

## Change of Mixing State of Polybutadiene Rubber-Polyolefin Resin Blend by Remilling and Heat Treatment

KUNIO SATAKE, *Synthetic Rubber Technical Service Laboratory, Asahi Chemical Ind. Co., Ltd., Kawasaki-shi, Japan*

### Synopsis

The change of the mixing state of polybutadiene rubber-polyolefin resin blend resulting from remilling and heat treatment was studied. Polyolefin resins studied here were high-pressure polyethylene, low-pressure polyethylene, and polypropylene. As in case of polybutadiene rubber-general purpose polystyrene resin blend, we made use of the results obtained through hardness and compression modulus measurement and microscopic observation. Even in case of polybutadiene rubber-polyolefin resin blend, the change of mixing state and the softening phenomenon by remilling were observed. The hardening phenomenon by heat treatment of the sample softened by remilling was also observed at high polyolefin resin content. But at low polyolefin resin content, the hardness which had increased once often decreased as the heat treating time increased, and in some cases the nonremilled sample was observed to soften with heat treatment. These phenomena attendant on heat treatment show that the intrinsic nature of a heterogeneous blend system also appears in a microheterogeneous polymer blend system.

### INTRODUCTION

In the previous experiment,<sup>1</sup> the studies on the mixing conditions, the mixing state, and the physical properties of unvulcanized samples of the polybutadiene rubber (BR)-general purpose polystyrene resin (GP polystyrene resin) blend showed that GP polystyrene resins could form either a continuous or a discontinuous phase, even if the polymer blend ratio was kept constant.

In the present paper, the change of the mixing state of BR-polyolefin resin (PO resin) blend with remilling and heat treatment was studied from the same point of view as in the previous report.<sup>1</sup> PO resins studied here were high-pressure polyethylene (HPPE), low-pressure polyethylene (LPPE), and polypropylene (PP).

There are several reports on a blend of rubber with PO resin,<sup>2</sup> also on a mixing method<sup>3</sup> and a mixing state.<sup>4</sup> However, the change of the mixing state and the softening phenomenon by remilling in these blend systems have not been reported yet. Therefore, in this report, the change of the mixing state of these blend systems by remilling was studied on the basis of the results of the previous paper.<sup>1</sup> Heat treatment and microscopic observation were made on the samples softened by remilling as stated in

the previous paper.<sup>1</sup> And further, the test of heat treatment was made on the nonremilled samples.

## EXPERIMENTAL

### Polymers

The polymers studied here are shown in Table I. These polymers are commercially available and were used for the experiment without purification.

TABLE I  
Polymers Used

Polymer	Trade name	Melt index (2160 g, 190°C), g/10 min	Vicat softening point, °C
Low- <i>cis</i> -BR	Asadene NF 35R	—	—
HPPE	Asahi-Dow polyethylene M6520	20	83
LPPE	Hizex 1200J	10	128
PP	Avisun 1016	2.4	149

### Procedure for Polymer Blend

A 10-in. diam × 20-in. length open mill (20 rpm and 24 rpm for front and back rolls, respectively) was used to blend polymers as described in the previous paper,<sup>1</sup> setting roll clearance about 0.9 mm. Blending was accomplished by adding PO resin to the BR band on the roll within about 10 min. The roll surface temperature was set at about 110°C for the blend of HPPE, 135°C for LPPE, and 165°C for PP, respectively. These temperatures are about 10°C higher than those at which PO resin melts apparently uniformly into the BR band. Sheeting-out was carried out with a roll clearance of about 1.5 mm.

### Procedure for Remilling

Remilling was performed with the same open mill and under the same conditions as mentioned above, except that roll surface temperature was set at 70°C in this case. Blends except those with high BR content were finely ground by remilling. However, as they are repeatedly fed into the mill and the roll clearance was made as narrow as possible, fragile bands were formed gradually. Remilling was continued for about 10 min.

### Heat Treatment of Polymer Blend

Heat treatment of the BR-PO resin blend was the same as in the case of the BR-GP polystyrene resin blend.<sup>1</sup> Cuboidal specimens, 1.5 cm × 3.0 cm × 3.0 cm, were heat treated in an air oven for the required time. The

temperature of heat treatment was set at 130°C for the HPPE blend, 150°C for LPPE, and 180°C for PP.

### Testing Methods of Physical Properties of Unvulcanized Specimens

**Hardness.** Hardness was measured by an Asker-C-type hardness tester, setting a contact time of 30 secs. The temperature was set as described in JIS (Japanese Industrial Standard) K 6301.

**Compression Modulus.** Using 17.8-mm diam  $\times$  12.7-mm high cylindrical specimens, the apparent initial modulus of compression was measured by an Instron-type universal tensile-compression tester at the compression speed of 0.5 mm/min. The temperature was set as described in JIS K 6301.

### Microscopic Observation

Micrographs were taken with a phase contrast microscope and a polarization microscope in order to investigate the state of dispersion of blend polymers. Specimens for the polarization microscopy were prepared by holding a thin, sliced sample together with a very small amount of BR between a slide glass and a cover glass and pressing them tightly. Specimens for the phase contrast microscopy were prepared by using liquid paraffin wax in place of BR.

## RESULTS AND DISCUSSION

### Hardnesses of Polymer Blend Before and After Remilling

The hardness of unvulcanized stocks before and after remilling of BR-HPPE, BR-LPPE, and BR-PP blends is shown in Figures 1, 2, and 3, respectively. As in the case of the BR-GP polystyrene resin blend, it is presumed from these experimental curves of hardness that the continuous phase of PO resin is fully formed in the stocks before remilling with more than 40% (wt-%, same hereinafter) PO resin content; on the contrary, in the stocks with less than 20% PO resin content, PO resin disperses in small particles in the BR phase.

The softening phenomenon by remilling is not observed in the stocks with less than about 20% PO resin content, although it differs depending upon the kind of resins used. This may be natural since PO resin does not form a continuous phase in the stocks before and after remilling.

The softening phenomenon by remilling is always observed in the stocks with more than 20% PO resin content. However, unlike the BR-GP polystyrene resin blend, the higher the content of PO resin, the more difficult it is to operate a mill, and remilling cannot be smoothly made. In case of HPPE, remilling was possible up to 70% HPPE content, and the softening phenomenon by remilling was observed. In case of the LPPE or PP, it was still more difficult to operate a mill, and it was impossible to remill the stocks with more than 40% PO resin content. In the stocks with less than

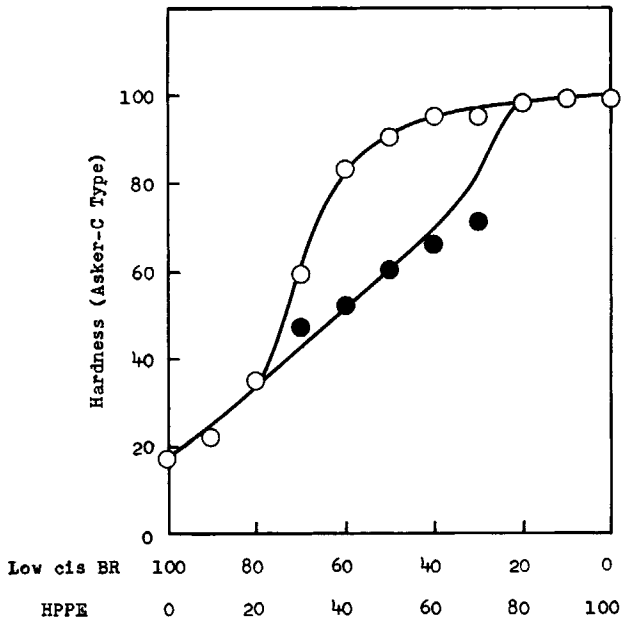


Fig. 1. Hardness of unvulcanized stocks (low-cis-BR-HPPE blend). (○) Nonremilled specimens; (●) remilled specimens.

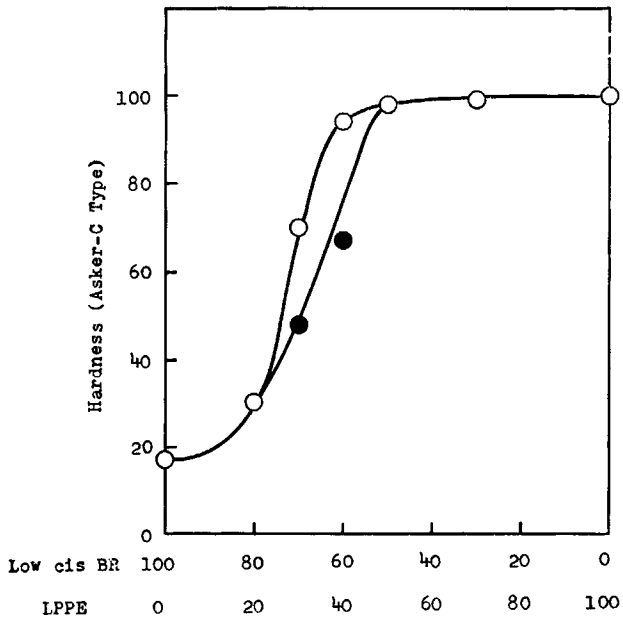


Fig. 2. Hardness of unvulcanized stocks (low-cis-BR-LPPE blend). (○) Nonremilled specimens; (●) remilled specimens.

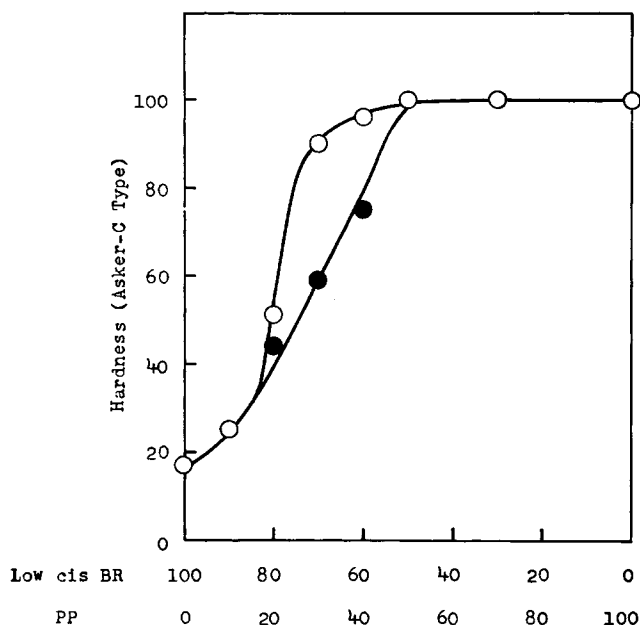


Fig. 3. Hardness of unvulcanized stocks (low-*cis*-BR-PP blend). (○) Nonremilled specimens; (●) remilled specimens.

40% PO resin content, the softening phenomenon by remilling was naturally observed. The softening phenomenon by remilling may be caused by the change of the continuous phase of PO resin into the discontinuous one, as in the case of the BR-GP polystyrene resin blend.

#### Compression Modulus of Polymer Blend Before and After Remilling

In order to obtain more definite information on the change of mixing state, the author studied the compression modulus. Figures 4 to 6 show the apparent compression modulus of BR-HPPE, BE-LPPE, and BR-PP blends before and after remilling, respectively. Curves I and II in these figures are the theoretical curves derived from the parallel model of Kawai and his co-workers,<sup>5,6</sup> in which stress is assumed to be additive. BR is taken as a continuous phase and PO resin, as a discontinuous phase in curve I (BR as sea, PO resin as island), and it is reversed in curve II. These figures demonstrate what was mentioned in the previous paragraph.

#### Micrographs of Polymer Blend Before and After Remilling

Micrographs of blends were taken with the phase contrast microscope in order to observe the fact that the softening phenomenon by remilling is caused by the change of the continuous phase of PO resin into the discontinuous one. Some examples of the results obtained are shown in Figures 7 to 12, and these figures clearly confirm the fact mentioned above.

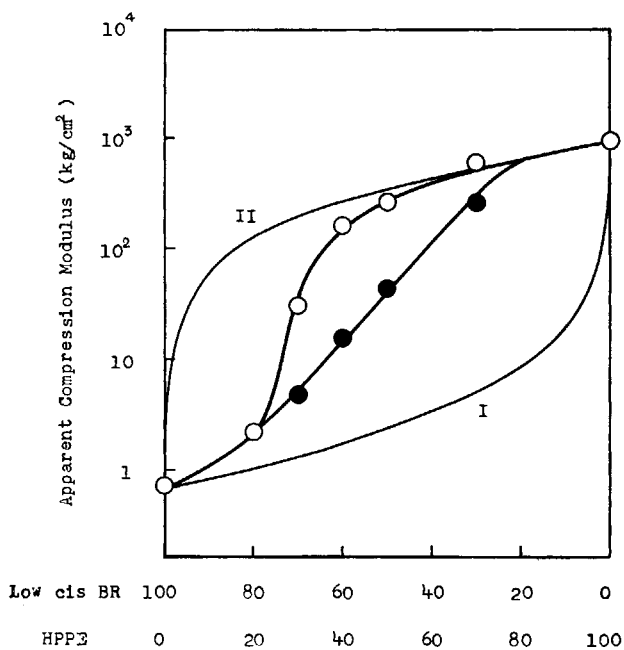


Fig. 4. Apparent compression modulus of unvulcanized stocks (low-cis-BR-HPPE blend). (○) Nonremilled specimens; (●) remilled specimens.

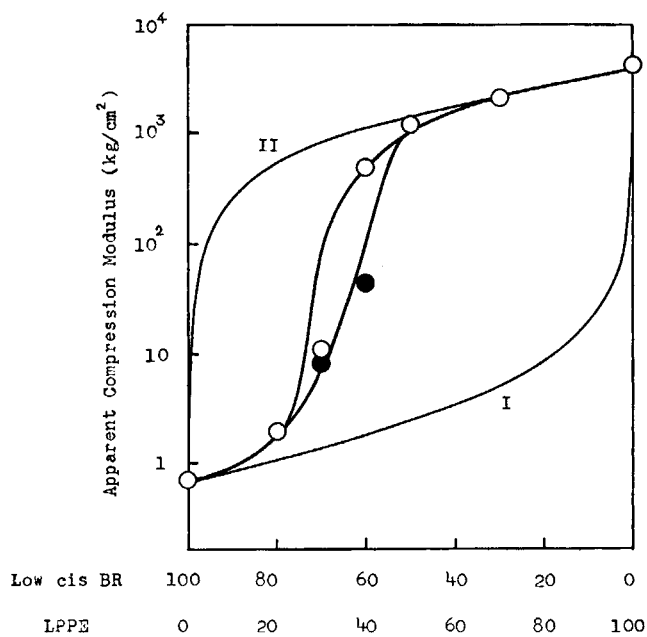


Fig. 5. Apparent compression modulus of unvulcanized stocks (low-cis-BR-LPPE blend). (○) Nonremilled specimens; (●) remilled specimens.

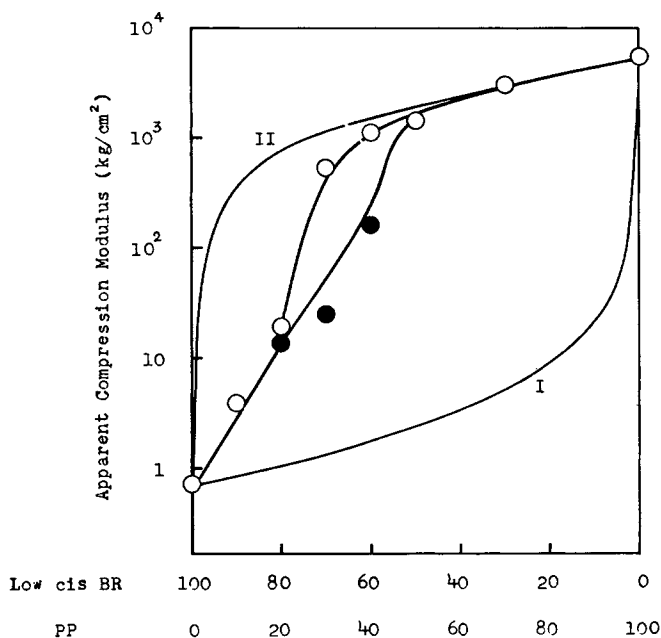


Fig. 6. Apparent compression modulus of unvulcanized stocks (low-*cis*-BR-PP blend). (○) Nonremilled specimens; (●) remilled specimens.

### Heat Treatment of Stocks Softened by Remilling

Heat treatment of the stocks softened by remilling was made in the same way as in case of the BR-GP polystyrene resin blend;<sup>1</sup> if the softening phenomenon is based on the mechanical destruction of the PO resin phase, as mentioned in the previous paper,<sup>1</sup> the hardening phenomenon is again expected upon further heat treatment.

In Figure 13, the Asker-C hardness of the stocks softened by remilling of HPPE blend is plotted against the time of the heat treatment, keeping the temperature of the heat treatment at 130°C. Figures 14 and 15 show the results obtained on LPPE blend (at 150°C) and PP blend (at 180°C) by the same experimental procedures. In Figures 13 to 15, hardening phenomena by heat treatment are observed in the stocks with 50% and 60% HPPE content, with 40% LPPE content, and with PP, and it is shown that the hardness of the specimen hardened by the heat treatment is restored up to a certain value which is closer to that of the nonremilled stocks. But it never reaches that value. In the stocks with 30% HPPE content and with 30% LPPE content, the hardness scarcely changes. It was observed that the stocks with 40% HPPE content exhibit a peculiar behavior: the hardness which had increased once decreased as the heat treating time increased.

In the previous paper,<sup>1</sup> it was reported that the hardening phenomena resulting from the heat treatment of the stock softened by remilling are widely observed in the BR-GP polystyrene resin blend and that they were caused

by the change of the discontinuous phase of GP polystyrene resin into the continuous phase due to the thermal flow and the reagglomeration of GP polystyrene resin during heat treatment. In the BR-PO resin blend, it is also presumed that the hardening phenomena by heat treatment of the stock

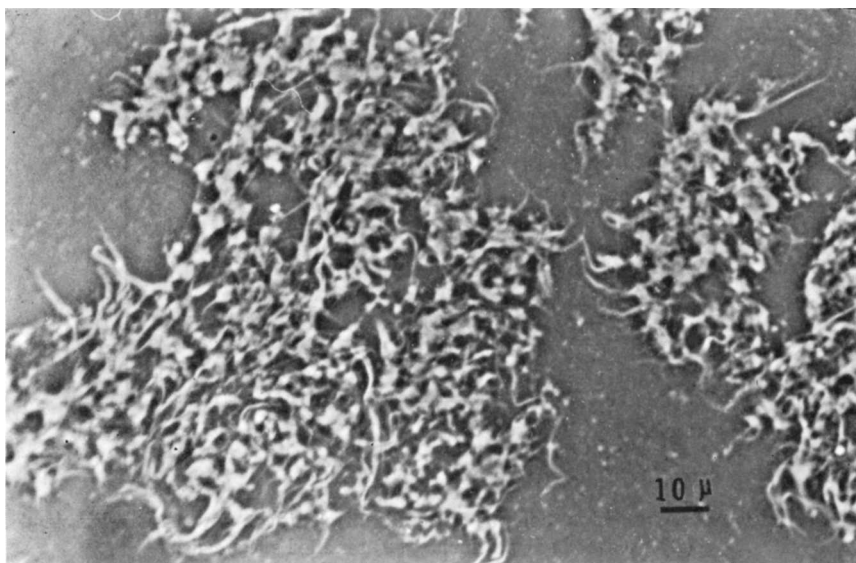


Fig. 7. Phase contrast-microscopic photograph of stock with 40% HPPE content. Nonremilled specimens; hardness (Asker-C-type): 96.

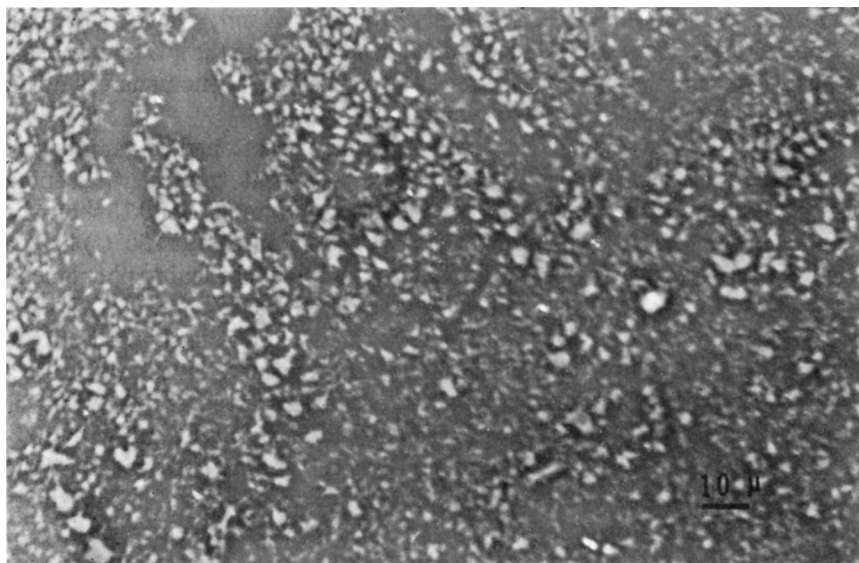


Fig. 8. Phase contrast-microscopic photograph of stock with 40% HPPE content. Remilled specimens; hardness (Asker-C-type): 75.



softened by remilling occur according to the same reason as mentioned above.

In the stocks with 40% HPPE content, the hardening phenomena are also observed if the time of heat treatment is short, and this also may be as-

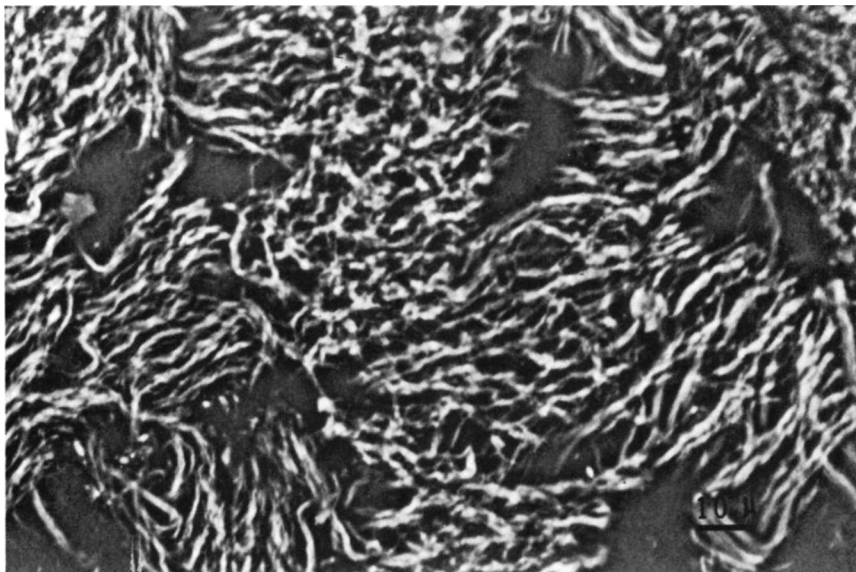


Fig. 9. Phase contrast-microscopic photograph of stock with 40% LPPE content. Non-remilled specimens; hardness (Asker-C-type): 94.

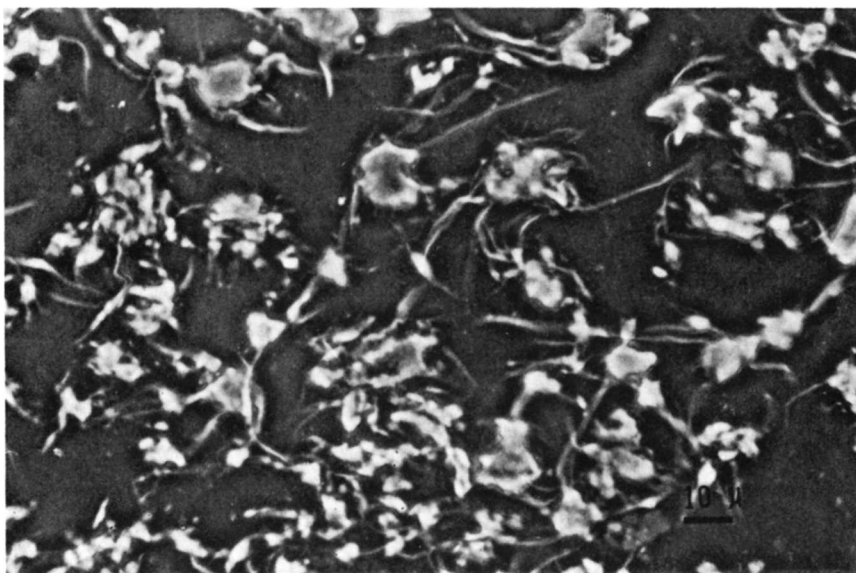


Fig. 10. Phase contrast-microscopic photograph of stock with 40% LPPE content. Remilled specimens; hardness (Asker-C-type): 67.

cribed to the same reason. In this case, however, the hardness decreases as the time of heat treatment increases. This is perhaps because the continuous phase of HPPE, formed imperfectly during the heat treatment, changes again into the discontinuous phase owing to granulation.

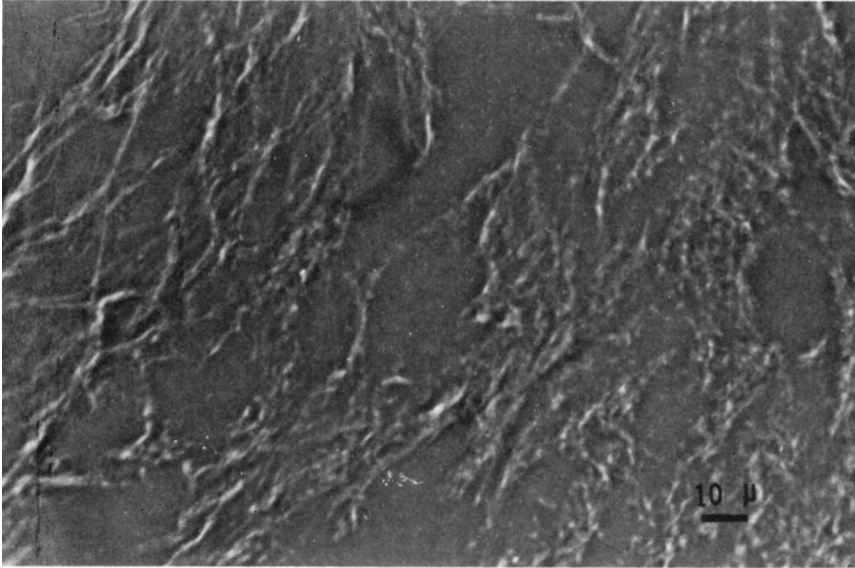


Fig. 11. Phase contrast-microscopic photograph of stock with 20% PP content. Non-milled specimens; hardness (Asker-C-type): 51.

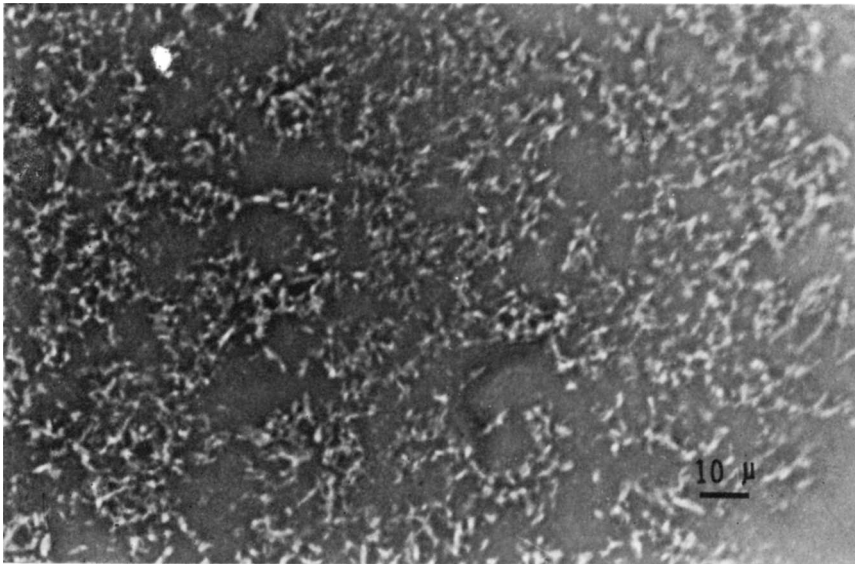


Fig. 12. Phase contrast-microscopic photograph of stock with 20% PP content. Remilled specimens; hardness (Asker-C-type): 44.

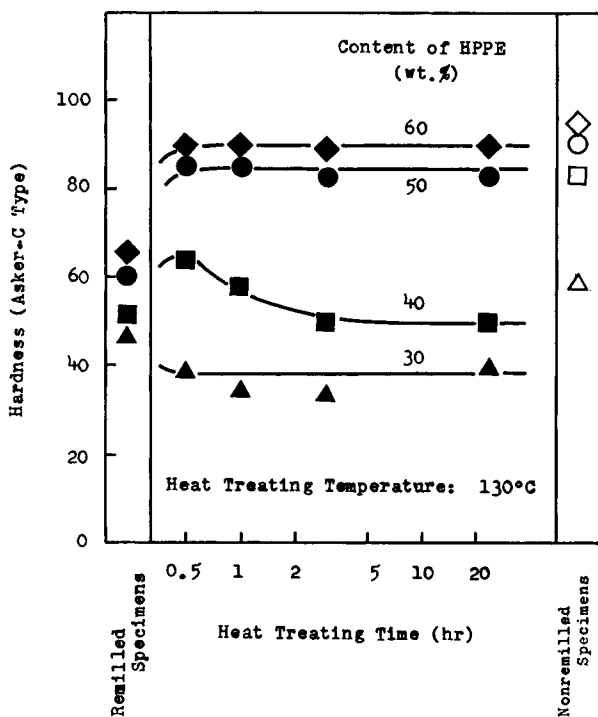


Fig. 13. Heat treatment of stock softened by remilling (low-*cis*-BR-HPPE blend)

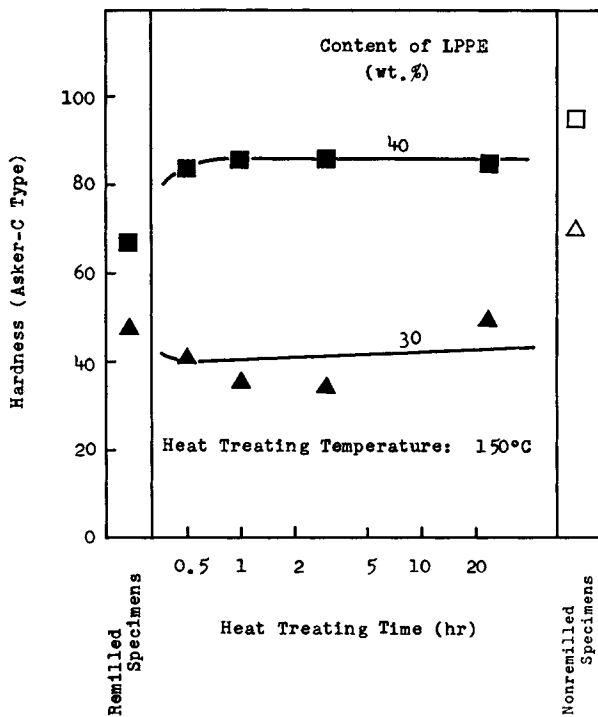


Fig. 14. Heat treatment of stocks softened by remilling (low-*cis*-BR-LPPE blend)

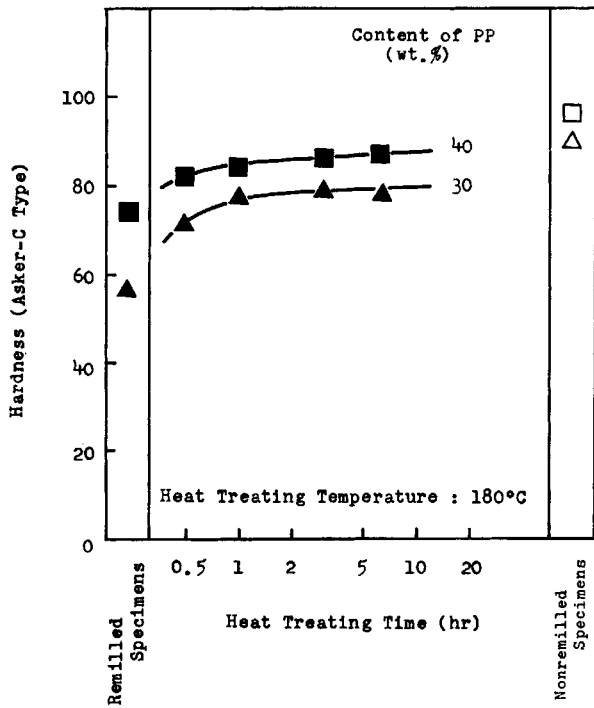


Fig. 15. Heat treatment of stocks softened by remilling (low-cis-BR-PP blend).

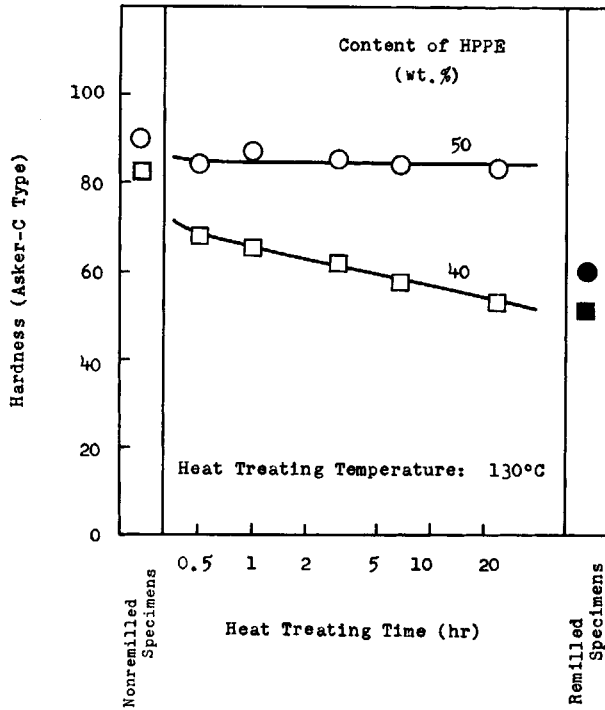


Fig. 16. Heat treatment of stocks before remilling (low-cis-BR-HPPE blend).

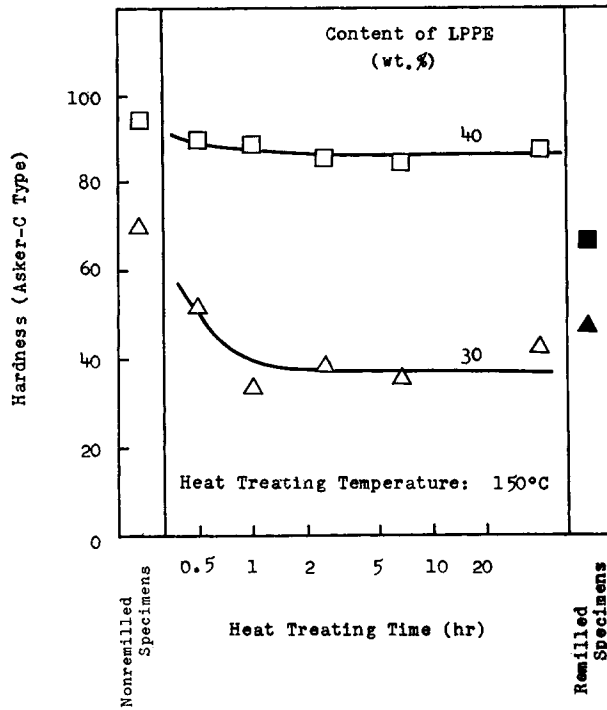


Fig. 17. Heat treatment of stocks before remilling (low-*cis*-BR-LPPE blend).

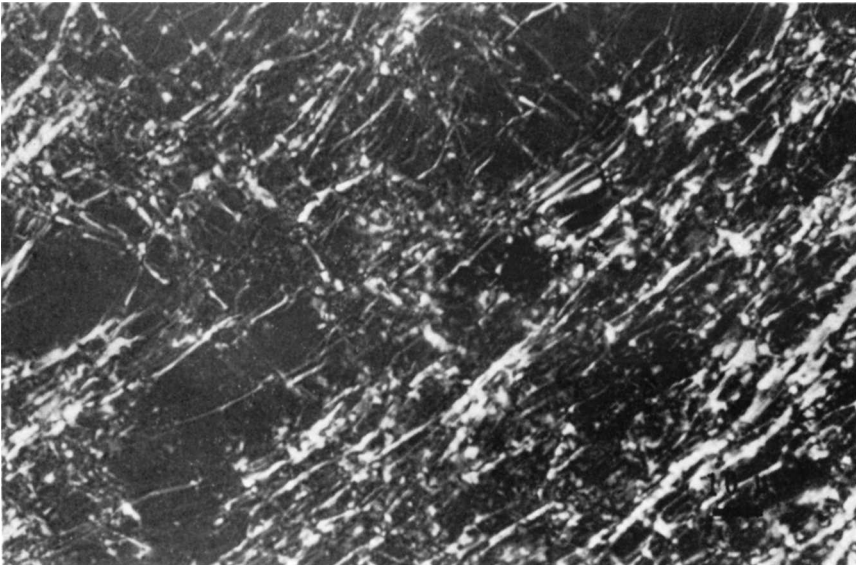


Fig. 18. Polarization-microscopic photograph of the stock with 30% LPPE content. Nonremilled specimens before treatment; hardness (Asker-C-type): 64.

### Heat Treatment of Stocks before Remilling

Based on the considerations in the foregoing paragraph, a further heat treatment of the stock before remilling was carried out, because the decrease in hardness was also expected as a result of the change of the continuous phase of HPPE into the discontinuous phase. Figure 16 shows the results of the heat treatment of a blend of BR and HPPE before remilling. As expected, in the stocks with 50% HPPE content, the decreasing of hardness is scarcely observed, and even if the time of heat treatment is long (10 or 20 hr), the hardnesses are maintained at a certain value which is closer to that of the nonremilled specimen before heat treatment. But the hardness of the stock with 40% HPPE content decreases with lapse of time of heat treatment and tends to come close to that of the stock softened by remilling.

The same experiments were made on a blend of BR and LPPE, and the results are shown in Figure 17. In this case, the same phenomenon is observed as in the blend of BR and HPPE. The change of the LPPE phases into the granular shape (discontinuous phase) by heat treatment is clearly shown in the polarization micrographs of the blend with 30% LPPE content (cf. Figs. 18 and 19).

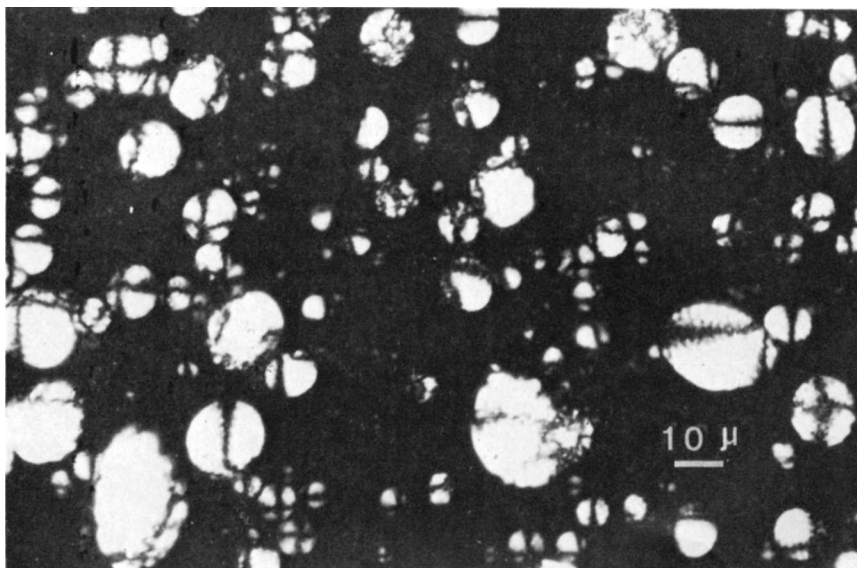


Fig. 19. Polarization-microscopic photograph of the stock with 30% LPPE content. Nonremilled specimens after heat treatment, 150°C for 75 hr; hardness (Asker-C-type): 36.

### Effects of Heat Treatment

As observed in the previous paragraphs, those two apparently contradictory phenomena—the increase and the decrease of hardness attendant on heat treatment—are explainable, considering the fact that both of them oc-

cur according to the intrinsic nature of a heterogeneous blend system to reduce the interface of polymers to a minimum when it is heat treated. But which phenomenon takes place depends upon the kind of blend polymer, the blend ratio, and the temperature and the time of heat treatment. In the

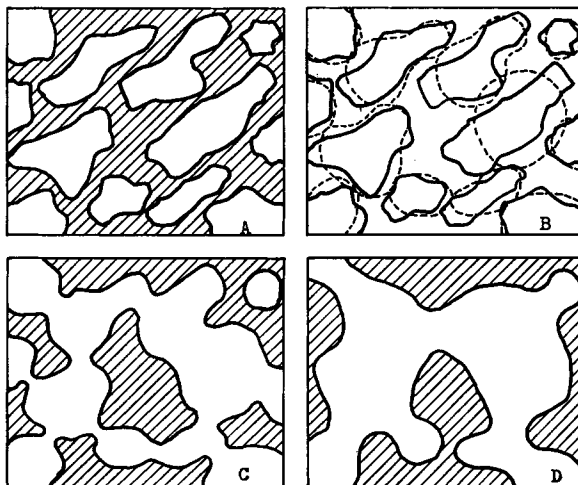


Fig. 20. Schematic diagrams of hardening process by heat treatment of stocks softened by remilling. The transient phenomenon proceeds from A to D. Vacant parts correspond to PO resin. In B, dotted lines show the transient state of the vacant parts encircled with solid lines from A to C. In C, hardening is shown to take place.

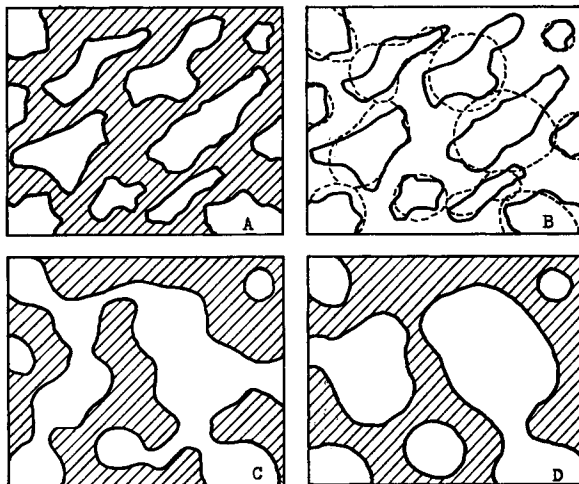


Fig. 21. Schematic diagrams of transient states by way of hardening to softening process by heat treatment of stocks softened by remilling. The transient phenomenon proceeds from A to D. Vacant parts correspond to PO resin. In B, dotted lines show the transient state of the vacant parts encircled with solid lines from A to C. The specimen is once hardened, as is shown in C, follow by softening, as in D.

case of heat treatment of remilled specimens, the reason why the hardness decreased after it had increased in the stocks with relatively low contents of HPPE (40%) might be that the blend was under such conditions that the once formed continuous phase of HPPE could become spheroidal (discontinuous phase). Namely, in case of low contents of HPPE, the HPPE phases are subject to a change in shape during the heat treatment and the continuous phase becomes spheroidal (discontinuous phase) (cf. Figs. 20 and 21).

On the other hand, in the case of heat treatment of nonremilled specimens, the reason why the hardness scarcely changed in the stocks with higher

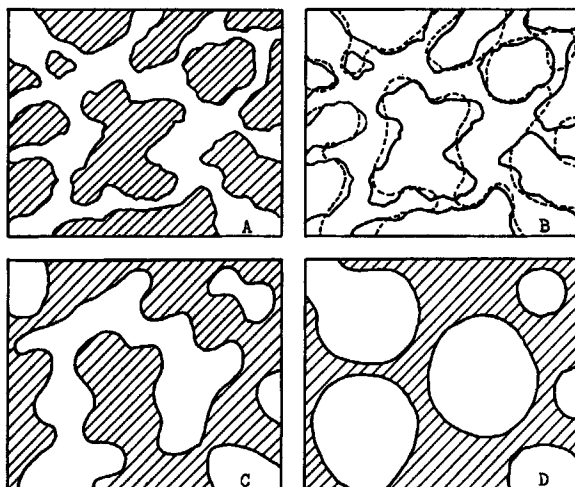


Fig. 22. Schematic diagrams of softening process by heat treatment of nonremilled stocks. The transient phenomenon proceeds from A to D. Vacant parts correspond to PO resin. In B, dotted lines show the transient state of the vacant parts encircled with solid lines from A to C.

HPPE or LPPE content and decreased in the stocks with lower HPPE or LPPE content might be considered as follows: In the stocks with higher content of HPPE or LPPE, the HPPE or LPPE phases are difficult to change in shape during the heat treatment, and the continuous phase of HPPE or LPPE does not become granular (discontinuous phase); therefore, little change in hardness occurs. On the other hand, in the stocks with lower HPPE or LPPE content, the HPPE or LPPE phase is subject to change in shape during heat treatment, and the continuous phase changes into the discontinuous phase; therefore, the hardness changes (cf. Fig. 22).

As mentioned above, it may be concluded that the changes in hardness of both remilled and nonremilled specimens caused by heat treatment occur according to the intrinsic nature of a heterogeneous blend system to reduce the interface of polymers to a minimum when it is heat treated.



## CONCLUSIONS

The change of the mixing state of BR-PO resin blend with remilling and heat treatment was studied. PO resins studied here were HPPE, LPPE, and PP. An investigation was made in accordance with the method used for the BR-GP polystyrene resin blend and some new methods. The following results were obtained:

1. In the BR-PO resin blend which is treated by an open mill under an ordinary condition, the phase inversion seems to occur in the PO resin content range of 20% to 40%; in the stocks with more than 40% PO resin content, the continuous phase of PO resin is fully formed. On the other hand, in the stocks with less than 20% PO resin content, it is presumed that PO resin is dispersed like "islands" in the BR phase.

2. Also, in the BR-PO resin blend, the change of the mixing state and the softening phenomenon by remilling are observed over a wide range of blend ratios.

3. The hardening phenomenon by heat treatment of the sample softened by remilling is observed at a high PO resin content.

4. In the sample softened by remilling with low PO resin content, the hardness which has increased once often decreased as the heat treatment time increased.

5. In some cases, a nonremilled sample with low PO resin content is observed to soften with heat treatment.

6. Such phenomena attendant on heat treatment as mentioned in (3) to (5) are caused by the intrinsic nature of a heterogeneous blend system to reduce the interface of polymers to a minimum when it is heat treated.

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