

일욕 현탁중합과 비누화에 의한 고분자량 폴리비닐알코올의 고수율 제조 및 그의 특성해석

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Synthesis of High Molecular Weight Poly(vinyl Alcohol) with High Yield by 1 Batch Suspension Polymerization and Saponification and Its Characterization

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1. Introduction

The poly(vinyl alcohol) (PVA) fiber is recognized as the best candidate because of its good mechanical properties together with excellent resistance to alkalis[1-5]. PVA cannot be prepared by the direct polymerization due to tautomerism of vinyl alcohol monomer. Thus PVA is obtained by the saponification of poly(vinyl ester) like poly(vinyl acetate) (PVAc). In general, four polymerization methods of vinyl acetate (VAc) (bulk, solution, emulsion, and suspension) have been known. Commercially important polymers and copolymers were manufactured by the suspension polymerization. High conversion can be achieved by suspension polymerization than by other polymerization methods[6-7]. Suspension polymerization generally has been used for the production of polymer particles of diameter in the range of 80-700 μ m. Polymer particles produced in suspension polymerization have applications in chromatographic separations, biochemical, bioengineering, drug delivery system, and cancel cell-killing embolic materials[8-9]. In this study, we tried continuous saponification process of PVAc prepared by suspension polymerization of VAc using a low-temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN). Generally, all PVA industries use 2 batch process in producing PVA. However, in this study, PVA was prepared by 1 batch process, which is very simple and effective method of continuous saponification process with high yield PVAc.

2. Experimental

2.1. Materials

VAc purchased from Shin-Etsu was washed with an aqueous solution of NaHSO₃, and water and dried over anhydrous CaCl₂, and then distilled under reduced pressure of nitrogen. The initiator ADMVN (Wako Co., 99%) was recrystallized twice from absolute methanol before use. PVA with molecular weight of 127,000 and degree of saponification of 88% (Aldrich Co.) was used as a suspending agent. Other extra-pure grade reagents were used without further purification. Water used for all the procedures was deionized.

2.2. Polymerization and Saponification

Suspension agent was dissolved in water under nitrogen atmosphere and constant stirring in a 250 ml reactor fitted with a condenser. VAc monomer along with the ADMVN after degassing were added all at once at a fixed polymerization temperature. After polymerization, immediately, the PVAc was saponified in alkali solution, and the saponification of PVAc was stirred for 2 day at constant temperature. Prepared PVA was filtered and washed with distilled water. Polymerization conditions are listed in Table 1.

2.3. Acetylation of PVA

A mixture of 1 g of PVA, 2 ml of pyridine, 20 ml of acetic anhydride, and 20 ml of acetic acid was stirred in a three necked flasks at 100 °C for 24 h under an atmosphere of nitrogen. Then the mixture was poured into cold water to precipitate PVAc. The PVAc thus produced was filtered and purified by repeating the reprecipitation from methanol and water.

2.4. Characterization

The number-average degree of polymerization (P_n) of PVAc was calculated by using Eq.1

$$[\eta] (\text{dL/g}) = 8.91 \times 10^{-3} [P_n]^{0.62} \quad (\text{in benzene at } 30 \text{ }^\circ\text{C}) \quad (1)$$

where $[\eta]$ is the intrinsic viscosity and P_n is a number-average degree of polymerization of PVAc. On the other hand, molecular weight of PVA was determined from that of PVAc produced by acetylation of PVA using Eq. (1).

The syndiotactic diad (S-diad) contents of PVA were determined using a proton-nuclear magnetic resonance (¹H-NMR) spectrometer (Varian, Sun Unity 300). The degree of saponification of PVA was determined by determined by weight loss after saponification and by the ratio of methyl and methylene proton peaks in the ¹H-NMR spectrum.

The degree of branching for the acetyl group (DB) of PVAc is calculated by Eq. (2)[2],

$$DB = (DP_1/DP_2)-1, \quad (2)$$

where DP_1 is P_n of PVAc and DP_2 is P_n of PVA prepared by saponifying PVAc.

3. Results and Discussion

Figure 1 shows the scanning electron micrograph of PVA beads prepared by continuous saponification process. We obtained the PVA beads with spherical shape, but particle size distribution of PVA beads was not uniform due to preparation of 1 batch process. Effect of initiator concentration on the conversion of VAc into PVAc suspension-polymerized at 50 °C is shown in Figure 2. The conversion rate increased as the ADMVN concentration was increased as the ADMVN concentration was increased, and the maximum conversion was reached over 95% all of the three initiator concentrations. Figure 3 shows plots of (P_n)s of PVA prepared 1 batch process at three different polymerization temperatures. The P_n of PVA obtained continuous process with high yield was over 5000. Figure 4 shows the effects of polymerization temperatures and initiator concentrations on the S-diad content of PVA prepared by 1 batch process. We prepared PVA with S-diad contents of 51-53%, which are described as atactic PVA. Properties of PVA beads prepared by 1 batch process were not different compared with those of general suspension polymerization.

4. Reference

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Table 1. Suspension polymerization conditions of VAc

Type of initiator	ADMVN
Type of suspension agent	PVA
Initiator concentration (mol/mol of VAc)	0.0002, 0.0005, 0.001
Suspending agent concentration (g/dl of water)	0.1
VAc/water (l/l)	1/2
Rpm	300, 400, 500, 600
Temperature (°C)	30, 40, 50

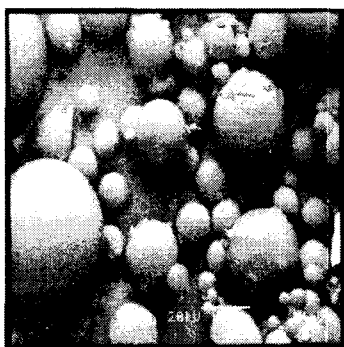


Figure 1. Scanning electron micrograph of PVA beads prepared by 1 batch process

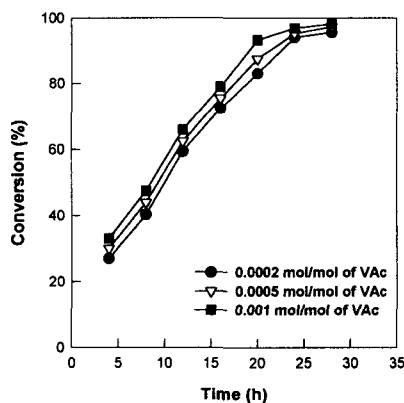


Figure 2. Conversion of VAc into PVAc obtained by suspension polymerization of VAc using ADMVN at 50 °C, suspension agent concentration of 0.5 g/dl of water, and VAc/water of 0.5 l/l

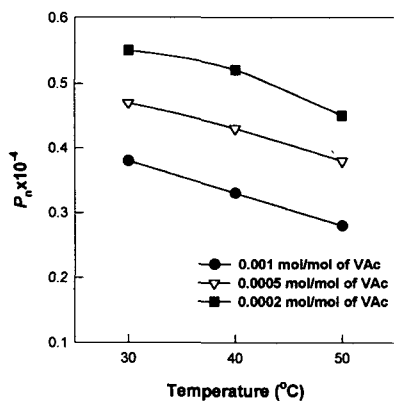


Figure 3. Plots of (P_n)s of PVA prepared by 1 batch process at 50 °C using suspension agent concentration of 0.5 g/dl of water and VAc/water of 0.5 l/l

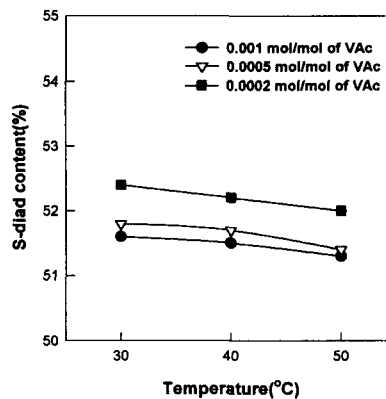


Figure 4. Effects of polymerization temperature and initiator concentration on the S-dial content of F prepared by 1 batch process