

폴리비닐알코올 수용액의 점성도 변화와 겔화 거동에 미치는 아세트산비닐의 유화중합조건의 영향

류원석, 염정현*, 이성민, 구강, 지병철*
영남대학교 섬유패션학부, *경북대학교 염색공학과

Effect of Emulsion Polymerization Conditions of Vinyl Acetate on the Viscosity Fluctuation and Gelation Behavior of Aqueous Poly(vinyl alcohol) Solution

Won Seok Lyoo, Jeong Hyun Yeum*, Seong Min Lee, Kang Koo, and
Byung Chul Ji*

School of Textiles, Yeungnam University, Kyongsan, Korea

**Department of Dyeing and Finishing, Kyungpook National University, Taegu, Korea*

1. Introduction

Poly(vinyl alcohol) (PVA) cannot be prepared from its structural monomer, vinyl alcohol (VA), for the instability of VA. Therefore saponification of precursors, such as poly(vinyl acetate) (PVAc), is unavoidable process. Molecular parameters of PVA can be effectively controlled due to these separated preparation methods; polymerization and saponification[1-7]. Complete saponification of precursor possibly results in PVA of linear molecular structure with hydroxyl group for each repeating unit. The many hydroxyl groups cause it to have a high affinity to water, with strong hydrogen bonding between the inter- and intramolecular hydrogen bonding of adjoining hydroxyl groups. It is well known that with an increase in the number of acetate groups, the negative heat of dissolution increases, the critical temperature of the phase separations is lowered, and the solubility at high temperatures decreases gradually[8].

Generally, viscosity of aqueous PVA solutions is considered as function of molecular weight and concentration of PVA. But the effects of structural regularity cannot be ignored. Molecular irregularities, including 1,2-glycol structure, are mainly determined by polymerization temperature of precursor. PVAc polymerized at higher temperature has more chances of forming head-to-head linkages for abundant activation energy[8]. But its effects on the physicochemical behavior of aqueous PVA solutions were not fully appreciated yet.

The object of our present study is to examine the gelation process of PVA by ageing and the effects of polymerization temperature. To achieve these purposes, completely saponified (PVA)s of similar molecular weights were prepared from various (PVAc)s polymerized at 40, 50, and 60 °C. (PVA)s having gradually differentiated molecular weights were also prepared at the same polymerization temperature.

2. Experimental

2.1 Materials

Vinyl acetate (VAc) purchased from Shin-Etsu was washed with an aqueous solution of NaHSO₃ and water and dried over anhydrous CaCl₂, flowed by distillation under reduced pressure of nitrogen. The other materials were used without further purification. Emulsion polymerizations were carried out in a three-necked round bottom stirred reactor. Polyoxyethylene nonylphenylether sodiumsulfate (LWZ, Cao Co.) and potassium peroxy disulfate (KPS) were used as emulsifier and initiator, respectively. The agitation was conducted at 250 rpm using a Teflon half-moon-shaped impeller blade mounted on a glass shaft and inserted in a glass adapter. The flask was purged with nitrogen for 30 minutes at room temperature and then heated. Once the polymerization temperature was attained, LWZ and VAc were added to the reactor. After 15 minutes, KPS was added. The reaction product was purified by reprecipitating three times into water, and then dried in vacuum at 50 °C. To a solution of 2 g of PVAc in 100 ml of methanol, 2.5 ml of 40% NaOH aqueous solution was added, and the mixture was stirred for 5 hours at room temperature to yield PVA. PVA produced was filtered and washed well with methanol. PVA samples showed the number-average degree of polymerization (P_n) of 2,300-3,300 and indicated the degree of saponification of over 99%. *Table I* shows the specification of (PVA)s used in this study.

2.2 Viscosity Measurement

PVA1-5 were dissolved in water at 80 °C to form stable aqueous PVA sol solutions without turbidity. Concentrations were varied 3, 5, and 7% (g/dl) for all specimens. The Ubbelodhe type of capillary viscometer was rinsed thoroughly many times with distilled water and dried with acetone initially as well as after each run. A constant temperature water bath with error range of 0.01 °C was used. A clamp was set up so the viscometer is placed inside the water bath, so the fiducial marks were visible below the water level. The relative viscosity (η_r) of the aqueous PVA solution was determined with a predetermined time interval at 30 and 60 °C, respectively.

3. Results and Discussion

In this study, (PVA)s having (P_n)s of 3,300, 2,800, and 2,300 were prepared from (PVAc)s emulsion polymerized at 60 °C, respectively. These (PVA)s were dissolved in water with concentrations of 3, 5, and 7%, respectively, and aged for a time. Viscosities of PVA solutions increased with an increase in the molecular weight, which was in good agreement with generally accepted tendency. This tendency is repeated in 5% solutions aged at 30 and 60 °C proved in *Figure 1*.

Figure 2 shows the viscosity changes of 3% aqueous solutions of PVA2, PVA4, and PVA5 aged at 30 and 60 °C with ageing time. Viscosities of PVA2, PVA4, and PVA5 maintain constant values. This value, however, for PVA2 shows relatively low compared with those of PVA4 and PVA5. Viscosity of PVA2 aged at 30 °C is even lower than those of PVA4 and PVA5 aged at 60 °C. This cannot be explained by classical theory solely depending on molecular weight and gel structure derived from molecular parameters can be considered as a new candidate. Viscosity of PVA solution may be affected by crosslinked molecular size. If there is no difference in molecular weights, crosslinked molecular size can be affected by crosslinkability of polymer chains. It is well known that polymer chains having superior regularity easily form physical crosslinking. Therefore, PVA4 and PVA5, which have more regular chain structure due to lower polymerization temperatures of (PVAc)s may be suspected to have higher values of crosslinked molecular size than that of PVA2.

4. References

- 1) W. S. Lyoo and W. S. Ha, *J Polym Sci Polym Chem* **35**, 55(1997).
- 2) W. S. Lyoo, B. C. Kim, C. J. Lee, and W. S. Ha, *Eur Polym J Short Commun* **33**, 785(1997).
- 3) W. S. Lyoo, J. Blackwell, and H. D. Ghim, *Macromolecules* **31**, 4253(1998).
- 4) W. S. Lyoo, S. G. Lee, J. P. Kim, S. S. Han, and C. J. Lee, *Colloid Polym Sci* **276**, 951(1998).
- 5) W. S. Lyoo and W. S. Ha, *Polymer*, **37**, 3121(1996).
- 6) W. S. Lyoo and H. D. Ghim, *Polymer*, **in press** (2001).
- 7) W. S. Lyoo, S. S. Han, J. H. Kim, W. S. Yoon, C. J. Lee, I. C. Kwon, J. Lee, B. C. Ji, and M. H. Han, *Die Angew. Makromol. Chemie*, **271**, 46(1999).
- 8) C. A. Finch, In *Polyvinyl Alcohol-Development*, Ed.; John Wiley & Sons: West Sussex, 1992.

Table I. (PVA)s used in viscometric experiment.

Sample No.	P_n	Polymerization temperature (°C)
	PVA (PVAc)	
PVA1	3,300 (18,000)	60
PVA2	2,800 (17,000)	60
PVA3	2,300 (8,800)	60
PVA4	2,800 (8,000)	50
PVA5	2,800 (6,700)	40

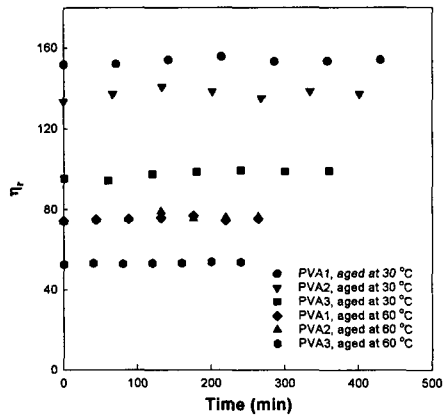


Figure 1. Relative viscosities of 5% aqueous solutions of PVA1, PVA2, and PVA3 with ageing time.

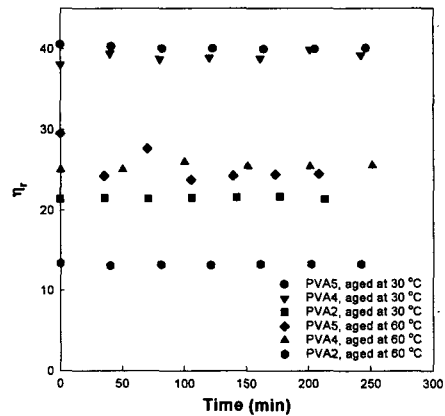


Figure 2. Relative viscosities of 3% aqueous solutions of PVA2, PVA4, and PVA5 with ageing time.