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Research Article

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Research on the mechanism of gel accelerator on gel transition of PAN solution by rheology and dynamic light scattering

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Abstract: The rheological properties of PAN/DMSO solution and the size and distribution of PAN coils were studied by rheology and dynamic light scattering (DLS) measurements. It was found that water could be used as a gel accelerator and increase the gel transition temperature T_{gel} and the storage modulus G' as well as decrease the damping factor $\tan\delta$ through rheological measurements. DLS test shows that the average size of PAN coils increases significantly with the increase in gel accelerator content. In addition, the gel accelerator can change the mobility of PAN chains during the cooling process. The results show that the gel accelerator can enhance the entanglement of PAN macromolecular chains and improve the formation of three-dimensional network gel structure, so that PAN solution is more prone to gel transition during the cooling process.

Keywords: gel accelerator, rheology, dynamic light scattering, gel transition

1 Introduction

In recent years, gel spinning was developed with the production of high quality PAN precursor for the manufacturing of high performance carbon fiber (1). In the solidification process, the gel fibers with three-dimensional network structure would be formed in the way of thermally induced gel transition (2). There is a thermal exchange between spinning solution and low temperature coagulation bath (3,4). In the initial stage of gel spinning, a certain amount of non-solvent was often added to the spinning solution as the gel accelerator to promote the gel transition in PAN solution. Previous research usually focused on the effect of gel accelerators on the mechanism of phase separation of polymer solutions. Tan et al. reported that there are nucleation and growth model in PAN solution without additive (5,6). Nandi et al. reported that there would be bi-continuous phase separation after adding water (7,8). Besides, sizes and their distribution of macromolecular random coils in original PAN spinning solution have an important effect on the gelation process. Thomas et al. reported that the drawability of the fiber will be impaired if the average coil size is too small (9). Taniguchi et al. reported that it will affect the uniformity of gel fibers when the size distribution is highly dispersed (10). However, the relationship between the gel accelerator and the size and distribution of random coils is rarely explored.

In this study, the mechanism of gel accelerator on the gelation of PAN solution was studied by rheology and dynamic light scattering (DLS) methods. The effect of gel accelerator was investigated from the perspectives of both the rheological properties and the size of PAN random coils in the spinning solution. The relationship between the formation of three-dimension gel structure and the morphology of PAN chains would be confirmed.

2 Experimental

2.1 Preparation of PAN solution

PAN co-polymer (the mass ratio of AN and IA is 98:2) with a viscosity-average molecular weight $\overline{M_{\mathrm{v}}} = 10 \times 10^4$ g/mol was provided by Jilin Chemical Fiber Group Co., Ltd. PAN

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powder with the mass fraction of 20% was added to a mixed solvent of DMSO and distilled water and swelled at room temperature for 24 h, and then stirred at 60°C for 15 h and defoamed in vacuum at 60°C for 1 h. The prepared PAN solution was stored at a constant temperature for rheological and DLS measurements.

2.2 Rheological characterization

Temperature dependence of dynamic rheological testing was carried out using a rotary rheometer (MCR101, Anton Paar, Austria) equipped with CP-25 cone plate fixture (constant 0.104 mm gap) from 60°C to 10°C with the cooling rate of 2°C/min at the constant frequency (10 rad/s). The storage modulus G' and loss modulus G'' varying with temperature during the cooling process were traced. The control-shear-strain (CSS) pattern was followed in this experiment. The strain amplitude should be set in the range of linear viscoelastic (LVE) region to ensure the maintenance of sample structure, which was set at 1% in this study.

2.3 Dynamic light scattering

The multi-angle laser light scattering gel chromatography system (DAWN HELEOS II, Wyatt, USA) was used in measuring the size of the poly-acrylonitrile coils at three constant temperatures (60°C, 40°C, and 20°C). The light source was a GaAs ($\lambda = 658$ nm) laser operating continuously and the power was 50 mW. All DLS measurements were made with a concentration of 0.1 wt% at a scattering angle $\theta = 90°$.

The diffusion coefficient D_t of the random coil was calculated by detecting the change of the intensity of the scattered light, and then the hydrodynamic radius R_h of the coils was calculated by the Stokes–Einstein equation (11–13):

$$D_t = \frac{kT}{6\pi\eta R_h}, \tag{1}$$

where k is the Boltzmann constant, T is the Kelvin temperature, η is the viscosity of the solvent, and R_h is the radius of the equivalent sphere with the same diffusion coefficient as the molecule in the sample, showing the size of the polymer random coils inside the solution.

3 Results and discussion

3.1 The effect of temperature on the rheological properties of PAN solution

Figure 1 shows the temperature dependence of the storage modulus G' and loss modulus G'' of PAN/DMSO solution. The storage modulus G' reflects the energy stored in the deformation process because of elastic deformation, which characterizing the elasticity of PAN solution. The loss modulus G'' reflects the energy that the solution consumes in the form of thermal loss during the deformation process, characterizing the viscosity. As shown in Figure 1, the loss modulus G'' is larger than the storage modulus G' at high temperature, which indicates that the viscosity is stronger than the elasticity in this solution. As the temperature decreases, the storage modulus G' and the loss modulus G'' gradually increase but show a different tendency. When the temperature tends to around 18°C, the growth rate of the storage modulus G' increased abruptly, indicating the formation of network-gel this time. As the temperature decreases further, the storage modulus G' gradually became greater than the loss modulus G'', indicating that the gel structure has been formed.

The corresponding temperature of the intersection of the storage modulus G' and the loss modulus G'' curves shown in Figure 1 is called the gel transition temperature T_{gel}, which is the critical temperature for PAN solution transformation from solution to gel during the cooling process (14).

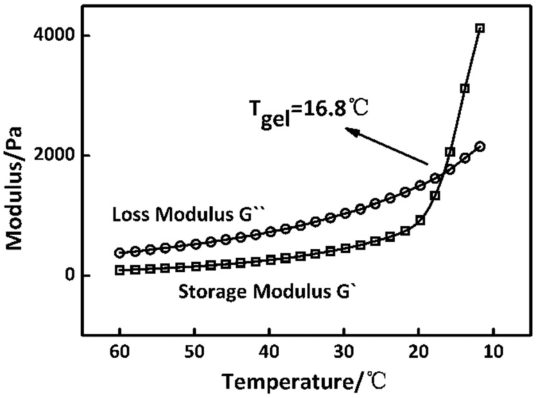

Figure 1: Temperature dependence of the storage modulus G' and the loss modulus G'' of PAN solution.

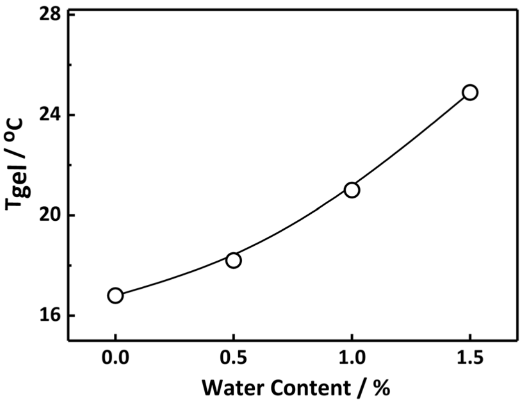

Figure 2: The gel transition temperature T_{gel} of PAN solution versus water content.

3.2 The effect of water on gel transition process

The effect of water, which was applied as the accelerator for gel transition, on the gel transition temperature of PAN solution is shown in Figure 2. The gel transition temperature of PAN solution without water is 16.8°C. With the increase in water content, the gel transition temperature gradually increases. It is suggested that water could act as a gel accelerator in PAN solution.

As shown in Figure 3a and b, compared with the neat PAN solution, the addition of water results in higher storage modulus G' and less damping factor tan δ, especially at lower temperature. It means that water, which acts as the gel accelerator, can enhance the elasticity of the PAN solution.

Figure 4 shows the frequency scanning curve of polyacrylonitrile gel with different water content. As shown in the figure, the high-frequency region is in a gel state because the action time of force is not long enough to destroy the gel structure. In the low-frequency region, the gel state is transformed into a solution state because of the relaxation of molecular chains. The storage modulus G' and loss modulus G'' were intersected at the point that was defined as gel transition frequency f_{gel}.

The effect of water on the gel transition frequency f_{gel} of PAN solution is shown in Figure 5. With the increase in water content in the solution, the gel transition frequency was decreased. It means that when the temperature is decreased, the gel transition could be prompted with the addition of water as the stability of PAN gel becomes higher.

The effect of water on the gel transition of PAN/DMSO solution could be interpreted by the theory of solvation and desolvation. At high temperature, the interaction between DMSO solvent and PAN segments is stronger than that between PAN segments. PAN chains tend to be separated from each other. However, this so-called solvation would be affected after the addition of water. Water and DMSO can form a strong intermolecular force because of hydrogen bonding. As a result, the interaction between DMSO and PAN was weakened by the addition of water. Therefore, the interaction of PAN segments was enhanced. PAN molecular chains tend to move closer to each other. This phenomenon is called the desolvation that promotes the entanglement of PAN chains. Thus, water can enhance the elasticity of the PAN macromolecules and promote its thermal gelation during the cooling process and promote the formation of a network structure named thermal-induced gelation during the cooling process.

3.3 The effect of water content on the dimension of PAN molecular random coils

DLS was applied to explore the mechanism of the gel acceleration by characterizing the size and distribution

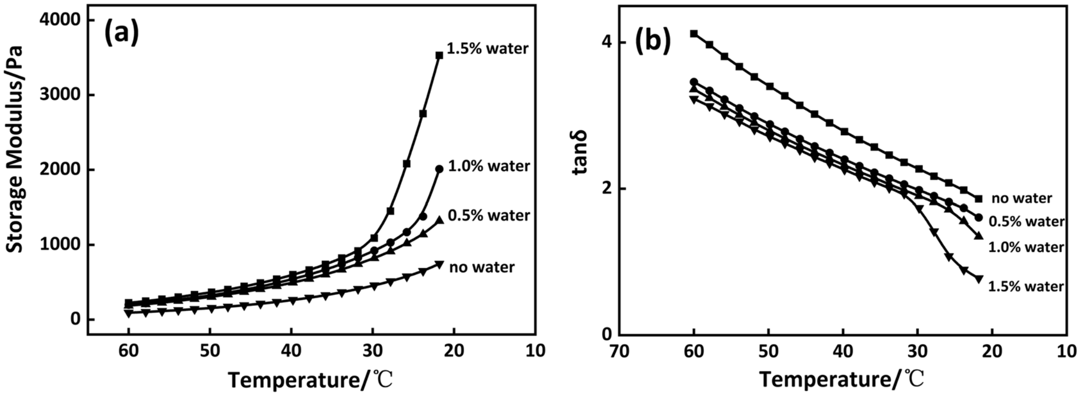

Figure 3: Temperature dependence of (a) G' and (b) tan δ of PAN solution with different water contents.

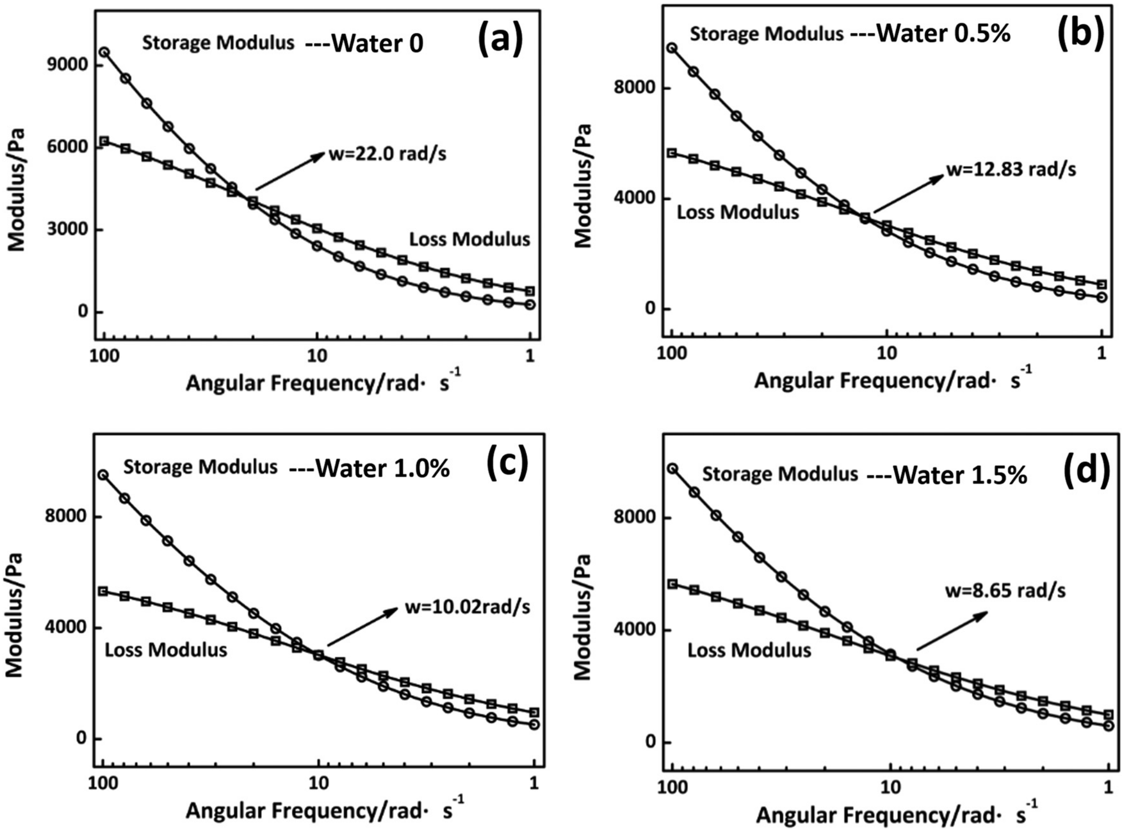

Figure 4: Frequency scanning for gel transition of PAN solutions with different water contents: (a) 0%, (b) 0.5%, (c) 1.0%, and (d) 1.5%.

of PAN molecular random coils. It can be seen from Figure 6 that the average size of random coils increases with the addition of water, which proves that the gel accelerator can promote the entanglement of PAN molecular chains. After adding water, PAN chains would be clustered and entangled with each other. The number of cross-linking points would be increased. The solid characteristics of the PAN solution become more obvious, which explains that the elasticity of PAN solution would be strengthened with the increase in water content. The higher the cross-link density of macromolecular chains, the easier it is to form the developed three-dimensional network gel structure. Therefore, thermally induced gel transition of PAN solution during the cooling process is easier by the addition of water.

It can be also seen in Figure 6 that the variation tendency of the average size of random coils is different with the water content. For non-aqueous solution, the average size decreased initially and then increased with the decrease in temperature. With the decrease in temperature, the solubility of PAN in DMSO was decreased. It indicated that the interaction between PAN segments was higher than that between PAN and DMSO solvent. This means that the shrinkage of PAN molecular coils is the domain transition during this temperature region. Apparently, the average size of PAN molecular coils was decreased. When the temperature decreased further, which was lower than 40°C, agglomeration phenomenon of PAN coils resulted from phase separation leads to the increase in the coil size. However, when the water content increases up to 10%, the

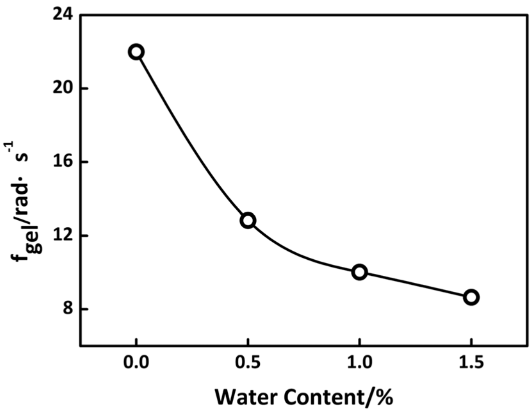

Figure 5: The gel transition frequency f_{gel} of PAN solution versus water content.

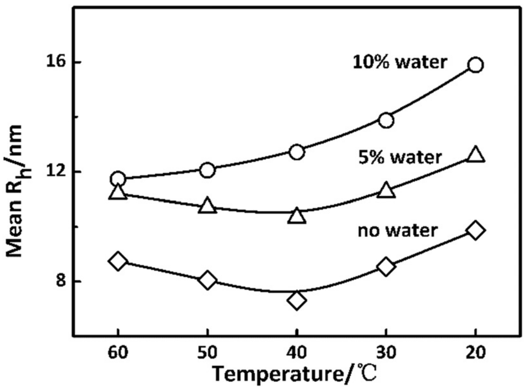

Figure 6: Average size of PAN coils in solution with different water content during cooling process.

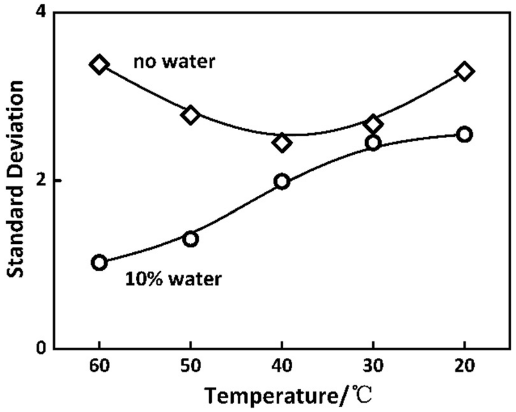

Figure 7: The standard deviation of size distribution of PAN coils in solution with 0% and 10% water during the cooling process.

average size increases continuously with the decrease in temperature. This means that the addition of water could prompt the gel transition and the stability of PAN gel.

As shown in Figure 7, water can also affect the size distribution of the random coils. With the addition of water, the standard deviation of the size of PAN coils became lower compared to the neat solution. It indicates that water can lead to more concentrated distribution of PAN random coils. Besides, the variation tendency of the standard deviation is also different with water content and similar to the variation tendency of the average size.

The model of the aggregation of PAN chains during gel transition without addition of water is shown in Figure 8a. During the initial cooling process, the decrease in the mobility of PAN molecular chains leads to the shrinkage of random coils themselves. Therefore, the average size of PAN chains was reduced apparently. However, as the temperature was decreased further, the neighboring coils would be physically cross-linked and merged with each other. In addition, some clusters with large size were gradually formed, resulting in the increase in coil size and its distribution. In the case of addition of 10% water, as shown in Figure 8b, water enhanced the interaction force between PAN segments and promoted the entanglement of PAN chains when the water content reached a critical value. Therefore, there would be the fusion of neighboring coils with the small size and the

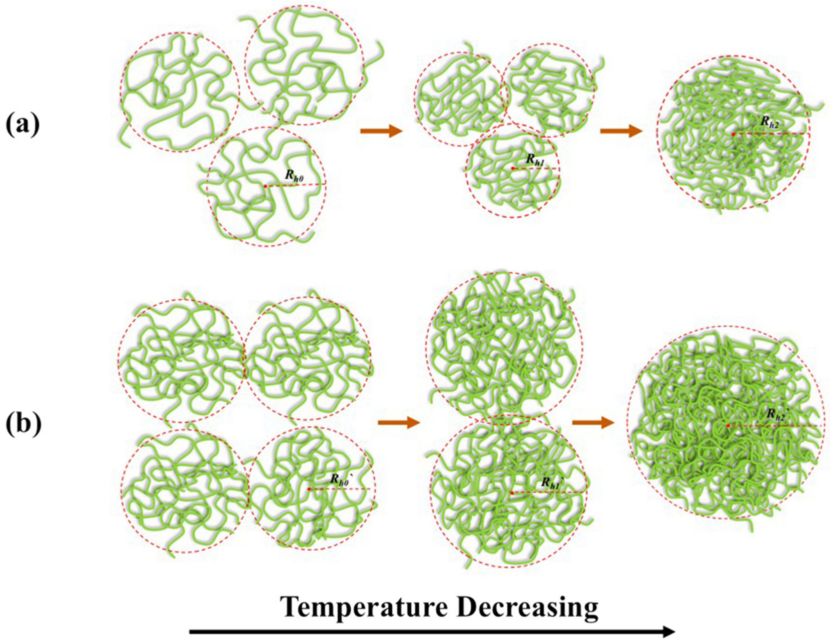

Figure 8: The schematic of the movement of PAN coils in solution: (a) without water and (b) with 10% water during the cooling process.

formation of larger size clusters in the first stage of the cooling process. As the temperature decreased further, the formed adjacent clusters coalesced with each other to form larger size clusters. It is opposite to the case of cooling process of PAN/DMSO neat solution, which leads to the continuous increase in average size and its distribution of PAN clusters. When the size of PAN clusters was larger enough, the three-dimensioned network gel structure would be formed which was named gel transition.

4 Conclusions

In this study, the mechanism of gel accelerator in PAN solution was studied, and water acts as the gel accelerator in PAN/DMSO solution. In neat solution, PAN macromolecular random coils undergo a process of individual shrinkage, and then adjacent random coils converge to form the larger clusters sequentially during the cooling process. The addition of a small amount of water to binary system results in the improvement and entanglement of the PAN molecular chains partly but could not change the mobility of PAN coils. When the water content becomes sufficient in ternary system, the average size of random coils would increase and the size distribution would be more concentrated. During the cooling process, adjacent random coils converge to form large-size clusters, and then adjacent clusters merge together to form larger size clusters. Therefore, a developed and stable gel network in PAN solution can be formed at higher temperature and the gel transition can be promoted.

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