

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

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ABSTRACT: To identify the effect of blend ratios of syndiotacticity-rich poly(vinyl alcohol) (s-PVA)/atactic PVA (a-PVA) having similar number-average degrees of polymerization (P_n)s of 4000 and degrees of saponification (DS)s of 99.9% on the rheological properties of s-PVA/a-PVA/water solutions, water-soluble s-PVA and a-PVA with different syndiotactic diad contents of 58.5 and 54.0%, respectively, were prepared by bulk copolymerization of vinyl pivalate and vinyl acetate (VAc) and solution polymerization of VAc, followed by saponifying the corresponding copoly(vinyl pivalate/vinyl acetate) and poly(vinyl acetate). The blend ratios played a significant role in rheological behavior. Over the frequency range of 10^{-1} – 10^2 rad/s, s-PVA/a-PVA blend

solutions with larger s-PVA content show more shear thinning at similar (P_n)s and (DS)s of polymer, suggesting that PVA molecules are more readily oriented as s-PVA content increases. Yield stress is higher for s-PVA/a-PVA blend solutions with larger s-PVA content at similar (P_n)s and (DS)s of polymer. This indicates that more domains with internal order are produced at larger s-PVA content in s-PVA/a-PVA blend solutions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3934–3939, 2006

Key words: blend ratios; s-PVA; a-PVA; rheological properties; shear thinning

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 a water-soluble polymer that has linear-flexible chains, a material of no toxicity for human, and biodegradable. It is used as coating in textiles, as stabilizer in industrial fields, polarizing film, sizing agent, adhesives, drug delivery carrier, contact lens, gels, biomaterials, and nanomaterials and its uses are expanded.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.^{2–6}

Generally, poly(vinyl acetate) (PVAc) has been used as the precursor of PVA, and atactic PVA (a-PVA) has been produced. a-PVA made from PVAc has a poor stereoregulation and dissolves in water. Syndiotacticity-rich PVA (s-PVA) with high stereoregularity would be made from poly(vinyl pivalate) (PVPi) having bulky side groups.^{2–6} Because s-PVA has a regular structure and the hydroxyl groups in the main chains are alternately arranged, it can easily form strong intermolecular hydrogen bond.^{7,8} Where only PVPi is used as the precursor of PVA, syndiotacticity-rich PVA does not dissolve in water above 120°C because of high syndiotacticity and high molecular weight (HMW).⁹ Thus, to prepare water-soluble s-PVA, the molecular weight and syndiotacticity need to be controlled using vinyl pivalate (VPi) and vinyl acetate (VAc) with various monomer feed ratios and resultant saponification. Since water-insoluble s-PVA is dissolved only in organic solvents, it causes toxicity in *in vivo* biomaterial uses. But, water-soluble s-PVA can be used for biomaterials with no toxicity. In addition, since water-soluble s-PVA is stronger than a-PVA in many physical properties, it can be used to prepare biomaterials with better physical and chemical properties.

The nomenclature in terms of tacticity seems not to be applied so literally to PVA as to other synthetic

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polyolefins. For example, the term “syndiotactic polymer” is used for the polymers with syndiotacticities higher than 95% in diad content in the case of polystyrene¹⁰ and poly(methyl methacrylate).¹¹ These peculiarities of PVA come from the fact that PVAs with syndiotacticity values close to either 100 or 0% have never been attained. Available PVAs are recognized to be in effect random mixtures of isotactic and syndiotactic sequences.

The most remarkable difference between s-PVA and a-PVA is revealed upon their crystallization, gelation, melting, and dissolution in bulk or solvents.¹² 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. The crystallization rate from aqueous solutions¹³ and the melting temperature of hydrogel¹⁴ are higher in s-PVA than in a-PVA. These findings indicate the difference in affinity of the polymer molecule with water. Tanigami et al.^{15,16} studied on the miscibility in the crystal phase of s-PVA/a-PVA blend films. According to their work, coexistence of the two melting temperatures indicated the presence of two types of crystal phases. That is, the high and low melting temperatures correspond to those of s-PVA-rich and a-PVA-rich phases, respectively.

PVA/water solution shows various rheological behaviors with regard to temperature, molecular weight, degree of saponification (DS), stereoregularity, and so on.^{17–20} It is natural that blend ratios have a significant influence on the rheological properties of s-PVA/a-PVA blends, because the difference in chemical composition gives rise to different physical properties. It is important to characterize the rheological properties of HMW s-PVA/HMW a-PVA blend solutions to manufacture the various products with excellent properties like biogels used *in vivo*. So in this study, to clarify the structural differences of the two PVAs, the rheological properties of s-PVA/a-PVA with similar number-average degrees of polymerization (P_n)s and (DS)s blend solutions was investigated.

EXPERIMENTAL

Preparation of s-PVA^{2,21}

To prepare a water-soluble s-PVA, copolymerization of VPi and 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 25–35% was performed, followed by saponification of copoly(VPi/VAc). Water-soluble s-PVA was prepared by saponifying with NaOH aqueous solution at 30°C.

Preparation of a-PVA²²

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

Determination of syndiotactic diad content and DS²

The syndiotactic triad and syndiotactic diad (s-diad) content of PVAs was determined by Varian Sun Unity 300 MHz proton-nuclear magnetic resonance (¹H NMR) spectrometer, using DMSO-d₆ as the solvent, based on the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm. DS was determined by the ratio of *tert*-butyl and acetyl and methylene proton peaks in the ¹H NMR spectrum.

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.

Measurement of rheological properties of s-PVA/a-PVA blend solutions

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 10⁻¹–10² rad/s.

Preparation of s-PVA/a-PVA blend films

s-PVA and a-PVA were dissolved for 2.5 and 5 g/dL water solutions at 120°C for 1 h, respectively, and then the blend solution was cast into casting plates. The plates were dried *in vacuo* at room temperature for 3 days.

Measurements of thermal properties of s-PVA/a-PVA blend films

Thermal properties of the blend films were measured using a differential scanning calorimeter (DSC, TA Instrument 2010, Dupont). The samples were heated at 10°C/min under a nitrogen atmosphere from 25 to 300°C.

TABLE I
Characteristics of s-PVA and a-PVA Prepared

	S-diad content (%)	P_n	DS (%)
s-PVA	58.5	4000	99.9
a-PVA	53.5	4000	99.9

RESULTS AND DISCUSSION

Generally, s-PVA with high tacticity and HMW is a water-insoluble polymer.⁹ In this study, to prepare a water-soluble s-PVA, tacticity and molecular weight were finely controlled to an appropriate level by adapting copolymerization of VPi and VAc. Table I shows the characteristic features of s-PVA and a-PVA. Two PVAs show similar (DS)s of 99.9% and (P_n)s of 4000. The difference in the syndiotacticity between the two PVAs was only 5% in diad content. Nevertheless, outstanding differences between s-PVA and a-PVA will still be expected to appear in rheological properties.

Figure 1 compares the behavior of the complex viscosities ((η^*) s) of 5% (g/dL) solutions of s-PVA/a-PVA blend with different blend ratios at 30°C. The state of all 5% (g/dL) blend solutions in this study is a solution state, which represents fluidity. Over the frequency (ω) range examined, the solutions of s-PVA/a-PVA blend with larger s-PVA content gave rise to greater η^* at given ω . Also, as ω was increased, all the specimens showed pseudoplasticity. In particular, for s-PVA/a-PVA blends with larger s-PVA content, the lower Newtonian flow region disappeared

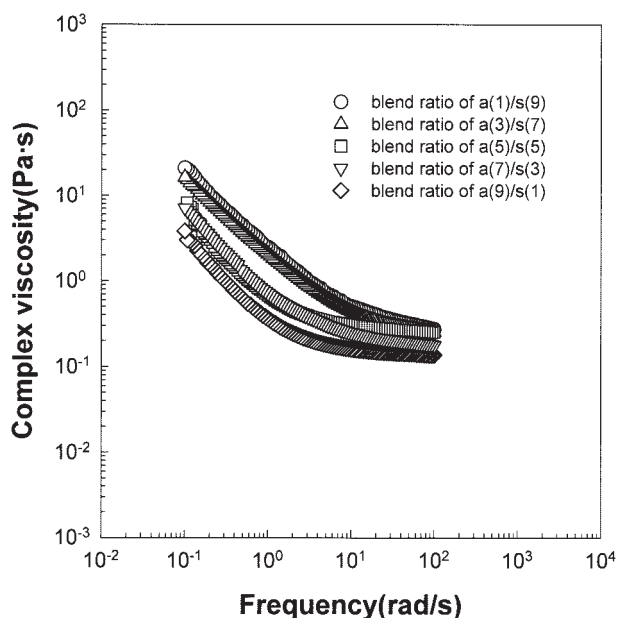


Figure 1 Complex viscosity of 5 g/dL s-PVA/a-PVA blend solutions with frequency at 30°C.

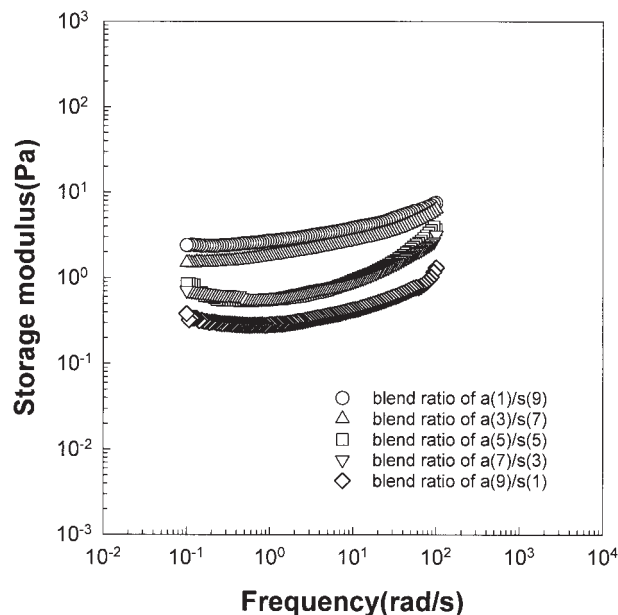


Figure 2 Storage modulus of 5 g/dL s-PVA/a-PVA blend solutions with frequency at 30°C.

and it exhibited 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. As s-PVA/a-PVA blends with larger s-PVA contents have regularly zigzag-arranged side groups and larger number of hydrogen bonds, it is expected that the molecules are more regularly packed which are more readily oriented by shear. If s-PVA content in s-PVA/a-PVA blends is high enough to reach such a physical state, the blend solutions have the heterogeneity similar to the anisotropic phase found in liquid crystal polymer systems, consequently, the lower Newtonian flow region disappears in the viscosity curve as shown in Figure 1. Comparison of the viscosity curves in Figure 1 indicates that the critical point of s-PVA content in s-PVA/a-PVA blend composition exists between 50 and 70%. This explains that s-PVA/a-PVA blends with s-PVA content over 70% have a high viscosity and Bingham flow properties, due to shear-orientation and hydrogen bonds.

Changes of storage modulus (G') and loss modulus (G'') of the s-PVA/a-PVA blend solutions with ω are presented in Figures 2 and 3, respectively. s-PVA/a-PVA blend solutions with larger s-PVA content had greater G' s and G'' s. Furthermore, the slope of G' of s-PVA/a-PVA blends with larger s-PVA content was nearly constant, irrespective of ω . Because s-PVA had strong intermolecular bonding related to tacticity, much higher values of G' and G'' with s-PVA content are easily observed in Figures 2 and 3. The plot of G'' against ω also had the higher values as s-PVA content increased in Figure 3. The s-PVA/a-PVA blend solu-

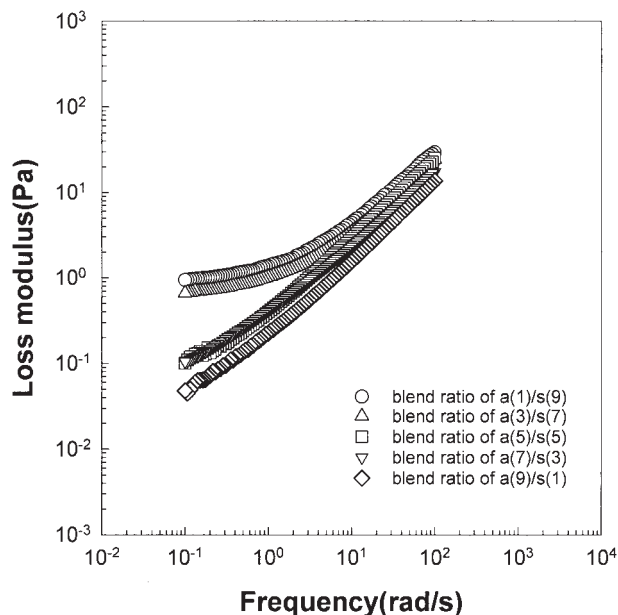


Figure 3 Loss modulus of 5 g/dL s-PVA/a-PVA blend solutions with frequency at 30°C.

tions with an s-PVA content below 50% had increased G' with ω , whereas specimens with s-PVA contents over 70% had nearly constant values of G' with low ω . This implies that s-PVA/a-PVA blend solutions with s-PVA contents below 50% are different from s-PVA/a-PVA blend solutions with s-PVA contents over 70% in internal structure of blend solutions. Because s-PVA/a-PVA blend solutions with s-PVA contents over 70% had superior intermolecular bonding, due to their regular arrangement of hydroxyl groups, it showed nearly constant G' at low ω . This represent that polymer chains of blend solutions are somewhat stiff above the critical point. It is well supposed that the G' and G'' are influenced by the effect of hydrogen bonding interactions because of different levels of hydroxyl groups.

Figure 4 shows plot of η^* against G'' for the solutions of the five different s-PVA/a-PVA blends in water. The slope of the viscosity curves demonstrates the effect of blend ratios on shear dependence of viscosity and yield behavior. s-PVA/a-PVA blend solutions with larger s-PVA content had the greater slopes of the viscosity curves. We reported that a-PVA had the constant η^* to G'' .²³ That is, it exhibited the behavior of Newtonian flow. However, s-PVA/water solution shows the behavior of non-Newtonian flow that the values of η^* against G'' decreased in previous study. As shown in Figure 4, all specimens exhibited the behavior of Newtonian and non-Newtonian flows. Disappearance of the lower Newtonian flow region indicates a heterogeneity of a system frequently observed in liquid-crystalline polymers and block copolymers. Three blend solutions with an s-PVA content below 50% showed lower slope behavior than the

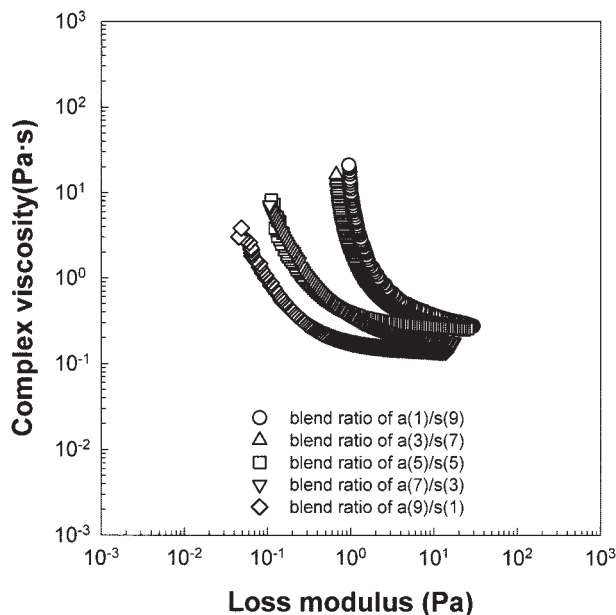


Figure 4 Complex viscosity of 5 g/dL s-PVA/a-PVA blend solutions with loss modulus at 30°C.

other two blend solutions, and blend solutions with an s-PVA content over 70% showed relatively unchanged G' with changes in viscosity. Therefore, it is supposed that some heterogeneous forms exist in system, and s-PVA/a-PVA blend solutions with larger s-PVA content have the greater heterogeneity. This implies that because of rigidity of molecules, though η^* changes, G' does not change relatively.

Figure 5 shows that the plot of G' against G'' , the so-called Cole-Cole plot, for the solutions of five s-PVA/

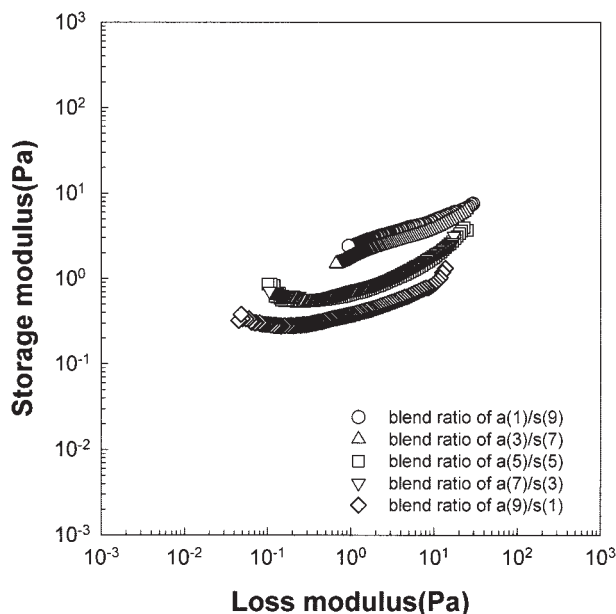


Figure 5 Storage modulus of 5 g/dL s-PVA/a-PVA blend solutions with loss modulus at 30°C.

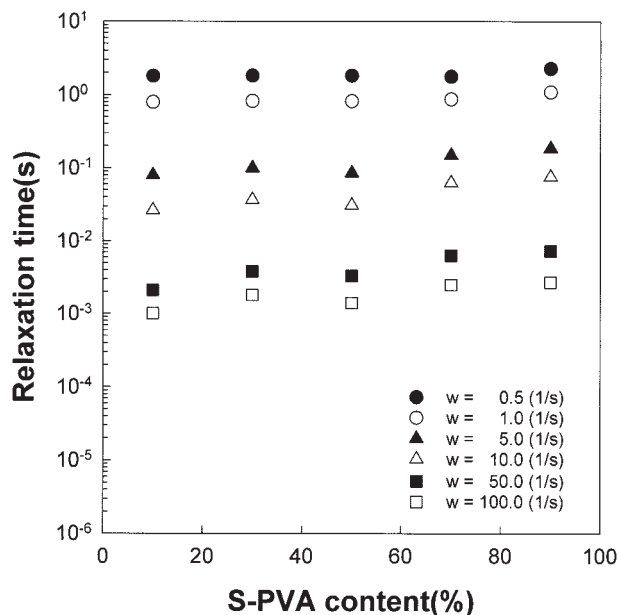


Figure 6 Relaxation time of 5 g/dL s-PVA/a-PVA blend solutions at various blend ratios at 30°C.

a-PVA blends in water with different blend ratios. In this plot, one sees the rheological responses more clearly by the replacement of ω with G'' in Figure 2. This logarithmic plot of G' against G'' , a Cole-Cole plot, gives a slope of 2 for most homogeneous and isotropic polymer melts and solutions. The slope of a homogeneous isotropic solution such as a-PVA is nearly 2, but the slope of a heterogeneous solution such as s-PVA is a lower value than 2.²⁴ In the cases of three blends with s-PVA content below 50% similar values are shown. However, at over 70% s-PVA content, a different behavior is shown. It can be thought that some heterogeneous structures are formed at over 70%. From these facts it was supposed that s-PVA/a-PVA blend solutions with s-PVA content over 70% had structures like mesophase. This confirms that the difference in stereoregularities influenced the appearance of the heterogeneous structure in s-PVA/a-PVA blend solutions.

Variation of relaxation time of 5% (g/dL) solutions of s-PVA/a-PVA blends in water with ω is shown in Figure 6. The relaxation time (λ) under dynamic shear may be calculated as,²⁵

$$J' = G' / ([\eta^*]\omega)^2 = \lambda / [\eta'] \quad (1)$$

where J' and G' are compliance and storage modulus, η^* and η' are complex viscosity and dynamic viscosity, respectively. All of λ for s-PVA/a-PVA blends reduced with ω . And, λ of s-PVA/a-PVA blend solutions hardly changed with s-PVA content, but s-PVA/a-PVA blends with s-PVA content over 70% showed the higher value than different s-PVA/a-PVA blend solutions. This indicates that s-PVA/a-PVA blend so-

lutions with s-PVA content over 70% have a long relaxation time because of internal strong structure.

Finally, to check the miscibility between HMW s-PVA and HMW a-PVA, we prepared s-PVA/a-PVA blend films. Blend films are prepared at various blend ratios of 10/0, 9/1, 7/3, 5/5, 3/7, 1/9, 0/10, and at two different polymer concentrations of 2.5 and 5% (g/dL), respectively. Melting temperature of blend films with various blend ratios estimated from the DSC melting endotherms is shown in Figure 7. Although s-PVA and a-PVA have different melting temperature of 235 and 226°C, respectively, all melting temperature of blend films at 2.5 and 5% (g/dL) show one value. From the fact described above, it was found that HMW s-PVA and HMW a-PVA have miscibility. In the case of glass transition temperature, it is very difficult to measure it owing to disappearance in DSC thermogram by very fast crystallization rate of HMW s-PVA.^{2,7-9} It is shown that the melting temperature of blend films was increased with an increase in the s-PVA content. Also, increasing rate of blend films at 2.5% (g/dL) was higher than that at 5% (g/dL). From the fact that the difference in slope of melting temperature varies between 5 and 2.5% (g/dL), it might be supposed that the gelation and crystallization of blend films was greatly influenced by the initial polymer concentration. That is, the crystallization rate increase by increasing s-PVA content was more dominant in lower initial polymer concentration.

CONCLUSIONS

The effect of blend ratios of s-PVA/a-PVA blends on the rheological properties of s-PVA/a-PVA/water so-

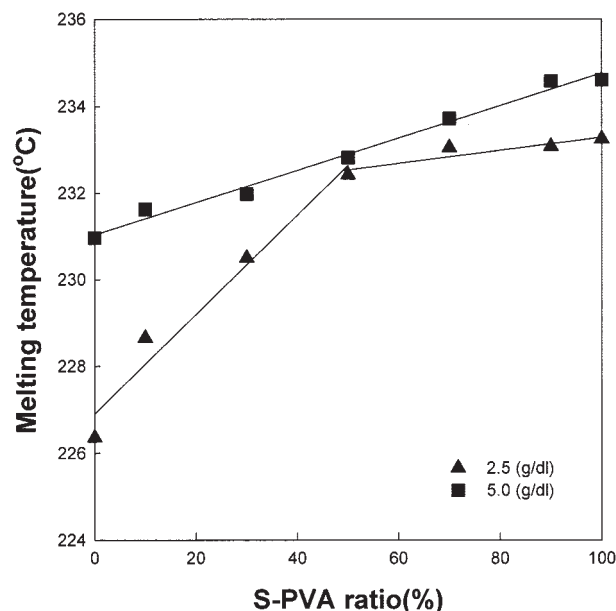


Figure 7 Melting temperature of s-PVA/a-PVA blend films cast at different blend ratios and at two initial polymer concentrations.

lutions by preparing five s-PVA/a-PVA blends with different blend ratios, similar (P_n)s, and (DS)s were identified. As was to be expected, blend ratios have a profound influence on the viscoelastic properties of s-PVA/a-PVA blend solutions. s-PVA/a-PVA blend solutions with larger s-PVA content had the higher η^* and the greater shear thinning effect. Because s-PVA/a-PVA blend solutions with larger s-PVA content have a regularly arranged structure and the large number of hydrogen bond and s-PVA molecules are stiff and oriented well, so it had the higher values of G' and G'' . Especially, s-PVA/a-PVA blend solutions, with s-PVA content over 70% had the higher shear thinning effect than other three s-PVA/a-PVA blend solutions, and nearly constant value of G' and G'' with low ω . This might be explained by the fact that the larger the s-PVA content, the greater the intermolecular hydrogen bonding in s-PVA/a-PVA blends. At s-PVA contents below 50%, it showed a lower yield stress with poor internal ordered structure, however, s-PVA/a-PVA blend solutions with s-PVA content over 70% had the greater pseudostructure like mesophase with larger relaxation time.^{23,24} That is, the critical point of s-PVA content in s-PVA/a-PVA blend composition exists between 50 and 70%. Therefore, it is evident that this blending will be a useful method by which the syndiotacticity of PVA materials can be controlled more finely. Also, blending of a small amount of s-PVA with a-PVA will be a useful technique to produce functional PVA materials with superior rheological properties from the cheaper a-PVA. In the near future, we will report on the preparation and characterizations of s-PVA/a-PVA blend films and fibers.

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