〈Research Paper〉

Rheological Measurement of Fiber Spinnability of PVA Solution Dopes in DMSO

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Abstract— The effects of molecular weight (MW) and concentration on the rheological properties of poly(vinyl alcohol) (PVA) solutions in dimethyl sulfoxide (DMSO) were investigated at 30 $^{\circ}$C. Ubbelohde viscometer and rotational rheometer were employed for dilute and concentrated regime, respectively. In the dilute regime, the Mark-Houwink exponent (α) of the solutions determined from three different MWs proved 0.73. The critical concentration (C*), in which the entanglement and overlap of polymer molecules began to take place, decreased with increasing the MW of PVA. Huggins constant (K_H) values ranged from 0.33 to 0.45 over the MW examined. In the log-log plot of η_{sp} versus [η]C, the PVA with higher degree of polymerization (DP) gave a greater slope exhibiting the inflection point in the vicinity of C*. In the dynamic viscosity (η') curve, the PVA solutions of DP 1700 presented Newtonian fluid behavior over most of the frequency range examined. However, the lower Newtonian flow region reduced with increasing the DP. As the PVA concentration increased, η' was increased and the onset shear rate for pseudoplasticity was decreased. In the Cole-Cole plot, PVA solutions showed almost a single master curve in a slope of ca. 1.65 regardless of the DP. However, the increase of the concentration from 8 to 12 wt% for PVA solutions of DP 5000 decreased the slope from 1.73 to 1.57. In the tan δ curve, the onset frequency for sol-gel transition was shifted from 154 to 92 rad/s with increasing the DP from 3300 to 5000 and from 192 to 46 rad/s with increasing the concentration from 8 to 12 wt%. In addition, longer relaxation time (λ) was observed with increasing the DP and concentration.

Keywords: *poly(vinyl alcohol) (PVA), dimethyl sulfoxide (DMSO), Mark-Houwink equation, dynamic viscosity, Cole-Cole plot, tanδ*

1. Introduction

Poly(vinyl alcohol) (PVA), one of the first synthetic polymers produced on a commercial scale, has been used in various applications such as high-performance fibers and functional films because linearity and zigzag conformation of molecules can give high fiber orientation[1]. Nowadays, because of its biodegradability, many attempts are made to apply the polymer to medical materials such as contact lens and cartilage. PVA containing polar hydroxyl groups in a unit chemical structure forms strong inter- or intra molecular hydrogen bonding. This may have a considerable effect on the viscoelastic properties of polymer solutions, exhibiting complicated phenomena such as phase separation and gelation. When determining the spinning condition for a given polymer, the investigation on viscoelastic properties is indispensible, which are strongly affected by molecular weight, concentration, and solvent, etc[2]. The viscosity, a measure of the resistance of a fluid which is being deformed by shear, is used as basic data to determine the spinning rate. Because the capacity of the motor used in the spinning process depends on the spinning rate, the viscosity of the polymeric system gives a clue to determining the capacity of motor as well. In addition, the storage modulus (G'), a measure of elastic properties, is used to determine the design of spinneret because a die swell is related with the elastic properties. Thus, the study on the viscoelastic properties of spinning material is prerequisite to understand a given spinning process and figure out the problems occurring in the process.

The strong physical interaction including hydrogen bonding hinders the orientation of polymer molecules.

Thus, PVA is frequently modified by means of

crosslinking in order to maximize the molecular orientation. Particularly with gel spinning, one of methods to obtain high performance PVA fibers, it is indispensable to add cations to cause cross-linking when water is used as a solvent of PVA[3-8]. This inevitably makes the solution basic resulting in the corrosion of spinning systems. However, one can avoid introducing cations by using dimethyl sulfoxide (DMSO) instead of water[9]. Therefore, the PVA/DMSO system seems to be advantageous to obtain high performance PVA fiber with highly oriented molecular structure. This study discussed the characteristic rheological responses of PVA solutions in DMSO in the low and high concentration regime varying the molecular weight and concentration.

2. Experimental

2.1 Materials

PVA (degree of saponification : 99 %), whose weight-average degree of polymerization (DP)s were 1700, 3300, and 5000, was purchased from Aldrich. The resin was vacuum dried at 80 ^{o}C for 24 hours prior to use. An extra pure DMSO was used as a solvent without further purification. PVA was dissolved in DMSO at 110 ^{o}C for 2 hours in a dry nitrogen atmosphere. The dilute solutions with the concentration range of 0.1 ~ 0.9 g/dl were filtered using a 0.45μm disk filter and then placed in an oven at a desired tem-perature for 24 hours to stabilize the solutions and prevent gelation before the measurement. The concentrated solutions with the range of 8 ~ 12 wt% were also prepared for the dynamic rheological measurements.

2.2 Measurement of flow behavior

Specific viscosity (η_{sp}) and intrinsic viscosity ([η]) were determined at 30 ^{o}C using an Ubbelohde viscometer (Schott Co.) over the concentration range of 0.1 ~ 0.9 g/dl. The variation of dynamic rheological properties of PVA solutions was measured with the DP at a given concentration of 10 wt% and with the concentration at a given

DP of 5000 using an Advanced Rheometric Expansion System (ARES, Rheometric Scientific. Co.). Parallel plate geometry with a diameter of 50 mm was adopted. The plate gap and strain level were 0.5 mm and 10%, respectively. Frequency sweep measurements were performed at 30 ^{o}C with liquid nitrogen purging. The solutions were kept for a given time prior to the measurement to relax residual stresses at the temperature. To prevent evaporation of the solvent during the measurement, a heavy mineral oil (Aldrich) was coated on the trimmed edge of the samples between plates.

3. Result and discussion

Fig. 1 exhibits the dependence of the intrinsic viscosity on the molecular weight for PVA solutions in DMSO at 30 ^{o}C. The Mark-Houwink exponent (α) is determined by Eq.(1):

$$[\eta] = K\ M^{\alpha} \tag{1}$$

where [η] is intrinsic viscosity, K, constant, and M, molecular weight of polymer. Although this equation was firstly devised for monodispersed polymers, it is widely used to polymers with narrow molecular weight distribution as well.
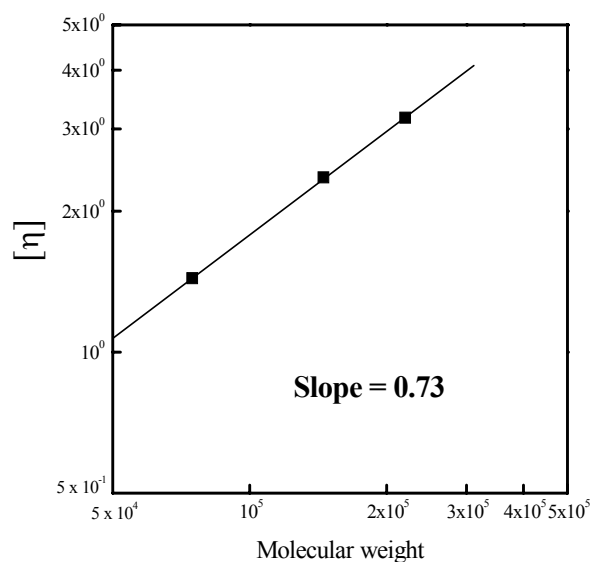

Fig. 1. Plot of [η] of PVA/DMSO solutions against molecular weight at 30 ^{o}C.

The α, dependent on the particular polymer-solvent system, may offer the information of the conformation of polymer molecules in the solution. The determined value of α is 0.73 over the range of molecular weight examined, which is higher than the reported values in the literatures for the PVA solutions in water or mixed solvent of water and phenol[10]. Generally, α varies from 0 to 2. α equals to zero for hard spheres, 0.5 to 0.8 for random coils, 1 for stiff coils, and 2 for rigid rods. We can infer that the hydrodynamic volume of PVA molecules dissolved in DMSO is larger than that of PVA molecules dissolved in aforementioned solvents[11].

In the dilute concentration regime, it is useful to cite some parameters including critical concentration (C*) and Huggins constant (K_H). Table 1 summarizes the values of [η], C*, and K_H of PVA solutions in DMSO for three different DPs. The C* refers to the concentration, in which the entanglement and overlap of polymer molecules begin to take place, and it is calculated by Eq.(2):

$$C* = \frac{1}{[\eta]} \qquad (2)$$

Table 1. Values of [η], C*, and K_H for PVA/DMSO solutions at several DPs

DP	1700	3300	5000
$[\eta]$	1.41	2.28	2.93
C^*	0.71	0.43	0.34
K_H	0.33	0.34	0.45

The C* is decreased with increasing the MW of polymer as expected. This indicates that higher MW PVA has larger hydrodynamic volume. K_H represents the degree of polymer-solvent interaction, and it is calculated by Eg.(3)[12]:

$$\frac{\eta_{sp}}{C} = [\eta] + K_H[\eta]^2 C \qquad (3)$$

where $\eta_{sp} = \eta/\eta_0 - 1$, η and η_0 are the viscosity of the polymer solution and that of the solvent, respectively. In a Θ solvent where the polymer chains take the unperturbed dimension the value of K_H equals to 0.52. In a good solvent where the polymer chains take extended conformations the value of K_H is less than 0.52. In a poor solvent where the polymer chains shrink the value of K_H is between 0.8 and 1.3[12]. Over the MWs examined K_H values are less than 0.52 suggesting that PVA molecules take an extended conformation in DMSO.

Frisch and Simha reported that the dynamic behavior of the polymer solution could be classified into several regions using the semi-empirical rules according to the interaction degree of the polymer with its environment. In ideal dilute polymer solutions, the slope is 1 on the logarithmic plot of η_{sp} versus [η]C. In the semi-dilute regime, however, the slope is increased due to the overlap between molecules[13]. Fig. 2 shows the log-log plot of η_{sp} versus [η]C of PVA solutions over three different DPs. The higher DP PVA gives greater slope with all DP solutions exhibiting the inflection point in the vicinity of C*. With an increase in the DP the hydrodynamic volume of polymer chain becomes large, giving rise to higher degree of entanglement and overlap of molecules. In addition, when the concentration of the polymer in the solution is raised above a critical level, the relative proximity of the neighboring chains allows polymer-polymer intermolecular interactions. This influences the motion of the polymer chains, producing the slope change in the curve.

For the high concentration regime, the effect of MW and concentration on the dynamic rheological properties of PVA/DMSO solutions was examined at 30 °C using a rotational rheometer. Figs. 3 (a) and (b) present the variation of dynamic viscosity (η') with the DP at 10 wt% and with the concentration at DP 5000, respectively. The η' is increased with increasing the concentration and DP as expected. PVA solutions show lower Newtonian flow region where η' is independent on the frequency, followed by shear thinning. PVA solutions of DP 1700 present Newtonian fluid behavior over most of the frequency range examined.
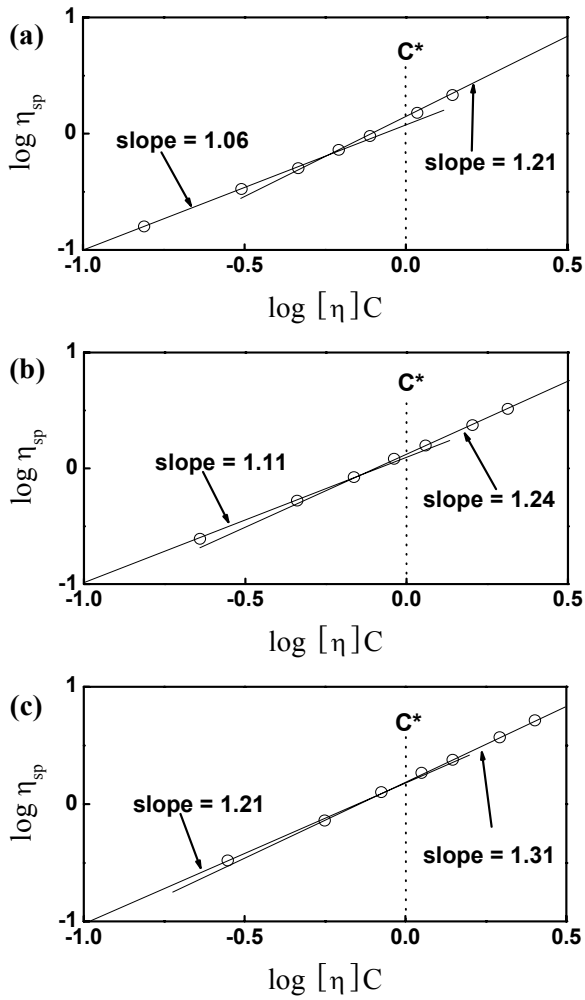
Fig. 2. Log–log plot of η_{sp} versus $[\eta]C$ for PVA/DMSO solutions at three different DPs: (a) DP 1700, (b) DP 3300, and (c) DP 5000.

Fig. 3. Variation of η' (a) with the DP at a concentration of 10 wt% and (b) with the concentration at a DP of 5000.

However, the lower Newtonian flow region reduces with increasing the DP, an indicative of a promoted physical association by inter- and intra-hydrogen bonding. Increasing the polymer concentration has similar effect on the rheological properties to increasing the DP. As the concentration is increased η' is increased and the onset frequency for shear thinning is decreased because of increased molecular entanglement density. That is, closer molecular packing with increasing concentration leads to more effective and stronger hydrogen bonding causing the formation of oriented structure to easily happen under shearing.

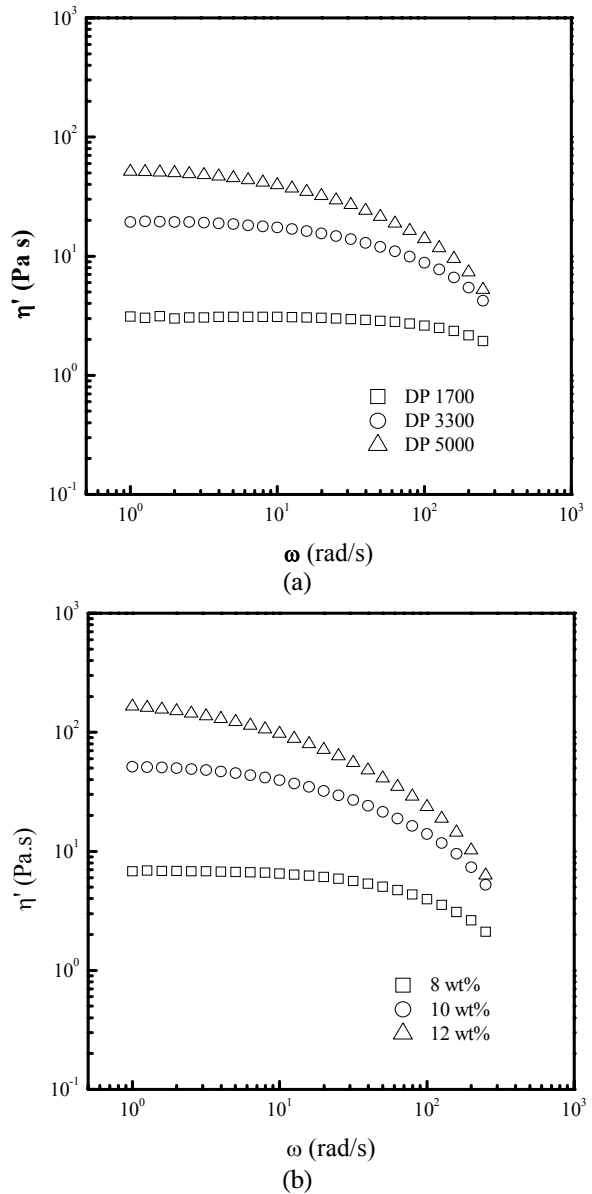For isotropic and homogeneous polymer solutions, the slope on the logarithmic plot of storage modulus (G') versus loss modulus (G"), which has been empirically recognized as Cole-Cole plot, is reported to be 2 because G' and G" is proportional to the second order and the first order of frequency, respectively[14]. Deviation from the slope 2 may be exploited in judging the heterogeneity of polymer solutions because the slope is decreased as the heterogeneity is increased[15-17]. Fig. 4 presents the logarithmic plot of G' against G" for PVA solutions in DMSO at 30 °C. The solutions show almost a single master curve in
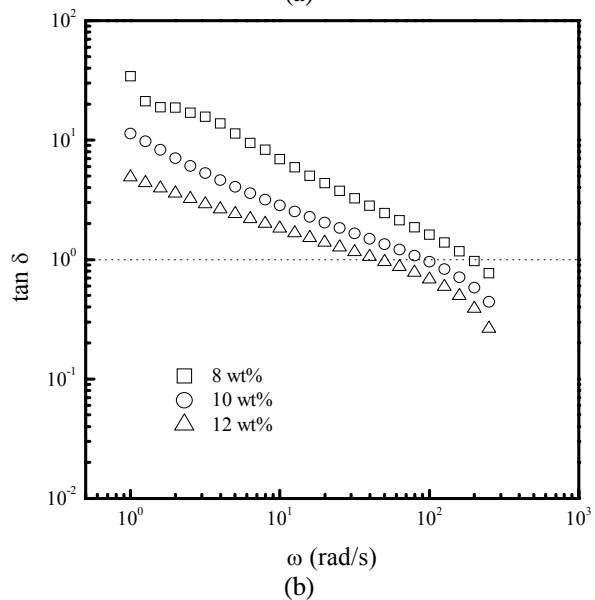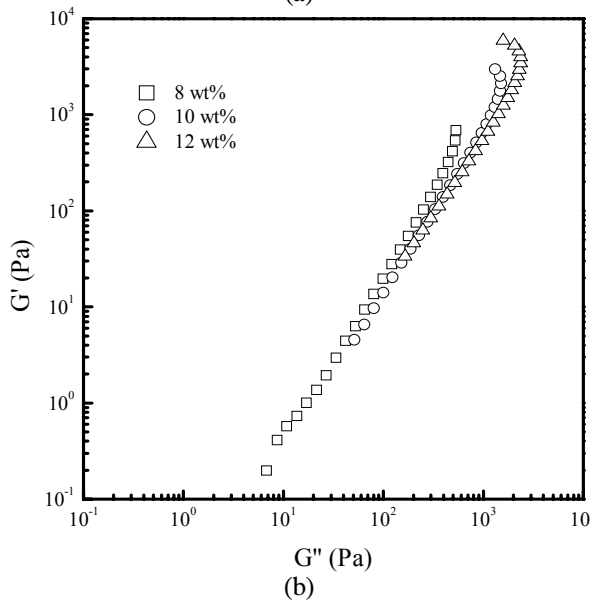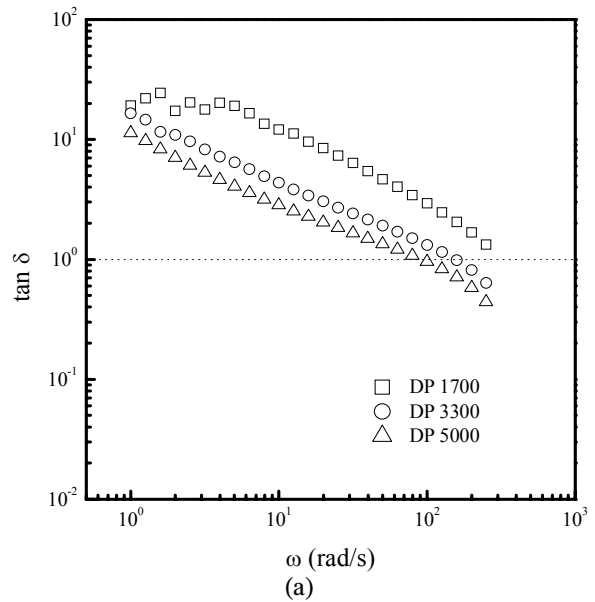
Fig. 4. Logarithmic plot of G' versus G" (a) at several DPs for 10 wt% PVA solutions and (b) at several concentrations for PVA solutions of DP 5000.
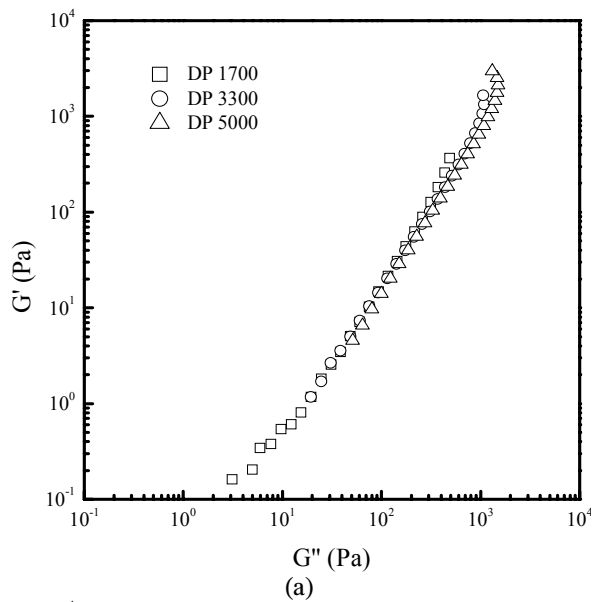

Fig. 5. Variation of tan δ (a) with the DP at a concentration of 10 wt% and (b) with the concentration at a DP of 5000.

a slope of ca. 1.65 within the DP applied. This suggests that molecular weight has little effect on the conformation of PVA chain in the solution. However, the increase of the concentration from 8 to 12 wt% for PVA solutions of DP 5000 decreases the slope from 1.73 to 1.57.

It is interesting to see that concentration has greater effect on the heterogeneity in polymeric system than molecular weight. Increasing concentration is more effective in enhancing hydrogen bonding than increasing MW.

That is, intermolecular hydrogen bonding density would be more rapidly increased than intramolecular hydrogen bonding with an increase of concentration.

Fig. 5 presents the plot of loss tangent (tanδ) against frequency (ω) at 30 °C. As known, tan δ is a quantitative measure of solid-like elastic or liquid-like viscose properties of a system. The loss tangent is decreased with increasing the DP and concentration, as expected. The population of the hydroxyl groups affects the elasticity through

the formation of pseudostructure. The mobility of PVA chain is restrained by a strong hydrogen bonding at a high DP and concentration. The increase in the chain rigidity through the interaction leads to an increase of elastic responses. Generally, the crossover point of G' and G", where the value of tan δ is 1, is considered as gelation point. While PVA solutions of DP 1700 show the ever-presence of sol structure at 10 wt% over the frequency range observed, PVA solutions of DP 3300 and DP 5000 show the sol-gel transition with increasing the frequency. In addition, within the concentration range applied, PVA solutions of DP 5000 show the sol-gel transition. The onset frequency for sol-gel transition is shifted from 154 to 92 rad/s with increasing the DP from 3300 to 5000 and 192 to 46 rad/s with increasing the concentration from 8 to 12 wt%. The decrease in the onset frequency for the gelation may result from greater intermolecular interactions at a higher DP and concentration.

The generation of pseudostructure by physical association affects the relaxation behavior of polymers as well[18,19]. For the polymeric systems in which some pseudostruture is involved, relaxation time (λ) under dynamic shear can be calculated by Eq.(4):

$$\lambda = \frac{G'}{|\eta^*|\omega^2} \qquad (4)$$

where G' is storage modulus, η^*, complex viscosity, and ω, frequency. Fig. 6 shows the variation of λ with the DP and concentration of PVA at two different frequencies. Longer λ is observed at lower frequency. The λ is increased with increasing the DP and concentration. If there is some molecular order or physical structure much longer λ is expected. That is, an increased number of entangled points and intermolecular hydrogen bonding with the MW and concentration of PVA interfere with the relaxation behavior of PVA molecules.
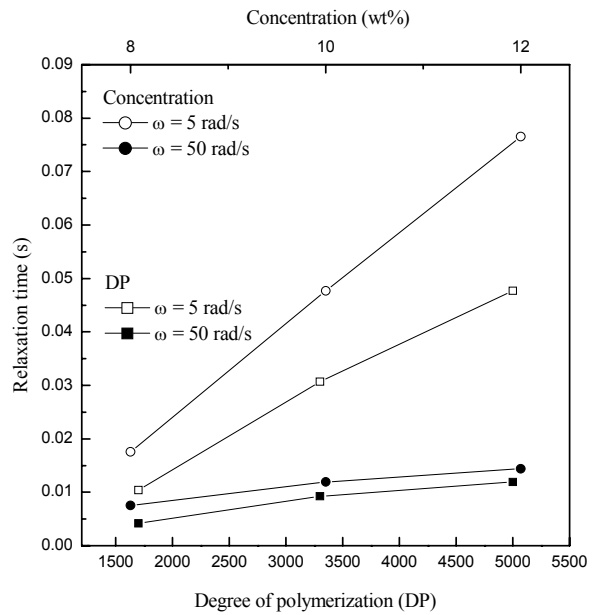

Fig. 6. Variation of λ with the DP and concentration of PVA at two frequencies.

4. Conclusions

The flow behavior of PVA/DMSO solutions affected by hydrogen bonding was studied in the low and high concentration regime varying the molecular weight and concentration of PVA. In dilute solution viscometry the determined value of Mark-Houwink exponent was 0.73 indicating greater expanding of the PVA chains in DMSO than in previously reported solvents such as water and mixed solvent of water and phenol. In addition, the value of Huggins constant (K_H) was less than 0.52 over the DPs examined, representing PVA chains have the extended conformation in DMSO. In the high concentration regime where dynamic rheological properties were examined, the dynamic viscosity increased with increasing the DP and concentration and the onset frequency for shear thinning decreased. The slope in the logarithmic plot of G' versus G" was little affected by the DP at a given concentration of 10 wt% but it decreased from 1.73 to 1.57 with increasing the concentration from 8 to 12 wt% at a given DP of 5000. This indicates that the concentration has more noticeable effect on the increase of heterogeneity than the DP, resulting from greater increase in the hydrogen bonding density. In

addition, the pseudostructure generated by physical association decreased the onset frequency for sol-gel transition and increased the relaxation time.

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