

PVA/DMSO 용액계의 유변학적 특성에 미치는 PVA의 분자량분포의 영향

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The Effects of Molecular Weight Distribution on the Rheological Behavior of PVA/DMSO Solution Systems

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초록 : 본 연구에서는 poly(vinyl alcohol) (PVA)를 dimethyl sulfoxide(DMSO)에 녹여 이 용액의 유변학적 특성에 미치는 PVA의 분자량분포의 영향에 관하여 고찰하였다. 동일 평균분자량인 경우에도 수지 혼합(resin blending)에 의해 분자량분포가 넓어지면 점도와 손실탄성률이 더 낮아짐을 알 수 있었다. 이것은 동일 평균 분자량의 경우 분자량분포가 넓은 PVA/DMSO 용액계의 자유체적이 증가되기 때문이라고 생각된다. 분자량 분포가 저장탄성률에 미치는 영향은, 14 wt% 용액의 경우에는, 1.3 rad/sec보다 낮은 진동수 영역에서는 동일 평균분자량의 경우 분자량분포가 넓은 PVA/DMSO 용액계가 탄성이 더 크고, 1.3 rad/sec보다 높은 진동수 영역에서는 분자량분포가 좁은 PVA/DMSO 용액계가 탄성이 더 크게 측정되었다. 14 wt% 용액의 경우에 Modified Cole-Cole plot에서의 기울기는 분자량분포가 넓어지면 진동수에 따른 상전이 현상이 더 뚜렷해졌다.

Abstract : The rheological properties of the solutions of atactic poly(vinyl alcohol) (PVA) in dimethyl sulfoxide (DMSO) were investigated in terms of molecular weight distribution (MWD) of the polymer. The dynamic viscosity (η') and loss modulus (G'') for the PVA/DMSO solutions with broader MWD were lower than those with narrower MWD at the similar M_w . It could be explained by the fact that the free volume for the solution with broader MWD at the similar M_w was increased. The storage modulus (G') of 14 wt% PVA/DMSO solutions with broader MWD was higher than that with narrower MWD at a lower frequency than 1.3 rad/sec, but lower than that with narrower MWD at a higher frequency (>1.3 rad/sec). The slopes of modified Cole-Cole plots of the 14 wt% solutions showed that as the MWD was broadened, the phase transition with frequency was more noticeable.

Keywords : PVA, DMSO, molecular weight distribution, rheological properties.

Introduction

PVA is a synthetic polymer in which polar hydroxyl groups alternately recur as pendent parts of the polymer main chain.^{1,2} Poly(vinyl alcohol) (PVA) is a crystalline polymer that forms a gel when the solution is cooled.³ PVA forms micro gel or gel by inter-molecular hydrogen bonding, intra-molecular hydrogen bonding, and interactions with PVA and solvent.^{4,5} PVA has good linearity, flat zigzag conformation, high crystallinity, alkali resistance that endures over pH 13.6, and adhesive property. Due to characteristics above mentioned,

high strength and elastic PVA fiber is possible, and it is widely used as the reinforcement of cement, concrete, plastic, asbestos substitution materials, tire cord, and film.⁶ DMSO and water as a solvent of PVA have been widely used. DMSO acts like good solvent and water acts like poor solvent for PVA.⁷⁻¹⁰

It is expected that the physical properties of syndiotactic PVA are good, but it has not been used commercially because of high cost of monomer and poor processibility. In contrast, atactic PVA is used more commercially due to various advantages. For atactic PVA that is mainly used in industry, practical research results on rheological characteristics and gelation behavior of macroscopic dimension as mentioned above have

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been reported intensively.^{11,12} However, in spite of practical importance, systematic and theoretical research on rheological characteristics for this solution system has been reported few. Proper choices such as MWD, molecular weight, concentration, the degree of saponification, solvent, and additive are important to produce high performance PVA fiber and film by using atactic PVA. Therefore, better understanding of the interrelationships that may exist between the molecular parameters and the rheological properties is very important to both the preparation of new polymers and their processing.

It is generally known that if the MWD is broad, high viscosity is shown at low frequency and low viscosity is shown at high frequency. This is due to the fact that if the MWD is broad, storage modulus shows high value resulting from the increase of intra-molecular elasticity and inhomogeneity of molecule. This leads to obvious advantages in processability of the polymer in equipment using high shear stresses.¹³ If the average molecular weights are similar, then it is expected that mechanical properties are similar. Therefore, if the MWD is broadened at the similar M_w , it is beneficial to the forming process due to the decrease of viscosity with the preservation of mechanical strength. In order to study this phenomenon for PVA solution, in this study, rheological analysis of solutions of atactic PVA with different MWD, but the similar M_w in DMSO was carried out to assess the effects of MWD on processability.

Experimental

Materials. In this study, PVA (Aldrich Chemical) with a degree of saponification greater than 99% was used. The PVA samples were coded according to their M_w ; A [A has M_w of 89000~98000], B [B has M_w of 85000~146000], C [C has M_w of 124000~186000], A6C3 [A6C3 was prepared by mixing A and C by 64:36 in weight percent]. B and A6C3 samples have similar M_w , but different MWD. DMSO (Aldrich Chemical) was used without further purification.

NMR Measurements. The syndiotactic dyad content determined by 300 MHz $^1\text{H-NMR}$ (Varian Gemini) was 52%. The $^1\text{H-NMR}$ of PVA was measured with solutions in $d\text{-DMSO}$ at 55 °C.¹⁴⁻¹⁶

Rheological Measurements. Since the method of preparing solutions showed significant effects on the rheological properties, PVA was dissolved in DMSO at 90 °C under the same dissolving procedure; stirred for the first 2 hr. and then placed still for 3 hr. To exclude the possibility of incomplete dissolution of the polymer in the solvent, the solution was optically examined.

The rheological properties were measured with an advanced rheometric expansion system (Rheometric Scientific) at 30 °C.

Parallel-plates were adopted whose diameter and gap were 50 and 1 mm, respectively. After being loaded between parallel plates, the solution specimen was fully relaxed for 20 min. Frequency sweep experiment was performed.

Results and Discussion

Figure 1 shows the effects of MWD and M_w on dynamic viscosity of 10 wt% and 14 wt% PVA/DMSO solutions. The solution with the smallest molecular weight, A, shows the Newtonian flow characteristics until 200 rad/sec, but the solution with the largest molecular weight, C, shows minor shear thinning even in low shear region. Figure 1 also shows that if the MWD is broadened due to the mixing of resin, then the viscosity is decreased in case of similar M_w . That is, A6C3 shows lower dynamic viscosity than B even through A6C3 and B have similar M_w . This phenomenon is more pronounced at low frequency region and the effects are decreased at high

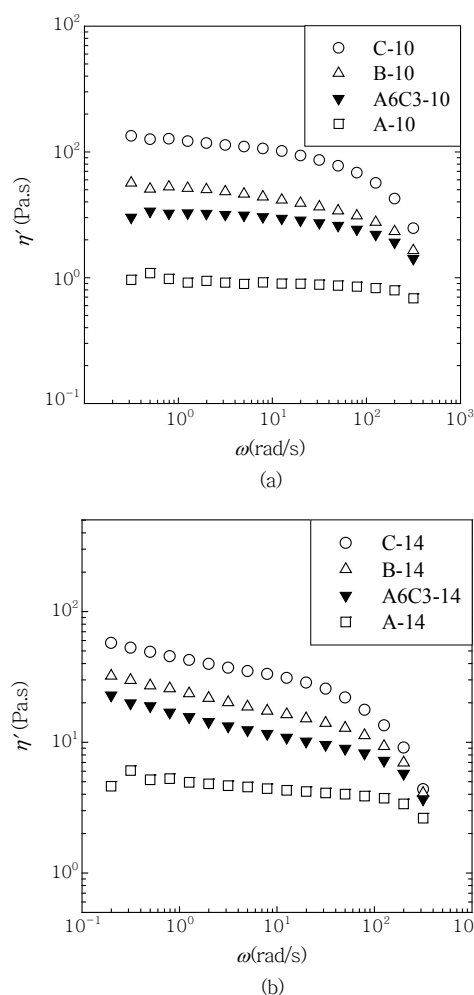


Figure 1. Dynamic viscosity (η') curves for PVA/DMSO solutions at 30 °C at four different molecular weights; (a) 10 wt% and (b) 14 wt%.

frequency region as shown in Figure 1. That is because free volume for the solution with broader MWD is increased due to the effect of chain end. It is considered that if the MWD is broadened, plasticity is increased because the fraction of molecular chain of PVA is increased. This phenomenon is more noticeable in low shear region with relatively low deformation of molecule. This agrees with the theoretical prediction by Middleman,^{17,18} qualitatively. Middleman suggested following equations for the effect of MWD on viscosity.

$$\frac{\eta - \eta_s}{\eta_0 - \eta_s} = \int_0^\infty \frac{M^2}{M_n} \frac{\Phi(M)F(\lambda_1, \dot{\gamma})}{M_w} dM \quad (1)$$

Where, $\Phi(M)$ is the MWD function. $F(\lambda_1, \dot{\gamma})$ can be expressed as following.

$$F(\lambda_1, \dot{\gamma}) = 1 - \frac{6}{n^2} \sum_{n=1}^N \frac{\lambda_1^2}{n^2} \frac{\dot{\gamma}^2}{(n^4 + \lambda_1^2 \dot{\gamma}^2)} / (2 - \frac{\lambda_1^2 \dot{\gamma}^2}{n^4 + \lambda_1^2 \dot{\gamma}^2}) \quad (2)$$

Where, M is M_w , λ_1 is relaxation time, and $\dot{\gamma}$ is shear rate. Figure 2 shows the plots of G' against ω for PVA/DMSO solutions at 30 °C with PVA/DMSO solutions. The effect of MWD on the elasticity of polymer is controversial, but it has been reported that elasticity is increased due to MWD broadening.^{13,19-22} Figure 2(a) shows that 10 wt% PVA/DMSO solutions represent larger storage modulus for solution with narrower MWD. In Figure 2(b), 14 wt% PVA/DMSO solution agrees with Ferry eq.²³ at lower frequency than 1.3 rad/s and it is also shown that PVA/DMSO solution with narrower MWD represents higher storage modulus at higher frequency than 1.3 rad/s. It is considered that as MWD is broadened, the phase transition with frequency is more noticeable. It could be inter-

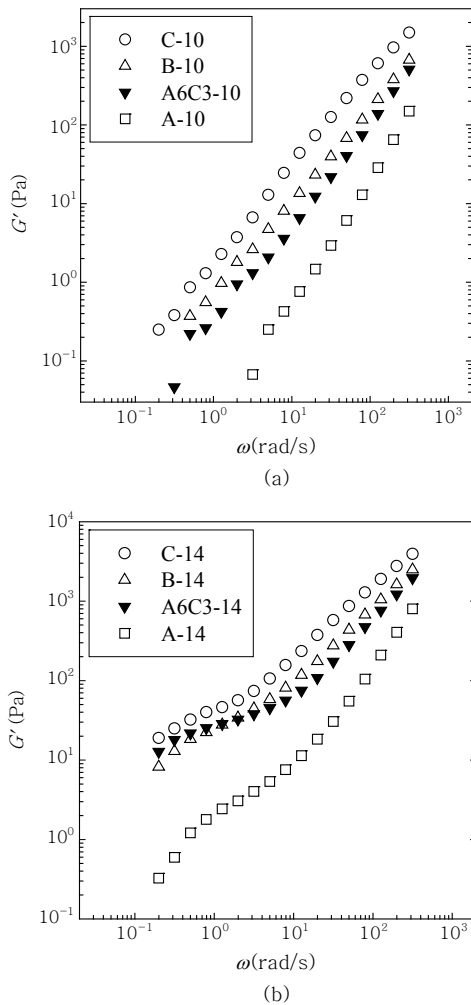


Figure 2. Plots of storage modulus (G') against frequency (ω) for PVA/DMSO solutions at 30 °C at four different molecular weights; (a) 10 wt% and (b) 14 wt%.

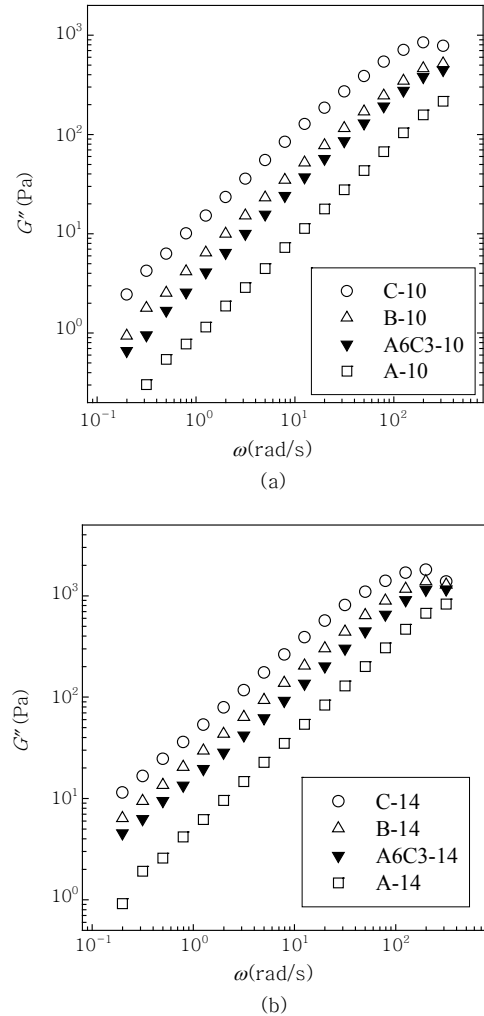


Figure 3. Plots of loss modulus (G'') against frequency (ω) for PVA/DMSO solutions at 30 °C at four different molecular weights; (a) 10 wt% and (b) 14 wt%.

preted as that the structure formation is easy at low frequency region, but this structure is more easily destroyed by frequency due to the lubrication effect of low molecular weight chains.

Figure 3 shows the plots of G'' against ω for PVA/DMSO solutions at 30 °C with PVA/DMSO solutions. The PVA solutions with higher M_w have a value of greater G'' at the given frequency. In these plots, the slopes represent the increase in energy dissipation for that frequency. The energy dissipation per cycle would be reduced if the internal structures exist in the solution because the deformation of the structures consumes additional energy.²⁴ It is also shown that as the concentration and the molecular weight are increased, the slopes of G'' for PVA/DMSO solutions are decreased. This means that the system is getting more heterogeneous due to polar interaction. The G'' for PVA/DMSO solutions with broader MWD was lower than that with narrower MWD at the similar M_w .

When the elasticity parameters are plotted against shear stress in stead of shear rate in steady-state rheology, and if the polymer solutions or polymer melts are homogeneous and isotropic, then it gives a master curve independent of the molecular weight, concentration (for solution), and temperature (for melt). This curve is called a Cole-Cole plot.^{25,26} This Cole-Cole plot in steady-state rheology may be applied to dynamic rheology. G' vs. G'' is expressed by logarithmic plot. This modified Cole-Cole plot is useful method to judge the molecular structure characteristics such as chemical structure, MWD, long chain branching, short chain branching, concentration, and method of preparation. For the same reason, a modified Cole-Cole plot shows one master curve independent of temperature and concentration and the slope is 2 if the polymer solution or melt is homogeneous.²⁷ This can be used to judge whether polymer solution or melt is homogeneous or inhomogeneous. According to Han and John,²⁸⁻³⁰ G' is related to G'' by eq. (3).

$$\log G' = 2 \log G'' + \log(6/5 G_N^0) \quad (3)$$

Where, G_N^0 is plateau modulus, G_N^0 is $\rho RT/M_e$, ρ is density, R is gas constant, T is absolute temperature, and M_e is entanglement molecular weight.

A modified Cole-Cole plot for PVA/DMSO solutions at 30 °C is shown in Figure 4. The PVA solutions give curves that vary with the concentration and molecular weight, and the slopes of plots are less than 2. This reconfirms that the PVA solutions are rheologically heterogeneous. The reduction of the slope with increasing concentration and M_w indicates that the PVA solution systems become more and more heterogeneous with increasing concentration and M_w . The

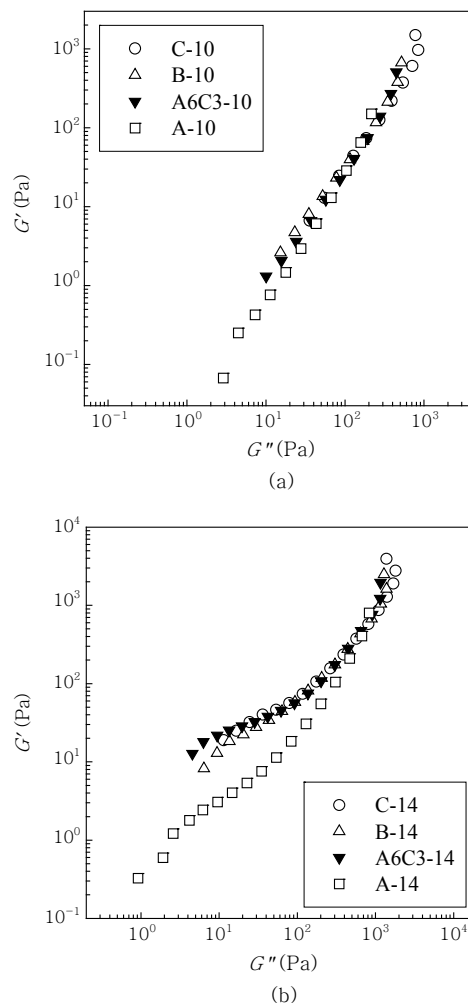


Figure 4. Cole-Cole type plots for PVA/DMSO solutions at 30 °C at four different molecular weights; (a) 10 wt% and (b) 14 wt%.

slope of plots are little dependent on the MWD as shown in Figure 4(a). In Figure 4(b), the slope of A6C3 is lower than that of B at low frequency region for 14 wt% solution. This represents that A6C3 is more heterogeneous than B at low frequency region. The slope of plots are little dependent on the MWD at higher frequency than 1.3 rad/sec, but the slope is lower than 2 in Figure 4(b). The slopes of modified Cole-Cole plots of the 14 wt% solutions show that as MWD is broadened, the phase transition with frequency is more noticeable.

The presence of pseudo-structure formed by physical aggregation can affect the relaxation behavior of polymer. That is, the relaxation time is increased by the limitation of molecular chain mobility if the physical bonding exists. It is generally known that the flexible chain polymer system has short relaxation time of 10^{-2} – 10^{-5} sec, but liquid crystal system or meso phase has relaxation time of longer than a few

seconds. The relaxation time under dynamic shear for polymeric systems including some pseudo-structures can be calculated by eq. (4) as suggested by Wissbrun *et al.*³¹

$$J' = G' / (\dot{\gamma}^* |\omega|^2) = \lambda / |\dot{\gamma}^*| \quad (4)$$

Where, J' and G' are compliance and storage modulus, respectively.

The relaxation times of PVA solutions at 30 °C, calculated by eq. (5), are plotted against several molecular weights in Figure 5. As the frequency is increased, relaxation time is generally decreased because the recovery of elasticity is rapid due to higher stress with the increase of strain for polymer chain. As predicted, as the frequency is increased, and as the concentration and the M_w are decreased, the relaxation time is decreased. The relaxation time of PVA/DMSO solutions with broader MWD was lower than that with narrower MWD

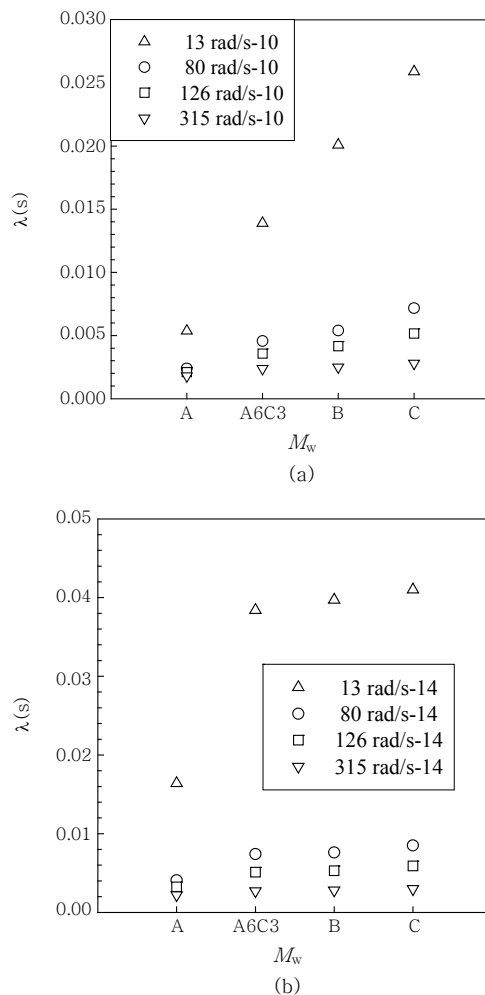


Figure 5. Variation of the relaxation time (λ) with four different molecular weights for PVA/DMSO solutions at 30 °C; (a) 10 wt% and (b) 14 wt%.

at the similar M_w at higher frequency than 13 rad/sec. Longer relaxation time is a direct evidence of the restriction of molecular chain by the formation of physical bonding with polar interaction. This also means that if some physical bonds by polar interactions are more effectively formed, the solution exhibits longer relaxation time.

Conclusions

The rheological behaviors for PVA solutions in DMSO were seriously affected by the MWD of the polymer and frequency. As the MWD was broadened at the similar M_w , it showed significant effects on the rheological properties of PVA/DMSO solution such as viscosity and elasticity. The slopes of modified Cole-Cole plots of the 14 wt% solutions showed that as the MWD was broadened, the phase transition with frequency was more noticeable. Precise control of rheological properties is very important in processing of PVA solutions such as film forming and fiber spinning, and thus these results can be effectively applied to fabrication process using PVA solutions.

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