Polymer Bulletin 47, 247–253 (2001)

Polymer Bulletin

Mechanochemical synthesis and characterization of poly(vinyl chloride) –*block*– poly(acrylonitrile-*co*-butadiene) copolymers by ultrasonic irradiation

Hideki Fujiwara

Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology,
16-1, Omiya 5-chome, Asahi-ku, Osaka 535-8585, Japan

Received: 4 September 2001/Accepted: 22 October 2001

Summary

Mechanical degradation and mechanochemical reaction in heterogeneous and homogeneous systems of poly(vinyl chloride) and poly(acrylonitrile-*co*-butadiene) polymer have been studied by ultrasonic irradiation at 30 °C. The rates of decrease in the number-average molecular weights of the degraded poly(vinyl chloride) and poly(acrylonitrile-*co*-butadiene) polymer in the swelled poly(vinyl chloride) – poly(acrylonitrile-*co*-butadiene) polymer solution were much faster than the homogeneous solution system and the final average chain lengths led to the smaller values than those in the latter system. On the other hand, mechanochemical reaction occurred by polymer radicals produced from the chain scissions of both polymers by ultrasonic irradiation. The changes in the composition of the total block copolymer, the unreacted poly(vinyl chloride), and the unreacted poly(acrylonitrile-*co*-butadiene) polymer in both reaction systems were obtained.

Introduction

In order to obtain a highly efficient poly(vinyl chloride), the reforming in the direction of the thermoplastic elastomers of poly(vinyl chloride) was studied (1–3). For example, the blending systems of poly(vinyl chloride) and the chlorinated acrylonitrile–butadiene rubber (1) or partly cross-linked acrylonitrile–butadiene rubber (3) have been carried out. As noted above, the development of the thermoplastic elastomers of poly(vinyl chloride) is performed through the polymer blend technique, but mechanochemical synthesis of the thermoplastic elastomer of all its own by ultrasonic irradiation was only the author's investigation at the reaction systems of poly(vinyl chloride) and poly(ethylene-*co*-propylene) polymer (4).

The present paper is concerned with ultrasonic mechanochemical reactions in heterogeneous and homogeneous systems of poly(vinyl chloride) and acrylonitrile–butadiene rubber that is excellent in oil, abrasion, and aging resistances.

Experimental

Materials

Suspension polymerized poly(vinyl chloride) sample PVC (Kane Vinyl XS-4000, Kanegafuchi Chemical Industry Co., Ltd.) was purified by extraction with hot pure benzene and methyl alcohol for 80 hr. The average particle diameter of PVC and the porosity in the PVC-grain particle were 150 µ *m* and 0.640 ml Hg/g PVC. The number-average molecular weight $\overline{M}_n$ of PVC determined by gel permeation chromatography was 1. 72xl0^5. Acrylonitrile–butadiene rubber NBR (N241H, JSR Co., Ltd.) was purified by the use of *o*-xylene–methyl alcohol system. The molar ratio of acrylonitrile and butadiene bonded in NBR was 0.29 vs. 0. 71 and the number-average molecular weight $\overline{M}_n$ was 1. 70x10^5. Purified *o*-xylene was used as the reaction solvent by considering the solubility of NBR. Purified tetrahydrofuran THF was used as the reaction solvent and the solvents for the determinations of the solution turbidity and the $\overline{M}_n$ of polymers. Purified methyl alcohol was used as a precipitating agent.

Apparatus and Procedures

Two types ultrasonic generator (Model USV-150V and UE-200Z 26S-1A, Cho-Onpa Kogyo Co., Ltd.) have been used for mechanical degradations and mechanochemical reaction of PVC and NBR. The USV-150V generator was equipped with a stepped horn of stainless steel on a magnetostrictive nickel vibrator of 25 kHz and the UE-200Z26S-1A generator was equipped with an electrostrictive PZT vibrator of 26 kHz. The output powers of these generators had respectively the intensities of 150 watts and 200 watts. When an ultrasonic waves from the upper part of the reaction system was irradiated, the USV-150V generator has been used and the stepped horn of stainless steel on the vibrator was contacted on the surface of the reaction solution. On the other hand, the PZT vibrator of the UE-200Z26S-1A generator has been used for the irradiation from the lower part of the reaction system and the center of the bottom of the reaction vessel was contacted on the surface of the vibrator.

The experiments of two kinds for mechanical degradations and mechanochemical reaction of both PVC and NBR were carried out in the following manner.

Experiment No. I : Swelled PVC–NBR solution system

In this reaction system, the mixture solvent of *o*-xylene/ THF (1. 0 vol. vs. 1. 0 vol.) has been used for the purpose of swelling of the PVC particle.

In a typical run for mechanical degradation, 2.00 g of PVC, 80. 0 ml of NBR–*o*-xylene/THF solution (NBR: 0. 800 g), and 1. 60 g of *p*-benzoquinone inhibitor were poured into a 300 ml special glass reaction vessel and the solution was permitted to stand for 2 hours at 30 °C. The original PVC particle expanded consequently by a factor of 2. 4. Ultrasonic irradiation was carried out for 60, 120, 180, 240, 300, and 360 min at the same time from the upper and the lower parts of the reaction 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 degraded PVC and NBR were fractionated by the use of *o*-xylene at 80 °C. The number-average molecular weights $\overline{M}_n$ of PVC and NBR at various stages of mechanical degradation were determined by gel permeation chromatography.

On the other hand, mechanochemical reaction of both PVC and NBR was carried out by the irradiation of the swelled PVC–NBR solution in the absence of *p*-benzoquinone. The reaction products were fractionated by the use of *o*-xylene at 80 °C. Infrared spectra of the *o*-xylene–insoluble and the *o*-xylene–soluble polymers were determined by the cast film technique from THF solution with a Shimadzu FTIR-8600PC spectrophotometer. The compositions of the block copolymer, the unreacted PVC, and unreacted NBR in the fractionated polymers were determined by turbidimetry (4, 5).

Experiment No. II : Homogeneous solution system

In this reaction system, THF has been used as a common solvent of both PVC and NBR. Further, mechanical degradations, mechanochemical reaction of both PVC and NBR, and the extraction separations of the polymers were carried out in a similar manner as above procedures.

Determination of the Number-Average Molecular Weights

The number-average molecular weights $\overline{M}_n$ of PVC and NBR at various stages of mechanical degradation were determined by gel permeation chromatography (Model HLC-8020, Tosoh Co., Ltd.) at 40 °C. Two G2000HXL TSK gel-columns and one each of G3000HXL and G4000HXL were connected to series in this order. THF was used as a solvent and a flow rate was 1. 0 ml/min. Molecular weights of PVC and NBR were calibrated with polystyrene standards.

Determination of Turbidities

The solution turbidities of PVC, NBR, and the fractionated polymers were determined with a turbidimetric titrator (Model NT-301H, Kotaki Works Co., Ltd.) at 30 °C. In the case of the *o*-xylene–insoluble polymer, the solvent and the precipitating agent were THF and distilled water. The polymer concentration was 0. 050 g/L.

On the other hand, the solvent and the precipitating agent for the *o*-xylene–soluble polymer were THF and methyl alcohol. The polymer concentration was 0. 030 g/L.

In preference to the above determinations, the turbidities of various kinds of the dilute solutions of PVC and NBR were determined and the calibration curves to both polymers were made up from the polymer concentration and the area under the peak of the turbidimetric titration curve (4, 5). The proportions of the unreacted PVC, unreacted NBR, and the block copolymer were calculated by the use of these calibration curves.

Results and Discussion

Mechanical Degradation

The changes in the number-average molecular weights $\overline{M_n}$ of PVC and NBR with respect to the irradiation times on mechanical degradation are shown in Figure 1 and 2. The values of $\overline{M_n}$ of PVC and NBR decreased with irradiation times and these results show that the chain scissions of PVC and NBR occurred at each reaction system. The rates of decrease in $\overline{M_n}$ of the degraded polymers in the swelled PVC–NBR solution system were much faster than the homogeneous solution system and the final average chain lengths led to the smaller values than those in the latter system. In general, mechanical degradation of polymers in solution by ultrasonic irradiation is known that polymer chain in good solvent is much more subject to scission than that in poor solvent (4, 6). However, the experimental result displayed the opposite phenomenon. This is thought that the viscosity of the homogeneous solution system is increased as compared to the swelled PVC–NBR solution system and the attenuation of ultrasonic waves was caused by its viscosity effect (7).

Mechanochemical Reaction

The end radicals of PVC and NBR resulted from mechanical degradation are responsible for the formation of mechanochemical PVC–*block*–NBR copolymer.

Infrared spectra of the *o*-xylene–insoluble and soluble polymers in the reaction product on the swelled PVC–NBR solution system are shown as examples in Figure 3 and 4.

The absorption spectra due to the -CN group at 2237 cm^{-1} and the -CH=CH- groups at 912, 968, and 1437 cm^{-1} with respect to the *o*-xylene–insoluble polymer in Figure 3 are respectively recognized. On the other hand, the spectrum of the C-Cl bond at 619 cm^{-1} with respect to the *o*-xylene–soluble polymer in Figure 4 is confirmed. A similar result

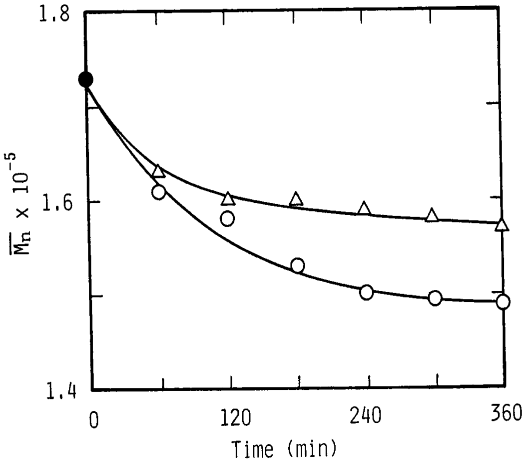

Figure 1. Mechanical degradation of PVC by ultrasonic irradiation. Reaction system: (○), Swelled PVC—NBR solution; (△), Homogeneous solution.

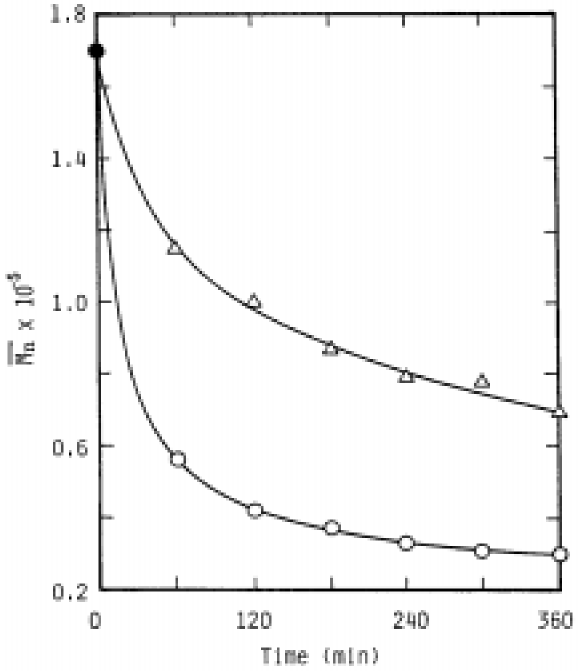

Figure 2. Mechanical degradation of NBR by ultrasonic irradiation. Reaction system: (○), Swelled PVC—NBR solution; (△), Homogeneous solution.

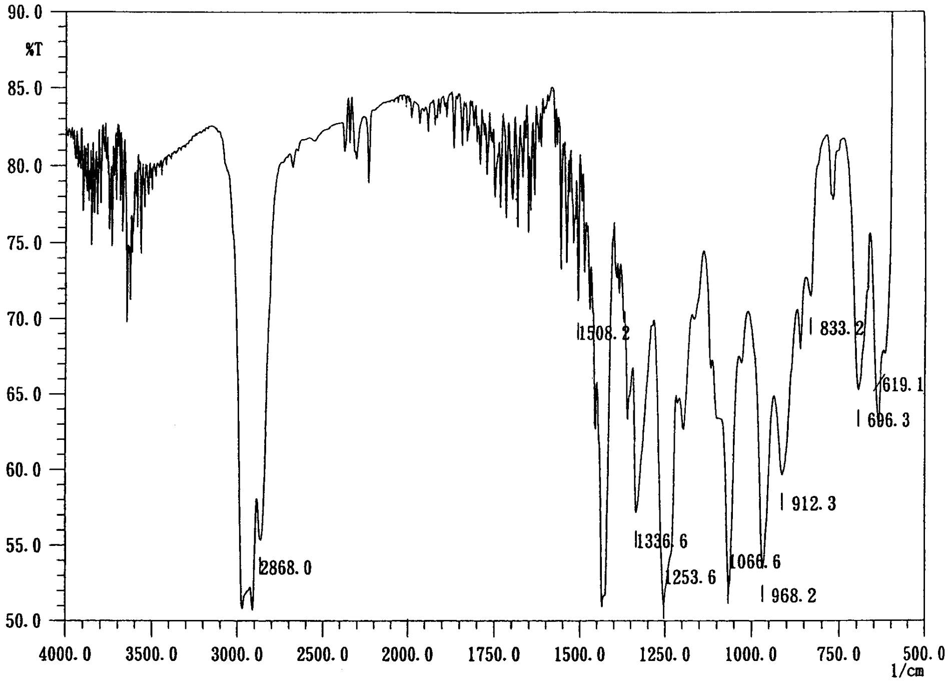

Figure 3. Infrared spectrum of the *o*-xylene—insoluble polymer in the reaction product on the swelled PVC—NBR solution system. Sample: 360 min treatment.

was observed for the absorption spectra of the *o*-xylene–insoluble and the *o*-xylene–soluble polymers in the homogeneous solution system. These results indicate that the PVC–*block*–NBR copolymers are present as the mixtures together with an unreacted PVC in the *o*-xylene–insoluble polymer and

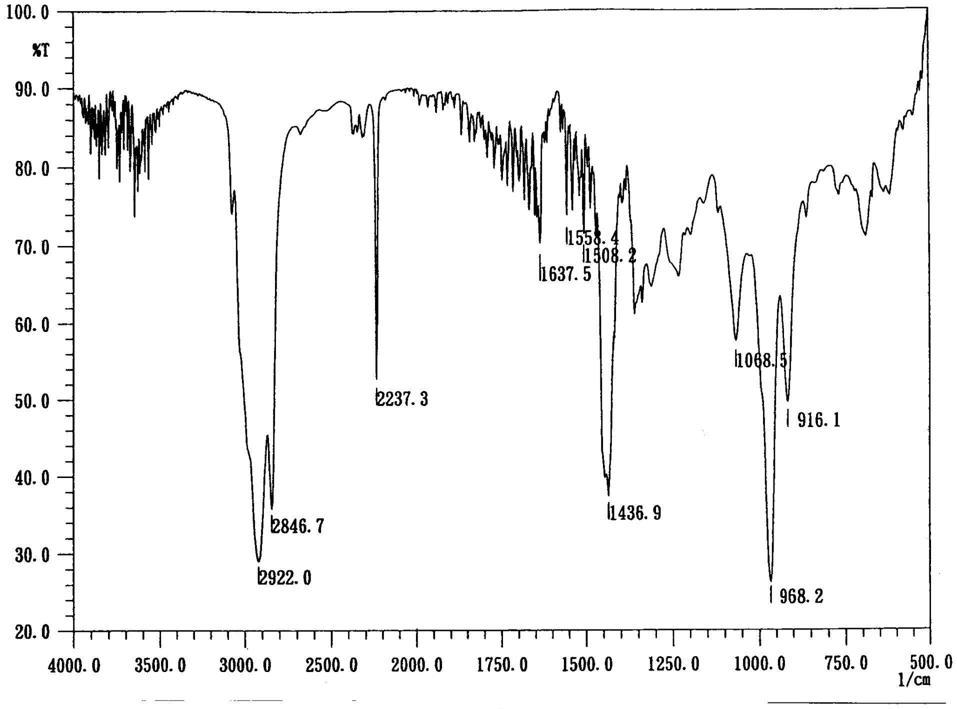

Figure 4. Infrared spectrum of *o*-xylene—soluble polymer in the reaction product on the swelled PVC—NBR solution system. Sample: 360 min treatment.

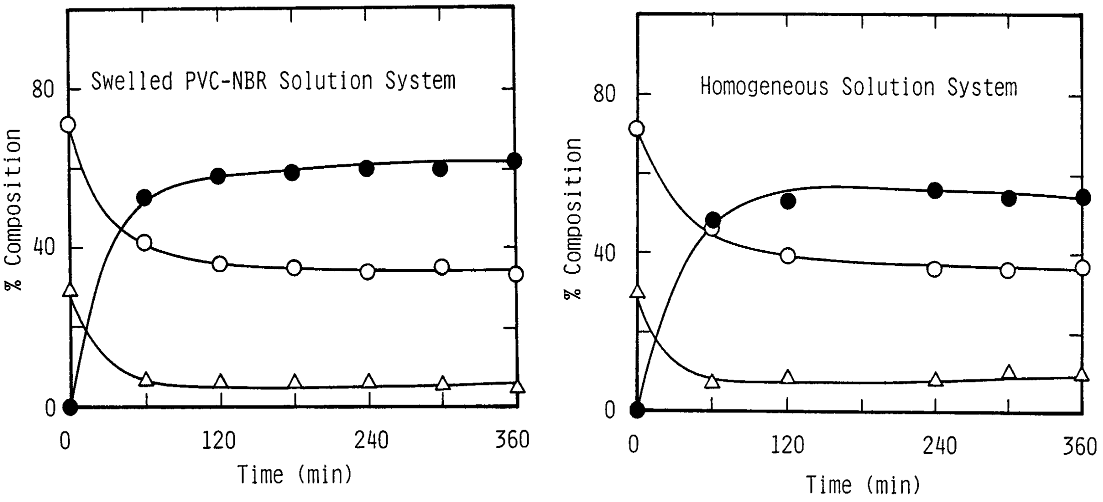

Figure 5. Changes in the composition of the total block copolymer and homopolymers in the reaction products in various kinds of the reaction systems. (●), Block copolymer; (○), PVC; (△), NBR.

an unreacted NBR in the *o*-xylene–soluble polymer.

The compositions of the total block copolymer, the unreacted PVC, and the unreacted NBR in the reaction products with respect to the irradiation time in the individual reaction systems were obtained from the turbidimetric titration curves. Those results are shown in Figure 5. In the swelled PVC–NBR solution system, the weight proportion of the total block copolymer increased rapidly at the initial irradiation time, and then slowly approached the constant ordinate. Its value after 360 min was 62 %. On the other hand, the proportions of the unreacted PVC and NBR decreased rapidly at the initial time, and then slowly approached the constant ordinates. It is thought that these results are attributable to the vigorous scissions of PVC and NBR at the initial irradiation time (by reference to Figure 1 and 2). In the homogeneous solution system, the weight proportion of the total block copolymer was undoubtedly lower than the swelled PVC–NBR solution system and its value after 300 min decreased a little.

On the other hand, the proportions of the unreacted PVC and NBR decreased with increasing the time, but the value of the unreacted NBR after 300 min increased slightly. This result suggests that the acrylonitrile-butadiene (NB) chain of the block copolymer underwent the scission at the prolonged irradiation and the unreacted NBR is formed consequently. In this instance it may be said that a long NB chain of the block copolymer was much more subject to the scission than the vinyl chloride (VC) chain of its copolymer. This is because mechanical degradation of NBR in the homogeneous solution system would not be so much caused (by reference to Figure 2) and the long NB chain was concerned with the formation of the block copolymer in the next mechanochemical reaction.

These results suggest that the synthesis of the PVC–*block*–NBR copolymers is no necessity for prolonged irradiation, that time suffices in 120 min, the swelled PVC–NBR solution system is preferred over the homogeneous solution system, and the VC and the NB segments in the block copolymer can be made to vary by changes in the experimental conditions.

Acknowledgments

I give thanks to Kanegafuchi Chemical Industry Co., Ltd. for the supply of the PVC sample and JSR Co., Ltd. for the supply of the NBR sample.

References

1. Schwarz H. F. : *Elastomerics*, Nov., 17 (1980).
2. Kawashima Y. : *Nippon Gomu Kyokaishi*, 57, No. 11, 736 (1984).
3. Wolfe J. R., Legge N. R., *et al.* : *Thermoplastic Elastomers*, 117 (1987).
4. Fujiwara, H. and Minamoto, Y. : *Polymer Bulletin*, 45, 137 (2000).
5. Fujiwara, H., Ishida, T., *et al.* : *Polymer Bulletin*, 42, 197 (1999).
6. Okuyama, M. : *Z. Elektrochem.*, 59, 565 (1955).
7. Chandra, S., Roy-Chowdhury, P., and Biswas, A. B. : *J. Appl. Polymer Sci.*, 10, 1089 (1966).