교대배열 폴리비닐알코올 수용액의 유변학적 특성에 미치는 비누화도의 효과

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

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1. Introduction

Recently, it was made the syndiotactic poly(vinyl alcohol) (PVA) of high stereoregularity, which was made with poly(vinyl pivalate) (PVPi) for precursors of PVA[1]. But, if PVPi is only used for precursors, syndiotactic PVA prepared cannot be dissolved in water. To prepare water soluble syndiotactic PVA, the molecular parameters of PVA such as molecular weight, stereoregularity, and degree of saponification should be controlled by copolymerization of VPi and VAc with various monomer feed ratio and by saponification of copoly(VPi/VAc). PVA is generally prepared by saponifying poly(vinyl ester) precursors such as poly(vinyl acetate) (PVAc) and poly(vinyl pivalate) (PVPi) since vinyl alcohol rearranges to give its tautormer, acetaldehyde, which cannot be polymerized[2,3]. So degree of saponification, one of molecular parameters of PVA is an important factor in preparation of PVA. It is also thought that the degree of saponification has a significant influence on the rheological properties of PVA because the difference in chemical composition gives rise to different physical properties[4,5]. It is important to characterize the rheological properties of PVA solution in order to manufacture the various products such as fiber, film, adhesive, sizing agent, with excellent properties[6]. It is object of this study to research about rheological properties which are showed to various degrees of saponification, about rheological behaviors to many rheological factors.

2. Experimental

2.1. Preparation of PVA

A water-soluble syndiotactic PVA was prepared by copolymerization of vinyl pivalate (VPi) and vinyl acetate (VAc) with feed ratio of mol_{VPi}/mol_{VAc} (2/8) and saponification of copoly(VPi/VAc). Copolymerization was performed with conversion of 25 to 35%, at 40 ℃, adding 5×10^{-4} mol/mol ADMVN for initiator[1]. To prepare specimens with various degrees of saponification, quantities of 40% sodium hydroxide aqueous solution appropriately were controlled and saponification was performed at 30 ℃ for 24 h.

2.2. Determination of degree of saponification and s-diad content

Degree of saponification and stereoregularity of prepared PVA was analyzed with using a proton-nuclear magnetic resonance (^{1}H-NMR) spectrometer, for solutions of PVA in DMSO. Degree of saponification was calculated by research of left content of acetyl group and pivaloyl group from about 1.1 ppm, 1.7 ppm peaks, and s-diad was calculated by 4.3, 4.5, 4.7 ppm peaks.

2.3. Preparation of PVA solution

Syndiotactic PVA was not dissolved in water at room temperature but dissolved in round flask at 100~110 ℃ for 1 hour to be 10 wt% solution.

2.4. Measurement of rheological properties of PVA solution

For rheological measurement, Advanced Rheological Expansion System(ARES) manufactured in Rheological Scientific, Inc. was used. In ARES measurement, a cone and plate type flow cell with diameter of 25 mm and degree of 0.04 rad was used. Test type and measurement type were strain control and dynamic frequency sweep test, respectively. Experimental was measured at fixed strain of 5%, at 25 ℃, at low frequency with range of 10^{-1} to 10^{2} rad/s.

3. Results and discussion

It is shown that the plot of complex viscosity against frequency for 10 wt% solutions of syndiotactic (PVA)s of different degrees of saponification in water at 25 ℃, respectively, in Figure 1. As frequency increase, all curves decrease and (PVA)s of higher degree of saponification have the greater curve slopes in decreasing. This indicates that if degree of saponification increases, syndiotactic PVA is oriented well and its solution has the greater heterogeneity, shear thining effect. Figure 2 shows the plot of storage modulus against loss modulus for the solutions of four (PVA)s in water with different degrees of saponification. The slope of homogeneous isotropic solution such as atactic PVA is in the vicinity of 2 irrespective of different factors, but the slope of heterogeneous solution such as syndiotactic PVA approaches in the near by 1[7]. In the plot, even if it has a small difference, the heterogeneous structure grows as degree of saponification increases. Bingham flow behavior gives rise to a non-zero yield stress, which represents that shear stress is in proportion to shear rate at the higher range than yield point and shear rate is not changed at the lower range than yield point. The yield stress of heterogeneous systems can be determined from the casson plot, similarly the intercept of loss modulus (G'') axis (G''_0) on the plot of the square root loss modulus (G'') against square root of frequency (ω) may be regarded as a measure of yield stress in dynamic shear measurement as[8]

$$G''^{1/2} = G''_0{}^{1/2} + K'\omega^{1/2}$$

All specimens have non-zero intercepts on the Casson-type plot, suggesting that pseudostructure exists in the system. Yield stress increases with degree of saponification, implying that syndiotactic (PVA)s of higher degrees of saponification have the greater properties of pseudostructure.

4. Reference

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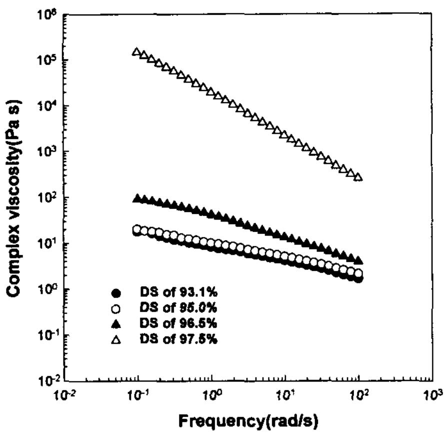

Figure 1. Complex viscosity curve of syndiotactic PVA solution in water

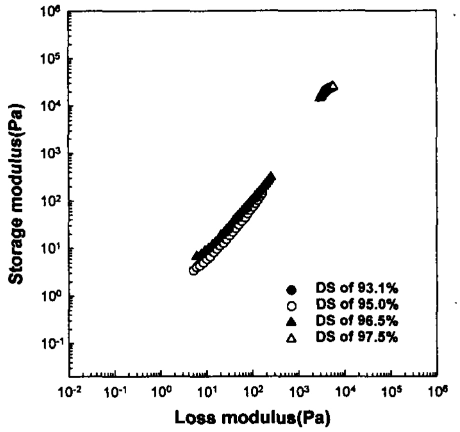

Figure 2. Plot of storage modulus vs loss modulus of syndiotactic PVA solution in water

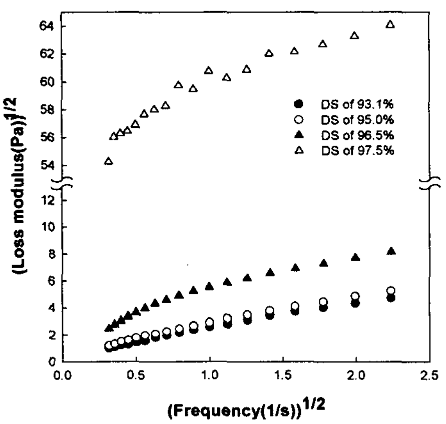

Figure 3. Plot of square root of loss modulus vs square root of frequency for 10wt% solution of syndiotactic PVA in water