

Effect of Degree of Saponification on the Rheological Properties of Syndiotactic Poly(vinyl alcohol)/Water Solution

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ABSTRACT: To identify the effect of degree of saponification (*DS*) of syndiotactic poly(vinyl alcohol)s (s-PVA)s having similar tacticity and molecular weight on the rheological properties of s-PVA/water solution, four kinds of (s-PVA)s with assigned (*DS*)s, from 93.1 to 97.5%, were prepared by copolymerization of vinyl pivalate (VPi) and vinyl acetate (VAc), followed by saponifying the corresponding copoly(VPi/VAc). The *DS* played a significant role in rheological behavior. Over the frequency range of 10^{-1} to 10^2 rad/s s-PVA with higher *DS* shows more shear thinning at similar molecular weight and tacticity of polymer, suggesting that PVA molecules are more readily oriented as *DS*

increases. This may provide indirect evidence of the spontaneous in situ orientation of s-PVA molecules at the late stage of saponification. Yield stress is higher for s-PVA with higher *DS* at similar molecular weight and tacticity of s-PVA. This indicates that more domains with internal order are produced at higher saponification. These facts result from increase in stiffness of s-PVA molecules with proceeding the saponification reaction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 463–467, 2002

Key words: degree of saponification; s-PVA; rheological property; orientation

INTRODUCTION

Recently, people have been concerned about environmental issues, 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 humans, and is biodegradable. It is used as a coating in textiles, a stabilizer in industrial fields, polarizing films, sizing agents, adhesives, drug delivery systems, contact lenses, bio-materials, nano-materials, etc.¹

Up until now, poly(vinyl acetate) (PVAc) have been used for the precursor of PVA, and atactic PVA (a-PVA) has been produced. But as vinyl acetate (VAc), a monomer of PVAc, has a small steric effect during polymerization, a-PVA made from PVAc has a poor stereosequences and is dissolved by water. Recently, syndiotactic PVA (s-PVA) with higher stereoregularity was made from poly(vinyl pivalate) (PVPi) having bulky side groups.^{2–9} Because s-PVA has a regular

structure and the hydroxyl groups in the main chains are alternately arranged, it is packed well with adjacent molecules, and it can easily form strong intermolecular hydrogen bonds.⁵ Where PVPi is used for the precursor, s-PVA, with a molecular structure finely packed due to higher syndiotacticity, is not dissolved in water above 120°C.²

To prepare a water-soluble s-PVA, the major molecular parameters of PVA such as molecular weight, stereoregularity, and degree of saponification (*DS*) need to be controlled using copolymerization of VPi and VAc with various monomer feed ratios and resultant saponification of copoly(VPi/VAc). Because water-insoluble s-PVA with a strong molecular structure 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, as water-soluble s-PVA is stronger than a-PVA in many physical properties, water-soluble s-PVA can be used to prepare biomaterials with better physical and chemical properties.

Because PVA is prepared by saponification of precursors like to PVPi and PVAc, *DS* of PVA is a very important molecular parameter. It is natural that *DS* has a significant influence on the rheological properties of PVA because the difference in chemical com-

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TABLE I
Characteristics of PVA Prepared

DS (%) ^a	s-Diad Content (%) ^a	P_n ^a
93.1	56.5	3900
95.0	56.5	3900
96.5	56.6	3900
97.5	56.5	3900

^a DS, s-diad content, and P_n are, respectively, degree of saponification, syndiotactic diad content, and number-average degree of polymerization of PVA.

position gives rise to different physical properties. PVA/water solution shows various rheological behaviors with regard to temperature, DS, molecular weight, stereoregularity, and so on.^{10–13} It is important to characterize the rheological properties of PVA solution to manufacture the various products such as fiber, film, adhesive, sizing agent, with excellent properties.¹⁴ In this study, the effect of DS on the rheological properties of s-PVA/water solutions was investigated.

EXPERIMENTAL

Preparation of S-PVA

To prepare a water-soluble s-PVA, copolymerization of VPi and VAc with feed ratio of $\text{mol}_{\text{VPi}}/\text{mol}_{\text{VAc}}$ (2/8) using ADMVN as initiator with conversions of 25 to 35%, was performed, followed saponification of copoly(VPi/VAc). Water-soluble (s-PVA)s with various (DS)s were prepared by saponifying with NaOH aqueous solution at 30°C for each determined time intervals, respectively.

Determination of syndiotactic diad content and DS

The syndiotactic triad and syndiotactic diad (s-diad) content of PVA were determined by Varian Sun Unity 300 MHz proton-nuclear magnetic resonance (¹H-NMR) spectrometer, using dimethylsulfoxide-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 PVA solution

S-PVA was hard to dissolve in water at room temperature, so it was dissolved in 10% water solution at 120°C for 1 h, and was kept for 30 min to ensure homogenization.

Measurement of rheological properties of PVA solution

For more precise rheological measurement, Advanced Rheometric Expansion System (ARES) manufactured in Rheometric Scientific, Inc. was used. In ARES measurement, a cone and plate-type flow cell with a diameter of 25 mm and a 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 a fixed strain of 5%, 25°C, low frequency with a range of 10⁻¹ to 10² rad/s.

RESULTS AND DISCUSSION

Generally, s-PVA with high tacticity and high molecular weight is a water-insoluble polymer. In this study, to prepare a water-soluble s-PVA, tacticity and molecular weight were finely controlled to an appropriate level by copolymerization of VPi and VAc. In addition, specimens with various (DS)s were prepared by controlling saponification conditions. Table I shows characteristic features of s-PVA prepared by saponification. All specimens show different (DS)s of 93.1 to 97.5% and similar s-diad contents of 57%, and similar (P_n)s of 3900, respectively.

Figure 1 compares behavior of the complex viscosities [η^*]s of 10% (g/dL) solutions of (s-PVA)s with different (DS)s at 30°C. Two things are worth noting in Figure 1. First, over the frequency range examined, the solution of s-PVA with higher DS gave rise to greater complex viscosity at given frequency. Second, s-PVA of DS 97.5% clearly exhibits a Bingham behavior. That

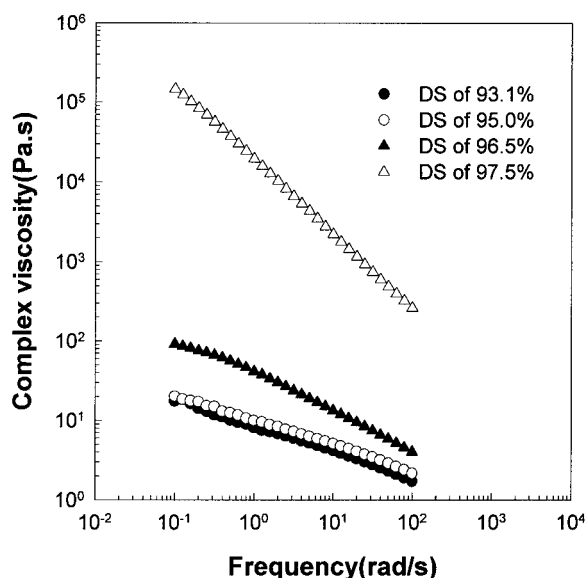


Figure 1 Complex viscosity of 10% (g/dL) s-PVA/water solution with frequency at 30°C.

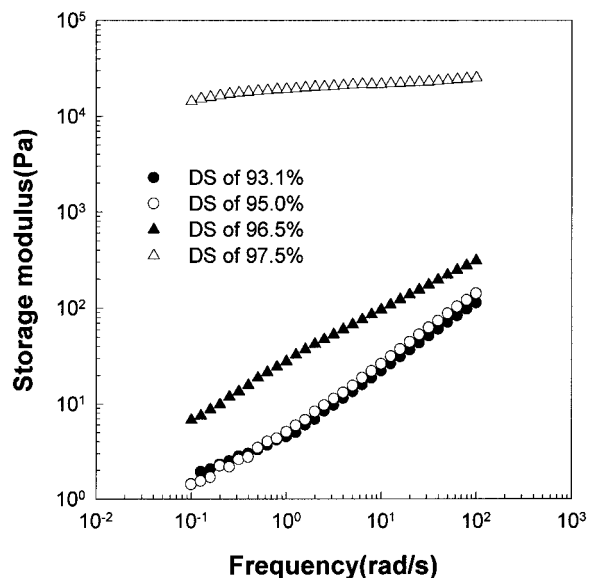


Figure 2 Storage modulus of 10% (g/dL) s-PVA/water solution with frequency at 30°C.

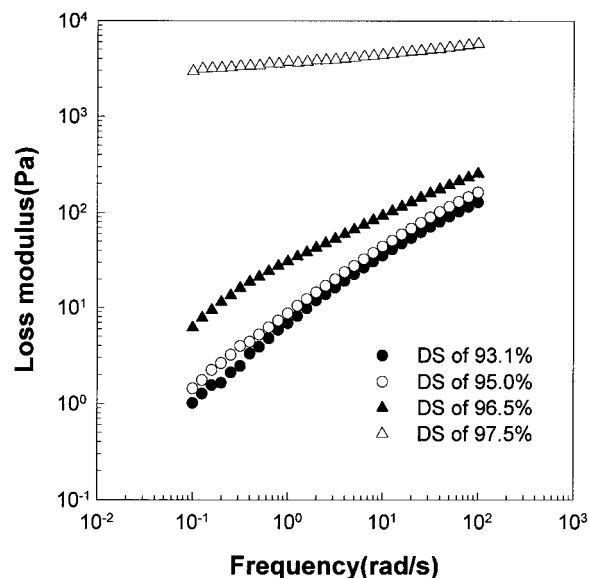


Figure 3 Loss modulus of 10% (g/dL) s-PVA/water solution with frequency at 30°C.

is, as frequency increased, all the specimens show pseudoplasticity. Particularly with s-PVA of higher *DS*, 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. As s-PVA has a regularly zigzag-arranged side groups and the large number of hydrogen bonds, it is expected that the molecules are more regularly packed, which are more readily oriented by shear. If *DS* is high enough to reach such a physical state, the solution has 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 curve in Figure 1 reveals that the critical point of *DS* exists between 96.5 to 97.5%. This explains that s-PVA of *DS* 97.5% has 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 solutions with frequency (ω) are presented in Figures 2 and 3, respectively. The slope of G' of s-PVA with *DS* of 97.5% shows are nearly constant value, irrespective of ω . It should be noticed that the slope is decreased with increasing *DS* but the magnitude of G'' is increased. Figure 3, the plot of G'' against ω , which is similar to Figure 2, also had the higher values as *DS* increased. It is well supposed that the G' and G'' are influenced by effect of hydrogen bonding interactions due to different levels of hydroxy groups. At 97.5%, as ω increases, it has nearly

constant modulus value. This represent that molecules bonds are stiff above the critical point.

Figure 4 shows plot of η^* against G'' for the solutions of the four (s-PVA)s in water. The slope of the viscosity curves demonstrates the effect of *DS* on shear dependence of viscosity and yield behavior. (S-PVA)s of higher *DS* have the greater slopes of the viscosity curves. Lyoo et al. noted that a-PVA had the constant η^* to G'' .¹⁵ 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 Figure 4. Therefore, it is supposed that heterogeneous forms exist in system

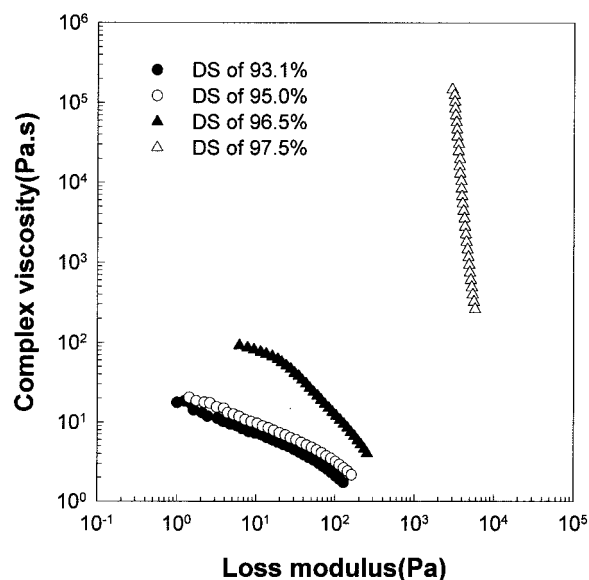


Figure 4 Complex viscosity of 10% (g/dL) s-PVA/water solution with loss modulus at 30°C.

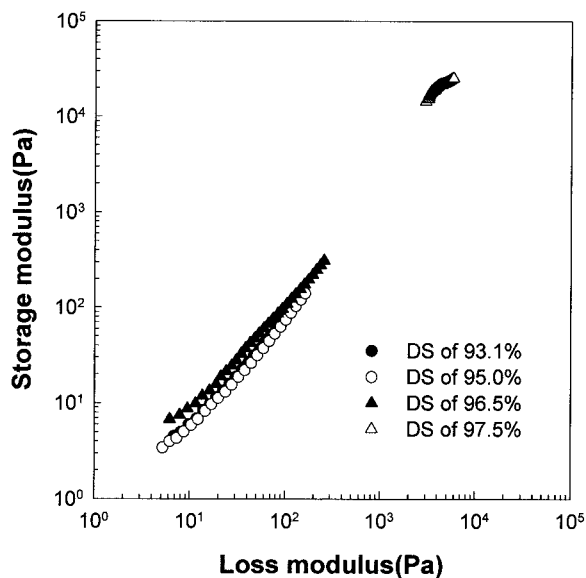


Figure 5 Storage modulus of 10% (g/dL) s-PVA/water solution with loss modulus at 30°C.

and s-PVA with higher DS has the greater heterogeneity of system. At the range of 93.1 to 96.5%, as η^* decreases, G'' changes. But nearly constant value is shown in the case of 97.5%. This implies that because of strong strength of molecules, though η^* changes, G'' does not change.

It is shown that the plot of G' against G'' , the so-called Cole–Cole plot, for the solutions of four (s-PVA)s in water with different (DS)s in Figure 5. The slope of homogeneous isotropic solution such as a-PVA is in the vicinity of 2, irrespective of different factors, but the slope of heterogeneous solution such as s-PVA approaches approximately 1.¹⁶ In Figure 5, the slopes of (s-PVA)s of (DS)s of 93.1, 95.0, 96.5, and 97.5% are 1.12, 1.09, 1.07, and 0.73, respectively. (S-PVA)s of higher (DS)s have the smaller slopes. In the cases of three (DS)s except of 97.5%, similar values are shown, however, at 97.5%, a different behavior is shown. It can be thought that some heterogeneous structures are formed at 97.5%. The inflection point is observed in case of DS of 97.5%, which suggests that s-PVA with DS over critical point produces more pre-ordered structure with disorder-to-order transition.

Bingham flow behavior gives rise to a nonzero yield stress, which represents that shear stress is proportional to shear rate at the higher range than yield point and shear rate is not changed at the lower range than yield point. This nonzero yield stress represents minimum energy required to break pseudostructures. The yield stress of heterogeneous systems can be determined from the Casson plot, plot of the square root of shear stress (τ) against square root of shear rate ($\dot{\gamma}$) in steady shear flow. The yield stress (τ_0) is obtained from,¹⁷

$$\tau^{1/2} = \tau_0^{1/2} + K\dot{\gamma}^{1/2} \quad (1)$$

Similarly, the intercept of loss modulus (G'') axis (G_0'') on the plot of the square root of G'' against the square root of ω may be regarded as a measure of yield stress in dynamic shear measurement as,¹⁸

$$G''^{1/2} = G_0''^{1/2} + K'\omega^{1/2} \quad (2)$$

The square roots of G'' of 10% (g/dL) solutions of (s-PVA)s of several different (DS)s in water are plotted against the square root of ω in Figure 6. This plot is the indirect method that determines the existence of internal order in the polymer using intercepts on the plot. Some specimens produce nonzero intercepts on the Casson-type plot, pointing out the existence of yield stress of positive values and pseudostructure in the system. On the plot, s-PVA with DS of 97.5% showed a very great value of nonzero yield stress. This implies that s-PVA over the critical point between 96.5 to 97.5% has rich internal orders.

Variation of relaxation time of 10% (g/dL) solutions of (s-PVA)s in water with ω is shown in Figure 7. The relaxation time (λ) under dynamic shear may be calculated as,¹⁹

$$J' = G'/([\eta^*]\omega)^2 = \lambda/[\eta'] \quad (3)$$

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)s reduced with ω , and λ of (s-PVA)s except to specimen with DS of 97.5% were hardly changed with DS , but s-PVA of DS of 97.5% showed the higher value than different (s-

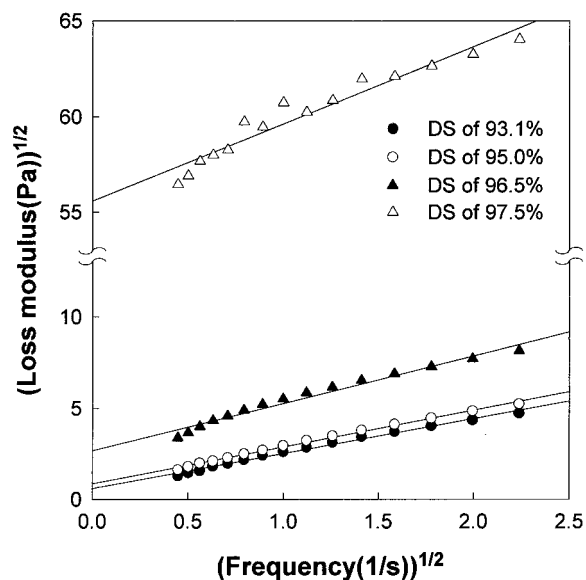


Figure 6 Square root of loss modulus of 10% (g/dL) s-PVA/water solution with square root of frequency at 30°C.

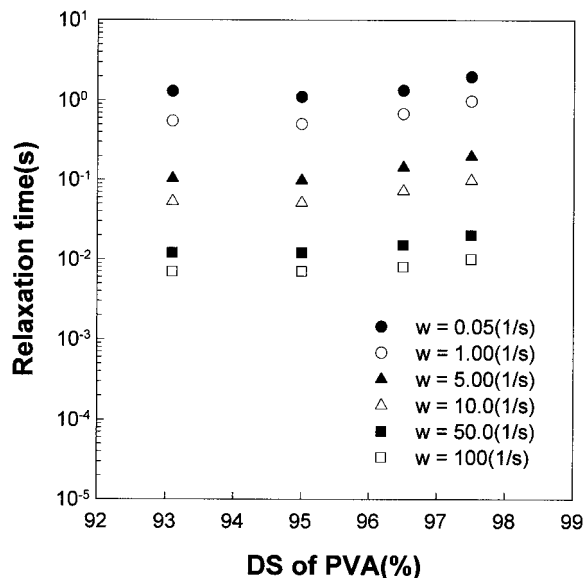


Figure 7 Relaxation time of 10% (g/dL) s-PVA/water solution at various degree of saponification at 30°C.

PVA)s. This indicates that s-PVA of *DS* of 97.5% has a long relaxation time due to internal strong structure.

CONCLUSIONS

The effect of *DS* of s-PVA was identified on the rheological properties of s-PVA/water solution by preparing four (s-PVA)s with different (*DS*)s, similar tacticity, and similar molecular weight. As expected, *DS* has a profound influence on the viscoelastic properties of PVA solution. S-PVA, with higher *DS*, had the higher η^* and the greater shear thinning effect. Because s-PVA of high *DS* has a regularly arranged structure and the large number of hydrogen bond and s-PVA molecules are stiff and oriented well, it had the higher values of G' and G . Especially, s-PVA of *DS* of 97.5% had the higher shear thinning effect than other three (s-PVA)s, and nearly constant value of G' and G with

ω . This suggested that s-PVA molecules are more oriented as *DS* increased. At (*DS*)s of 93.1 to 96.5%, it showed a lower yield stress with poor internal ordered structure; however, s-PVA of *DS* of 97.5% had the greater pseudostructure like a mesophase with a higher nonzero yield stress and larger relaxation time. In the near future, we will report the effects of tacticity and molecular weight on the rheological properties of s-PVA/water solution.

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