

혼성 배열 폴리비닐 알코올/디메틸 설펝시드 용액의 유변학적 특성에 미치는  
분자량 분포의 영향

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**Effect of molecular weight distribution 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 crystalline polymer that forms a gel when the solution is cooled [1]. Polyvinyl alcohol forms micro gel or gel by intermolecular hydrogen bonding, intramolecular hydrogen bonding and interaction with polyvinyl alcohol and solvent [2]. Polyvinyl alcohol is a synthetic polymer in which polar hydroxyl groups alternately recur as pendent parts of the polymer main chain [3]. Polyvinyl alcohol 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 polyvinyl alcohol fiber is possible, and it is widely used as reinforcement of cement, concrete, plastic, asbestos substitution materials, tire cord, and film [4]. A good balance of property and processibility of polymer products can be obtained by proper manipulation of molecular weight distribution. In this study, rheological analysis of solutions of atactic polyvinyl alcohol with different molecular weight distributions, but the same average molecular weight in dimethyl sulfoxide (DMSO) was carried out to assess the effect of

molecular weight distribution on processibility.

## 2. Experimental

Polyvinyl alcohol (Aldrich Chemical Co. Inc.) in which the degree of saponification is over 99% was used. The polymer 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 solution was optically examined. Rheological characteristics of the solutions of polyvinyl alcohol in dimethyl sulfoxide were measured using an Advanced Rheometric Expansion System (ARES, Rheometric scientific. Co.).

## 3. Results and Discussion

Fig 1. shows the variation of dynamic viscosity ( $\eta'$ ) with frequency ( $\omega$ ) for polyvinyl alcohol/dimethyl sulfoxide solutions (14 wt.%) with the same average molecular weight but different molecular weight distributions. Molecular weight of A is 89,000-98,000, that of B is 85,000-146,000 and that of C is 124,000-186,000. B and A64C36 have same average molecular weight but different molecular weight distributions, which was prepared by mixing A and C by 64:36 in weight percent. It is noted in Fig. 1 that the viscosity of polyvinyl alcohol with wider molecular weight distribution is lower than that of polyvinyl alcohol with narrower molecular weight distribution at the same average molecular weight. This agrees well with the theoretical prediction by Middleman [5]. Over the frequency range examined, the polyvinyl alcohol solutions show non-Newtonian flow behavior.

Fig. 2 shows the variation of dynamic viscosity ( $\eta'$ ) with molecular parameter such as molecular weight and molecular weight distribution at three different frequencies. As the molecular weight is increased, viscosity is increased. This qualitatively agrees with the well known expression,  $\eta_0 = k \overline{M}_n^w$  [6], in which  $\eta_0$  is zero-shear viscosity. As a rule, the viscosity of polyvinyl alcohol with wider

molecular weight distribution is lower than that of polyvinyl alcohol with narrower molecular weight distribution. We can see this phenomenon more clearly in Fig 2.

Fig. 3 shows the relationship between storage modulus ( $G'$ ) and loss modulus ( $G''$ ) for polyvinyl alcohol/dimethyl sulfoxide solutions at 30°C (14 wt.%). The slope of A64C36 is lower than that of B in the terminal zone. This means that the solution of polyvinyl alcohol of wider molecular weight distribution is more heterogeneous at the same molecular weight.

Fig. 4 shows the variation of stress relaxation time of polyvinyl alcohol solutions in dimethyl sulfoxide with frequency. At low frequency, polyvinyl alcohol with wider molecular weight distribution exhibits a little longer relaxation time. This means that polyvinyl alcohol with wider molecular weight distribution forms more effective hydrogen bonds. As predicted, however, the relaxation time of polyvinyl alcohol solutions is decreased with increasing frequency and the effect of molecular weight distribution on the relaxation time disappears at high frequency region.

Figs. 5 and 6 show the variation of  $G'$  with molecular parameter such as molecular weight and molecular weight distribution at 0.8 and 80 rad/sec. At low frequency, 0.8 rad/sec, polyvinyl alcohol with wider molecular weight distribution gives greater storage modulus at the same molecular weight.

#### 4. References

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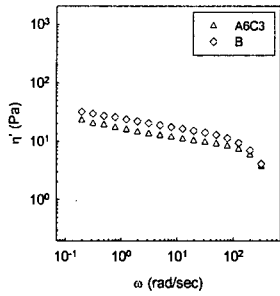


Fig. 1. Dynamic viscosity curves for PVA solutions (14 wt.%) in DMSO at 30 °C.

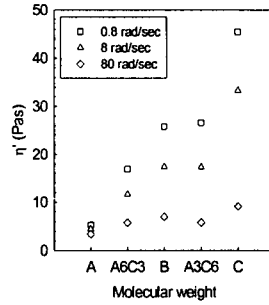


Fig. 2. Dynamic viscosity curves for PVA solutions in DMSO (14 wt.%)

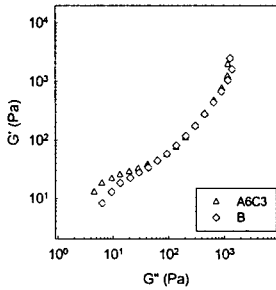


Fig. 3. Storage modulus vs. loss modulus for PVA solutions (14 wt.%) in DMSO at 30 °C.

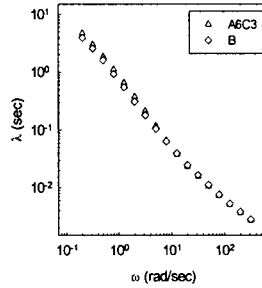


Fig. 4. Variation of relaxation time with frequency for PVA solutions (14 wt.%) in DMSO at 30 °C.

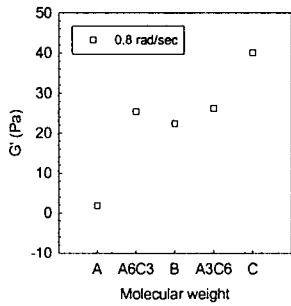


Fig. 5. Storage modulus vs. molecular weight of PVA solutions in DMSO (14 wt.%).

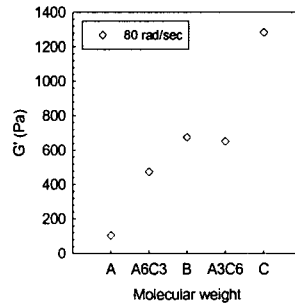


Fig. 6. Storage modulus vs. molecular weight of PVA solutions in DMSO (14 wt.%).