RHEOLOGICAL PROPERTIES OF PVA SOLUTIONS IN THE MIXED SOLVENT OF DMSO AND WATER

Seung Gyoo Kim, Jeong Ryeon Han, and Byoung Chul Kim*

Department of Textile Engineering, Dankook University
*Polymer Hybrid Center, Korea Institute of Science and Technology

1. INTRODUCTION

To increase the tensile strength and modulus of polyvinylalcohol (PVA) fiber by utilizing polymer with medium molecular weight, several spinning techniques have been developed with significant commercial importance. To name of them includes gel spinning[1] and crosslinking spinning[2]. The former uses organic solvents while the latter adopts inorganic salts. As might be supposed, it is prerequisite to understand the characteristic features of PVA solutions to properly design the spinning process of PVA because some microgels may be formed through hydrogen bonding between hydroxy groups or complexation by aid of inorganic ions such as cupric, borate and vanadate ions[3].

To develop high-performance PVA fiber and medical PVA substituents many researchers have been studied the characteristic rheological behavior of PVA/water and PVA/dimethylsulfoxide(DMSO)/water systems[4-8]. Yamaura *et al.*[9] observed that gels are formed in the mixture of DMSO and water. They reported that properties of the gels are dependent on the ratio of DMSO/H_2O. Cha *et al.*[1] succeeded in manufacturing high strength and high modulus PVA fibers by drawing gels prepared from DMSO/water mixture. Up to now, however, problems associated with applying these gel systems to the actual spinning processes still remains controversial.

Owing to the strong inter and intramolecular interactions, however, PVA exhibits very unusual rheological responses depending on measuring conditions and time scale of measurement. This study investigates the effect of water level on the rheological properties of PVA solutions in DMSO.

2. EXPERIMENTAL

PVA sample was prepared by bulk polymerization. The number-average degree of polymerization of polymer was 1700 and degree of saponification was 99.5 mol%. PVA solution was prepared from pure DMSO, pure water, or mixture of DMSO/water. The ratio of DMSO to water was 90/10~10/90 by weight. The polymer solutions were homogenized at 120 ℃ in nitrogen atmosphere to prevent oxidative degradation.

The rheological measurements were performed with a Rheometrics mechanical spectrometer (RMS, Rheometrics Scientific Rhios) using a cone-and-plate geometry. The diameter, angle, and gap of the cone were 50 mm, 0.1 °, and 30 μm, respectively. The temperature range was 30 to 60 ℃ within the accuracy of ±0.1 ℃.

3. RESULTS AND DISCUSSION

To investigate the effect of DMSO/water ratio of the mixed solvent on the rheological properties of PVA solution, the complex viscosity ($\eta*$) of 12 wt% solutions of PVA of P_n of 1700 is plotted against frequency (ω) in Figure 1. PVA is soluble in both DMSO and water. Of the two solvents, DMSO proved to be a better solvent than water. However, the PVA solution in DMSO forms a strong gel only when freezing and subsequent thawing procedures are repeated. PVA forms a strong gel in the mixture of DMSO/water when the solution is cooled to room temperature. DMSO is known to be a polar solvent, and it has a strong affinity to water. The interactions of DMSO/water by NMR[10], neutron scattering[11] revealed the structure of a hydrated compound of DMSO to be $(CH_3)_2 \cdot SO \cdot 2H_2O$ or $(CH_3)_2 \cdot SO \cdot 3H_2O$. The oxygen of N-O appendage of N-methyl morpholine-N-oxide (MMNO, $CH_3C_4H_8NO_2$) is able to form one or two hydrogen bonds with hydroxylated substances such as water and alcohol. When the dissolution of cellulose occurs in the presence of water, there is a competition between water and cellulose for the MMNO molecules. It has turned out that NMMO prefers water to cellulose.[12] Similar hydrogen bonding is also believed to occur with PVA. The variation of the $\eta*$ of PVA solutions with mixture ratio of DMSO/water is shown in Figure 2. As seen in the figure, the $\eta*$ of PVA solution exhibits a maximum over the mixing range of DMSO and water. At the mixing ratio of DMSO/water 60/40 by weight, the $\eta*$ shows a maximum value. In

addition, the $\eta*$ of the PVA solution in DMSO is higher than that in pure water. On the whole, the mixed solvent acts as a new solvent which differs from pure DMSO and pure water. Hence the mixed solvent system gives unique rheological responses.

For homogeneous isotropic solutions of polymers, G′ is related to G″ by Eq.(1)[13]:

$$logG' = 2logG'' - logG_o \quad ----------- \quad (1)$$

in which $G_o=c_lkT/M_e$, c_l is a constant, k is the Boltzmann constant, T is the absolute temperature, and M_e is the average molecular weight between entanglement points. On the empirical and theoretical bases slope 2 on this plot for a polymer solution indicates that the solution is isotropic and homogeneous. This expression offers a very useful tool for tracing the conformational information of polymer molecules in solutions. Through the strong interactions between solvent molecules and PVA chains, the physicochemical character of solvent may affect the spatial arrangement of PVA molecules.

Change in conformations of PVA molecules through changing the mixing ratio of DMSO to water is assessed by plotting the G′ of the PVA solutions against G″ in Figure 3. On the so-called Cole-Cole type plots, the slope of PVA solution in pure DMSO go to 1.73, and the slopes approach 1.09 and 1.12 at the ratio of DMSO/water 80/20 and 60/40, respectively. However, in case of PVA solutions in water-rich solvent and pure water, the slopes approache 1.52. Cha *et al.*[1] reported that water and DMSO molecules can associate to form a 1 : 1 molar complex in the 80/20 DMSO/H_2O mixture. In principle, a good solvent does not lead to formation of gels but a homogeneous solution, whereas a poor solvent causes formation of large crystallites through phase separation, ultimately leading to formation of a weak gel. As might be imagined, the slope on the Cole-Cole plot would be decreased if the solution systems get more heterogeneous. In other words, the ratio of G′ to G″ will be decreased because of existence of irregular gels with long relaxation time. The gels are readily oriented even by a weak shear, which leads to an increase of viscous dissipation. In consequence, it may be said that PVA may form heterogeneous solutions including some gel structure in the mixed solvents of DMSO and water. Loss tangent data in Figure 4 further ascertain the result.

4. REFERENCES

1. W. I. Cha, S. H. Hyon, and Y. Ikada, *J. Polym. Sci. Polym. Phys.*, **32**, 297 (1994).
2. K. S. Hwang, C. A. Lin, and C. H. Lin, *J. Appl. Polym. Sci.*, **52**, 1181 (1994).
3. M. Shibayama, M Adachi, F. Ikkai, H. Kurokawa, S. Sakurai, and S. Nomura, *Macromolecules*, **26**, 623 (1993).
4. T. Takigawa, H. Kashihara, K. Urayama, and T. Masuda, *Polymer,* **33**, 2334 (1992).
5. W. I. Cha, S. H. Hyon, D. Graiver, and Y. Ikada, *J. Appl. Polym. Sci.*, **47**, 339 (1993).
6. M. Watase and K. Nishinari, *Polymer J.* **21**, 567 (1989).
7. M. Matsuo, Y. Harashina, and T. Ogita, *Polymer J.* **25**, 319 (1993).
8. C. Sawatari and Y. Yamamoto, N. Yanagida, and M. Matsuo, *Polymer.* **34**, 954 (1993).
9. K. Yamaura, T. Karasawa, and S. Matsuzawa, *J. Appl. Polym. Sci.,* **37**, 2709 (1989).
10. K. J. Packer and D. J. Tomlinson, *Trans. Faraday Soc.,* **67**, 1302 (1971).
11. G. T. Safford, P. C. Schaffer, P. S. Leung, G. F. Doebbler, G. W. Brady, and E. F. X. Lyden, *J. Chem. Phys.,* **50**, 3140 (1969).
12. H. Chanzy, S. Nawrot, A. Peguy, and P. Smith, *J. Polym. Sci. Polym. Phys. Ed.,* **20**, 1909 (1994).
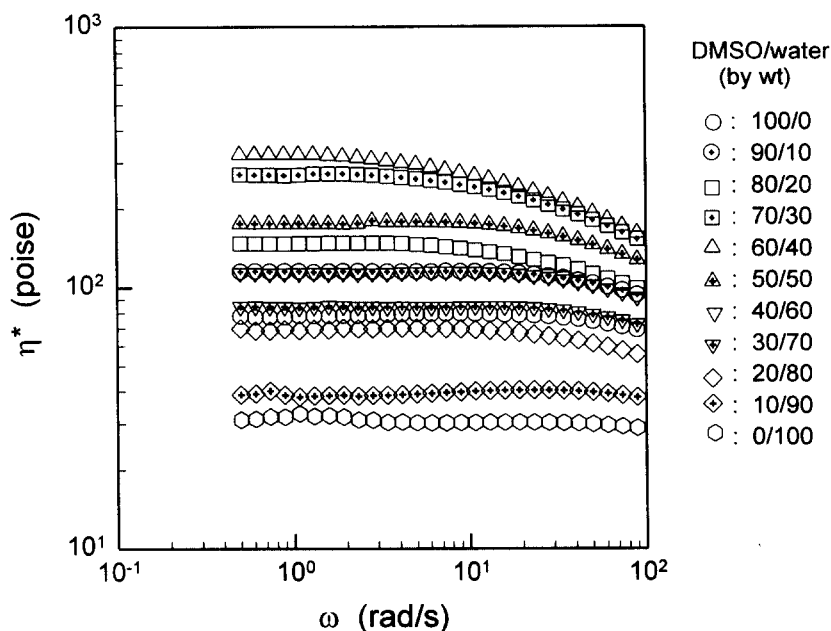13. C. D. Han and M. S. John, *J. Appl. Polym. Sci.,* **32**, 3809 (1986).

Fig. 1. Complex viscosity (η^*) curves of 12 wt% PVA (P_n=1700) solutions in DMSO/water with various water levels at 30 $^\circ$C.
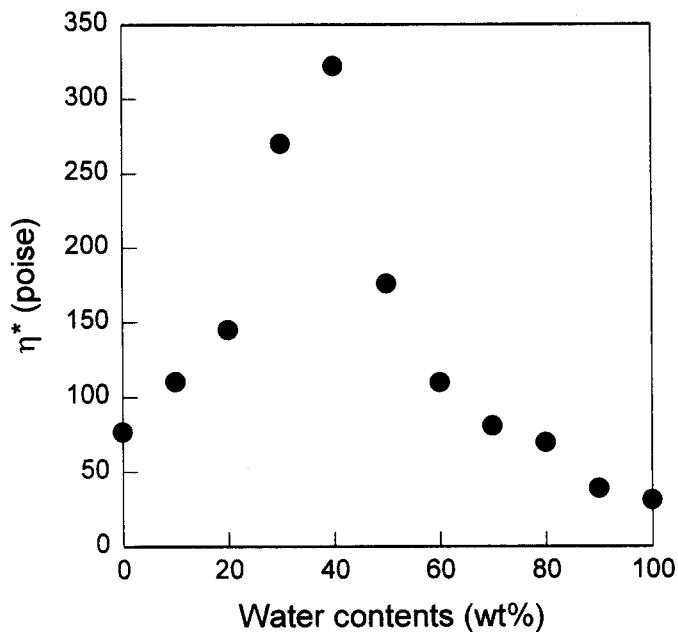

Fig. 2. Variation of complex viscosity (η^*) of PVA (P_n=1700) solutions in DMSO/water mixtures with water contents at 0.5 rad/s and 30 $^\circ$C.
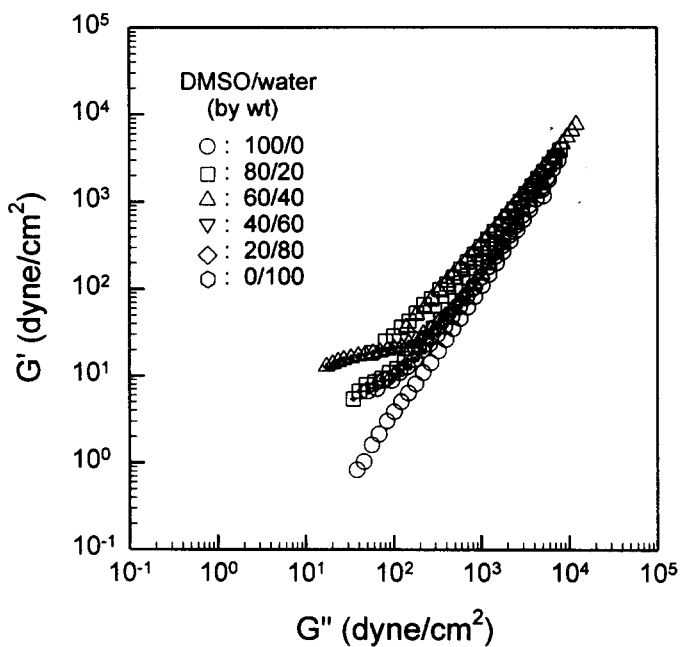
Fig. 3. Plot of storage modulus (G') vs. loss modulus (G") for 12 wt%
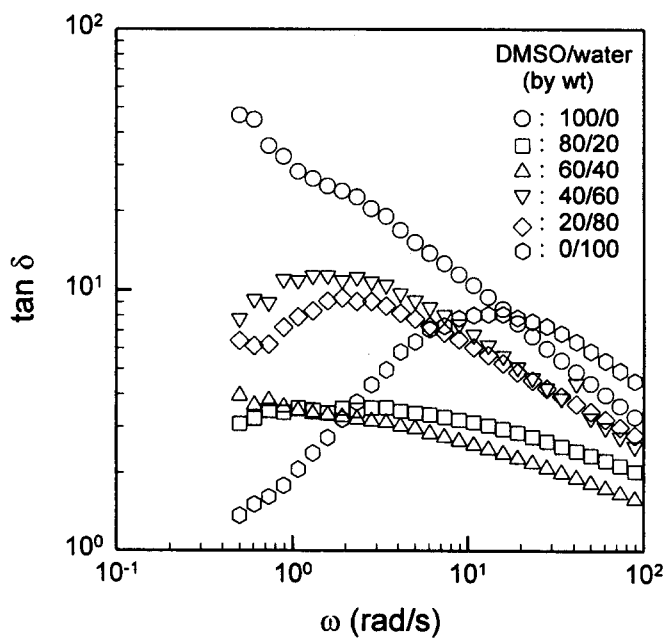PVA (P_n=1700) solutions in DMSO/water with different water
contents at 30 °C.

Fig. 4. Variation of loss tangent (tan δ) with frequency (ω) for 12 wt%
PVA (P_n=1700) solutions in DMSO/water with different water
contents at 30 °C.