AAPH를 이용한 아세트산비닐의 유화중합

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Emulsion Polymerization of Vinyl Acetate Using AAPH

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1. Introduction

Vinyl acetate monomer can be polymerized through bulk, solution, emulsion, and suspension polymerization processes. However, in the preparation of PVA from bulk or solution polymerization, there are several technical limitations for obtaining high yield and high molecular weight simultaneously. Thus, the improvement of polymerization method is necessary to prepare the PVA with high yield and high molecular weight because that the difficulty in control of high viscosity and in removal of the heat of polymerization, which might lead to side reactions like branching. In general, it is known that molecular weight and conversion of monomer to polymer were increased simultaneously by emulsion polymerization. Emulsion polymerization process among many polymerization methods for preparation the high molecular weight atactic PVA has studied[1-3]. In this study, we conducted the emulsion polymerization of VAc with AAPH (2,2'-azobis(2-amidinopropane) dihydrochloride) as an initiator and sodium dodecylsulfate (SDS) as an emulsifier to prepare PVA with high molecular weight and high yield by controlling the polymerization factors. The effect of polymerization factors that affect the conversion and the molecular weight is investigated. And, PVA/PVAc (skin/core) microspheres were prepared through the surface saponification of PVAc microspheres. Monodispersed PVA/PVAc microspheres with uniform size distribution via emulsion polymerization of VAc and surface saponification of resultant PVAc can be used as biomaterials like embolic materials and electrical applications like toner particles.

2. Experimental

2.1. Materials and method

VAc was washed with an aqueous solution of $NaHSO_3$ and water and dried over anhydrous $CaCl_2$, followed by distillation under reduced pressure of nitrogen. The initiator, AAPH, the emulsifier, SDS, and other reagents were used without further purification. Water used for all the procedures was deionized. Water and emulsifier in a 250 ml three-necked round bottom flask were flushed with nitrogen through the pyrogallol-alkaline solution trap and agitated for 30 min and then VAc was added into the flask with slow agitation. After 30 min, the initiator, AAPH, was added into the reaction mixture at predetermined polymerization temperature. Particle shaped polymer resin obtained by deemulsification using Na_2SO_4 solution was washed with warm water and dried in a vacuum oven at 60 ℃ for 1 day.

2.2. Surface saponification of PVAc microspheres

PVAc microspheres obtained by emulsion polymerization were sieved with standardized mesh

sieves. 0.5 g of PVAc microspheres were added slowly into a 500 ml flask was filled with 200 ml alkaline solution with stirring at predetermined temperature. After predetermined time, microspheres were poured in cold water and filtered with cool water several times and dried in vacuum oven at 40 ℃

2.3. Characterization

The conversion of VAc into PVAc was obtained from the percent ratio of the weight of polymer formed to the weight of monomer used and the molecular weight of PVAc and the degree of branching (DB) were calculated by using Eq. (1) and Eq. (2)[4] respectively.

$[\eta] = 8.91 \times 10^{-3} [P_n]^{0.62}$ in benzene at 30 ℃ (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).

$DB = (DP_1/DP_2) - 1$ (2)

Where DP_1 is P_n of PVAc and DP_2 is P_n of PVA prepared by saponifying PVAc in Eq. (2). The surface morphology of microsperes were observed using optical microscope (Olympus co. Japan, BH-2) and scanning electron microscope (SEM, Hitachi co. Japan, S-4100).

3. Result and discussion

It is important to select the optimum emulsion polymerization factors among the emulsion polymerization conditions that affect the conversion and molecular weight such as initiation method, volume ratio of monomer to water, amount and type of initiator, amount and type of emulsifier, agitation method and agitation speed, polymerization temperature, and polymerization time. In general, it has been reported that the values of volume ratio of monomer to water, amount of initiator and oxygen and polymerization temperature should be minimum. Moreover, amount of emulsifier is optimum one to obtain the high molecular weight polymer relatively[1]. The P_n of PVAc and PVA obtained by emulsion polymerization at 50 °C was higher than that of PVAc and PVA obtained by emulsion polymerization at 60 °C.

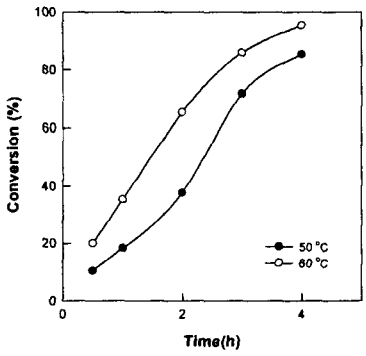

Fig 1. Plots of conversion of VAc into PVAc obtained by emulsion polymerization of VAc at 50 and 60 ℃ vs. polymerization times.

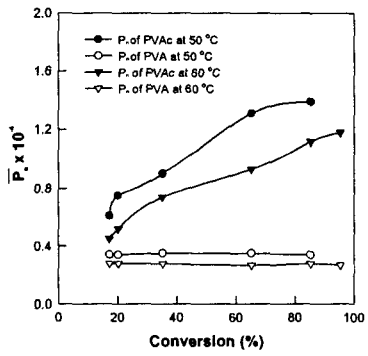

Fig 2. Plots of P_n of PVAc obtained by emulsion polymerization of VAc at 50 and 60 ℃ and resulting PVA vs. conversions.

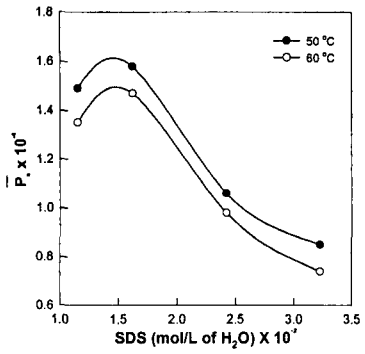

Fig 3. Effect of the amount of SDS on the P_n of PVAc (polymerization condition: AAPH 3.7×10^{-3} mol/L of H_2O ; 50 and 60 ℃; 4 h).

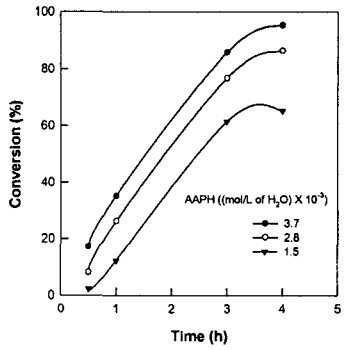

Fig 4. Plots of conversion of VAc obtained by emulsion polymerization of VAc at 60 ℃ vs. AAPH concentrations.

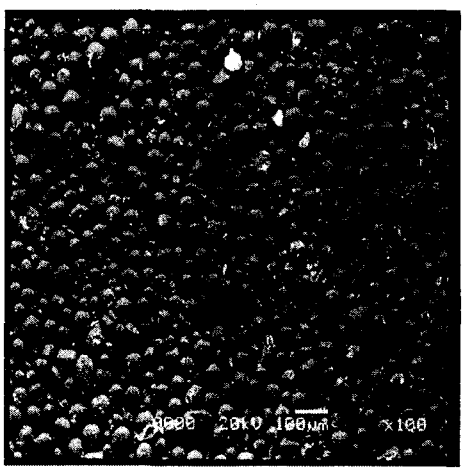

Fig 5. Scanning electron micrograph of PVAc microspheres obtained by the emulsion polymerization of VAc (before separation).

Fig 6. Optical micrograph of PVA/PVAc microspheres with skin/core structure obtained by surface saponification in alkali solution at 40 ℃ for 10 h.

Fig 1. illustrates conversion-time plots for temperatures of 50 °C and 60 °C. The conversion of VAc into PVAc represented 80 - 90% in 4 h and the rate of conversion was increased with increasing polymerization temperature. The rate of conversion was high at the early stage of polymerization at both temperatures but the ultimate conversion was lower. Increase in conversion with time was abruptly diminished during polymerization, probably due to the inefficient transfer and diffusion of heat because of formation of PVAc at the early stage of polymerization. Effect of polymerization temperature on the conversion of VAc into PVAc and P_n of PVAc obtained by emulsion polymerization of VAc and resulting PVA is shown in Fig 2.. The P_n of PVAc was increased with increasing conversion, but the P_n of PVA was almost uniform because of frequent chain transfer reactions above a certain extent of initial conversion in emulsion polymerization. As a rule, the branches occurred by chain transfer and by disproportionation termination are hydrolyzed via saponification process. Thus, (P_n)s of PVA are almost constant regardless of each

(P_n)s of precursor, PVAc[1]. Fig 3. shows the effect of the amount of SDS on P_n of PVAc at each polymerization temperatures. The emulsion system was unstable below an SDS concentration of 1.15 x 10^{-2} mol/L of H_2O because these concentrations of SDS was not enough to effectively emulsify VAc so that, the effective polymerization could not occur. In an optimum emulsifier concentration, higher molecular weight of PVAc was synthesized than in other emulsifier concentrations at same polymerization condition. Fig 4. illustrates conversion-time plots for polymerization temperatures of 60 °C vs. AAPH concentrations. It has been reported that initiator concentration must be optimum value to raise conversion and molecular weight. The conversion rate was increased as the AAPH concentration was increased. High ultimate conversion up to 95% was obtained at AAPH concentration of 3.7 x 10^{-3} mol/L of H_2O. The P_n of PVAc increased as the AAPH concentration was decreased. PVAc microspheres obtained by emulsion polymerization of VAc were saponified in alkaline solution for determined time and as a result, PVA/PVAc skin/core microspheres, revealing about 16% of the degree of saponification, were prepared. Fig 5. is the SEM photograph of PVAc microspheres obtained by emulsion polymerization of VAc. The average diameters were in the range of 125 - 150 μm. Fig 6. is the optical micrograph of PVA/PVAc microspheres with skin/core structure obtained by the surface saponification in alkaline solution. In this study, the effect of polymerization temperature on the DB for acetyl group of PVAc at a similar conversion was investigated. DB at 60 °C was 3.6 - 3.7 and DB at 50 °C was 3. 4 - 3.6. Like this, the extent of increasing DB was more prominent at higher polymerization temperature. Crystal melting temperatures of PVA obtained by saponification of PVAc at emulsion polymerization temperature of 50 °C and 60 °C, respectively, were measured on a differential scanning calorimeter (DSC).

4. Conclusion

Conversion of VAc into PVAc obtained at higher polymerization temperature is higher than that at lower temperature. Molecular weight of PVAc at lower temperature is higher than that of PVAc at higher temperature. PVA having maximum P_n of 3,400 could be prepared by complete saponification of PVAc having maximum P_n of 13,900 obtained with 1.62 x 10^{-2} mol/L of H_2O of SDS and 3.7 x 10^{-3} mol/L of H_2O of AAPH at 50 °C. PVAc with high conversion above 95% was prepared at same content of SDS and AAPH at polymerization temperature of 60 °C, but P_n of this PVAc was 11,200. DB for acetyl group in this polymerization system was about 3.0 - 3.7. Emulsion polymerization of VAc is a powerful method for producing PVAc microspheres with various particle sizes and uniform size distribution to a high yield. The diameter of precursor PVAc microspheres was in the range between 60 μm and 100 μm. These prepared PVAc microspheres were surface-saponified, and then PVA/PVAc microspheres with skin/core structure were obtained. Separated PVA/PVAc microspheres are expected to be formed with coloring matter or charge control agent.

5. References

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