

Heat Curing of Radiation-Induced Crosslinked Syndiotactic 1,2-Polybutadiene

INTRODUCTION

The effect of radiation on 1,2-polybutadiene has been studied by Heusinger et al.¹ They have reported that $G(\text{crosslink})$ and $G(-\text{vinyl})$ are ca. 10 and 110, respectively, and suggested that crosslinking and cyclization take place via a chain reaction mechanism. The authors also investigated gel formation and vinyl consumption on the irradiation of syndiotactic 1,2-polybutadiene (syndio-1,2-PB), and determined that $G(\text{crosslink})$ and $G(-\text{vinyl})$ are ca. 14 and 120, respectively. In this report, the effects of oxygen and an antioxidant on gel formation are studied in the irradiation of syndio-1,2-PB. Further, heat treatment of crosslinked product is carried out in order to obtain information about the thermal property.

EXPERIMENTAL

Syndio-1,2-PB used was synthesized with the use of cobalt octoate– $\text{Al}(\text{C}_2\text{H}_5)_3$ – CS_2 – CH_3OH catalyst²: melting point, 143°C; \bar{M}_n , 11.3×10^4 (by osmometry); \bar{M}_w/\bar{M}_n , ca. 2 (by GPC); vinyl content, 82.2% (by NMR); crystallinity, 45% (by x-ray diffraction). The polymer was used in film or sheet form which contained 2,6-di-*tert*-butyl-*p*-cresol (BHT) as conventional antioxidant. In some cases BHT was removed by extraction in a Soxhlet extractor using methanol.

Irradiation by electron beam was carried out at room temperature using a linear accelerator. The current density of the electron beam was 0.25–1.0 $\mu\text{A}/\text{cm}^2$.

Gel fraction measurement was carried out as follows. A portion of the irradiated sample of about 0.5 g was accurately weighed out into a 100-mesh stainless-steel basket. The sample was extracted with boiling benzene containing 0.5 wt-% BHT for 24 hr by changing to fresh benzene every 8 hr and then dried under reduced pressure at room temperature. The weight ratio of insoluble polymer to original polymer was defined as the gel fraction.

Heat treatment of the irradiated product was carried out in a salt bath or a special electric furnace. A glass ampoule which contained the sample was degassed, sealed off, and then kept in the salt bath. After a fixed time the ampoule was cooled in water. Or, the sample was placed in the electric furnace and heated by N_2 gas being passed through the furnace.

Infrared spectra of films 15–20 μm thick were obtained by the use of a Hitachi EPI-2 infrared spectrometer. Specific gravity was determined by means of a Beckmann 930 pycnometer. Thermal expansion behavior was studied using a Rigaku Denki thermal expansion apparatus. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on a Rigaku Denki 8002 thermal analyzer. Tests for tensile property, flexural property, Izod impact strength, and Rockwell hardness were carried out at room temperature by the ASTM D-638, D-790, D-256, and D-785 methods, respectively.

RESULTS AND DISCUSSION

In general, it is of advantage from a practical point of view that radiation-induced crosslinking of polymers is carried out in air using an electron beam rather than γ -rays. The rate of crosslinking is, however, affected by air, especially oxygen. In addition, the rate is also affected by various additives which are contained in the polymers. The effects of oxygen and BHT as conventional antioxidants on gel fraction are shown in Figure 1. BHT is found to retard gel formation as illustrated in the case of irradiation in vacuo. Oxygen also retards gel formation, and the retardation becomes more serious the thinner the specimen is. This may be attributed to diffusion of oxygen into the film. From these facts, it is suggested that this crosslinking and cyclization proceeds via a radical mechanism.

As a rule, one of the characteristic changes by crosslinking of a polymer is that the polymer does not melt and flow when heated above the melting point. Figure 2 shows the relation between dose or gel fraction and thermal expansion behavior measured in nitrogen atmosphere. As the dose in-

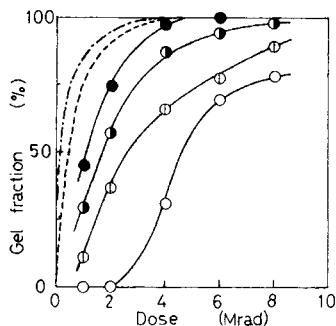


Fig. 1. Effect of film thickness on gel fraction in irradiation of film with BHT in air: BHT, 0.2 wt-%; current density, $0.5 \mu\text{A}/\text{cm}^2$; (O) 15 μm ; (\odot) 0.1 mm; (\bullet) 0.5 mm; (\bullet) 3.0 mm; (- - -) irradiation in vacuo; (- · - · -) without BHT, irradiation in vacuo.

creases, a bend around 50°C becomes smaller and the coefficient of linear expansion reaches a constant in the region up to about 130°C . The sample melts and flows at the melting point below 0.75 Mrad. In the case of 1.5 Mrad, the specimen contracts temporarily around the melting point and expands again in the higher temperature region above the melting point, but contraction takes place around 280°C . Around the melting point, the specimen contracts a little at 5 Mrad but expansion is observed at 18 Mrad. Above 1.5 Mrad, the coefficients of linear expansion obtained in the region from 10 to ca. 250°C except for the melting point region are $(18\text{--}20) \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ regardless of dose, which are nearly equal to that of low-density polyethylene. The opaque, white, soft sample which had been irradiated with more than 1.5 Mrad became transparent, pale yellow, and very hard during this thermal expansion measurement. In the case of measurement in air, the sample became opaque, black, and hard.

The TG/DTA diagram of the product irradiated with 5 Mrad is shown in Figure 3. The melting point of the product is lower compared with that of the original. After a remarkably large exothermic peak around 350°C , the weight of the sample begins to decrease at ca. 410°C , accompanied by a large endothermic peak which is due to thermal degradation. The exothermic peak and the weight decrease were not affected by the dose and were almost the same. It can be seen from Figures 2 and 3 that both the contraction and the exothermic peak appear in approximately the same temperature region. Considering also the change in appearance, the contraction and the exothermic peak can be ascribed to a heat curing reaction. Thus, the crosslinked and cyclized syndio-1,2-PB is heat cured above the original melting point without melting and flowing.

These results are correlated with a change in infrared spectrum as shown in Figure 4. The vinyl groups at 3080 , 1840 , 1640 , 995 , and 910 cm^{-1} decrease, while CH_2 groups at $2990\text{--}2860$ and 1460 cm^{-1} increase upon heat treatment. Further, the band at 965 cm^{-1} increases appreciably, which

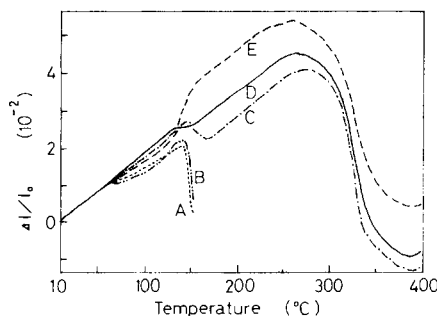


Fig. 2. Relation between dose or gel fraction and thermal expansion behavior: sample, injection-molded test piece, 3.0 mm thick; BHT 0.2 wt-%; irradiation, $1.0 \mu\text{A}/\text{cm}^2$, in air. Dose (gel fraction): (A) 0 Mrad (0%); (B) 0.75 Mrad (41.3%); (C) 1.5 Mrad (76.8%); (D) 5.0 Mrad (100%); (E) 18.0 Mrad (100%). Thermal expansion measurements: l_0 , 11.5 mm; atmosphere, nitrogen; heating rate, $2.5^\circ\text{C}/\text{min}$; load, 1 g.

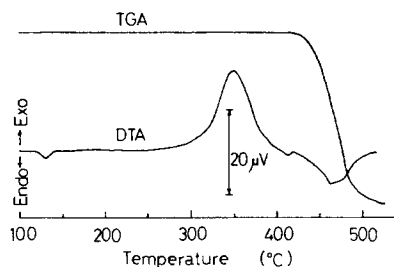


Fig. 3. TG/DTA diagram of irradiated syndio-1,2-PB. Sample is same as (D) in Figure 2. TG/DTA measurements: sample, 8 mg; atmosphere, nitrogen; heating rate, 10°C/min; sensitivity, $\pm 100 \mu\text{V}$.

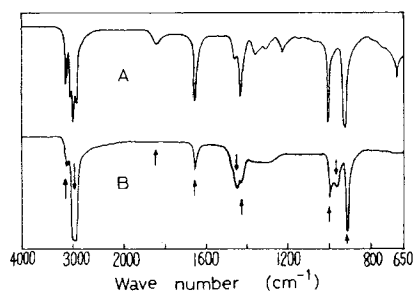


Fig. 4. Change in infrared spectrum of irradiated syndio-1,2-PB by heat treatment: sample, without BHT; irradiation, $1.0 \mu\text{A}/\text{cm}^2$, 4 Mrad, in vacuo; (A) untreated; (B) heat treatment in vacuo, 275°C, 4.0 hr.

TABLE I
Changes in Mechanical Properties by Heat Treatment^a

Properties	Original	Irradiation	Heat treatment
Specific gravity (20/20°C) ^b	0.920	0.921	0.970
Tensile strength, kg/cm ²	185	187	344
Elongation, %	340	126	2.6
Elastic modulus, kg/cm ²	1670	2060	19700
Flexural strength, kg/cm ²	112	144	633
Izod impact strength, kg-cm/cm	not broken	not broken	2.3
Rockwell hardness (R scale)	65.6	82.8	113.6

^a Test piece, sample B, injection molding (BHT 0.2 wt-%); irradiation, $1.0 \mu\text{A}/\text{cm}^2$, 8 Mrad, in air; heat treatment, 280°C, 2 hr in nitrogen (the time needed to reach 280°C was ca. 1 hr).

^b (20/20°C) means the value of the sample at 20°C as a standard of water at 20°C.

can be assigned to a cyclic structure as already pointed out by Golub.^{3,4} From these changes, the heat curing is found to be essentially a cyclization reaction in which the vinyl group plays an important role.

Table I shows the changes in mechanical properties by heat treatment. Rigidity increases to some extent by irradiation. Heat treatment is found to bring about a remarkable increase in specific gravity, hardness, and various strengths except for impact strength. These mechanical properties can be further improved by using inorganic fillers such as glass fiber and asbestos.

The authors wish to express their sincerest thanks to Professor Koichiro Hayashi of Osaka University for valuable suggestions and discussions.

References

1. A. V. Raven and H. Heusinger, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2255 (1974).
2. H. Ueno, K. Oizumi, H. Ishikawa, H. Hamada, and H. Aikawa, Jpn. Pat. 59,480 (1975).
3. M. A. Golub and R. J. Gargiulo, *J. Polym. Sci., Polym. Lett. Ed.*, **10**, 41 (1972).
4. M. A. Golub and M. Sung, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 129 (1973).

HIDEMASA OKAMOTO*
TADASHI IWAI

Central Research Laboratory
Ube Industries, Ltd.,
Ube, Yamaguchi 755, Japan

Received February 14, 1978

Revised April 6, 1978

*Present address: Hirakata Plastics Laboratory, Ube Industries, Ltd., Hirakata, Osaka 573, Japan.