this temperature for 24 h before the rheological experiments (this

Table 1. Concentration of PAN and H_2O in Each Sample

Samples	S0	S1	S2	S3	S4	S5	S6
PAN (wt %)	20	20	20	20	20	23	25
H_2O (wt %)	0	3	4	5	6	5	5

operation is safe and the possible rheological change of the solutions is negligible). The concentration (weight percent wt %) of each sample was listed in Table 1.

Rheological Test

The rheological measurements were conducted in a stress-controlled rheometer, RS150L (HAAKE, Germany) using the 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 due to evaporation during the measurement. The steady shear measurements were carried out by a stepwise programmation of the shear rate from 800 to 0 s^{-1}. The storage modulus G' and loss modulus G'' as functions of frequency at a given temperature was conducted with frequency ranging from 0.01 to 100 Hz. For the gel point experiments, the temperature dependence of the viscoelastic behavior were obtained from the frequency scanning data measured at various temperatures by a cooling procedure. Before the test at each temperature, all the samples were kept at that temperature for an adequate time period to eliminate the influence of the thermal history, and a new solution was chosen for each test to avoid the memory effects.

RESULTS AND DISCUSSION

Static Rheological Measurements

Viscosity of PAN Solutions Under Shear Rate Scan

Figure 1 shows the viscosity change of the PAN solutions of different concentration under various shear rates. At low shear rate range, a higher concentration leads to a greater viscosity, which decreases sharply with increasing shear rate until a critical level. Above this level, which seems to be independent of the concentration, the viscosity stabilizes regardless of either the shear rate or the concentration. This can be explained by shear alignment of the molecules and breaking of the

Figure 1. Viscosity of sample S3, S5, and S6 under shear rate scan. The PAN concentration is 20, 23, and 25%, respectively. H$_2$O content is 5%.

entangled networks formed between the PAN molecules due to intermolecular van der Waals force, leading to the decrease of the viscosity before a critical shear rate.[21,22] Such reorientation and disentanglement will complete once the shear rate reaching a critical level, and the viscosities of all the samples level off to almost the same value.

Orientation Maintaining

Whether the polymer solutions can maintain the aligned chain orientation once reached is very important for spinning process. The chain orientation in the solution determines the final orientation of the fibers. Therefore the viscosity of sample S6 (25% PAN and 5% H$_2$O) was examined under shearing and relaxation conditions to check how well the orientation in the solution can be retained, as seen in Figure 2. In each experiment, a constant shear rate was applied for 300 s, and then the shear action was stopped to let the solution relax for 0 s (first), 90 s (second) and 900 s (third), respectively. Similar to Figure 1, the flow curves decrease quickly and then level off. The starting viscosity of the second experiment after the first relaxation period (90 s) is almost the same as that before the relaxation. That means, after 90 s, the achieved higher chain orientation, as reflected by a reduced viscosity, has not been lost significantly. That is to say, after the first waiting period, the orientation is held well. Even for the third experiment, the viscosity still has not recovered to the original value right after the shearing. That is, even after 900 s, the chain ori-

entation formed has not worsened significantly, a favorable discovery for fiber spinning.

Dynamic Rheological Measurements

Temperature Effect on G' and G''

Figure 3 shows the effect of temperature on G' and G'' against the frequency for sample S3 (20% PAN and 5% H$_2$O). As can be seen, a steady increase of both G' and G'' with oscillation frequency is observed at all four temperature levels. At a given testing frequency, a sample exhibits higher G' and G'' at lower temperatures, which is consistent with the phenomenon when no H$_2$O added,[19,20] reflecting the temperature sensitivity of both parameters.

Homogeneity and Polydispersity

The log G'−log G'' plots have been widely applied to interpret the homogeneity and polydispersity of the polymer systems.[23,24] This method was also applied in our system to retrieve information about the effect of miscibility on the visco-elastic behavior of the PAN systems. Figure 4 show the log G'−log G'' plots for sample S3 (using the same data in Fig. 3). As known, for compatible and mono-disperse polymer blends, the log G'−log G'' plot should be independent of both composition and temperature change.[24] In Figure 4, the 70 and 80 °C curves overlap well, and so do the 50 and 60 °C ones. This means the PAN dope at 70 and 80 °C essentially belongs to one state and at 50 and 60 °C to another state. Within each state, the curves become temperature

Figure 2. Viscosity change in cycles of applying and releasing shearing for Sample S6 (25% PAN and 5% H$_2$O).

Figure 3. G' (a) and G'' (b) changes of sample S3 with increasing frequency at different temperatures. PAN = 20%, H_2O = 5%.

independent. This temperature independence within each state can be attributed to the good miscibility and narrow dispersity of the systems. Yet the dope state changes over wider range of temperatures, that is 60–70 °C, which is higher than the system that no H_2O added.[19]

Gel Point of Sample S3

As we mentioned earlier, the state of the dope changes during 60–70 °C, so it is necessary to determine the gel point of sample S3. As a common practice, many researchers use the crossover point of storage modulus G' and loss modulus G'' as the gel point, a simple and convenient method.[25] In this article, we also used this criterion, as seen in Figure 5. It is obvious that the gel point temperature of sample S3 is about 62 °C, which is higher than 45 °C, the gel point when no H_2O was added.[19] Combining Figures 4 and 5, a conclusion can be made that 50 and 60 °C corre-

Figure 4. Logarithmic relationship between G' and G'' of sample S3 at different temperatures. PAN = 20%, H_2O = 5%.

spond to the gel state and 70 and 80 °C to the solution state. Then 60–70 °C lay within the sol-gel transition range.

H_2O Effect on the Viscoelasticity of PAN Solutions

The effect of nonsolvent, H_2O, on the viscoelasticity of PAN solutions under different frequency has also been examined as shown in Figure 6. Both G' and G'' increase with the oscillation frequency for H_2O content involved, and a sample with higher H_2O content exhibits greater G' and G'' values, showing the modulus sensitivity to H_2O content in the PAN solutions.

Figure 5. G' and G'' of sample S3 as a function of temperature. PAN = 20%, H_2O = 5%.

Figure 7. Logarithmic relationship between G' and G'' of sample S0, S1, S2, S3, and S4 at 70 °C. PAN = 20%, H$_2$O = 0, 3, 4, 5, and 6%, respectively.

Theoretical Interpretation of Log G' Versus Log G''

By definition, the state change takes place over the gel point. Right at the gel point however, the samples can be in any of the three states: solution state, sol-gel state and gel state, respectively. In Figures 4 and 7, all the curves at either solution state or the gel state have the slope around 1, which could be explained through Doi-Edwards theory.[24]

$$\log G' = n \log G'' - \log cT + \log(M_e)$$

where c is a material constant, T the absolute temperature, M_e the average molecular weight

Figure 6. G' (a) and G'' (b) changes of sample S0, S1, S2, S3, and S4 with increasing frequency at 70 °C. PAN = 20%, H$_2$O = 0, 3, 4, 5, and 6%, respectively.

Log G' − Log G'' Plots of PAN Solutions with Different H$_2$O Content

We also used the log G' − log G'' plot to study the homogeneity and polydispersity of 20% PAN solutions with different H$_2$O content at 70 °C, illustrated in Figure 7 (with the same data from Fig. 6). All the curves with different H$_2$O content at 70 °C coincide with one another well, indicating that all these solutions fall into the same state, owing to the good miscibility and narrow dispersity. The gel point of the sample S4 (6% H$_2$O) was also determined in Figure 8. It can be seen that the gel point of S4 sample is about 67 °C, so the sample S4 with lowest H$_2$O content will be at solution state now $T = 70$ °C. Considering the fact that solutions with higher nonsolvent content possess higher gel points when other conditions are constant, all the samples S0, S1, S2, S3, and S4 in Figure 6 should be at solution state, and thus no sol-gel transition occurs at 70 °C.

Figure 8. G' and G'' of sample S4 as a function of temperature. PAN = 20%, H$_2$O = 6%.

between the entanglement points, and n the slope of a log G' − log G'' plot.

For common systems, $n = 2$, whereas for a perfectly compatible and mono-disperse system, $n = 1$, and the value exceeding two is the evidence of polydispersity. In our study, the slopes of the log G' − log G'' plots in Figures 4 and 7 are about 1, revealing that the PAN solutions with regular low molecular weight used in this study, whether containing H_2O or not, behave very close to a mono-disperse system. That is to say, the PAN solutions, with conventional PAN molecular weight and relatively high PAN concentration, are suitable for gel spinning.

CONCLUSIONS

PAN/DMSO/H_2O systems, with relatively high PAN concentration of regular molecular weight, have been investigated under static and dynamic conditions using rheological methods.

1. The viscosities of the solutions decreased with the rising of shear rate, and then leveled off to almost the same value, regardless of the PAN concentration. This is due to the shear alignment of the molecular chains and breaking of the entangled networks, and once the orientation has been completed under a sufficient shear condition, the viscosity does not change anymore under further shearing.
2. The PAN system used in our work can hold this chain orientation formed under the shear rate, favorable to the fiber spinning process.
3. G' and G'' steadily increase with oscillation frequency, and lower temperature and/or higher H_2O content lead to greater G' and G'' values.
4. For systems with 20% PAN and 5% H_2O, the 70 and 80 °C curves overlap well, indicating both are at the solution state. Similarly 50 and 60 °C curves belong to the gel state. Within each state, the curves become temperature independent, attributed to the good miscibility and narrow dispersity of the systems.

Resulted from the theoretical study, the PAN systems with conventional PAN molecular weight is close to mono-disperse systems, which are very suitable for gel spinning.

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