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Mechanochemical synthesis and characterization of poly(vinyl chloride)-*block*-poly(vinyl alcohol) copolymers by ultrasonic irradiation

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Summary

Mechanical degradation and mechanochemical reaction in heterogeneous systems of the solid poly(vinyl chloride)-poly(vinyl alcohol) aqueous solutions have been studied by ultrasonic irradiation at 30 °C. The rate of decrease in the viscosity-average degree of polymerization of the degraded poly(vinyl chloride) was much faster than that of the degraded poly(vinyl alcohol). Mechanochemical reaction occurred by free radicals produced from the chain scissions of both polymers by ultrasonic waves. The copolymer was obtained and the molar ratio of the vinyl chloride and the vinyl alcohol units in its copolymer can be determined. In addition, the changes in the composition of the total block copolymer, the unreacted poly(vinyl chloride), and the unreacted poly(vinyl alcohol) were obtained.

Introduction

The heat stability of poly(vinyl chloride) is of great importance in its molding and fabricating. An investigation of the particular stability has been advanced widely from the directions of the polymerization kinetics of vinyl chloride, the function of heat stabilizer, and the techniques of the molding and fabricating. In particular, it is known that polyols of an auxiliary agent to heat stabilizer as metallic soap exhibit excellent retardation effect on the heat coloring of poly(vinyl chloride) film (1). This is because a complex is formed between the metallic chloride produced by heat treatment and polyols (1). When polyhydric alcohols of low molecular weight as polyols have been used, those alcohols are generated as the bleeding on the film. In addition, when poly(vinyl alcohol) as polyol has been used, its compatibility for poly(vinyl chloride) is very poor.

On the other hand, the another disadvantage of poly(vinyl chloride) is poor in the wettability. In particular, the wettability of the surface of its film in the presence of water vapor in much larger quantities is very poor. This

is because poly(vinyl chloride) does not have hydroxy groups in its molecule.

In order to improve these disadvantages, it is thought that a block copolymer or graft copolymer composed of both a chain having the compatibility for poly(vinyl chloride) and a chain having the retardation effect on the heat coloring or hydroxy groups in one molecule is utilized as a improvement agent. Therefore, the author has been used an ultrasonic waves for the synthesis of the block copolymer as one of such copolymers. In earlier papers, the studies of mechanochemical block copolymerizations in suspensions systems of poly(vinyl alcohol) aqueous solutions-methyl methacrylate (2) and in heterogeneous systems of the solid poly(vinyl chloride)-styrene-sodium dodecyl sulfate aqueous solutions (3) by ultrasonic irradiation were shown respectively.

On the other hand, mechanochemical reaction in heterogeneous systems of a solid polymer A-polymer B solution by ultrasonic irradiation has not been entirely studied. The present paper is concerned with mechanochemical reaction in heterogeneous systems of the solid poly(vinyl chloride)-poly(vinyl alcohol) aqueous solutions affected by ultrasonic irradiation.

Experimental

Materials

Suspension polymerized poly(vinyl chloride) sample PVC (Kane Vinyl 25L-56, Kanegafuchi Chemical Industry Co., Ltd.) was purified by extraction with hot pure benzene and methyl alcohol for 80 hr. The average particle diameter D of PVC and porosity P in the PVC-grain particle were 89 μ*m* and 0.637 ml Hg/g PVC. The viscosity-average degree of polymerization $\overline{P}_v$ was 4,220. Poly(vinyl alcohol) PVA (Gohsenol NH-26, Nippon Synthetic Chemical Industry Co., Ltd.) was purified by extraction with hot pure benzene and methyl alcohol for 80 hr. The viscosity-average degree of polymerization $\overline{P}_v$ was 2,030. The water H_2O was doubly distilled. Purified methyl alcohol was used as a precipitating agent. Purified tetrahydrofuran THF was used as a solvent of fractional extraction of poly(vinyl chloride)-*block*-poly(vinyl alcohol) copolymers and a solvent for the determination of the solution turbidities of polymers. Purified cyclohexanone was used as a solvent for the measurement of the viscosity-average degree of polymerization of PVC.

Apparatus and Procedures

The porosity P in the PVC-grain particle was determined with a digital readout porosimeter (Model 5-7121B, American Instrument Co., Inc.) under absolute pressure from 20 *psi* to 1,000 *psi* at 25 °C (3).

An ultrasonic generator (Model USV-150V, Cho-Onpa Kogyo Co., Ltd.) equipped with a stepped horn of stainless steel on a magnetostrictive nickel vibrator of 25 kHz. The output of this generator had an intensity of 150 watts.

In a typical run for mechanochemical reaction, 3.000 g of the solid PVC, 50.0 ml of PVA aqueous solution (PVA: 1.000 g) were poured into a 300 ml special glass reaction vessel.

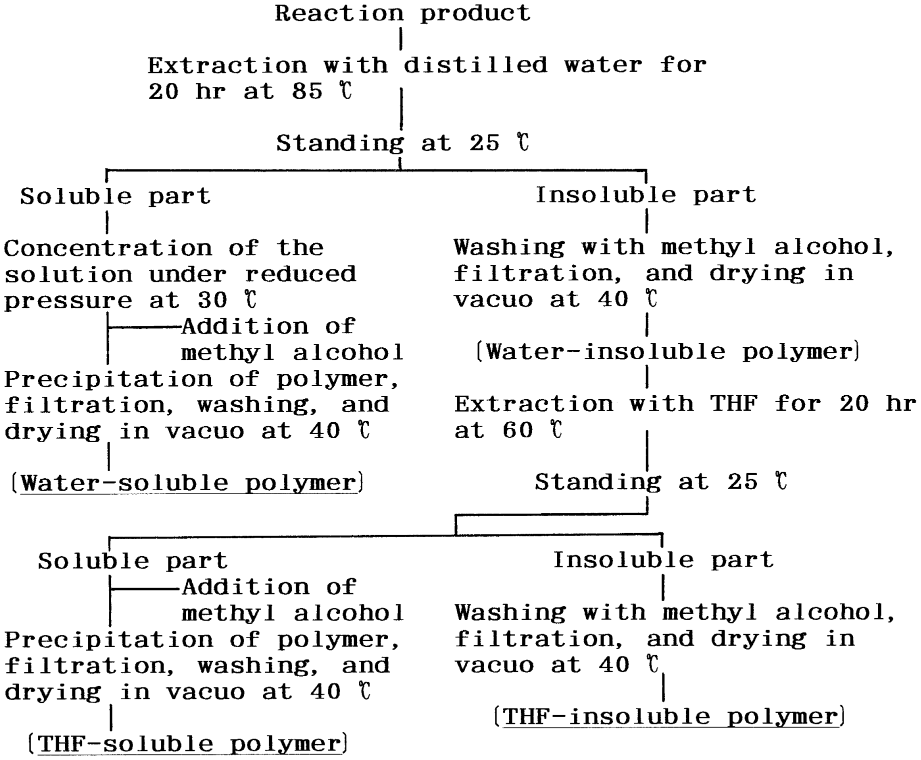
Ultrasonic irradiation was carried out for 30, 50, 90, 120, 150, and 180 min with the stepped horn in contact with the surface of the solution under one atmospheric pressure of dry nitrogen at 30 ± 0.1 °C. After the reaction, the solution was poured into a large amount of methyl alcohol containing *p*-benzoquinone inhibitor. The precipitated polymer was filtered, washed, and dried in vacuo at 40 °C. The reaction products were fractionated by the procedure shown in Table 1. The compositions of the block copolymer and unreacted PVC in the polymer of both the water-insolubilization and the THF-solubilization were determined by turbidimetry (3).

In other experiments, mechanical degradations of PVC and PVA were carried out by the irradiation of the solid PVC-PVA aqueous solutions in the presence of *p*-t-butylcatechol inhibitor. The degraded PVC and PVA were fractionated in accordance with the procedure of Table 1. The viscosity-average degrees of polymerization $\overline{P}_v$ of PVC and PVA at various stages of the degradation were determined by viscometry.

Determination of Turbidity

The solution turbidity of the polymer of both the water-insolubilization and the THF-solubilization was determined with a turbidimetric titrator (Model NT-301H, Kotaki Works Co., Ltd.) at 30 °C. The solvent and precipitating agent were THF and distilled water. The polymer concentration

TABLE I. Method of fractional extraction



was 0.0600 g/l.

Determination of the Viscosity-Average Degrees of Polymerization

The viscosity-average degrees of polymerization $\overline{P_v}$ of PVC and PVA at various stages of mechanical degradation were calculated from the intrinsic viscosities determined in cyclohexanone and distilled water at 30 ± 0.02 °C with the aid of the following relationships (4, 5).

$$\text{PVC: } \overline{P_v} = (\text{Antilog } (\eta) \ / \ 0.197 - 1\ ) \times 500$$

$$\text{PVA: } (\eta) = 66.6 \times 10^{-3}\ \overline{M_v}^{\,0.64} \qquad \overline{P_v} = \overline{M_v} \ / \ 44.1$$

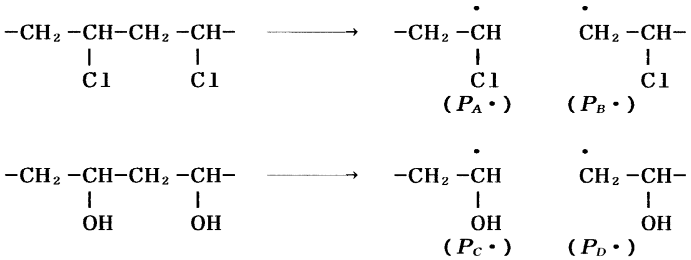
Results and Discussion

Mechanical Degradation

The weight composition and the changes in the viscosity-average degrees of polymerization $\overline{P_v}$ of polymers with respect to the irradiation time in mechanical degradation system are shown in Figure 1. The compositions of the water-insoluble and the water-soluble polymers, namely PVC and PVA, were not changed at before and after the degradation. The values of $\overline{P_v}$ of PVC and PVA decrease rapidly during the initial step, and then slowly approach the constant ordinates. The rate of decrease in $\overline{P_v}$ of the degraded PVC was much faster than that of the degraded PVA. It is thought that the reason for this phenomenon is due to the differences in the initial degrees of polymerization of PVC and PVA. These results show that the chain scissions of both polymers occurred, but both mechanochemical reactions were inhibited completely in the presence of *p-t*-butylcatechol.

Mechanochemical Reaction

The end radicals of PVC and PVA resulted from ultrasonic degradation are expressed in the following manner and these active ends are responsible for the formation of mechanochemical block copolymer.



$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \longrightarrow \underset{(P_A\cdot)}{-CH_2-\underset{Cl}{\dot{C}H}} \quad \underset{(P_B\cdot)}{\dot{C}H_2-\underset{Cl}{CH}-}$$

Mechanical degradation

$$-CH_2-\underset{OH}{CH}-CH_2-\underset{OH}{CH}- \longrightarrow \underset{(P_C\cdot)}{-CH_2-\underset{OH}{\dot{C}H}} \quad \underset{(P_D\cdot)}{\dot{C}H_2-\underset{OH}{CH}-}$$

Mechanical degradation

$$P_A\cdot + P_C\cdot \longrightarrow P_A-P_C$$
$$P_A\cdot + P_D\cdot \longrightarrow P_A-P_D$$
$$P_B\cdot + P_C\cdot \longrightarrow P_B-P_C$$
$$P_B\cdot + P_D\cdot \longrightarrow P_B-P_D$$

Formation of PVC-*block*-PVA copolymers

The compositions of the water-insoluble and the water-soluble polymers with respect to the irradiation time in mechanochemical reaction are shown in Figure 2. The weight proportions of the water-insoluble polymer increased with the progress of the reaction, but those of the water-soluble polymer decreased. In particular, the changes in the composition of both polymers become greater with increasing the additional amount of PVA. The reason for this phenomenon is thought that the number of chain scissions of PVA was increased with increasing the additional amount of PVA and the block copolymer was made up in larger quantities.

Infrared spectra of the water-insoluble and the water-soluble polymers in the reaction product were determined by the KBr disk technique with a Japan Spectroscopic FT/IR-3 spectrophotometer. These spectra are shown as examples in Figure 3. The absorption spectra due to the -OH groups at

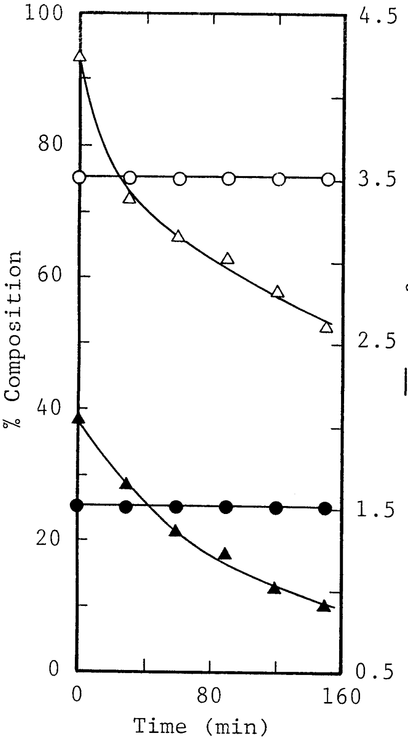


Figure 1. The weight composition and the changes in $\overline{P}_v$ of polymers on mechanical degradation by ultrasonic irradiation. Composition vs. time: (○), PVC; (●), PVA. $\overline{P}_v$ vs. time: (△), PVC; (▲), PVA. PVC: 3.000 g. PVA: 1.000 g. H_2O: 50.0 ml. *p*-*t*-butylcatechol: 0.20 g.

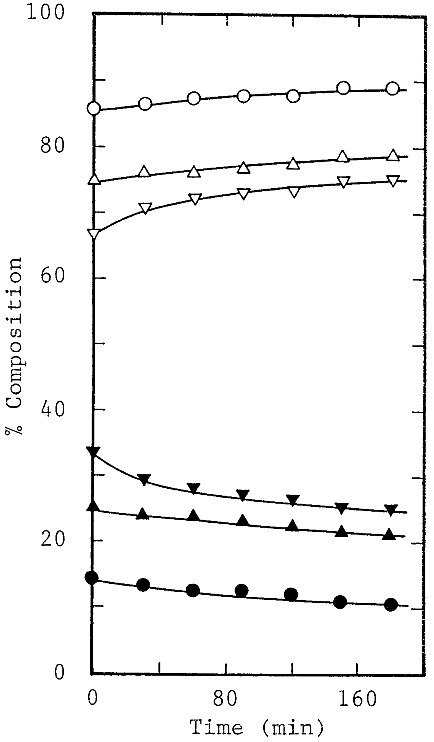


Figure 2. Changes in the composition of the water-insoluble and the water-soluble polymers in the reaction products. Water-insoluble polymer: (○), (△), (▽). Water-soluble polymer: (●), (▲), (▼). PVA: (○), (●), 0.500 g; (△), (▲), 1.000 g; (▽), (▼), 1.500 g. H_2O: 50.0 ml. PVC: 3.000 g.

3,400 cm^{-1} and the C-Cl bond at 620 cm^{-1} with respect to the water-insoluble polymer (WI) and the -OH groups at 3,400 cm^{-1} with respect to the water-soluble polymer (WS) are respectively recognized, but the spectrum of the C-Cl bond in the water-soluble polymer (WS) is not recognized. These results indicate that the PVC-*block*-PVA copolymer is present as the mixtures together with an unreacted PVC in the water-insoluble polymer and the water-soluble polymer is only an unreacted PVA.

The water-insoluble polymers were fractionated by extraction with THF for 20 hr at 55 °C. The compositions of the THF-insoluble and the THF-soluble polymers with respect to the irradiation time are shown in Figure 4. The weight proportion of the THF-insoluble polymer increased slowly with increasing the time and its value after 180 min was approximately 25 %. It is thought that this THF-insoluble polymer, namely the polymer of both the water- and the THF-insolubilizations, is the PVC-*block*-PVA copolymer.

Infrared spectra of the THF-insoluble (TI) and the THF-soluble (TS) polymers are shown as examples in Figure 5. The absorption spectra due to the

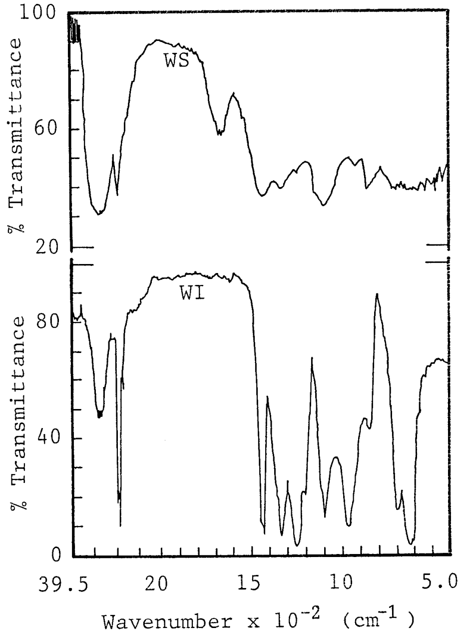


Figure 3. Infrared spectra of the water-insoluble and the water-soluble polymers. Sample (PVC: 3.000 g. PVA: 1.000 g. H_2O: 50.0 ml.): reacted sample, 180 min treatment. (WI), water-insoluble polymer; (WS), water-soluble polymer.

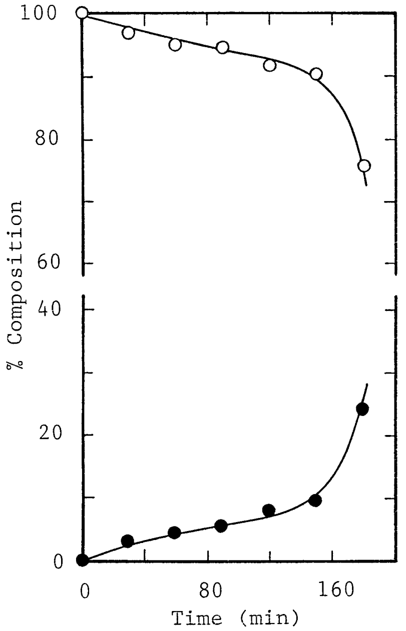


Figure 4. Changes in the composition of the THF-insoluble and the THF-soluble polymers. Sample: water-insoluble polymers at before and after the reaction (PVC: 3.000 g. PVA: 1.000 g. H_2O: 50.0 ml.). (●), THF-insoluble polymer; (○), THF-soluble polymer.

-OH groups at 3,400 cm^{-1} and the C-Cl bond at 620 cm^{-1} with respect to the polymer in each case are recognized. These results indicate that the THF-insoluble polymer (TI) is the block copolymer and the THF-soluble polymer (TS) is the mixture of the block copolymer and the unreacted PVC. For the purpose of determination of the total chlorine content in the THF-insoluble polymer (TI), a Yanaco Micro Determining for Elements (Model MU-2) by the silver absorption method was used. The total chlorine content and the molar fraction of a vinyl chloride VC unit calculated from the total chlorine content in the THF-insoluble polymers are shown in Table II. The proportions of the decrease in the total chlorine content and in the molar fraction of the VC unit after 180 min were approximately 15 wt% and 0.34. This result indicates that the molar ratio of the VC and the vinyl alcohol VA units in the block copolymer formed after 180 min is 6.6 : 3.4.

On the other hand, the proportions of the block copolymer and the unreacted PVC in the THF-soluble polymers (TS) were obtained from the turbidimetric titration curves. Those results are shown in Table III. The proportion of the block copolymer tends to increase with the progress of the time, but its value after 180 min decreases. The block copolymer in the THF-soluble polymer can be presumed that its VA unit has lower value in comparison with that in the THF-insoluble polymer. In addition, the proportion of the unreacted PVC tends to decrease with increasing the time, but its value after 180 min increases. This result suggests that the VC chain of the block copolymer in the THF-soluble polymer undergoes the scission at the prolonged irradiation and PVC is formed consequently. Accordingly, the proportion of the block copolymer decreases and that of the unreacted PVC increases.

The sum of the quantities of the THF-insoluble polymer (TI) and the block copolymer

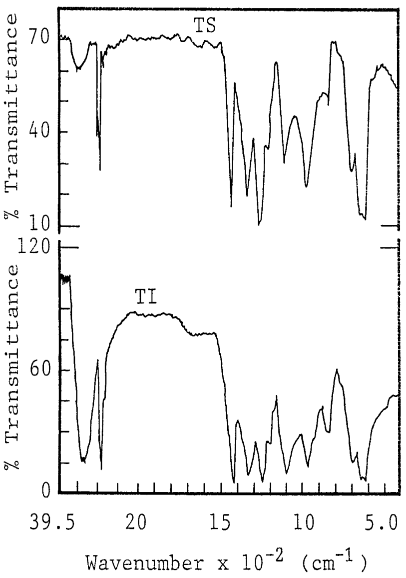


Figure 5. Infrared spectra of the THF-insoluble and the THF-soluble polymers. Sample (PVC: 3.000 g. PVA: 1.000 g. H_2O: 50.0 ml.): reacted sample, 180 min treatment. (TI), THF-insoluble polymer; (TS), THF-soluble polymer.

TABLE II. Total chlorine content and the molar fraction of the vinyl chloride unit

Time (min)	Cl (wt%)	VC unit (mol)
0	56.98	1.00
60	46.76	0.768
120	41.92	0.666
180	41.54	0.659

TABLE Ⅲ. Proportions of the block copolymer and the unreacted PVC in the THF-soluble polymers TS

Time (min)	Block copolymer (wt%)	Unreacted PVC (wt%)
0	0	100.0
30	19.7	80.3
60	16.2	83.8
90	29.7	70.3
120	33.3	66.7
150	34.6	65.4
180	22.0	78.0

in the THF-soluble polymer leads to the total amount of the block copolymer. The changes in the composition of the total block copolymer, the unreacted PVC, and the unreacted PVA in the reaction products with respect to the time are shown in Figure 6. The proportion of the total block copolymer increased and its value after 180 min was approximately 32 wt%, but those of the unreacted PVC and the PVA decreased. The rate of decrease in PVC was much faster than that of PVA. This result is thought to be due to a difference in the extent of mechanical degradation of both polymers.

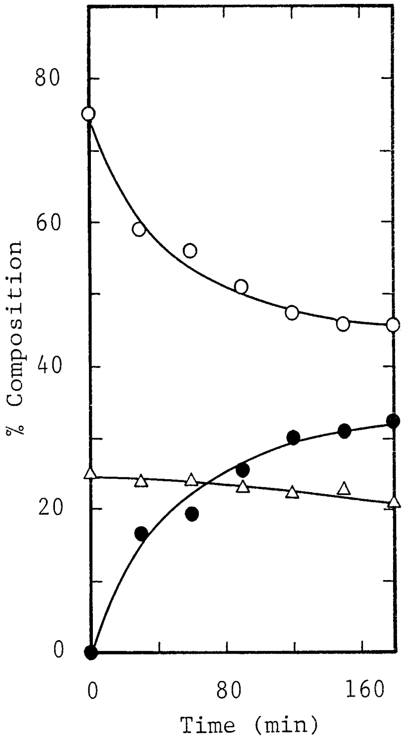


Figure 6. Changes in the composition of the total block copolymer and homopolymers in the reaction products. The reaction condition: PVC, 3.000 g; PVA, 1.000 g; H_2O, 50.0 ml. (○), PVC; (●), Block copolymer; (△), PVA.

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