혼성 배열 폴리비닐 알코올/디메틸 설폭시드 용액의 유변학적 특성

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The rheological properties of the solution of atactic poly (vinyl alcohol) in dimethyl sulfoxide

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1. Introduction

Polyvinyl alcohol (PVA) is a zigzag chain polymer, in which hydroxyl groups form hydrogen bonding. Polyvinyl alcohol is a synthetic polymer, precursor polymers such as poly (vinyl acetate) (PVAc) and poly (vinyl pivalate) (PVPi) are utilized in preparing polyvinyl alcohol [1]. Polyvinyl alcohol is a crystalline polymer that forms micro gel or gel by intermolecular hydrogen bonding, intramolecular hydrogen bonding and interaction with polyvinyl alcohol and solvent [2-3]. Hydrogen bonding has a profound effect on the rheological and mechanical properties of the polymer, which is largely determined by the density and spatial arrangement of hydroxyl groups. Thus, it has a significance to control the degrees of saponification and syndiotactic diad content as well as molecular weight and concentration in designing polyvinyl alcohol products such as fibers, films, medical substitutes, and adhesives. Some results on the rheological properties of syndiotactic polyvinyl alcohol have been reported by Kim et al. [4-5]. It would be also imagined that atactic polyvinyl alcohol also shows concentration-dependent rheological response. In this study, we investigated the effect of molecular weight and concentration on the rheological properties of the solutions of atactic polyvinyl alcohol in dimethyl sulfoxide (DMSO).

2. Experimentals

Polyvinyl alcohol (Aldrich Chemical Co. Inc.) in which the degree of saponification is over 99% was used. The polyvinyl alcohol samples were coded

according to molecular weight (MW); A (MW = 85,000 ~ 146,000) and B (MW = 124,000 ~ 186,000). Polyvinyl alcohol was dissolved in dimethyl sulfoxide in a well stirred silicon oil bath, which was heated to 90°C for 5 hours. To exclude the possibility of incomplete dissolution of the polymer in the solvent, the resultant solution was optically examined. The rheological properties of the polyvinyl alcohol solution in dimethyl sulfoxide were measured by Advanced Rheometric Expansion System (ARES, Rheometric scientific. Co.).

3. Results and Discussion

Figure 1 shows dynamic viscosity (η') curves of polyvinyl alcohol solutions in dimethyl sulfoxide at 30°C at several concentrations. Dynamic viscosity is increased with increasing the concentration of polyvinyl alcohol. Over the frequency range examined, the polyvinyl alcohol solutions show non-Newtonian flow behavior, which is more noticeable at higher concentration. Figure 2 shows variation of G' and G" with frequency for polyvinyl alcohol solutions in dimethyl sulfoxide at 30°C at several concentrations. It is worth mentioning in the Figure 2 that the solutions do not give the slope 2 and 1 for G' and G" curves and give the slope less than the predicted values. Further, the slopes are slightly decreased with increasing concentration. 14 wt.% polyvinyl alcohol solutions show very complicated behavior. The slopes change with shear rate and give distinctly different regions. The heterogeneity of a system can verify by the existence of a positive value of yield stress (τ_y). The modified Casson plots for polyvinyl alcohol solutions at 30°C at several concentrations are shown in Figure 3. On this plot, the intercept on G" axis can be regarded as the square root of yield stress ($Go"^{1/2}$). 10 wt.% polyvinyl alcohol solutions give negligible yield stress, but 12 and 14 wt.% polyvinyl alcohol solutions give definite yield stress, which is increased with increasing concentration. To examine the phase transition with shear rate, tan δ of polyvinyl alcohol solutions in dimethyl sulfoxide at 30°C at several concentrations is plotted against frequency in Figure 4. 10 and 12 wt.% polyvinyl alcohol solutions give the value of tan δ greater than 1 in the terminal zone. On the other hand, 14 wt.% polyvinyl alcohol solutions have the lowest values of tan δ among polyvinyl alcohol solutions and give inflection points. According to winter's view [6] on gelation, 14 wt.% polyvinyl alcohol solutions undergo a very complicated phase transition.

4. References

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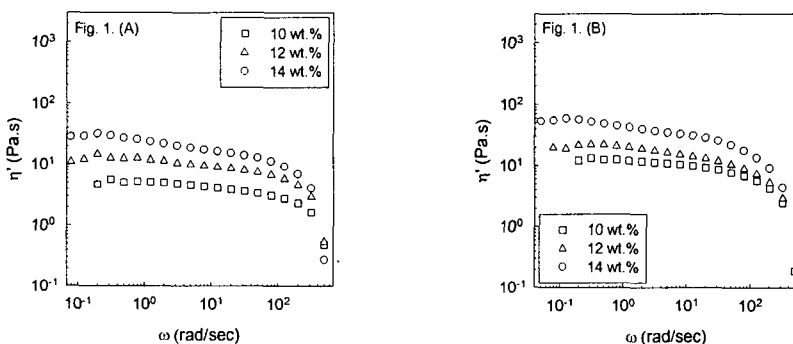6) H. H. Winter and F. Chambon, J. Rheol., **30**, 367 (1986).

Fig. 1. Dynamic viscosity (η') curves of PVA solutions in DMSO at 30°C.
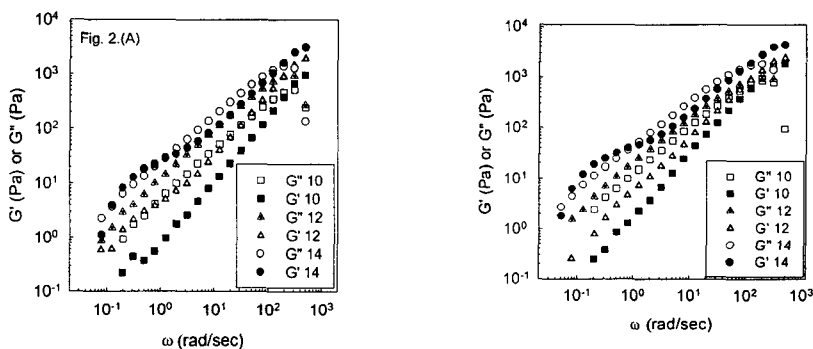
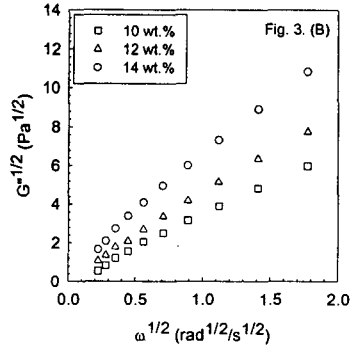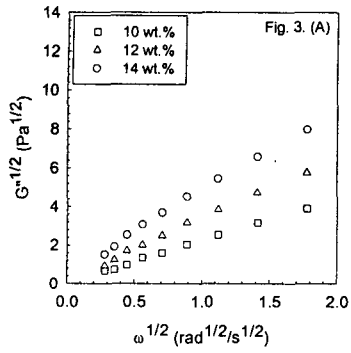Fig 2. Plots of storage modulus (G') and loss modulus (G").

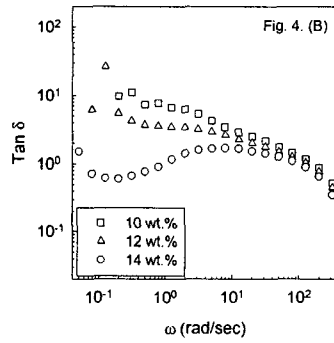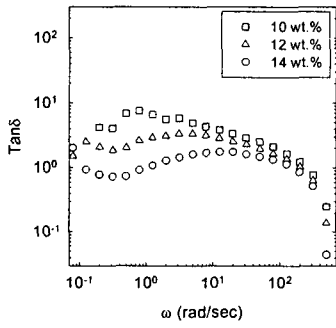Fig. 3. Casson type plots for PVA solutions in DMSO at 30°C.

Fig. 4. Variation of tan δ with frequency (ω) for PVA solutions in DMSO.