

혼성 배열 폴리비닐 알코올/디메틸 설펝시드 용액의 유변학적 특성의
시간 의존성

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**Time-dependence on 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 synthetic polymer, in which polar hydroxyl groups give rise to hydrogen bonding. Owing to the keto-enol tautomerism of vinyl alcohol monomer, 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 a gel by gradual increase in viscosity when the solution is cooled [2]. Polyvinyl alcohol has good linearity, flat zig-zag conformation, high crystallinity, alkali resistance that endures over PH 13.6, and adhesive property. Lots of rheological studies have been made on polyvinyl alcohol solutions in water [3], water/dimethyl sulfoxide (DMSO), and other solvents [4]. Some results on the rheological properties of syndiotactic polyvinyl alcohol have been reported by Kim et al. [5]. It is impossible to manufacture high strength and elastic fiber because superdrawing is impossible if strong hydrogen bond due to hydroxyl group and strong crystal due to hydroxyl group is not eliminated or relaxed [6]. It is important to optimize the processing parameters with consideration of viscoelasticity of polyvinyl alcohol solution in order to manufacture polyvinyl alcohol fiber and film with excellent properties. In this study, time-dependence of the dynamic rheological properties of polyvinyl alcohol/dimethyl sulfoxide system was investigated.

2. Experimentals

Polyvinyl alcohol (Aldrich Chemical Co.) in which the degree of saponification is over 99% was used. 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 was measured by Advanced Rheometric Expansion System (ARES, Rheometric scientific. Co.). Time sweep experiment was performed at the frequencies of 2 and 200 rad/s at 30 °C, by repeating the following procedure 3 times; 10 minutes' rheological measurement and 5 minutes' relaxation in the rheometer.

3. Results and Discussion

The modified Cole-Cole plot for 14 wt.% polyvinyl alcohol (MW=85,000-146,000) solution in dimethyl sulfoxide at 30 °C is shown in Figure 1. The slope of the solution is less than 2, indicating that the polyvinyl alcohol solution is rheologically heterogeneous system. It should be noted in Figure 1 that the variation of G' with G'' for 14 wt.% polyvinyl alcohol solution shows very complicated behavior. The slope changes with shear rate and gives distinctly different regions. Figure 2 shows dynamic viscosity curve of polyvinyl alcohol (MW=85,000-146,000) solution in dimethyl sulfoxide at 30 °C at the frequencies of 2 rad/s (a) and 200 rad/s (b), respectively. Dynamic viscosity is increased with repeating the procedure at 2 rad/s. However the frequency of 200 rad/s gives little change in dynamic viscosity. This indicates that dynamic viscosity of polyvinyl alcohol solution depends on the time at 2 rad/s with this polymer concentration. That is, low shear like 2 rad/s gives slight orientation. So, the possibility of effective hydrogen bonding seems to be more increased under low shear.

Figure 3 traces time dependence of storage modulus (G') for 14 wt.% polyvinyl alcohol (MW=85,000-146,000) solution in dimethyl sulfoxide at 30 °C at the frequencies of 2 (a) and 200 rad/s (b). G' is increased with repeating the time sweep at the frequency of 2 rad/s. All the G' tends to increase with time and the G' at the first procedure shows the highest increasement than others. The slope is slightly decreased with repeating the procedure. However, G' at the frequency of 200 rad/s shows a little change in spite of repeating the procedure.

Loss tangent ($\tan \delta$) of polyvinyl alcohol (MW=85,000-146,000) solution in

dimethyl sulfoxide at 30 °C at the frequencies of 2 rad/s (a) and 200 rad/s (b) is plotted against frequency in Figure 4. According to Winter's view [7], the gelation point can be defined, at which G' is equivalent to G'' ($\tan \delta=1$). $\tan \delta$ shows the reverse tendency with G' . At the first time sweep, $\tan \delta$ is decreased under the gelation point with time. It means that the gel structure is formed by shear. At the second and third time sweep, the solid like character is more noticeable. However, there is a little change of $\tan \delta$ at the frequency of 200 rad/s.

4. References

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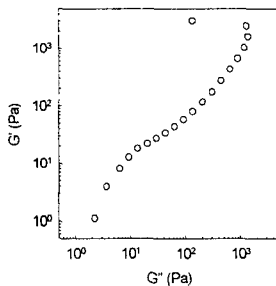


Fig. 1 Storage modulus vs. loss modulus for PVA solution in DMSO at 30 °C. (14 wt.%)

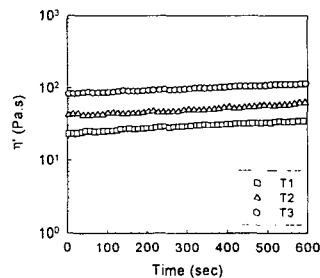


Fig. 2. (a) Plots of dynamic viscosity as a function of time for 14 wt.% PVA solution in DMSO at 30 °C. (frequency 2 rad/sec)

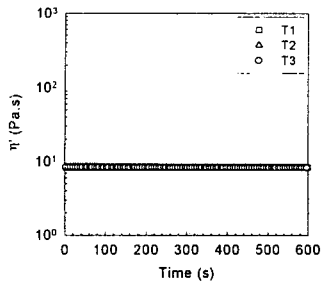


Fig 2. (b) Plots of dynamic viscosity as a function of time for 14 wt.% PVA solution in DMSO at 30°C. (frequency 200 rad/s.)

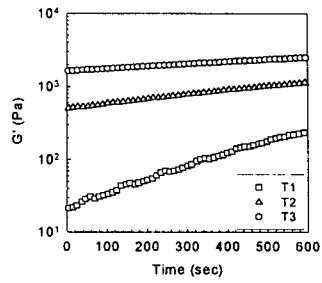


Fig. 3. (a) Plots of storage modulus with time for 14 wt.% PVA solution in DMSO at 30°C. (frequency 2 rad/sec)

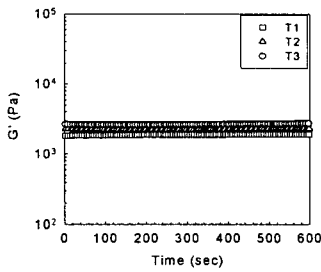


Fig. 3 (b) Plots of storage modulus with time for 14 wt.% PVA solution in DMSO at 30°C. (frequency 200 rad/sec)

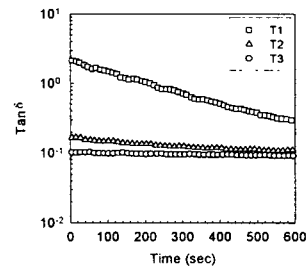


Fig. 4. (a) Plots of $\tan \delta$ with time for 14 wt.% PVA solution in DMSO at 30°C. (frequency 2 rad/sec)

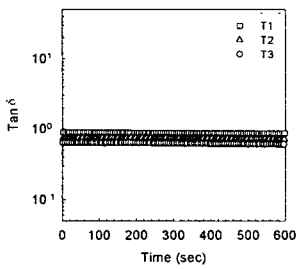


Fig. 4. (b) Plots of $\tan \delta$ with time for 14 wt.% PVA solution in DMSO at 30°C. (frequency 200 rad/sec)