

Effects of Mixing States on Physical Properties of Vulcanizates of Polybutadiene Rubber-General Purpose Polystyrene Resin Blend

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Synopsis

The effects of the continuous phases of general purpose polystyrene resins upon the physical properties of the vulcanizates were studied using the polybutadiene rubber-general purpose polystyrene resin blend. The unvulcanized samples were prepared according to the method already mentioned in our previous report,¹ and the radiation cure was adopted so that a change of state during cure might be avoided. Some physical properties like hardness, modulus, elongation, permanent set, and resilience are much influenced by the existence of the continuous phases even if the polymer blend ratios are kept constant, whereas tensile strength at failure is mainly determined by the polymer blend ratio. The physical properties which belong to the former group are found to be controlled more strongly by the polymer which forms the continuous phase.

INTRODUCTION

In the previous paper¹ it was reported that general purpose polystyrene resin (GP polystyrene resin) can have both continuous and discontinuous phases by a change of blend conditions in the polybutadiene rubber (BR)-GP polystyrene resin blend, even if the polymer blend ratio is kept constant. However, the previous report did not deal with the effects of the change of state of GP polystyrene resin phase on the properties of the vulcanizates. These effects have not been studied so far, and therefore the author studied them in this paper. The radiation cure was adopted in this report so that the change of blend state which will possibly occur in case of high temperature vulcanization such as sulfur vulcanization might be avoided. Hardness, compression modulus, and benzene extraction tests were carried out on vulcanizates cured by radiation to observe the state of phases to some extent. In addition, tests of various properties were made in order to study the influence of the change of state of GP polystyrene resin phases on the properties of the vulcanizates.

EXPERIMENTAL

Polymers

Commercial grades were used for both BR and GP polystyrene resin as described in the previous paper¹: low *cis* BR ASADENE NF 35R as BR and Styron 683 as GP polystyrene resin.

Procedure for Polymer Blend and Remilling

A 10 in. ϕ \times 20 in. l open mill (rotation speed: 20 rpm and 24 rpm for front and back rolls, respectively; roll clearance: about 0.9 mm) was used to blend polymers as described in the previous paper, and the roll surface temperature was about 140°C. Polymer blend was accomplished by adding GP polystyrene resin to BR band within about 10 min. A half of blended stocks was remilled for 20%–60% (wt-%, same hereinafter) GP polystyrene resin content. Based on the results in the previous paper, the remilling was made with 10 in. ϕ \times 20 in. l open mill (rotation speed: 20 rpm and 24 rpm for front and back, respectively) at the surface temperature of 70°–110°C for 10–40 min.

Vulcanization

As reported in the previous paper,¹ the remilled softened stocks are hardened due to the change of state which is caused by heating these stocks to the temperature necessary for the sulfur vulcanization. The radiation cure was adopted to avoid this change of state.

The radiation cure was undertaken at Takasaki Radiation Chemistry Research Establishment. A 71,000-ci source of Co 60 was used and the radiation dose rate was $1\text{--}5 \times 10^5$ rad/hr. Since it has been proved that a radiation cure result is scarcely influenced by this change of radiation dose rate,² studies on properties were made by maintaining only the radiation dose at a constant level. The radiation dose was 1.1×10^7 rad and the sample was irradiated at room temperature in air.

The preliminary compression molding was carried out prior to irradiation to eliminate air bubbles in stocks. The compression temperature was 90°C for stocks with less than 10% GP polystyrene resin content and remilled stocks and 140°–180°C for other stocks. The compression time was 10 min. There is no difference in hardness of stock before and after molding, and therefore it is presumed that no change in the state of phase is caused by preliminary compression molding. The sizes of molded stocks were 150 mm \times 150 mm \times 12.7 mm and 200 mm \times 150 mm \times 2 mm. Specimens were prepared by punching and milling.

Testing Methods of Physical Properties

Hardness of Unvulcanized Samples. Hardness was measured by an Asker-C-type hardness tester and the values after 30 sec of contact were adopted.

Hardness of Vulcanizates. The test was carried out by a JIS (Japanese Industrial Standard) spring-type hardness tester which is provided in JIS K6301.

Compression Modulus. 17.8 mm ϕ \times 12.7 mm high cylindrical specimens were used to measure the apparent initial modulus of compression, using an Instron-type universal tensile-compression tester at the compres-

sion speed of 0.5 mm/min. The temperature was adjusted to the standard of JIS K6301.

Tensile Strength. The tensile test was carried out in accordance with JIS K6301 and the rate of stretching was adjusted to 50 mm/min. An Instron-type universal tensile-compression tester was used for measuring tensile strength.

Compression Permanent Set. Compression permanent set was measured at 70°C after 22 hr in accordance with JIS K6301. Compression ratio was 25% regardless of hardness of the specimen.

Resilience. Resilience was measured using a Dunlop Tripsometer in accordance with BS 903. The temperature was adjusted to the standard state in accordance with JIS K6301.

Benzene Extraction Test of Vulcanizates

By using a specimen of 20 mm × 10 mm × 2 mm, the benzene extract was continuously measured with a Soxhlet extracting apparatus for 46 hr. (It was confirmed by preliminary experiments that extracts of every stock are saturated by extracting continuously for 46 hr.) After leaving the extraction residues overnight in air and drying them under vacuum for 6 hr at room temperature, they were weighed. The extract was precipitated with methanol and, after filtering and drying, it was dissolved in CS₂ solvent. Then the infrared absorption spectrum of this solution was measured with a Hitachi infrared spectrophotometer EPI-G2 type. BR and GP polystyrene resin contents of the extract were determined by Hampton's method.³

RESULTS AND DISCUSSION

Hardness of Unvulcanized Materials

The properties of unvulcanized materials were already reported in detail in the previous paper.¹ Again, hardness of unvulcanized stocks before and after remilling is shown in Figure 1, as it is an important property. Again it is presumed that most of GP polystyrene resins form continuous phases in stocks before remilling with more than 20% GP polystyrene resin content, whereas GP polystyrene resins form discontinuous phases in remilled softened stocks with less than 60% GP polystyrene resin content and stocks with 10% GP polystyrene resin content.

Hardness and Compression Modulus of Vulcanizates

Hardness after irradiation with γ -rays is shown in Figure 2. It may be seen that the state of phase of unvulcanized samples is retained even after radiation cure.

Figure 3 shows the apparent compression modulus of blend compounds after being irradiated with γ -rays. The curves (I) and (II) in Figure 3 are theoretical curves led by the parallel model of Kawai and his co-workers,⁴

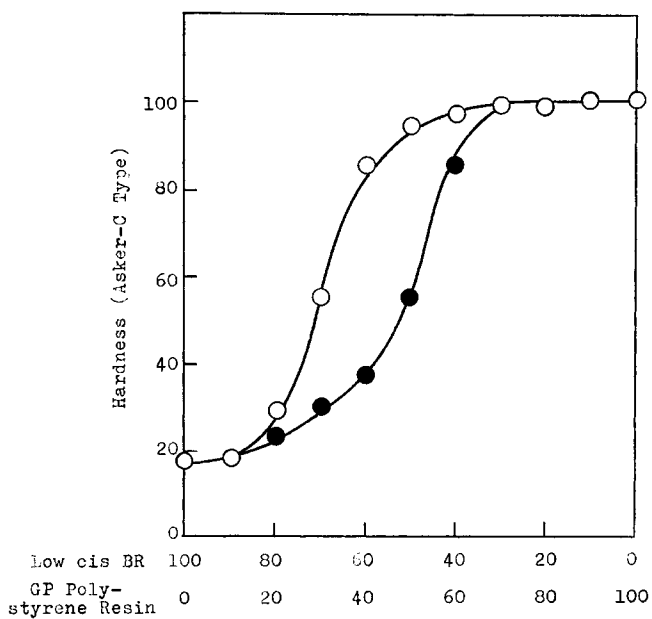


Fig. 1. Hardness of unvulcanizates: (○) un-remilled specimens; (●) remilled specimens.

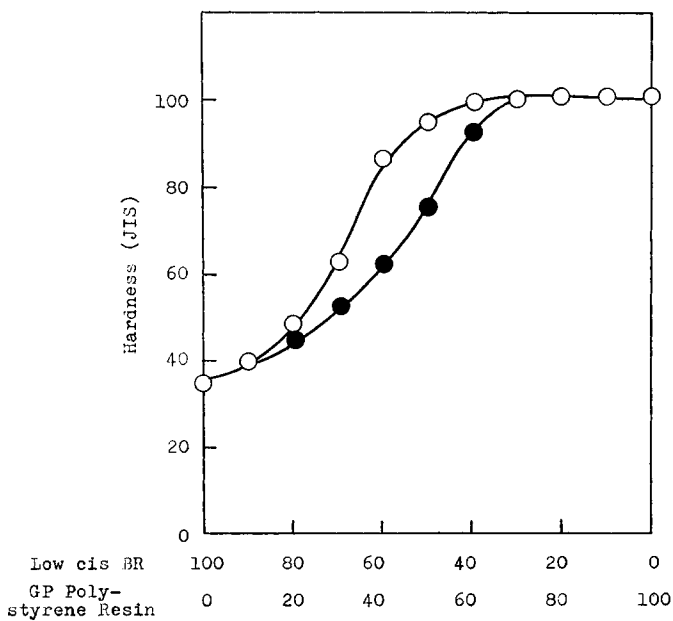


Fig. 2. Hardness of vulcanizates: (○) un-remilled specimens; (●) remilled specimens.

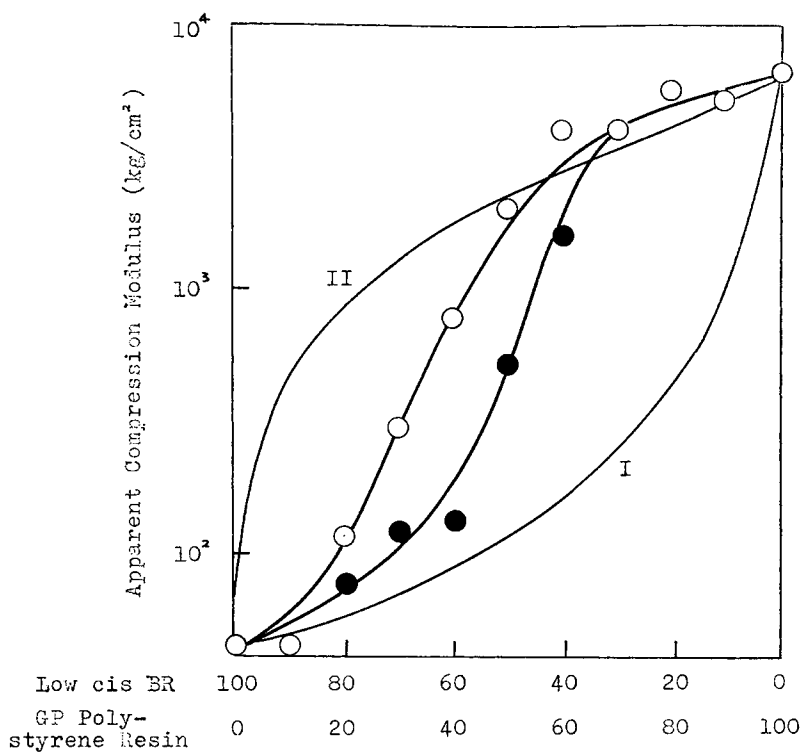


Fig. 3. Apparent compression modulus of vulcanizates: (O) un-remilled specimens; (●) remilled specimens.

in which stress is assumed to be additive. BR is taken as a continuous phase and GP polystyrene resin as a discontinuous phase in curve (I), and it is reversed in curve (II). Again the figure shows that the dispersion state in the unvulcanized materials is retained even in the vulcanizates by the radiation cure.

Benzene Extraction of Vulcanizates

Figure 4 shows the results of the benzene extraction test on the blend after being irradiated with γ -rays (specimen size: 20 mm \times 10 mm \times 2 mm). Figure 5 shows the infrared spectrum of the extract of the stocks with 30% GP polystyrene resin content after remilling. In this case, the benzene extraction ratio is 3.8% (2.4% for BR and 1.6% for GP polystyrene resin). The following discussion is based on these facts.

The radiation cure is fully accomplished in case of 100% BR, whereas crosslinking is not caused by the radiation cure in case of 100% GP polystyrene resin. Therefore, if GP polystyrene resin forms entirely continuous phases in the blend, all GP polystyrene resins may be possibly extracted by benzene. On the contrary, if GP polystyrene resin forms en-

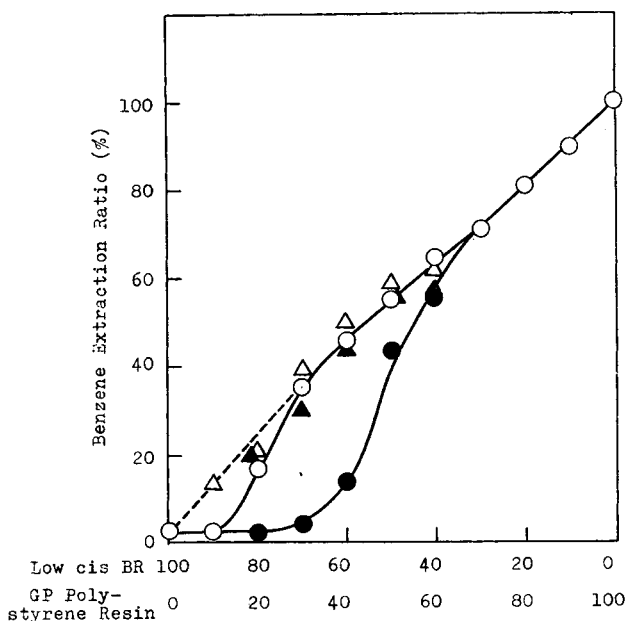


Fig. 4. Benzene extraction ratio of vulcanizates: (○) un-remilled specimens; (●) remilled specimens; (△) ground un-remilled specimen; (▲) ground remilled specimens.

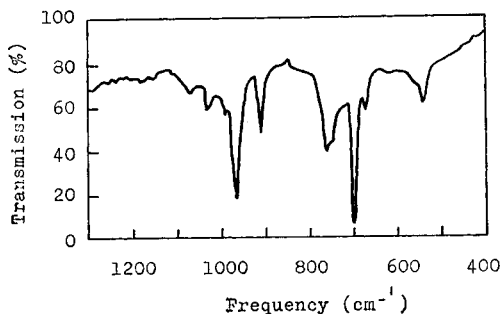


Fig. 5. Infrared spectra of benzene-extracted polymer of remilled vulcanizates composed of 30 wt-% of GP polystyrene resin.

tirely discontinuous phases, the extracted quantity by benzene must be kept at a lower level.

Actually, the extracted quantity by benzene nearly corresponded to the GP polystyrene resin content for the stocks with more than 30% GP polystyrene resin content before remilling, whereas it was much less than the GP polystyrene resin content for the stocks after remilling. The infrared spectrum of the extract also shows that GP polystyrene resin is hardly extracted in case of the stocks after remilling. In other experiments, before the extraction test the stocks were passed through a 3 in. ϕ \times 7.5 in. l open mill (rotation speed: 16.4 rpm and 18.7 rpm for front and back rolls,

respectively) with a narrow clearance (about 0.1 mm) at room temperature and were ground into pieces. In the previous paper,¹ it was found that the continuous phases of GP polystyrene resin were mechanically destroyed and dispersed at a magnitude of a few microns after remilling. Walters and his co-workers⁵ also report that the zone size of a few microns is observed for the rubber blends mixed by an open mill, using a phase contrast microscope technique.

Based on these facts, it may be presumed that during milling mechanical destructive force may act upon the stocks cured after remilling and the

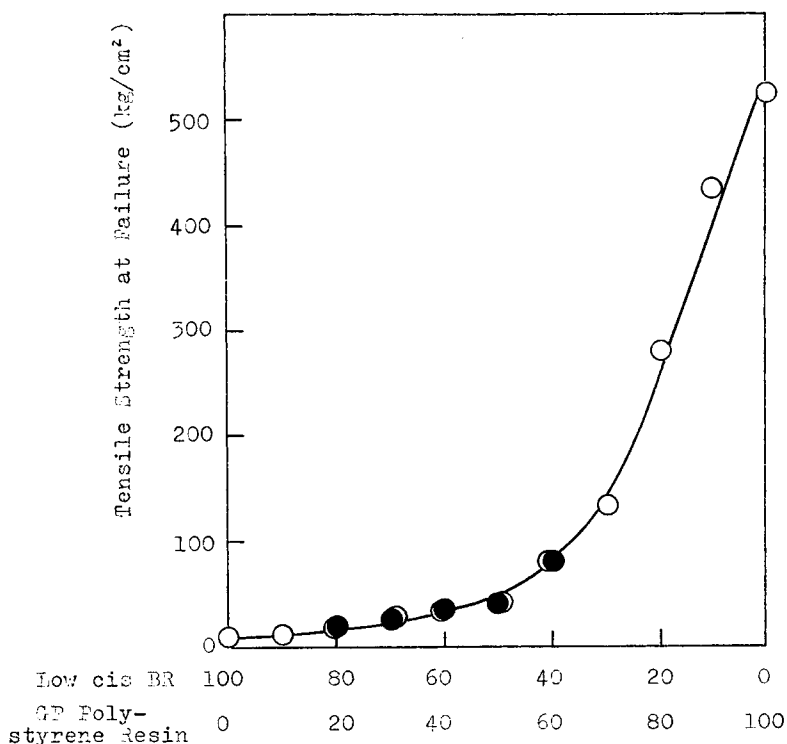


Fig. 6. Tensile strength of vulcanizates: (O) un-remilled specimens; (●) remilled specimens.

continuous phases of BR are destroyed so that the discontinuous phases of GP polystyrene resin are exposed and the extraction of GP polystyrene resin becomes as easy as in the case of stocks before remilling. As shown in Figure 4, no difference is observed before and after remilling and the extracted quantity by benzene almost corresponds to the GP polystyrene resin content. From the above points of view, it is found that most of GP polystyrene resins form continuous phases before remilling and discontinuous phases after remilling in stocks with more than 30% polystyrene resin content.

It is presumed that most of GP polystyrene resins form continuous phases also in stocks with 20% GP polystyrene resin content before remilling. It is probably because continuous phases are not fully developed that a part of GP polystyrene resins remains not to be extracted.

State of Phase and Properties of Vulcanizates

The state of phases of blend compounds after being irradiated with γ -rays is explicit as mentioned above. On the basis of the knowledge obtained so far, the author studied the effects on the properties of vulcanizates by whether GP polystyrene resin forms continuous phases or not. Hardness and compression modulus were already studied and are therefore omitted here.

Tensile Strength at Failure. Figure 6 shows the tensile strength at failure of blend compounds after being irradiated with γ -rays. No difference is observed between the continuous phase and the discontinuous phase of GP polystyrene resin. It means that whether the ultimate failure occurs in GP polystyrene resin phase or in BR phase does not depend upon whether GP polystyrene resin forms a continuous or discontinuous phase, but primarily upon the blend ratio.

Elongation. Figure 7 shows the elongation of blend compounds after being irradiated with γ -rays. The elongation does not change uniformly with the blend ratio and makes a curve with a maximum at a rather low GP polystyrene resin content, which is probably due to the reinforcing effect of GP polystyrene resin. The existence of a continuous phase of GP poly-

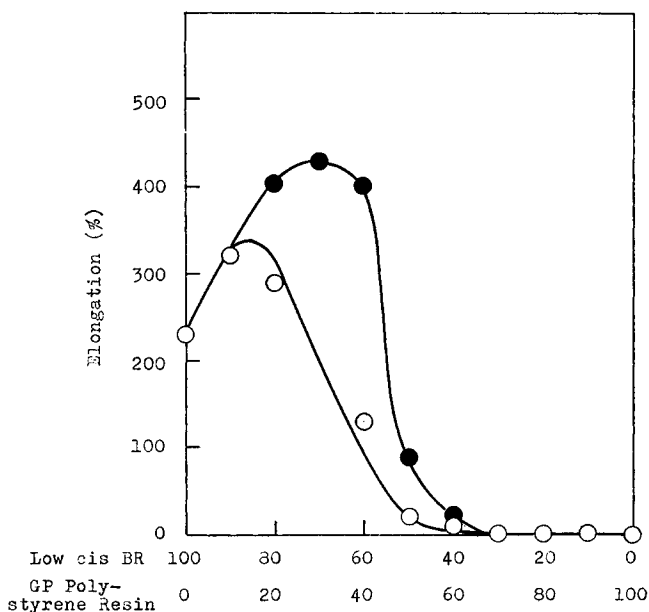


Fig. 7. Elongation of vulcanizates: (○) un-remilled specimens; (●) remilled specimens.

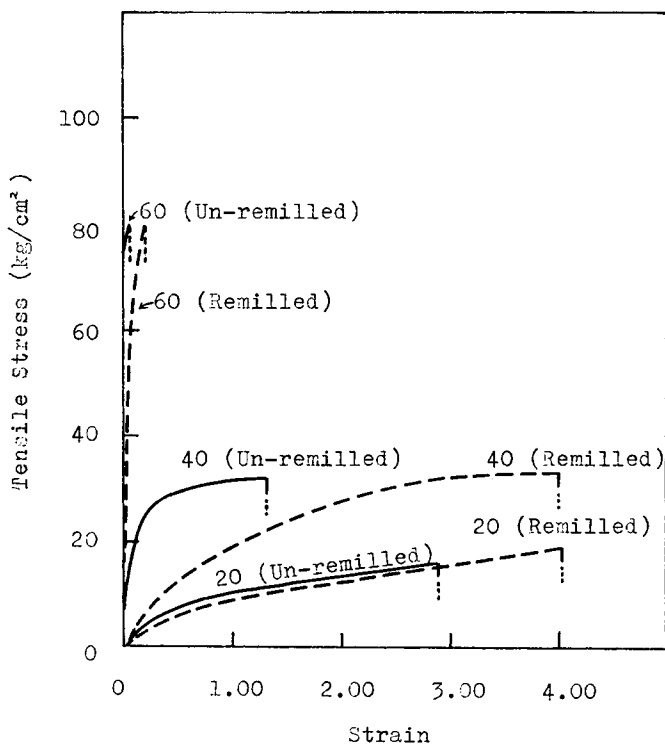


Fig. 8. Tensile stress-strain curves of vulcanizates. Numbers on curves are GP polystyrene resin contents, wt-%.

styrene resin has a great effect on elongation values. The elongation is much smaller in the case of continuous phases than in the case of discontinuous phases. The GP polystyrene resin content marking maximum elongation varies with stocks before and after remilling. There is not yet a generally accepted theory concerning the failure of heterogeneously dispersed polymer blends. The author looks at these phenomena as follows: In case GP polystyrene resin forms continuous phases, GP polystyrene resin does not elongate with rubber when stocks are stretched and the failures in GP polystyrene resin phases cause the stress concentration followed by the low elongation, as shown in Figure 7.

Stress-Strain Curve. Figure 8 shows an example of stress-strain curve of blend compounds after being irradiated with γ -rays. It makes a rather big difference in curves whether GP polystyrene resin forms continuous phases or not. This difference is remarkable in 40% GP polystyrene resin content. Physical properties of GP polystyrene resin are prominent in stocks before remilling and those of BR are prominent in stocks after remilling.

Compression Permanent Set. Figure 9 shows the test results of compression permanent set on the blend compounds after irradiating with

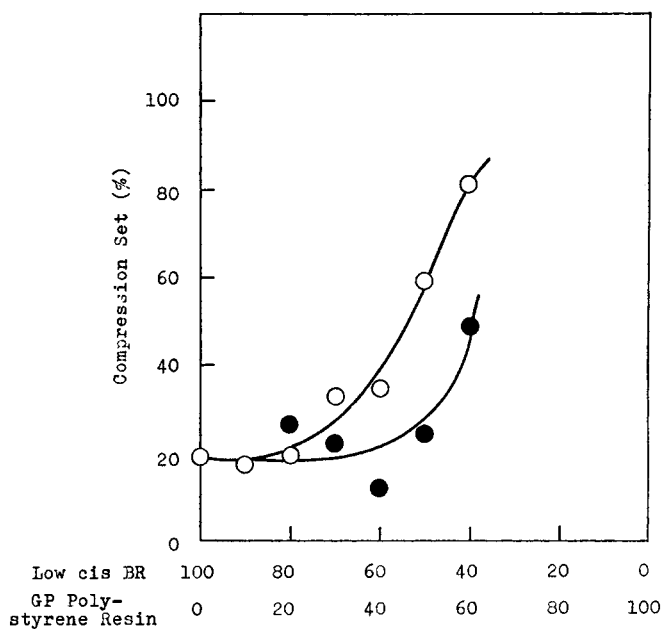


Fig. 9. Compression set of vulcanizates: (○) un-remilled specimens; (●) remilled specimens.

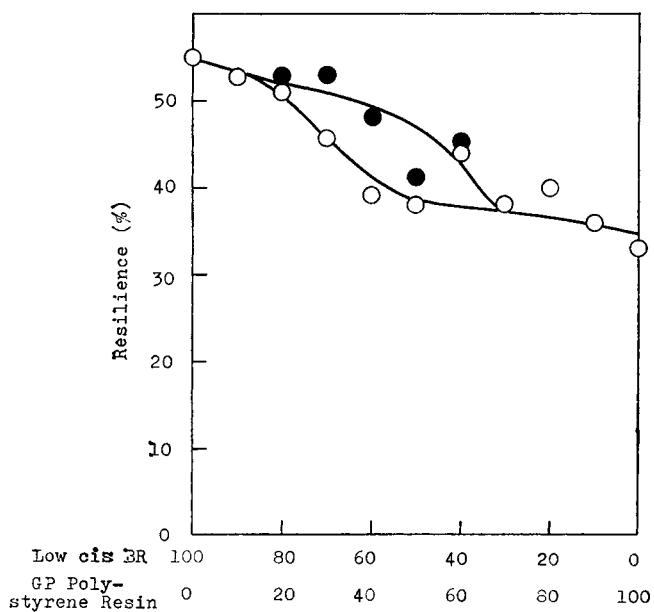


Fig. 10. Resilience of vulcanizates: (○) un-remilled specimens; (●) remilled specimens.

γ -rays. The stocks with high GP polystyrene resin content before remilling possess higher compression permanent set than the stocks after remilling. The compression permanent set of the stocks with less than 50% GP polystyrene resin content is almost same as that of 100% BR. The existence of continuous phases seems to have a great influence upon compression permanent set of stocks.

Resilience. Figure 10 shows the results of resilience test on blend compounds after irradiation with γ -rays. Resilience of 100% BR is high, whereas that of 100% GP polystyrene resin is low. In case of stocks with 20%–60% GP polystyrene resin content, the resilience of stocks after remilling is higher than that of stocks before remilling. The resilience of stocks before remilling approaches that of 100% GP polystyrene resin, whereas the resilience of stocks after remilling approaches that of 100% BR. Therefore, the continuous phase must have a great influence upon resilience.

CONCLUSION

The effects of the continuous phases of GP polystyrene resins on the physical properties of the vulcanizates were studied using the BR–GP polystyrene resin blend. The specimens were prepared with the radiation cure in combination with the methods as described in the previous paper.¹ Some studies were made on the state of phases of vulcanizates by the radiation cure, and the following results were obtained:

(1) The state of phase of unvulcanized stocks seems to be almost retained even after being irradiated with γ -rays under ordinary conditions.

(2) Tensile strength at failure is determined only by the blend ratio whether GP polystyrene resin forms continuous phases or not.

(3) Hardness, modulus, elongation, permanent set, and resilience are largely influenced by whether GP polystyrene resin forms continuous phases or not, even if the blend ratio is kept constant. In this case, the characteristics of a polymer which forms continuous phases is prominent in polymer blend compounds.

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