

Changes in Mixing States of Styrene-Butadiene Copolymer Rubber and General-Purpose Polystyrene Resin Mill Blend by Heat Treatment

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Synopsis

The effect of heat treatment in the so-called phase inversion region was studied using uncured mill blends of various commercial styrene-butadiene copolymer rubbers (styrene content, 23.5 to 48 wt-%; styrene block, 0 to 18 wt-%) with general-purpose polystyrene resin (blend ratio, 80-40: 20-60, in wt-%). It was found that the effect of heat treatment on the hardening or softening phenomenon of blends is different in the random type from that in the block-type styrene-butadiene copolymer rubber. A thorough discussion led us to conclude that this difference is caused by the strong interaction between the polystyrene block of the copolymer and the styrene homopolymer of general-purpose polystyrene resin.

INTRODUCTION

In a previous paper,¹ uncured mill blends of various kinds of styrene-butadiene copolymer rubber (SBR) with general-purpose polystyrene resin (GP polystyrene resin) were studied from various points of view. It was clear that they were a microheterogeneous polymer blend system and that, furthermore, both the hardness and the compression modulus changed in S-shaped curves versus blend ratio, as observed in the blends of low *cis*-polybutadiene rubber (low *cis*-BR) with GP polystyrene resin^{2,3} or polyolefin resin (PO resin).⁴ Further studies on the phase inversion region of these systems clarified that the behavior of random SBR differed from that of block SBR on GP polystyrene resin. That is, in the blend of random SBR, the phase of GP polystyrene resin was almost the same as that in the blend of low *cis*-BR with GP polystyrene resin,² whereas in the blend of block SBR, the phase of GP polystyrene resin was dispersed in the states of spherical or round rod particles having diameters of 0.1 to 0.4 μ . The firm continuous phase of GP polystyrene resin, although it is observed in the blend of random SBR, is not easily formed, and the softening phenomenon by remilling is not observed. This difference is thought to be based on the fact that in the blend of block SBR, the interaction between the polystyrene block of block SBR and styrene homopolymer of GP polystyrene resin is so strong that block SBR acts like a surface-active agent.

In the previous paper,¹ nothing was mentioned as to how the polystyrene block of SBR affects the GP polystyrene resin when the blends are heat treated in the phase inversion region; but we did study the effects of heat treatment using the mill blends of low *cis*-BR with GP polystyrene resin² or PO resin.⁴ It was stated that all phenomena attendant on heat treatment occur according to the intrinsic nature of a heterogeneous blend system to reduce the interface of polymers to a minimum. Now, if block SBR acts like a surface-active agent on GP polystyrene resin, its effect will be undoubtedly intensified by heat treatment. The heat treatment on the mill blend of styrene-butadiene-styrene block copolymer (SBS block copolymer) with GP polystyrene resin has already been discussed,⁵ but the effect of polystyrene block was not studied in detail.

In this paper, the authors studied mill blends of various SBR's with GP polystyrene resin, with respect to how the polystyrene block of SBR affects the state of dispersion of GP polystyrene resin in the phase inversion region when the stock is heat treated.

EXPERIMENTAL

Polymers

The polymers studied here are the same as those in the previous paper,¹ and their characteristics are shown in Table I. These polymers are commercially available and were used for the experiment without purification.

Procedure for Polymer Blend

A 10-in.-diameter \times 20-in.-long open mill (20 rpm and 24 rpm for front and back rolls, respectively) was used to blend polymers, setting the roll surface temperature about 150°C and the roll clearance about 0.9 mm. Blending was accomplished by adding GP polystyrene resin to the SBR band on the roll within about 10 min. Pure polymer was also milled under the same conditions.

Procedure for Remilling

Remilling was performed with the same open mill and under the same conditions as mentioned above, except that the roll surface temperature was set at 70° to 90°C in this case.

Heat Treatment of Uncured Mill Blends

Heat treatment was made in the same way as with the blends of low *cis*-BR with GP polystyrene resin² or PO resin.⁴ Cuboidal specimens, 2 cm \times 3 cm \times 5 cm, were heat treated in an air oven, for the required time. The temperature of heat treatment was set at 150°C in accordance with the study of the blend of low *cis*-BR with GP polystyrene resin,² at which temperature thermal flow and reagglomeration of GP polystyrene resin should occur readily.

TABLE I
Polymers Used

	SBR-A	SBR-B	SBR-C	SBR-D	SBR-E	GP polystyrene Resin
Styrene content, wt-%	23.5	25	25	46	48	100
Styrene block, wt-%	0	0	18	0	11	(100)
Styrene sequence distribution	random	random	block	random	block	—
Mooney viscosity						
ML ₁₊₄ (100°C)	52	56	47	45	45	—
Mooney viscosity						
MS ₁₀₊₄ (150°C)	15	11.5	4	10	3	25.5
Specific gravity	0.94	0.94	0.94	0.97	0.97	1.05
Polymerization method	emulsion	solution	solution	emulsion	solution	radical

Testing of Hardness

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

Microscopic Observations

A phase contrast microscope was used to investigate the changes of the state of dispersion of GP polystyrene resin by heat treatment. The specimen was prepared as follows: a thin section was mounted on a slide glass, SBR was dissolved out by *n*-hexane, and one drop of cedar oil was dropped on the residue and pressed firmly with a cover glass.

RESULTS AND DISCUSSION

Heat Treatment and Change of Hardness of Uncured Mill Blend

Heat Treatment of Random SBR Blends

Figures 1 to 3 show the changes in hardness by heat treatment of the mill blends of random SBR's, SBR-A, -B, and -D, with GP polystyrene resin.

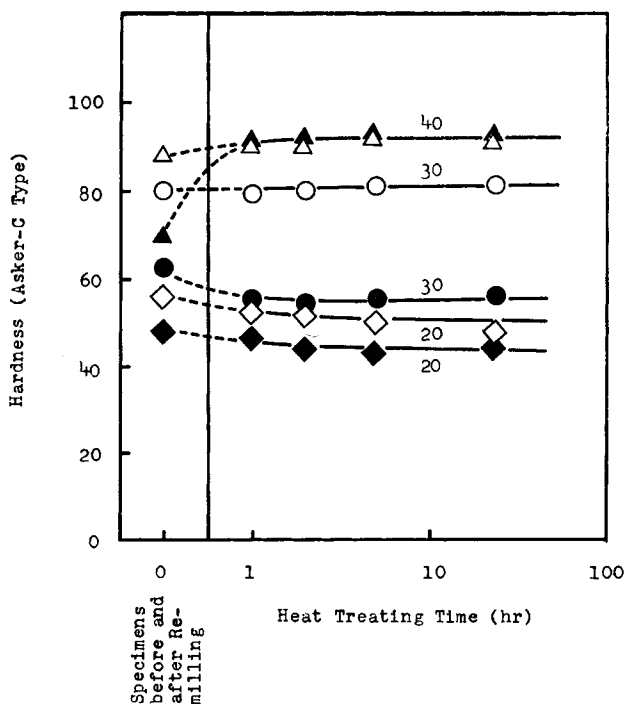


Fig. 1. Heat treatment of uncured blend stocks of SBR-A (23.5% styrene content, without block) and GP polystyrene resin, prepared by mill blend: (○, △, ◇) unremilled specimens; (●, ▲, ◆) remilled specimens. Numbers on curves are GP polystyrene resin contents, wt-%. Heat-treating temperature: 150°C.

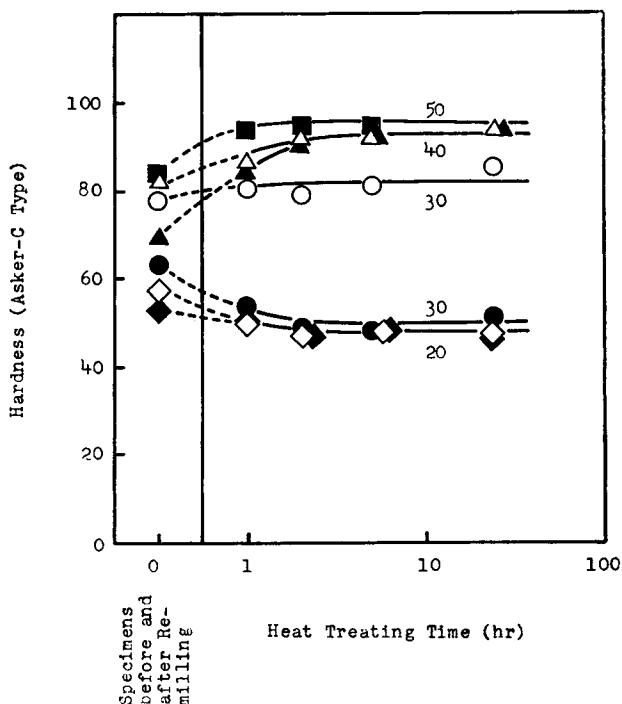


Fig. 2. Heat treatment of uncured blend stocks of SBR-B (25% styrene content, without block) and GP polystyrene resin, prepared by mill blend: (O, Δ, ◇) unmilled specimens; (●, ▲, ◆, ■) remilled specimens. Numbers on curves are GP polystyrene resin contents, wt-%. Heat-treating temperature: 150°C.

The hardening and softening phenomena by heat treatment reflect the change in the state of dispersion of blend polymers, as stated in the previous papers;^{2,4} therefore, examination of changes in hardness serves to elucidate the state of dispersion of polymers.

As is evident from Figures 1 to 3, the effect of heat treatment on the blend of random SBR's is almost similar to that on the blend of low *cis*-BR with GP polystyrene resin shown in Figure 4, although the polymerization methods and the styrene contents of the random SBR's are different.

In stocks containing GP polystyrene resin, 20% (wt-%, the same hereinafter) GP polystyrene resin, is not enough in quantity to develop a firm continuous phase of GP polystyrene resin. Therefore, even in the unmilled stocks, in which a continuous phase is slightly formed, a slight softening phenomenon is observed because the continuous phase changes into the discontinuous one by heat treatment. The decrease in hardness may be partly because the particles of dispersed polymers become spherical by heat treatment. In any case, the hardening phenomenon caused by thermal flow and reagglomerations of GP polystyrene resin is not observed.

In the unmilled stocks containing 30% GP polystyrene resin, a considerably firm continuous phase of GP polystyrene resin is formed, and there-

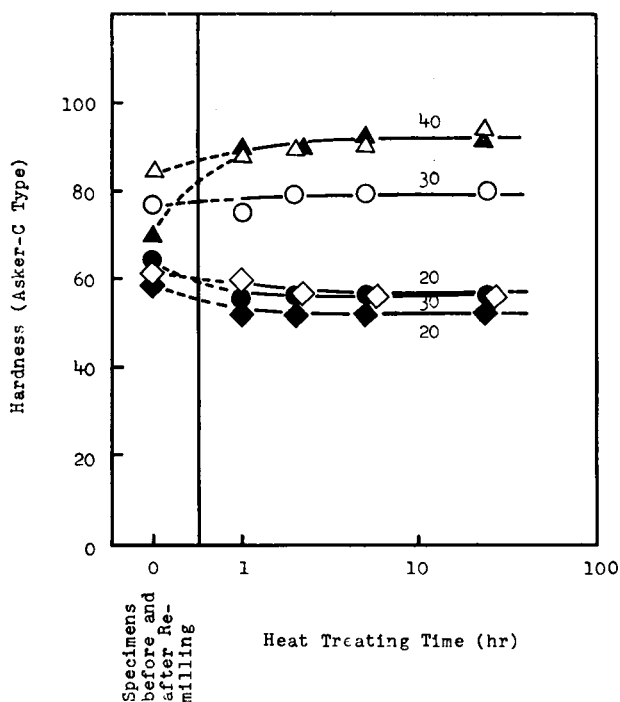


Fig. 3. Heat treatment of uncured blend stocks of SBR-D (46% styrene content, without block) and GP polystyrene resin, prepared by mill blend: (O, Δ, ◇) unremilled specimens; (●, ▲, ◆) remilled specimens. Numbers on curves are GP polystyrene resin contents, wt-%. Heat-treating temperature: 150°C.

fore never changes into the discontinuous phase by heat treatment, resulting in no change in hardness. Moreover, in the blend of low *cis*-BR with GP polystyrene resin, it seems that the continuous phase of GP polystyrene resin becomes more firm by heat treatment, resulting in a slight increase in hardness.

On the other hand, in the remilled stocks containing 30% GP polystyrene resin, the hardness decreases to some extent by heat treatment. This may be caused by the fact that the discontinuous phase of GP polystyrene resin, once formed by remilling, never changes into the continuous phase because the GP polystyrene resin content is not large enough to reform the continuous phase of GP polystyrene resin by the reagglomeration with heat treatment, and also by the fact that the dispersed particles of GP polystyrene resin become more spherical by heat treatment.

In the unremilled stocks containing 40% GP polystyrene resin, it seems that the continuous phase of GP polystyrene resin becomes more firm by heat treatment, and therefore the hardness increases to some extent. Moreover, in the remilled stocks containing 40% GP polystyrene resin, the hardening phenomenon by heat treatment is observed. This may be caused by the fact that the discontinuous phase of GP polystyrene resin, once

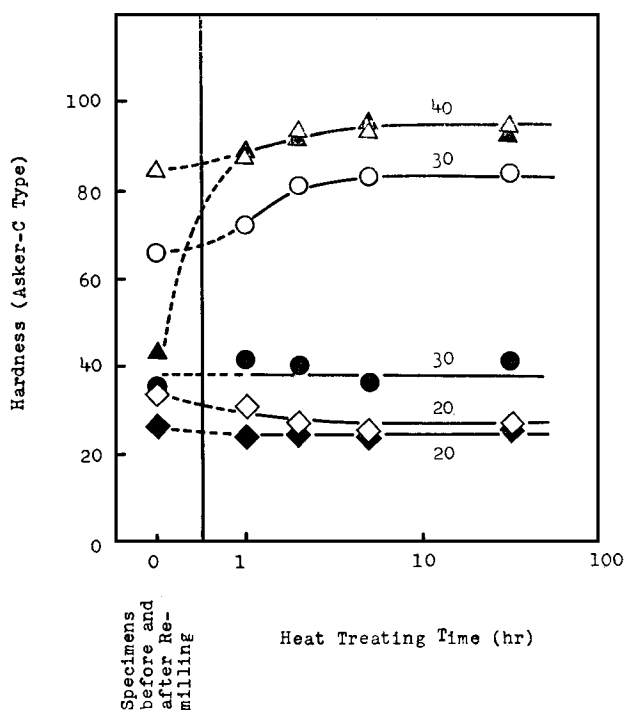


Fig. 4. Heat treatment of uncured blend stocks of low *cis*-BR and GP polystyrene resin, prepared by mill blend: (O, Δ , \diamond) unmilled specimens; (\bullet , \blacktriangle , \blacklozenge) remilled specimens. Numbers on curves are GP polystyrene resin contents, wt-%. Heat-treating temperature: 150°C.

formed by remilling, changes into the firm continuous one because the GP polystyrene resin content is large enough to reform the continuous phase of GP polystyrene resin by reagglomeration upon heat treatment.

Heat Treatment of Block SBR Blends

Figures 5 and 6 show the changes in hardness by heat treatment of the uncured mill blend stocks of block SBR's, SBR-C and -E, with GP polystyrene resin.

In the stocks containing 30% GP polystyrene resin, the GP polystyrene resin phase is dispersed in small and spherical particles, as shown in the previous paper,¹ and is not reagglomerated by heat treatment; consequently, a slight softening phenomenon occurs.

Now, in the stocks containing 40% GP polystyrene resin, with blends of random SBR with GP polystyrene resin (as shown in the previous paragraph), the discontinuous phase of the latter, which is formed by the destruction of continuous phase by remilling, reagglomerates upon heat treatment into the continuous phase, showing a hardening phenomenon. On the other hand, with blends of block SBR, SBR-C, with GP polystyrene

resin, the hardness decreases noticeably upon heat treatment even in the unmilled stocks, although the GP polystyrene resin content is large enough to form a continuous phase.

Moreover, in the present study, the effect of remilling on the SBR-E blend system containing 40% GP polystyrene resin was clearly shown, whereas it had been vague in the previous paper.¹ That is, hardness increases in unmilled stocks, but decreases in remilled stocks when they are heat treated.

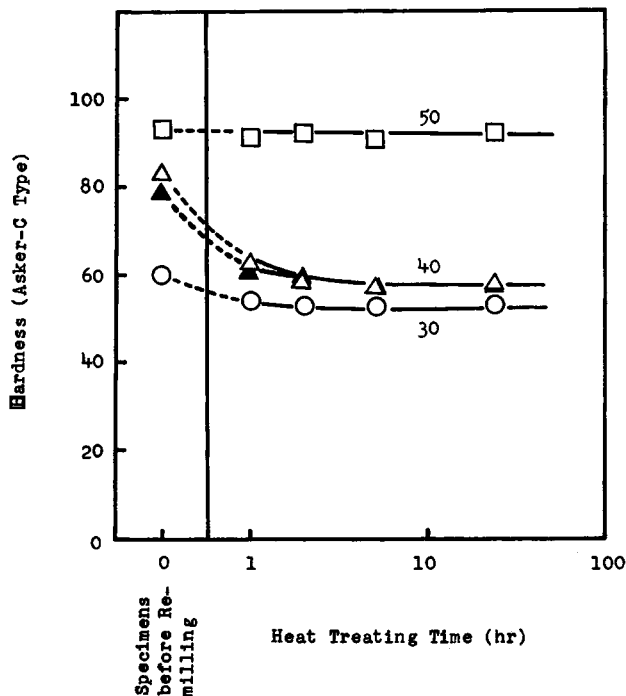


Fig. 5. Heat treatment of uncured blend stocks of SBR-C (25% styrene content, 18% styrene block) and GP polystyrene resin, prepared by mill blend: (O, Δ , \square) unmilled specimens; (\blacktriangle) remilled specimens. Numbers on curves are GP polystyrene resin contents, wt-%. Heat-treating temperature: 150°C.

In the block SBR blend systems containing 50% GP polystyrene resin, no hardening phenomenon is observed upon heat treatment, because the continuous phase of GP polystyrene resin is assumed not to grow any further. However, this is not conclusive because the hardness before heat treatment is already near to full-scale value on the hardness tester. To support the above assumption, we would like to refer to our previous paper⁵ on 40/60 mill blend of SBS block copolymer with GP polystyrene resin, in which the apparent compression modulus was examined and the existence of the softening phenomenon by heat treatment was reported, showing that the GP polystyrene resin phase is likely to become discontinuous very easily.

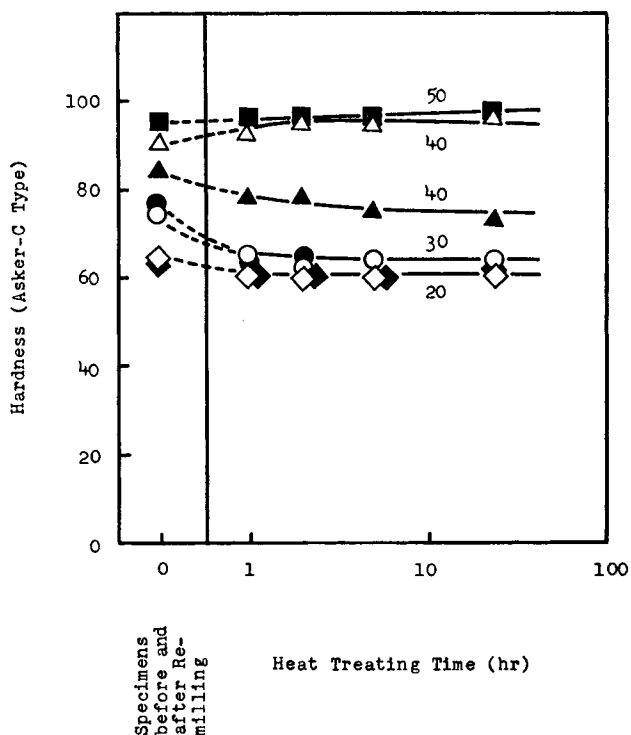


Fig. 6. Heat treatment of uncured blend stocks of SBR-E (48% styrene content, 11% styrene block) and GP polystyrene resin, prepared mill blend: (O, Δ , \diamond ,) unremilled specimens; (\bullet , \blacktriangle , \blacklozenge , \blacksquare) remilled specimens. Numbers on curves are GP polystyrene resin contents, wt-%. Heat-treating temperature: 150°C.

The hardening and softening phenomena by heat treatment, caused by changes in GP polystyrene resin into the continuous or the discontinuous phase, are affected very little by styrene content, but are greatly governed by whether the polystyrene block exists or not. The authors think that this is because the degree of growth of the continuous phase of GP polystyrene resin varies between block SBR and random SBR according to their difference in surface-active effect.

Microscopic Observation

In Figures 7 to 10 are shown the phase contrast micrographs of 70/30 blends of random SBR, SBR-B, with GP polystyrene resin before and after heat treatment. In the unremilled stocks, the continuous phase of GP polystyrene resin seems not to be destroyed by heat treatment, and the hardness increases slightly by agglomeration. In the remilled stock before heat treatment, the continuous phase of GP polystyrene resin seems to be destroyed considerably but not completely. Once this remilled stock is heat treated, its continuous phase is completely destroyed, and it is dispersed in spherical particles.

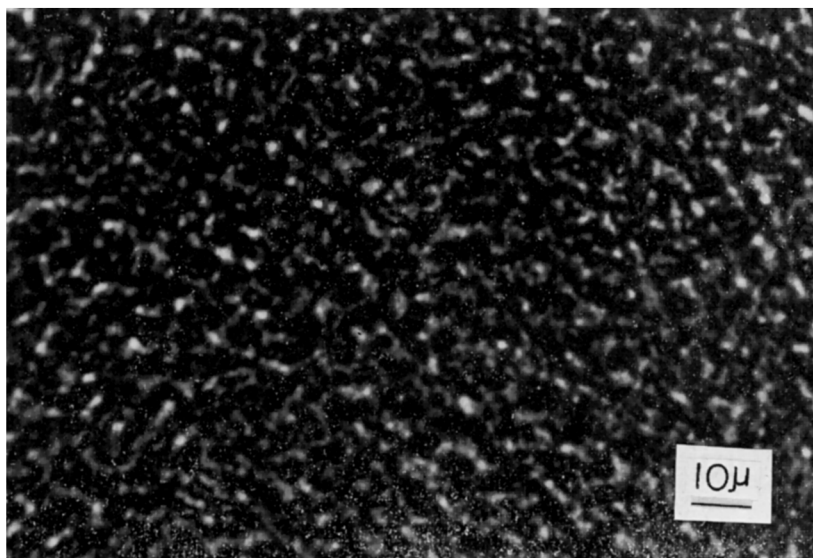


Fig. 7. Phase contrast micrograph of SBR-B (25% styrene content, without block)-GP polystyrene resin blend (70/30 weight ratio, before remilling), prepared by mill blend; before heat treatment. Asker-C hardness: 78.

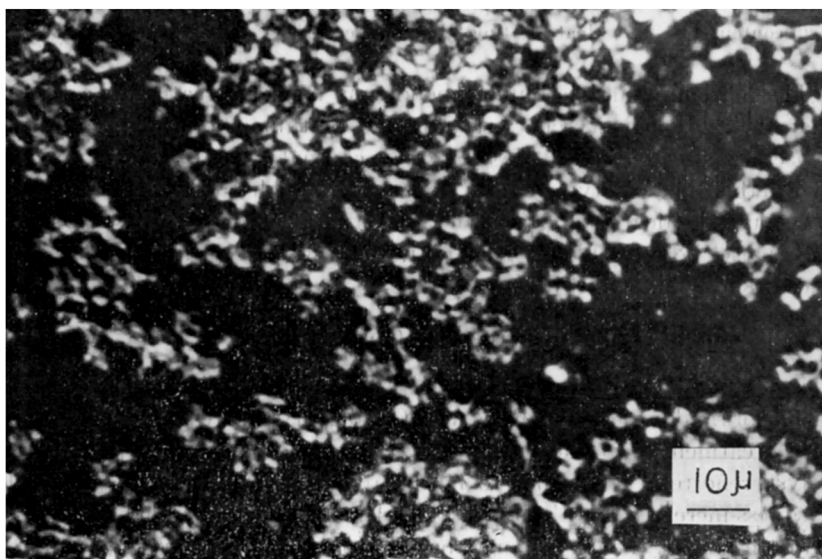


Fig. 8. Phase contrast micrograph of SBR-B (25% styrene content, without block)-GP polystyrene resin blend (70/30 weight ratio, before remilling), prepared by mill blend. Heat treatment: $150^{\circ}\text{C} \times 5$ hr. Asker-C hardness: 81.

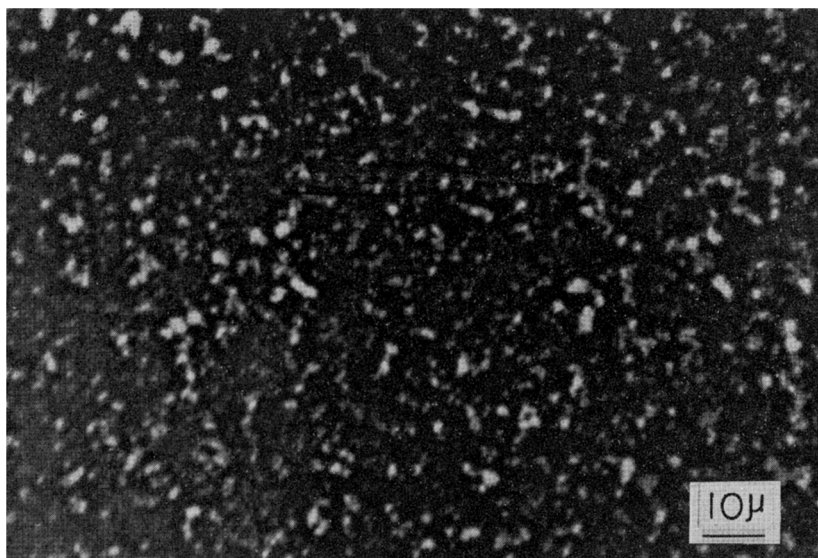


Fig. 9. Phase contrast micrograph of SBR-B (25% styrene content, without block)-GP polystyrene resin blend (70/30 weight ratio, after remilling), prepared by mill blend; before heat treatment. Asker-C hardness: 64.



Fig. 10. Phase contrast micrograph of SBR-B (25% styrene content, without block)-GP polystyrene resin blend (70/30 weight ratio, after remilling), prepared by mill blend. Heat treatment: 150°C \times 5 hr. Asker C hardness: 48.

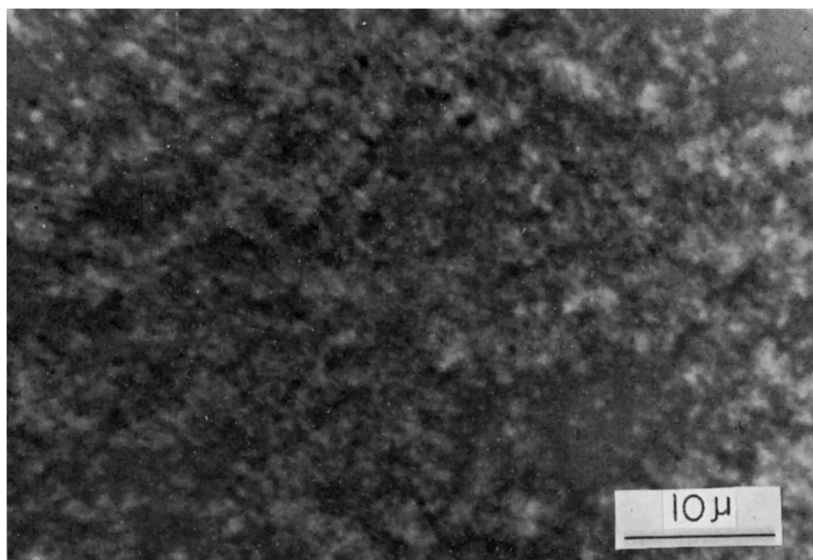


Fig. 11. Phase contrast micrograph of SBR-C (25% styrene content, 18% styrene block)-GP polystyrene resin blend (60/40 weight ratio, before remilling), prepared by mill blend; before heat treatment. Asker-C hardness: 83.

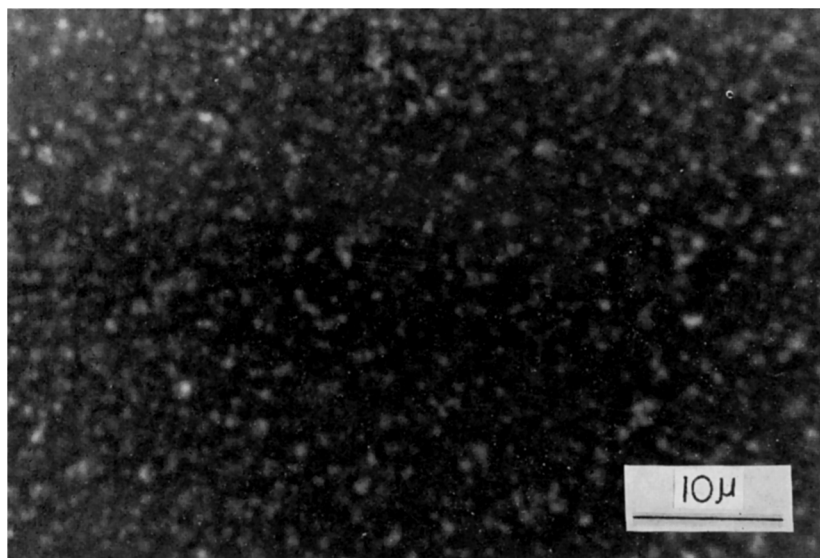


Fig. 12. Phase contrast micrograph of SBR-C (25% styrene content, 18% styrene block)-GP polystyrene resin blend (60/40 weight ratio, before remilling), prepared by mill blend. Heat treatment: 150°C × 5 hr. Asker-C hardness: 58.

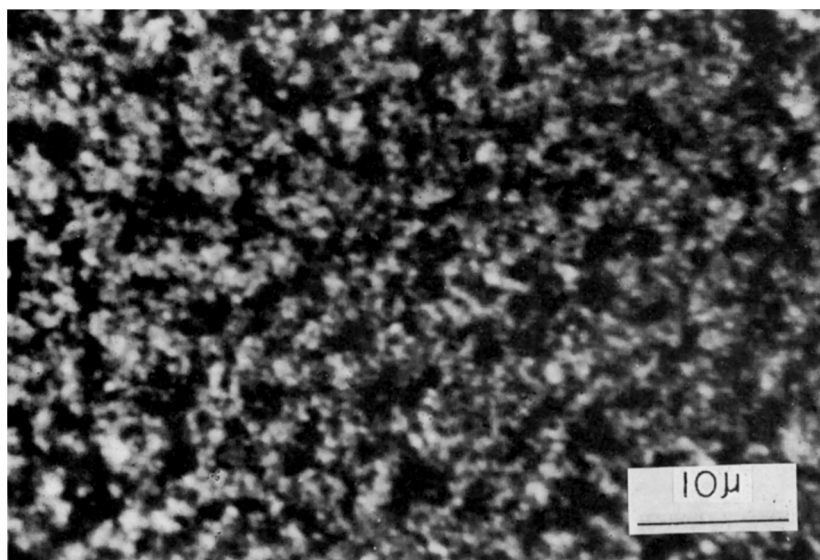


Fig. 13. Phase contrast micrograph of SBR-E (48% styrene content, 11% styrene block)-GP polystyrene resin blend (60/40 weight ratio, before remilling), prepared by mill blend; before heat treatment. Asker-C hardness: 90.

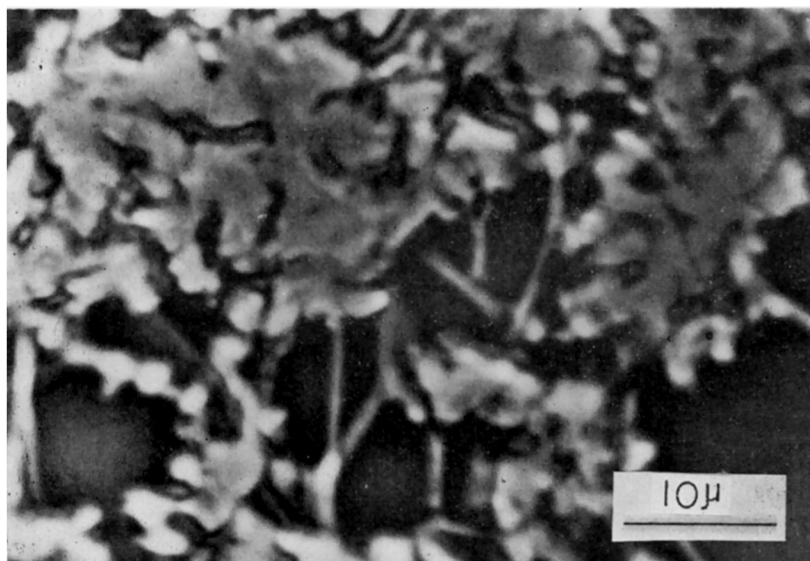


Fig. 14. Phase contrast micrograph of SBR-E (48% styrene content, 11% styrene block)-GP polystyrene resin blend (60/40 weight ratio, before remilling), prepared by mill blend. Heat treatment: $150^{\circ}\text{C} \times 5$ hr. Asker-C hardness: 94.

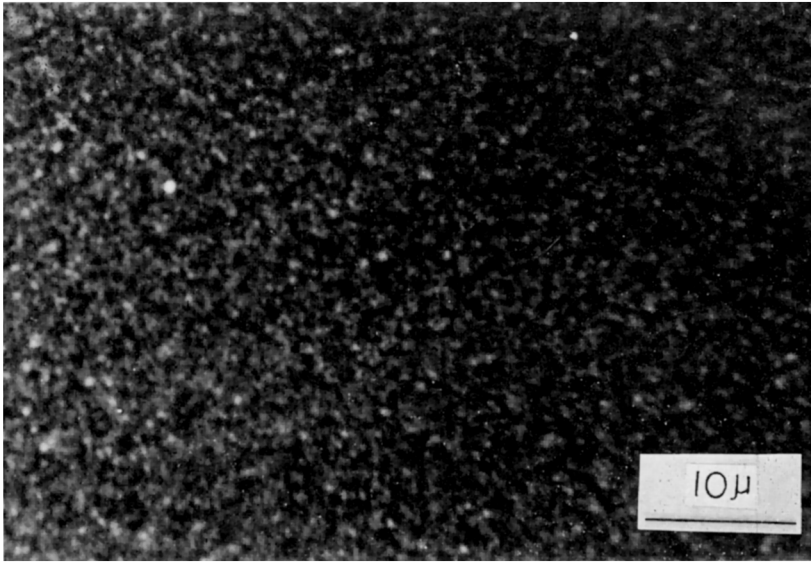


Fig. 15. Phase contrast micrograph of SBR-E (48% styrene content, 11% styrene block)-GP polystyrene resin blend (60/40 weight ratio, after remilling), prepared by mill blend; before heat treatment. Asker-C hardness: 83.

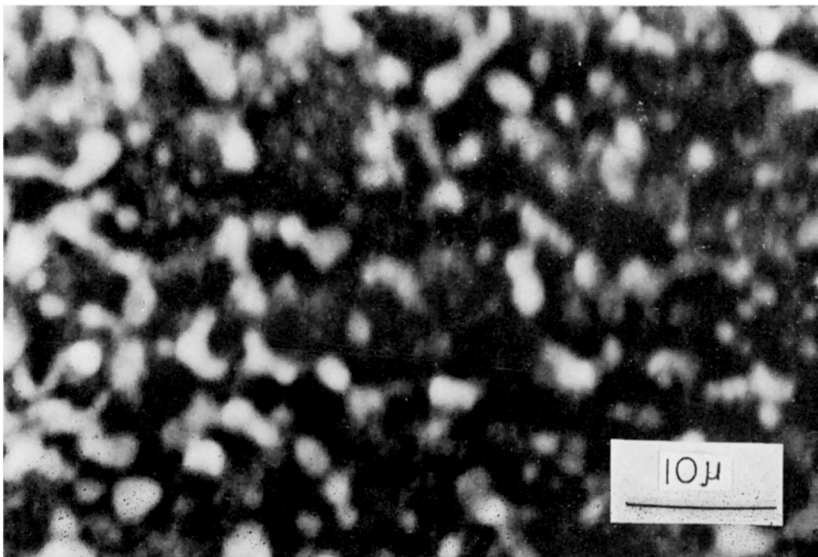


Fig. 16. Phase contrast micrograph of SBR-E (48% styrene content, 11% styrene block)-GP polystyrene resin blend (60/40 weight ratio, after remilling), prepared by mill blend. Heat treatment: 150°C \times 5 hr. Asker-C hardness: 75.

These phenomena probably occur because of the intrinsic nature of a heterogeneous polymer blend system to reduce the interface of polymers to a minimum when they are heat treated.

In Figures 11 and 12 are shown the phase contrast micrographs of 60/40 blends of block SBR, SBR-C, with GP polystyrene resin before and after heat treatment. From the results of the previous paper,¹ it is known that the cotton-like phase of GP polystyrene resin in the stocks before heat treatment is the finely dispersed aggregate of GP polystyrene resin of particle size 0.1 to 0.4 μ . In Figure 12 it is shown that this phase becomes spherical, approximately 0.5 μ in size, and is dispersed by heat treatment.

In Figures 13 to 16 are shown the phase contrast micrographs of 60/40 blends of block SBR, SBR-E, with GP polystyrene resin before and after heat treatment. As is evident in these micrographs, no noticeable difference is observed between the state of dispersion of GP polystyrene resin before and after remilling when the stocks are not heat treated. This observation supports the results reported in the previous paper¹ that the effect of remilling is small in the blend systems of block SBR's with GP polystyrene resin.

The phase contrast-micrographic observation reveals that the effect of remilling is not obvious in the stocks before heat treatment, but becomes marked after heat treatment. In the unremilled stocks, the firm, continuous phase of GP polystyrene resin is formed upon heat treatment as a result of the reagglomeration of GP polystyrene resin phase, whereas in the remilled stocks, GP polystyrene resin phase is dispersed in spherical particles and the softening phenomenon is observed.

The results of the phase contrast-microscopic observations confirm that, as was reported in the previous papers,^{2,4} the hardening phenomenon by heat treatment represents the tendency of the phase of GP polystyrene resin to become continuous or that of the continuous phase to become more firm, whereas the softening phenomenon represents the opposite.

CONCLUSIONS

The effect of heat treatment on uncured mill blends of various commercial SBR's (styrene content, 23.5 to 48%; styrene block, 0 to 18%) with GP polystyrene resin was studied in the phase inversion region (blend ratio, 80 to 40:20 to 60, in wt-%). The following results were obtained:

1. The effect of heat treatment on the mill blends of various SBR's with GP polystyrene resin differs between block and random SBR.
2. In the blend systems of random SBR's, the formation of a continuous phase of GP polystyrene resin starts with lower blend ratios of GP polystyrene resin than in block SBR's. Moreover, by the heat treatment the continuous phase is made more firm, and consequently the hardening phenomenon is observed.
3. This difference is attributed to the different degree of growth of the continuous phase of GP polystyrene resin between block and random SBR's according to their difference in surface-active action due to block SBR.

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