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Rheological Properties of High Molecular Weight (HMW) Syndiotactic Poly(vinyl alcohol) (PVA)/HMW Atactic PVA Blend Solutions

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1. Introduction

Recently, people are gradually concerned about environmental issue, bionics, environmental-friendly or biocompatible materials. Poly(vinyl alcohol) (PVA) is suitable for these materials, because it is typically water-soluble polymer that have linear-flexible chains, a material of no toxicity for human, and biodegradable polymer[1]. One of the most effective factors that dominate the properties of PVAs is tacticity. The tacticity of PVA is controlled by the structure and properties of the corresponding monomeric vinyl ester or vinyl ether and their polymerization conditions. The most remarkable difference between atactic PVA (a-PVA) and syndiotactic PVA (s-PVA) is revealed upon their crystallization, gelation, melting and dissolution in bulk or solvents[1]. These transition behaviors can be mainly correlated with the properties of the crystal phase such as crystallization rate and heat of fusion. These properties seem to be higher in s-PVA than in a-PVA. The difference between the two PVAs becomes more pronounced on comparing their behavior in solutions. It is important to characterize the rheological properties of s-PVA/a-PVA blend solutions in order to manufacture the various products with excellent properties. So in this study, the effect of blend ratios on the rheological properties of s-PVA/a-PVA/water blend solutions was investigated.

2. Experimental

2.1. Preparation of S-PVA[2]

To prepare a water-soluble s-PVA, copolymerization of vinyl pivalate (VPi) and vinyl acetate (VAc) with feed ratio of $\text{mol}_{\text{VPi}}/\text{mol}_{\text{VAc}}$ (4/6) using 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) as initiator with conversions of 25 to 35%, was performed, followed saponification of copoly(VPi/VAc). Water-soluble s-PVA was prepared by saponifying with NaOH aqueous solution at 30 °C.

2.2. Preparation of A-PVA

To prepare a water-soluble a-PVA, solution polymerization of VAc in dimethyl sulfoxide (DMSO) using ADMVN as initiator with conversions of 25 to 35%, was performed, followed saponification of poly(VAc).

2.3. Preparation of S-PVA/A-PVA Blend Solutions

S-PVA and a-PVA were dissolved for 5 g/dl water solution at 120 C for 1 h, and were kept

for 30 min to ensure homogenization.

2.4. Measurement of Rheological Properties of PVA Solution

For more precise rheological measurement, Physica USD 200 Rheometer was used. In Rheometer measurement, a cone and plate type flow cell with diameter of 25 mm and degree of 0.04 rad was used to effectively accommodate the torque of the solutions. Test type and measurement type were strain control and dynamic frequency sweep test, respectively and the measurement was performed at fixed strain of 5%, 30 °C, low frequency with range of 10^{-1} to 10^2 rad/s.

3. Results and Discussion

Figure 1 compares behavior of the complex viscosities of 5 g/dl solutions of s-PVA/a-PVA blend with different blend ratios at 30 °C. Over the frequency range examined, the solution of s-PVA/a-PVA blend with larger s-PVA content gave rise to greater complex viscosity at given frequency. Also, as frequency increased, all the specimens show pseudoplasticity. Particularly with s-PVA/a-PVA blend with larger s-PVA content, the lower Newtonian flow region disappears and it exhibits much greater decreasing rate of viscosity in the viscosity curve. This kind of viscosity behavior is reported to be frequently encountered in inhomogeneous systems such as polymer gels, block copolymers, and liquid-crystalline polymers. Changes of storage modulus of the s-PVA/a-PVA blend solutions with frequency are presented in Figure 2. The slope of storage modulus of s-PVA/a-PVA blend with larger s-PVA content is nearly constant value, irrespective of frequency.

4. References

1. C. A. Finch, Polyvinyl Alcohol-Developments, John Wiley and Sons, New York, 1991.
2. W. S. Lyoo, J. Blackwell, and H. D. Ghim, *Macromolecules*, **31**, p. 4253 (1998).

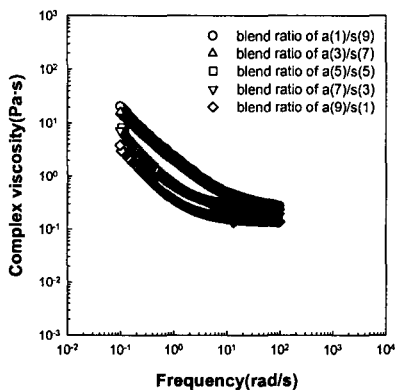


Figure 1. Complex viscosity of 5 g/dl s-PVA/a-PVA blend solutions with frequency at 30 °C.

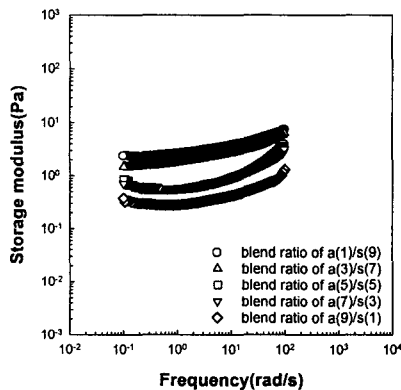


Figure 2. Storage modulus of 5 g/dl s-PVA/a-PVA blend solutions with frequency at 30 °C.