고농도 폴리비닐 알코올/디메틸 설폭사이드 용액의 유변학적 특성의 시간 의존성

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Time-Dependence of the Rheological Properties of Concentrated PVA Solution in DMSO

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요 약

검화도와 분자량이 상이한 폴리비닐 알코올을 디메틸 설폭사이드에 녹여 폴리비닐 알코올/디메틸 설폭사이드 용액을 준비하고, 동적 유변학적 특성에 대한 시간과 온도 의존성을 고찰하였다. 고농도 폴리비닐 알코올 용액의 유변학적 특성은 시간 의존성을 보여주었다. 복합 점도와 저장 탄성률은 시간에 따라 증가하였다. 또한, 저장 탄성률과 손실 탄성률의 그래프에서 저장 탄성률은 시간에 따라 증가하였으나, 기울기는 시간에 따라 감소하였다. 유변학적 특성의 시간 의존성은 분자량이 높을수록, 측정 온도가 높을수록 더 두드러지게 나타났다.

Abstract — Polyvinyl alcohol (PVA) with different degrees of saponification and molecular weights was prepared. Time-dependence of the dynamic rheological properties of the concentrated solution of PVA in dimethyl sulfoxide (DMSO) was investigated in terms of degree of saponification, molecular weight, and temperature. The concentrated PVA solution in DMSO exhibited time-dependent rheological responses. Both complex viscosity (η^*) and storage modulus (G') were increased with time. On the plot of G' against loss modulus (G"), the G' was increased with time, but its slope was decreased. Further, time dependence of the rheological properties was more noticeable in PVA with higher molecular weight and at higher temperature.
Keywords: PVA, degree of saponification, time-dependence, storage modulus, loss modulus, heterogeneous system

1. Introduction

PVA is a synthetic polymer in which polar hydroxyl groups alternately recur as pendent parts of the polymer main chain[1]. Owing to strong polarity of the hydroxyl groups, PVA decomposes prior to melting. PVA is generally prepared by saponifying polyvinyl ester precursors such as polyvinyl acetate (PVAc) and polyvinyl pivalate (PVPi) since vinyl alcohol rearranges to give its tautomer, acetaldehyde, which can not be polymerized[2]. PVA is a crystalline polymer that forms a gel when the solution is cooled. It has been known from 1950's that the concentrated solution of PVA produces gel by gradual increase in viscosity when it was maintained below room temperature[3]. In most PVA, the degree of saponification generally ranges 85 to 99+% to meet the diverse requirements of various industrial fields.

Lots of rheological studies have been made on PVA solution in water[4-9], water/DMSO[10], and other solvents[11]. However, only a few reports on the rheological properties of PVA solution in DMSO[12], ethylene glycol [13], glycerin[14], and N-methylpyrrolidone[15] are available in spite of industrial importance for the production of PVA fiber and film. It is obvious that the degree of saponification has a significant influence on the rheological properties of PVA because the difference in chemical composition gives rise to different physical properties. The molecular weight of polymer may affect the rheological properties as well. It is important to characterize the PVA solution and gel rheologically in order to manufacture PVA fiber and film with excellent properties.

In this study, PVA with different degrees of saponification and molecular weights was prepared, and time-dependence of the dynamic rheological properties of the con-

centrated solution of PVA in DMSO at different temperatures was investigated.

2. Experimental

PVA (Aldrich Chemical Co. Inc.) with molecular weight of 85,000~146,000 and degree of saponification of 96~100% was used as the base polym polymer. The polymer was dissolved in DMSO (Junsei Chemical Co. Ltd) in a well stirred silicon oil bath which was heated to 120°C. The rheological properties of the solution of PVA in DMSO were measured by using a Rheometrics mechanical spectrometer (RMS 800) in the dynamic oscillatory mode in a nitrogen atmosphere. Specimens were shaped as a circular sheet form to fit in the RMS plate. In the RMS measurements, the parallel-plate and conicylinder fixtures were adopted. The diameters of plates were 12.5 mm and 25 mm.

3. Results and Discussion

From a molecular theory, Han and Jhon[16] related G' to G" by Eq. (1):

$$logG' = 2logG" + log(6/5G_N^0) \tag{1}$$

in which $G_N^0 = \rho RT/M_e$, ρ is density, R is the gas constant, T is temperature, and M_e is entanglement molecular weight, respectively. This equation is proposed to be well adapted in the terminal region. This theoretical prediction indicates that the polymer solution gives a slope of 2 if it is isotropic and homogeneous. This principle had also been empirically verified before Han and Jhon gave a theoretical significance. It has been proven useful thing in characterizing molecular parameters for a homopolymer series. For solution of a polymer with a given molecular parameter, it can provide information on the solution morphology[17]. It has been recognized that the heterogeneous polymeric systems such as thermotropic liquid-crystalline polymers in the nematic phase decrease the slope to below 2 on the plot of G' against G"[18].

In the case of solution of PVA with high syndiotactic content, the slope was less than 2, and dependent on the molecular weight of polymer in a similar manner to the liquid crystalline polymers. The solution of PVA with high syndiotactic content exhibited more noticeable heterogeneous characteristics at higher molecular weight[17].

3.1. Rheology of 10 wt% PVA solution in DMSO

Fig. 1 shows a plot of G' against G" for 10 wt% PVA solution in DMSO at 35°C at the time interval of 47 min. The molecular weight of polymer was 86,000 and the degree of saponification was 100%. G' is linearly related with G" for the 10 wt% PVA solution. The slope does not change during 47 min. Its solpe is 1.86, which is slightly lower than the theoretically predicted value 2 for the isotropic homogeneous solution. This suggests that the phase morphology of the PVA solution remains unchanged within the experimental time scale. The slight deviation of slope from 2 may be partly ascribed to a little heterogeneity of the solution system. However, it may be said that the solution is almost homogeneous. Fig. 2 traces time dependence of η^* and G' for 10 wt% PVA solution in DMSO at 35°C. There is little time dependence in the rheological parameters at this polymer concentration and at this temperature.

3.2. Rheology of 15 wt% PVA solution in DMSO

Fig. 3 shows a plot of G' against G" for 15 wt% PVA solution in DMSO at 30°C at the time interval of 47 min. The molecular weight of polymer was 86,000 and the degree of saponification was 100%. G' is linearly related
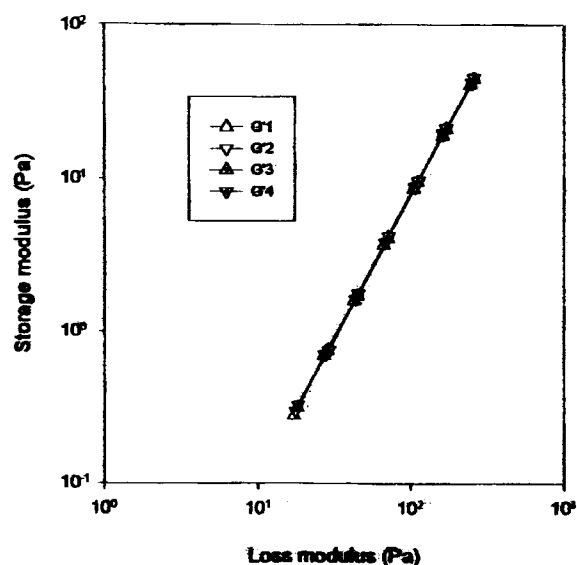

Fig. 1. Plots of storage modulus and loss modulus for PVA1-10 at 35°C (M.W. = 86,000, D.S. = 100%). Symbol : G' is the storage modulus. 1 represents data from the first frequency sweep experiment, 2 represents data from the second frequency sweep experiment carried out 430 seconds after the first frequency sweep experiment, 3 represents data from the third frequency sweep experiment carried out 430 seconds after the first time sweep experiment, and 4 represents data from the fourth frequency sweep experiment carried out 430 seconds after the second time sweep experiment.
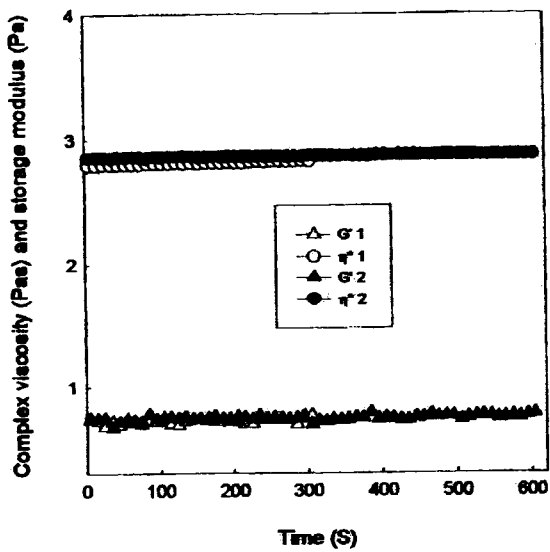
Fig. 2. Plots of storage modulus and complex viscosity as a function of time for PVA1-10 at 35°C (M.W. = 86,000, D.S. = 100%). Symbol : G' is the storage modulus, η* is the complex viscosity. 1 represents data from the first time sweep experiment carried out 300 seconds after the second frequency sweep experiment and 2 represents data from the second time sweep experiment carried out 600 seconds after the third frequency sweep experiment.

Fig. 4. Plots of storage modulus and complex viscosity as a function of time for PVA1-15 30°C (M.W. = 86,000, D.S. = 100%). Symbol is the same as in Fig. 2.

with G" for the 15 wt% PVA solution. Its slope is slightly lower than the theoretically predicted value 2, and it slightly decreases from 1.72 to 1.64 at the time interval of 36.5 min. The slight deviation of slope from 2 may be partly ascribed to heterogeneity of the solution system. Fig. 4 traces time dependence of η* and G' for 15 wt% PVA solution in DMSO at 30°C for the same polymer as shown
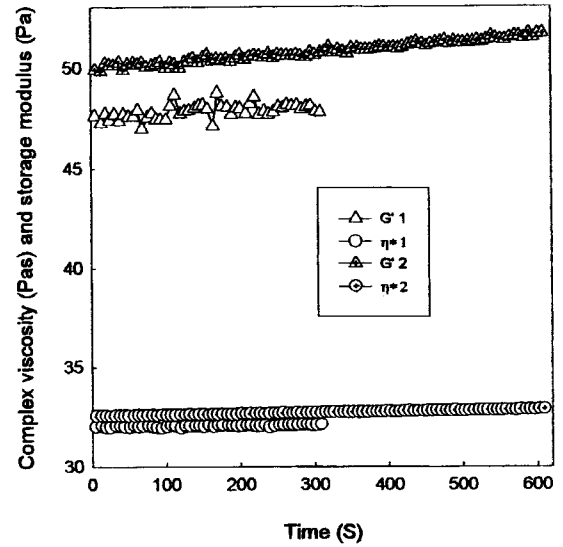
in Fig. 3. This ascertains that there is time dependence in the rheological parameters at this polymer concentration.

Fig. 5 shows a plot of G' of 15 wt% solution of PVA in DMSO against G" at 30°C at the time interval of 47 min. The molecular weight of polymer was between 85,000 and 146,000, and the degree of saponification was 96%. G' is linearly related with G" for the 15 wt% PVA solution. The slope is decreased from 1.81 to 1.58 as shown in Fig. 5. The slope of PVA 2 is closer to the value 2 predicted for the isotropic homogeneous solution than that of PVA 1 in spite of higher molecular weight. This in-
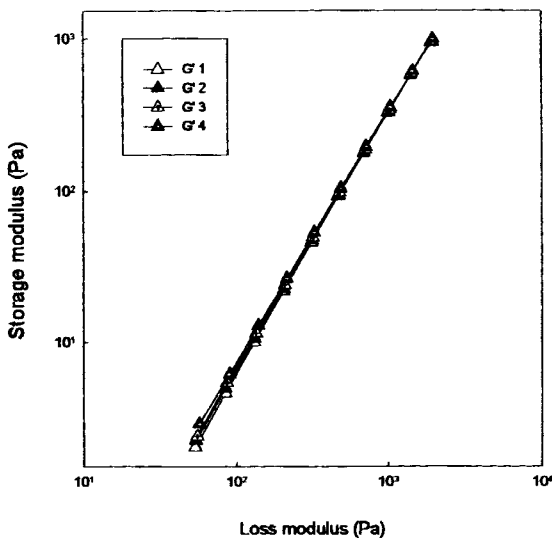

Fig. 3. Plots of storage modulus and loss modulus for PVA1-15 at 30°C (M.W. = 86,000, D.S. = 100%). Symbol is the same as in Fig. 1.
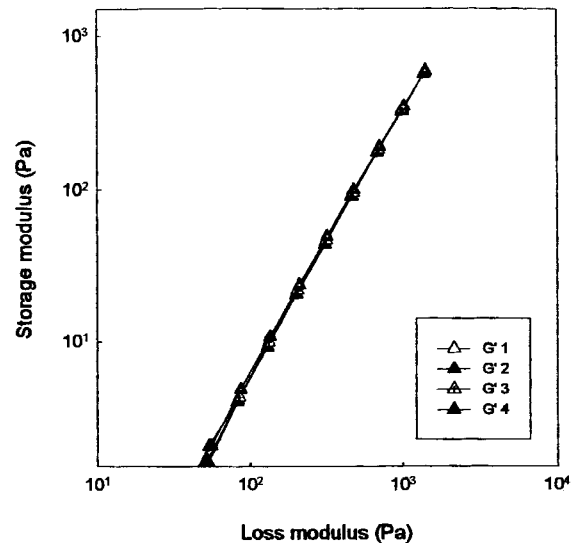

Fig. 5. Plots of storage modulus and loss modulus for PVA2-15 at 30°C (M.W. = 85,000~146,000, D.S. = 96%). Symbol is the same as in Fig. 1.

dicates that the degree of saponification has an effect on the rheological behavior of PVA solution in DMSO. It appears that the lower degree of saponification leads to the weaker intermolecular attractions through polar hydroxyl groups because of lower frequency of hydroxyl groups in the main chain. Hence, a more isotropic and homogeneous solution would be produced by PVA with lower degree of saponification in DMSO.

Fig. 6 traces time dependence of η^* and G' for the 15 wt% PVA solution in DMSO at 30°C for the same polymer as shown in Fig. 5. This ascertains that there is time dependence in the rheological parameters at this polymer concentration.

3.3. Rheology of 25 wt% PVA solution in DMSO

The G' of 25 wt% solution of PVA in DMSO at 45°C is plotted against G" at the time interval of 47 min. as shown in Fig. 7. The molecular weight of polymer was 86,000 and the degree of saponification was 100%. This plot shows reduction in slope with time, suggesting that a morphological change takes place with time. Also, it is estimated that the system is getting more and more solid like with increasing polymer concentration because frequency is reapplied to the heterogeneous system before the molecular relaxation is completed. This suggests that this solution contains more microdomains which make the system heterogeneous than Figs. 1 and 3. Fig. 8 gives plots of G' and η^* as a function of time for 25 wt% PVA solution in DMSO at 45°C for the same PVA as shown in Fig.
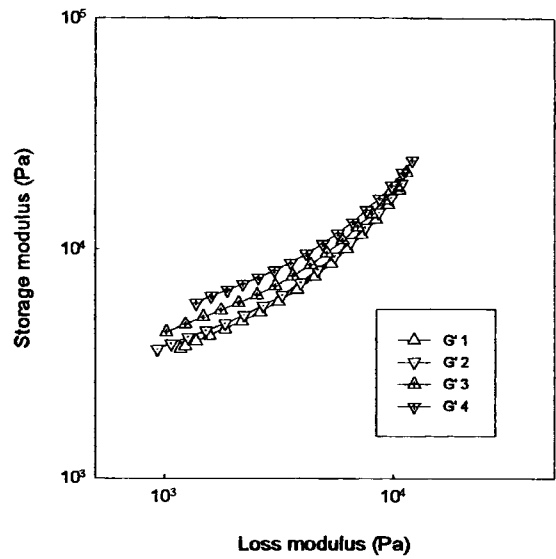

Fig. 7. Plots of storage modulus and loss modulus for PVA1-25 at 45°C (M.W. = 86,000, D.S. = 100%). Symbol is the same as in Fig. 1.

7. It shows that G' and η^* are increased with time. This suggests that heterogeneous solution seems to contain some internal orders. This indicates that there is time dependence in the rheological parameters at this polymer concentration.

Fig. 9 shows a plot of G' of 25 wt% solution of PVA in DMSO against G" at 30°C at the time interval of 24.3 min. The molecular weight of polymer was 85,000~146,000 and the degree of saponification was 96%. A decrease in slope is observed, from 1.23 to 0.89 after 17.2 min. Com-
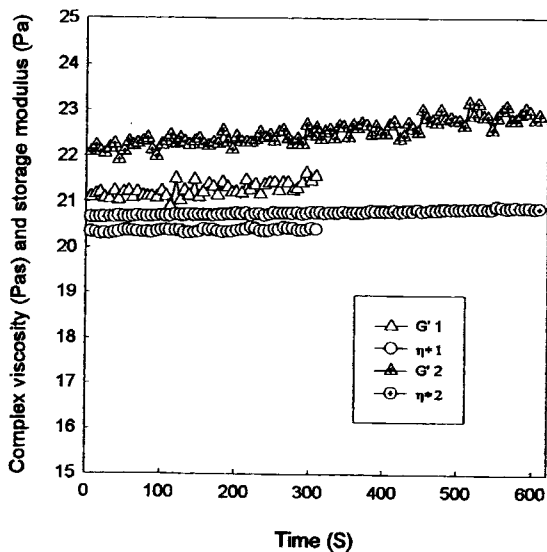

Fig. 6. Plots of storage modulus and complex viscosity as a function of time for PVA2-15 at 30°C (M.W. = 85,000~146,000, D.S. = 96%). Symbol is the same as in Fig. 2.
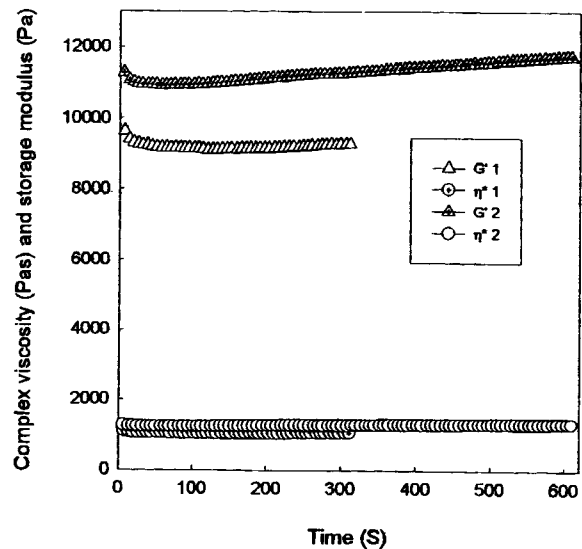

Fig. 8. lots of storage modulus and complex viscosity as a function of time for PVA1-25 at 45°C (M.W. = 86,000, D.S. = 100%). Symbol is the same as in Fig. 2.
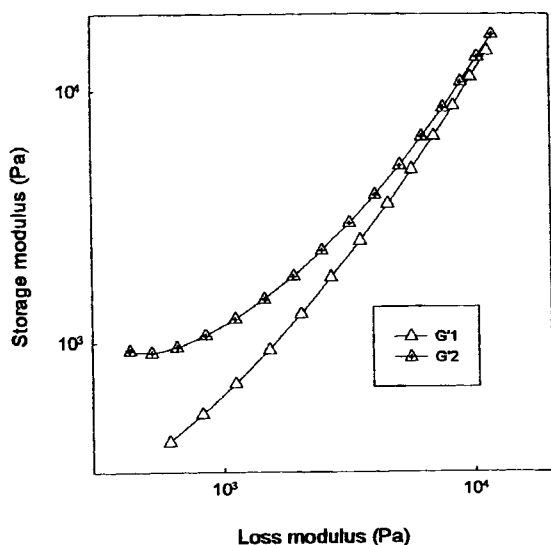
Fig. 9. Plots of storage modulus and loss modulus for PVA2-25 at 30°C (M.W. = 85,000~146,000, D.S. = 96%). Symbol : G' is the storage modulus. 1 represents data from the first frequency sweep experiment, 2 represents data from the second frequency sweep experiment carried out 430 seconds after the first time sweep experiment.

parison of Figs. 9 with 5 suggests that the morphological change resulting from the formation of heterogeneous domains is increased with increasing the polymer concentration.

Fig. 10 gives plots of G' and η^* as a function of time for 25 wt% PVA in DMSO at 30°C, 45°C, and 60°C, respectively. The molecular weight of polymer was 85,000
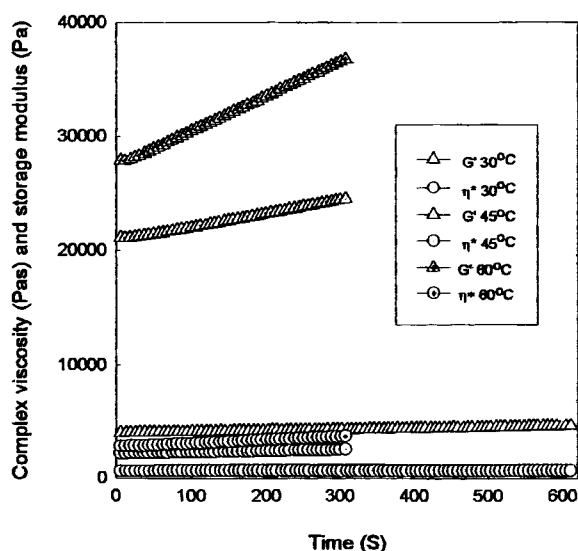

Fig. 10. Plots of storage modulus and complex viscosity as a function of time for PVA2-25 at 30°C, 45°C, and 60°C (M.W. = 85,000~146,000, D.S. = 96%). Symbol : G' is the storage modulus, η^* is the complex viscosity.

Table 1. Recipe for PVA solution

Sample code	M.W. of PVA	D.S. of PVA (%)	Polymer concentration
PVA1-15	86,000	100	15
PVA1-25	"	"	25
PVA2-15	85,000~146,000	96	15
PVA2-25	"	"	25

~146,000 and the degree of saponification was 96%. It is clearly seen that G' and η^* are increased as time. This ascertains that there is time dependence in the rheological parameters at this polymer concentration. This figure ascertains a gradual build up of internal structures. Temperature has an influence on the rheological properties of the solution of PVA as well. One can estimate the influence of temperature on the time-dependent rheological properties of the PVA solution at the identical molecular parameters by Fig. 10. The heterogeneous internal structure seems to be more readily developed at higher temperature. Up to now, the reason is under search.

4. Conclusions

PVA with different degrees of saponification and molecular weights was prepared, and time-dependence of the dynamic rheological properties of the concentrated solution of PVA in DMSO at different temperatures was investigated. Main results are as follows.

(1) PVA exhibits time-dependent rheological responses at concentrated polymer concentration. That is, both η^* and G' are increased with time. On the plot of G' and G", G' is increased with time, but its slope is decreased with time. The deviation of slope may be partly ascribed to heterogeneity of the solution system. The decrease in the slope implies that the phase morphology of the PVA solution is slightly changed within the experimental time scale.

(2) Time dependence of the rheological properties is more noticeable in PVA with higher molecular weights and at higher temperatures. Further studies require to clarify the reason for the effect of temperature, so it will be carried out.

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