Softening Phenomenon by Remilling of Styrene–Butadiene Copolymer Rubber–General-Purpose Polystyrene Resin Blend

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Synopsis

The softening phenomenon by remilling of uncured blends of various commercia styrene–butadiene copolymer rubber (styrene content, 23.5 to 48 wt-%, styrene block 0 to 18 wt-%) with general-purpose polystyrene resin was mainly studied by examining the blend ratio dependence of hardness and compression modulus (in logarithmic form), with special attention to the state of dispersion of the polymers. It was found that the blend of styrene–butadiene copolymer rubber with general-purpose polystyrene resin forms a microheterogeneous polymer blend system and that the hardness and the compression modulus change in S-shaped curves versus blend ratio. However, the degree of softening phenomenon by remilling (roll surface temperature, 70°–90°C) was found to be different for the two blend systems, i.e., random styrene–butadiene copolymer rubber and block styrene–butadiene copolymer rubber. The softening phenomenon is more pronounced in random-type rubbers; and in some block-type rubbers, no softening phenomenon was observed. The influence of the styrene content of the polymer is small. Further discussions have shown us that the strong interaction between the polystyrene block of the copolymer and the styrene homopolymer of the general-purpose polystyrene resin controls the state of dispersion of polymers thereby causing this difference in the softening phenomena among the different kinds of styrene–butadiene copolymer rubbers.

INTRODUCTION

In previous papers,[1–10] mill blends of rubber with plastics and of rubber with rubber were studied, and the following results were obtained. When interaction between the blended polymers is weak, a firm, continuous phase of one of the polymers is formed corresponding to the blend ratio, and a phase inversion region exists between the two continuous phases, so that physical properties such as hardness and compression modulus change in S-shaped curves versus blend ratio. Even in this phase inversion region, the firm continuous phase of the polymer with higher compression modulus tends to form, and so the softening phenomenon is observed if the firm continuous phase is broken by remilling under suitable conditions.

On the other hand, when interaction between the blended polymers is strong, small molecular aggregates of one of the polymers invade the mass of

the other polymer, and as a result a continuous phase of the latter polymer does not form, but a very complicated blend system of two polymers appears. In such cases the dependence of physical properties such as hardness and modulus on the blend ratio is monotonic rather than S-shaped, and consequently softening phenomenon by remilling is not observed.[5]

If interaction between the polymers is moderate, the behavior of the system has an intermediate tendency between the two cases discussed above.

The authors found many interesting facts, especially by studies of the blend of general-purpose polystyrene resin (GP polystyrene resin) with low cis-polybutadiene rubber (low cis-BR) or styrene–butadiene–styrene block copolymer (SBS block copolymer).[1,6,7] We believe that these phenomena are governed by the styrene content or the structure of the styrene unit of the blended polymer.

In order to obtain more definite information on this point, the authors studied mill blend systems of GP polystyrene resin with the styrene–butadiene copolymer rubbers (SBR), whose styrene contents or structures of styrene units were different from each other and, therefore, the interactions with GP polystyrene resin might be considered different, paying attention to these influences on the state of dispersion of polymers or on the softening phenomenon by remilling.

On the blend of SBR with GP polystyrene resin, many studies have been made because it is of great interest from the industrial point of view in relation to the problem of high-impact polystyrene resin (HI polystyrene resin). However, there is no report concerning the blend system over all blend ratios, especially from the viewpoint of the phase inversion phenomenon.

From that viewpoint, the authors studied mill blend systems of GP polystyrene resin with various commercial SBR's, and the results obtained are reported in this paper.

EXPERIMENTAL

Polymers

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

Procedure for Polymer Blends

A 10-in.-diameter × 20-in.-long open mill (20 rpm and 24 rpm for front and back rolls, respectively) was used to blend polymers as described in the previous paper,[3] setting roll clearance about 0.9 mm and roll surface temperature about 150°C. 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.

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 ML_{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

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° to 90°C.

Procedure for Molding

The compression molding of the specimens for the measurement of physical properties was carried out essentially as described in the previous paper.[3] The compression temperature was 150°C for unremilled stocks and 70° to 90°C for remilled stocks. There were no differences in hardness between the stocks before and after molding, showing that there were no changes in the state of phase by compression molding.

Testing Methods of Physical Properties of Uncured Specimens

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.

Compression Modulus. Using cylindrical specimens 17.8 mm in diameter and 12.7 mm high, the stress–strain curves at compression were measured by an Instron-type universal tensile compression tester at a compression speed of 0.5 mm/min. Next, as an apparent compression modulus, the value of the rate constant was calculated from the slope of the straight-line part of the initial stress–strain curve at compression. The temperature was set as described in JIS K 6301.

Phase Separation Test of Polymer Solutions

Benzene solutions of blends of various concentrations between 1 to 10 wt-% (total concentration of both polymers) were prepared; three blend ratios were used (wt-%, the same hereinafter): 30/70, 50/50, and 70/30. These solutions were sealed in a container for four weeks, and the critical concentration for phase separation was determined by observing at which point the solutions were separated into two phases.

Microscopic Observations

A phase contrast microscope and an electron microscope (JEM-T6 NIHONDENSHI) were used in order to investigate the state of dispersion of blended polymers. The specimen for phase contrast microscopy 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. Specimens for the electron microscope were prepared as follows: a thin section was cut out by an ultramicrotome and exposed to the vapors from a water solution of osmic acid, which stained the sites of double bonds in the molecules.

RESULTS AND DISCUSSION

Hardness of Uncured Stocks Prepared by Mill Roll Blending

The Asker-C hardnesses of the uncured mill blends, before and after remilling, are shown in Figures 1 to 5. The broken lines in these figures are the corresponding curves of the blend of low cis-BR with GP polystyrene resin, which was reported before.[2]
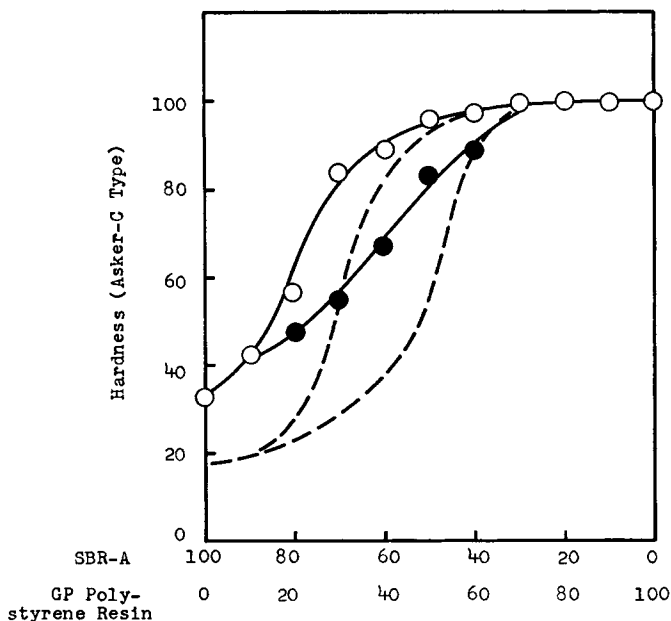

Fig. 1. Asker-C hardness of uncured blend stocks of SBR-A ((23.5% styrene content, without block) and GP polystyrene resin, prepared by mill blend: (O) unremilled specimens; (●) remilled specimens. Broken lines are hardness of low cis-BR–GP polystyrene resin blend system.

As is evident from the figures, the hardness of the mill blends of various SBR's (as shown in Table I) with GP polystyrene resin change in S-shaped curves versus blend ratio, as those of the mill blend of low cis-BR with GP polystyrene resin. In addition, the following is observed:

1. There is no difference in the behavior between the emulsion and solution SBR.

2. It seems that the effect of the softening phenomenon by remilling decreases to some extent with increase in styrene content.

3. The effect of the softening phenomenon by remilling disappears in block SBR.

In the mill blends of random SBR's, SBR-A, -B, and -D, with GP polystyrene resin, the hardness changes in S-shaped curves versus blend ratio,
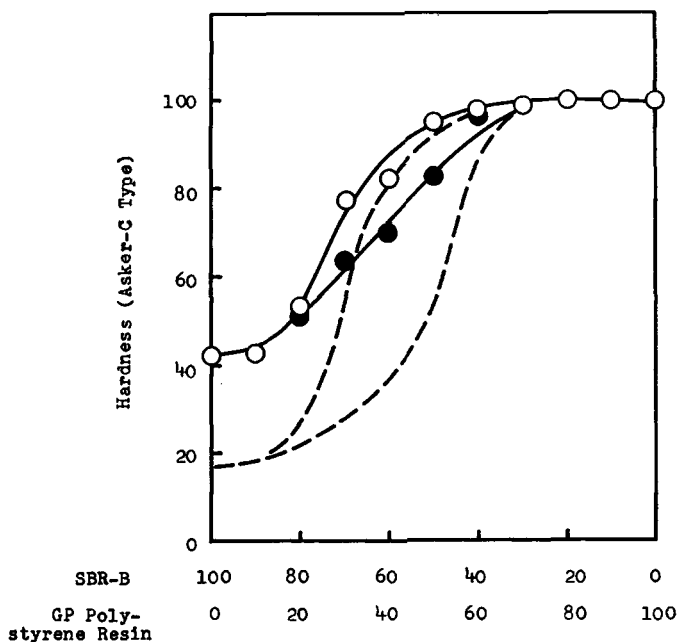
Fig. 2. Asker-C hardness of uncured blend stocks of SBR-B (25% styrene content, without block) and GP polystyrene resin, prepared by mill blend: (O) unremilled specimens; (●) remilled specimens. Broken lines are hardness of low *cis*-BR–GP polystyrene resin blend system.
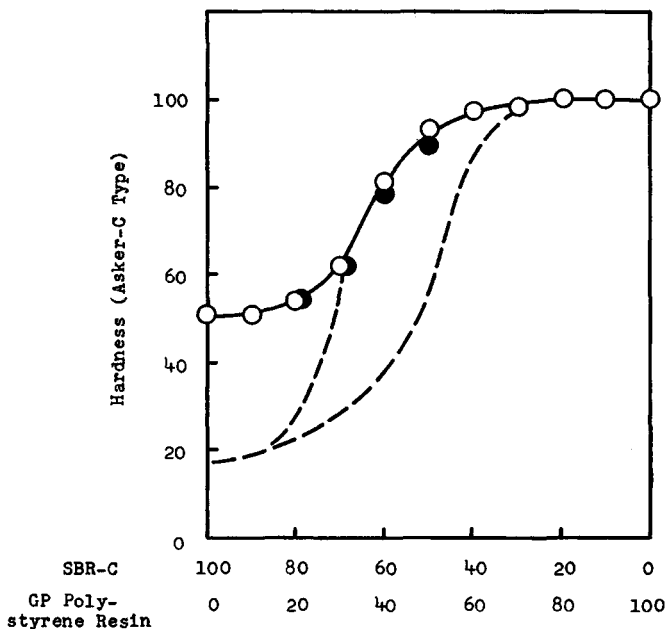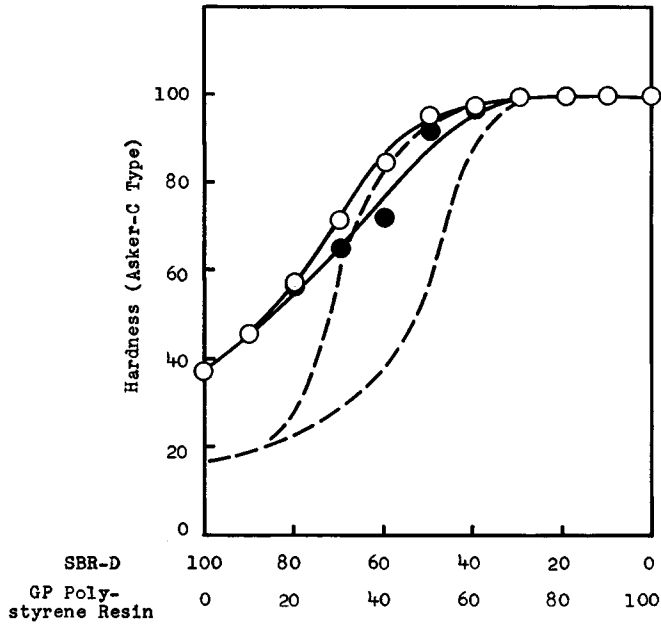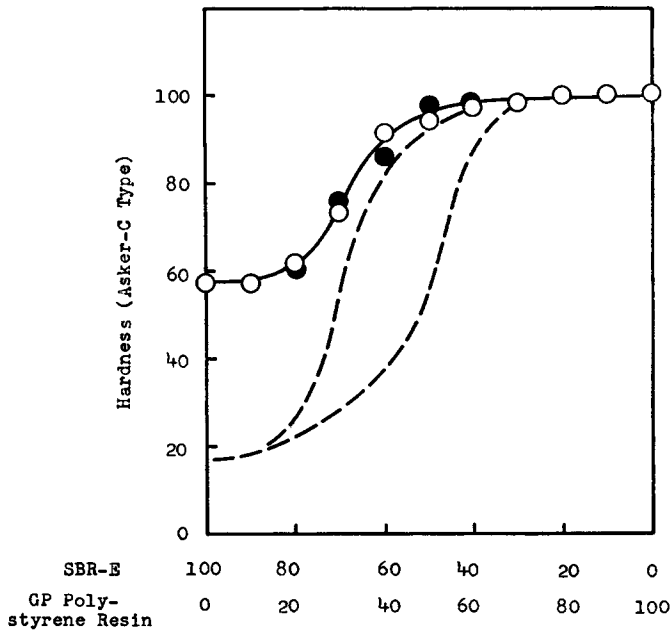

Fig. 3. Asker-C hardness of uncured blend stocks of SBR-C (25% styrene content, 18% styrene block) and GP polystyrene resin, prepared by mill blend: (O) unremilled specimens; (●) remilled specimens. Broken lines are hardness of low *cis*-BR–GP polystyrene resin blend system.

Fig. 4. Asker-C hardness of uncured blend stocks of SBR-D (46% styrene content, without block) and GP polystyrene resin, prepared by mill blend: (O) unremilled specimens; (●) remilled specimens. Broken lines are hardness of low *cis*-BR–GP polystyrene resin blend system.

Fig. 5. Asker-C hardness of uncured blend stocks of SBR-E (48% styrene content, 11% sytrene block) and GP polystyrene resin, prepared by mill blend: (O) unremilled specimens; (●) remilled specimens. Broken lines are hardness of low *cis*-BR–GP polystyrene resin blend system.

and the softening phenomenon by remilling is observed in the region of 20% to 60% GP polystyrene resin content. From these facts, it may be assumed that in the unremilled stock the continuous phase of GP polystyrene resin begins to form when its content becomes more than 20%, as in the case of the mill blend of low cis-BR with GP polystyrene resin.[2]

On the other hand, in the mill blends of block SBR's, SBR-C and -E, with GP polystyrene resin, the effect of the softening phenomenon by remilling is not observed, although the physical properties change in S-shaped curves versus blend ratio. These facts suggest that the states of dispersion are different to some extent in the two types of SBR's. From the fact that the hardness before and after remilling is almost the same, it may be assumed that the discontinuous phase of GP polystyrene resin is formed up to the regions of rather high blend ratios since, because of the contribution of the polystyrene block of block SBR, the firm continuous phase of GP polystyrene resin is not easily formed, as was previously observed in the blend system of SBS block copolymer with GP polystyrene resin.[7]

Compression Modulus of Uncured Stocks Prepared by Mill Roll Blending

In order to obtain more definite information on the state of dispersion of polymers, the authors examined the compression modulus. The results are shown in Figures 6 to 10. Curves I and II in these figures are the theo-
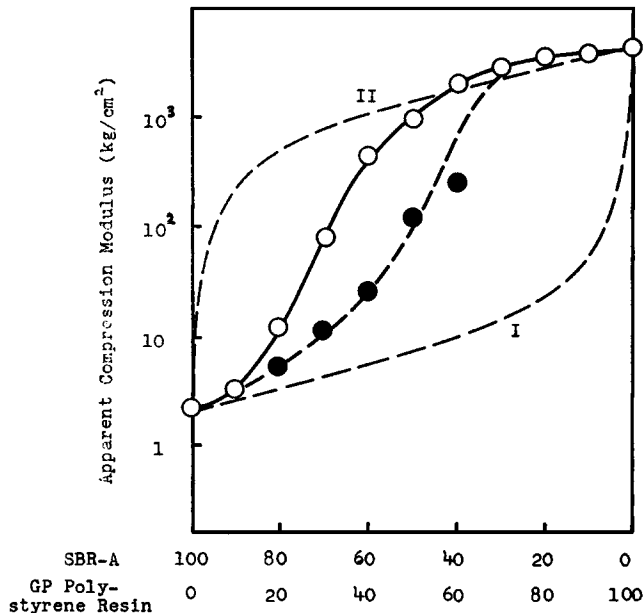

Fig. 6. Apparent compression modulus of uncured blend stocks of SBR-A (23.5% styrene content, without block) and GP polystyrene resin, prepared by mill blend: (O) unremilled specimens; (●) remilled specimens.
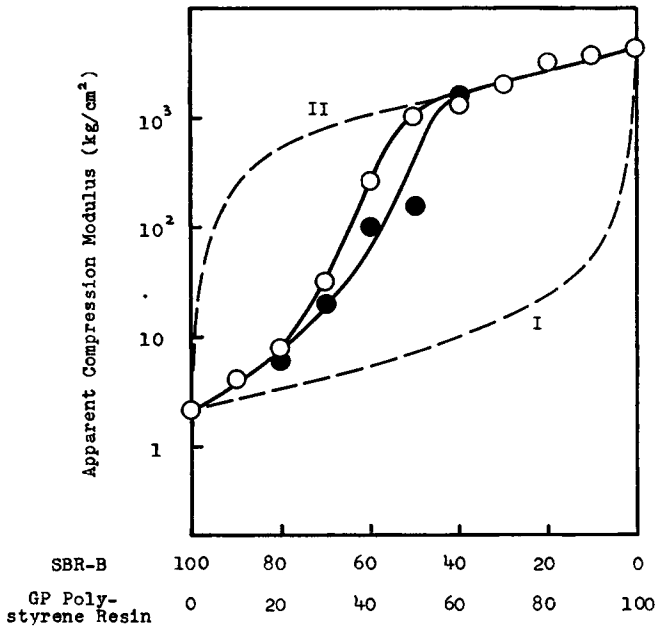
Fig. 7. Apparent compression modulus of uncured blend stocks of SBR-B (25% styrene content, without block) and GP polystyrene resin, prepared by mill blend: (O) unremilled specimens, (●) remilled specimens.
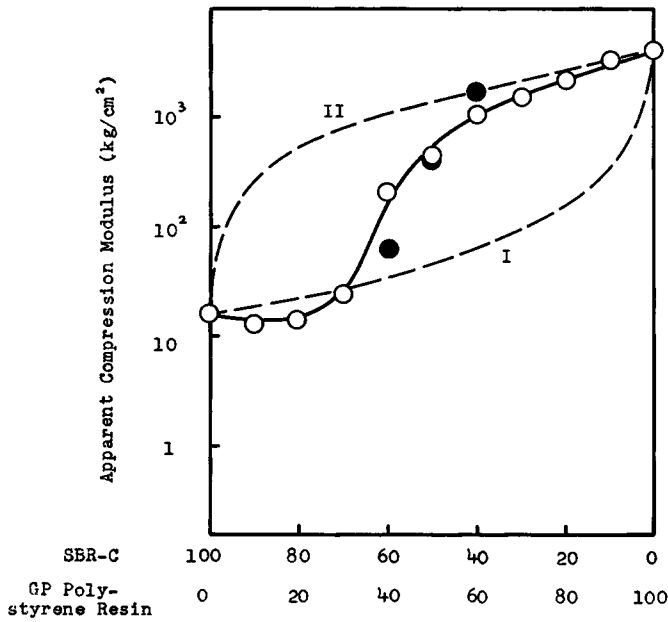
Fig. 8. Apparent compression modulus of uncured blend stocks of SBR-C (25% styrene content, 18% styrene block) and GP polystyrene resin, prepared by mill blend: (O) unremilled specimens; (●) remilled specimens.
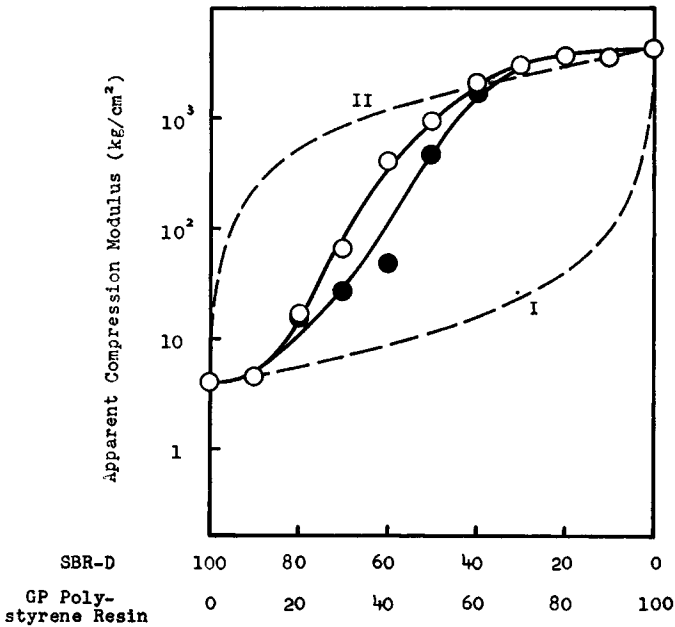
Fig. 9. Apparent compression modulus of uncured blend stocks of SBR-D (46% styrene content, without block) and GP polystyrene resin, prepared by mill blend: (○) unremilled specimens; (●) remilled specimens.
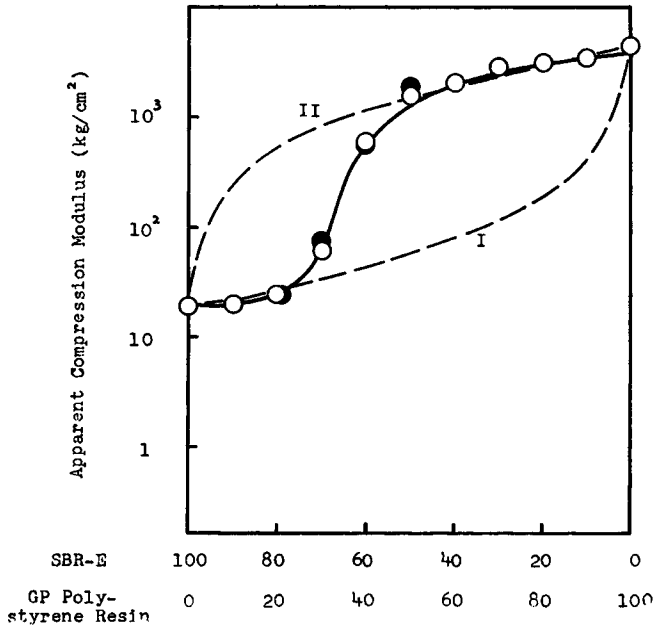

Fig. 10. Apparent compression modulus of uncured blend stocks of SBR-E (48% sytrene content, 11% styrene block) and GP polystyrene resin, prepared by mill blend: (○) unremilled specimens; (●) remilled specimens.

retical curves of the parallel model of Kawai and his co-workers,[11] in which stress is assumed to be additive. SBR is taken as a continuous phase and GP polystyrene resin as a discontinuous phase in curve I, and they are reversed in curve II.

The results confirm the assumptions stated above: no difference between the polymerization methods, little effect of change in styrene content, and a remarkable effect of the structure of the styrene unit.

More precisely, in both of the mill blends of block SBR's, SBR-C and -E, with GP polystyrene resin, the curves seem to coincide with curve I (the theoretical curve based on the model of Kawai and his co-workers:[11] SBR—sea, GP polystyrene resin—island) in the region up to approximately 30% GP polystyrene resin content. From the fact that the softening phenomenon by remilling was not observed as mentioned in the previous paragraph, the discontinuous phase of GP polystyrene resin may be considered to form in the region up to approximately 30% GP polystyrene resin content; and even in the phase inversion region, between 40% and 60% GP polystyrene resin content, the firm continuous phase of GP polystyrene resin may be considered to form with difficulty, in contrast with the blend system of random SBR or low cis-BR with GP polystyrene resin.[2]

As mentioned above, the shapes of the curves of compression modulus versus blend ratio differ between the blend systems of random SBR and those of block SBR. This difference may be attributed to the strong inter-

TABLE II
Phase Separation in Polymer Solutions[a]

Polymer blend system	Polymer blend ratio, wt-%	Critical concentration of phase separation,[b] wt-%
SBR-A/GP polystyrene resin	30/70	4.4–4.8
	50/50	4.4–4.8
	70/30	4.4–4.8
SBR-B/GP polystyrene resin	30/70	4.9–5.4
	50/50	4.9–5.4
	70/30	4.4–4.9
SBR-C/GP polystyrene resin	30/70	7.4–7.9
	50/50	7.1–7.4
	70/30	6.3–6.7
SBR-D/GP polystyrene resin	30/70	5.4–5.9
	50/50	5.4–5.9
	70/30	5.9–6.4
SBR-E/GP polystyrene resin	30/70	
	50/50	7.9–8.3
	70/30	7.4–7.8
Low cis-BR/GP polystyrene resin	30/70	3.8–4.0
	50/50	3.3–3.6
	70/30	3.3–3.6

[a] In benzene.
[b] Total concentration of both polymers.

actions between the polystyrene block in block SBR and the styrene homo-polymer of GP polystyrene resin.

Phase Separation Test of Polymer Solutions

In order to evaluate the mutual solubility of the blended polymers, a phase separation test of the polymer solution was made. The results are shown in Table II, in which some parts of the results from the previous paper[6] are quoted for reference. It seems that the solubility of polymer/GP polystyrene resin blends increases in the following order:

low *cis*-BR < SBR-A, SBR-B, SBR-D < SBR-C, SBR-E

From these results, it is clear that the solubility of the GP polystyrene resin blend is more affected by the structure of the styrene unit of SBR than the styrene content in SBR. It seems that these results confirm the assumptions in the previous paragraphs.

Microscopic Observations

A phase contrast microscope and an electron microscope were used in order to investigate directly the state of dispersion of polymers. The phase contrast micrographs of blends are shown in Figures 11 to 15. All these blends contained 30% GP polystyrene resin.

As is evident from these figures, in the mill blends of random SBR's, SBR-A, -B, and -D, with GP polystyrene resin, a continuous phase of GP polystyrene resin is found, as in the mill blend of low *cis*-BR with GP polystyrene resin.
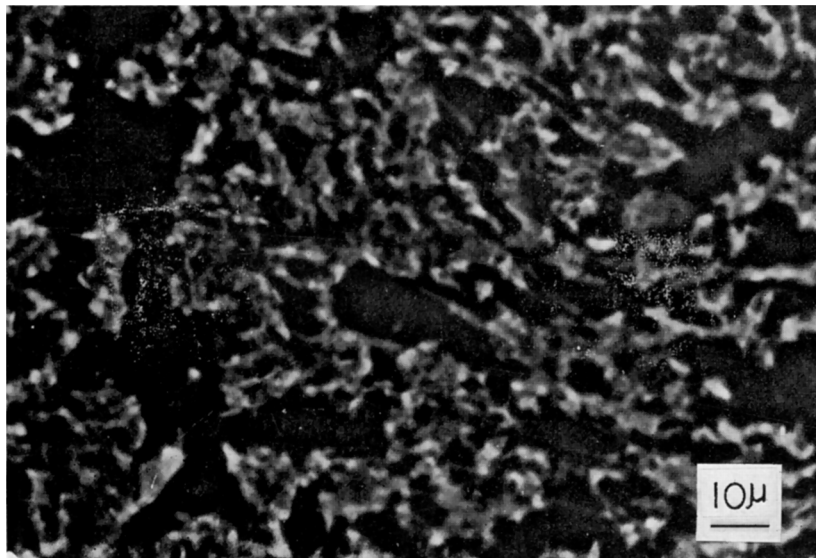

Fig. 11. Phase contrast micrograph of SBR-A (23.5% styrene content, without block)-GP polystyrene resin blend (70/30 weight ratio, before remilling), prepared by mill blend.

Unlike in the random SBR, in the mill blends of block SBR's, SBR-C and -E, with GP polystyrene resin, the firm, continuous phase of GP polystyrene resin is not found, but the state of cotton-like dispersion is observed. Figures 16 and 17 are the electron micrographs of this state. From these
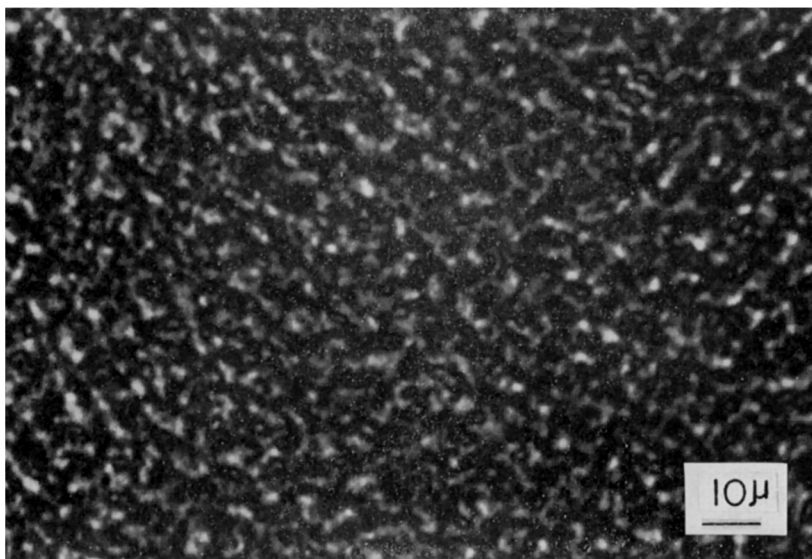

Fig. 12. Phase contrast micrograph of SBR-B (25% styrene content, without block)–GP polystyrene resin blend (70/30 weight ratio, before remilling), prepared by mill blend.
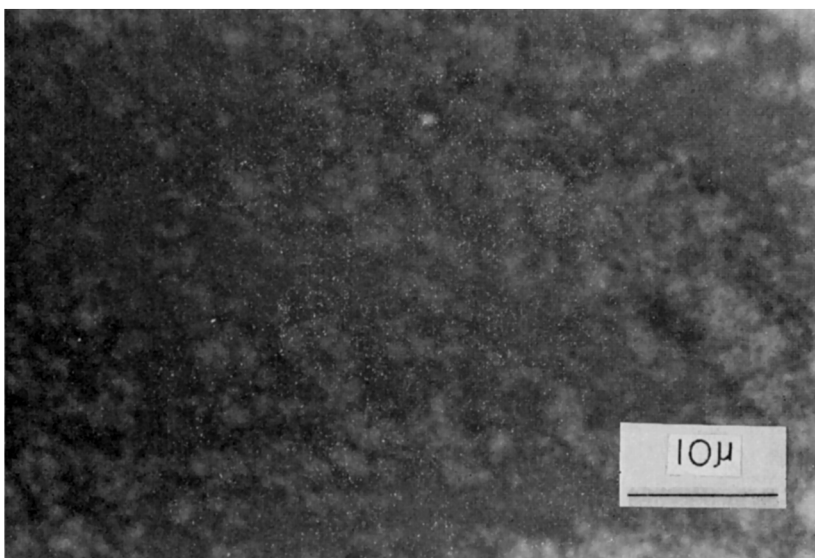

Fig. 13. Phase contrast micrograph of SBR-C (25% styrene content, 18% styrene block)–GP polystyrene resin blend (70/30 weight ratio, before remilling), prepared by mill blend.

micrographs, it can be seen that the phase of the GP polystyrene resin that .
looks like cotton through a phase contrast microscope consists of aggregates
of spherical or nearly round dispersed particles of GP polystyrene resin 0.1
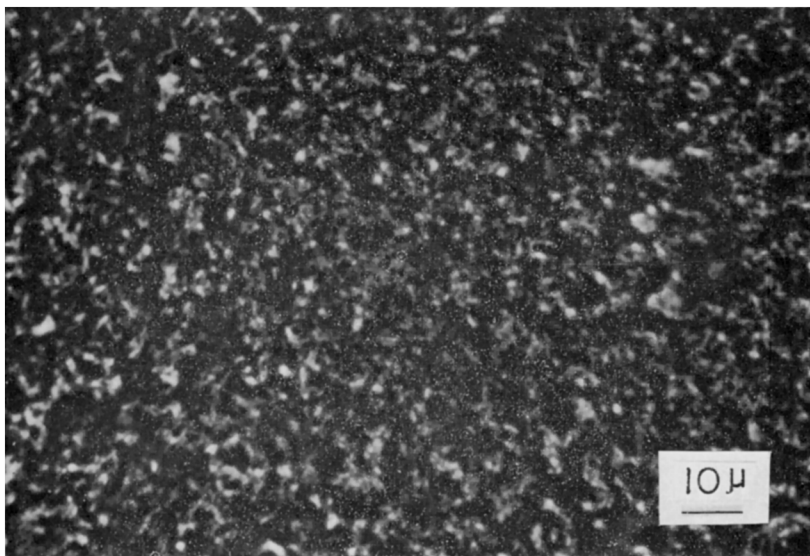to 0.4 μ in diameter, and therefore does not form such a firm continuous

Fig. 14. Phase contrat micrograph of SBR-D (46% styrene content, without block)–
GP polystyrene resin blend (70/30 weight ratio, before remilling), prepared by mill
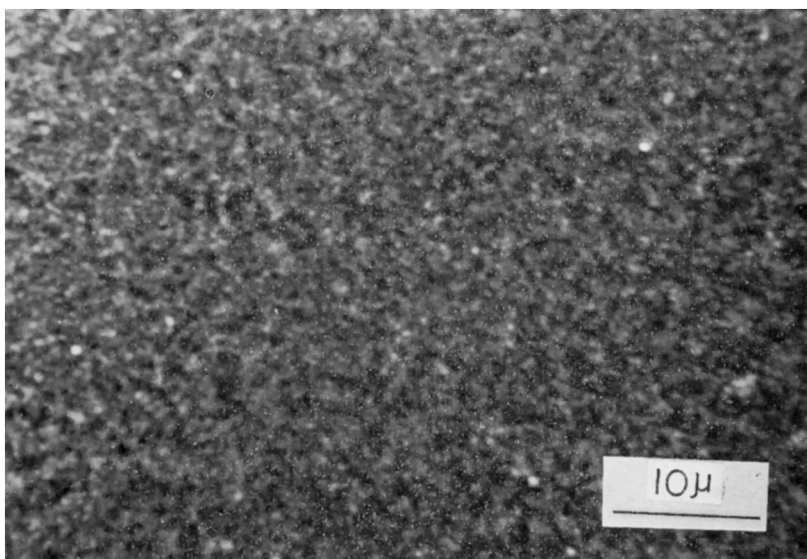blend.

Fig. 15. Phase contrast micrograph of SBR-E (48% styrene content, 11% styrene
block)–GP polystyrene resin blend (70/30 weight ratio, before remilling), prepared by
mill blend.

phase as is observed in random SBR, but forms a discontinuous phase. This confirms our next assumption which was derived from the shape of the curves of the physical properties versus blend ratio and from the softening phenomenon by remilling.
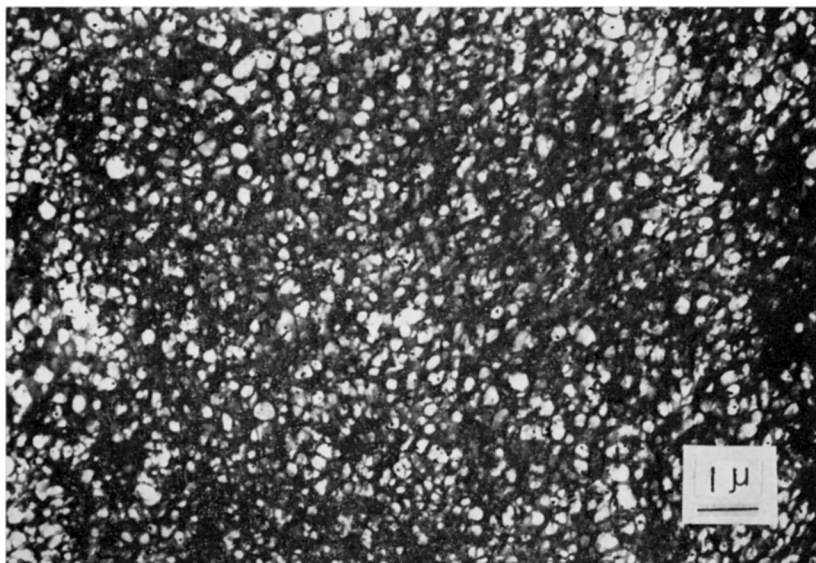

Fig. 16. Electron micrograph of SBR-C (25% styrene content, 18% styrene block)—GP polystyrene resin blend (70/30 weight ratio, before remilling), prepared by mill blend.
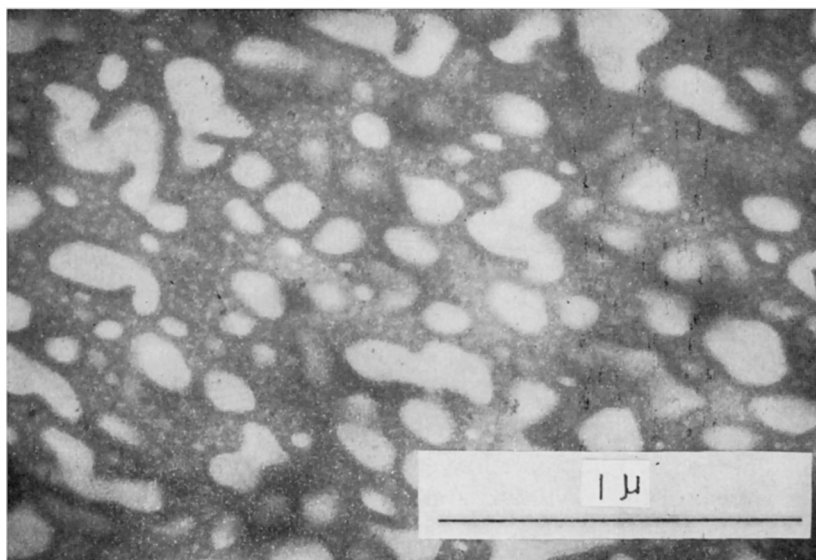

Fig. 17. Electron micrograph of SBR-E (48% styrene content, 11% styrene block)–GP polystyrene resin blend (70/30 weight ratio, before remilling), prepared by mill blend.

In the mill blend of random SBR with GP polystyrene resin, the interface of the polymers tends to become a minimum, thus forming the continuous phase of one of the polymers; whereas in the block SBR, GP polystyrene resin becomes the small and round dispersed particles and tends to form the discontinuous phase, and therefore its continuous phase is not easily formed.

In the mill blend of block SBR with GP polystyrene resin, the former is thought to act like a surface-active agent upon the latter because of the strong interaction between them. This effect is considered to be one of the reasons for the phenomena described above. As experimental evidence of the existence of this surface-active effect, the authors would like to refer to the report of Riess and his co-workers[12] who showed that in the blend of homopolymer A and B the mutual solubility increased if A–B-type block copolymer was added to the system.

CONCLUSIONS

The softening phenomenon by remilling of uncured blends of various commercial SBR's (styrene content, 23.5 to 48 wt-%, styrene block, 0 to 18 wt-%) with GP polystyrene resin was mainly studied by examining the blend ratio dependence of hardness and compression modulus (in logarithmic form), with special attention to the state of dispersion of polymers. The following results were obtained:

1. The hardness and compression modulus (in logarithmic form) change in S-shaped curves versus blend ratio, suggesting the formation of sea–island-type microheterogeneous blend systems. However, the structures of the blend systems are different to some extent between the random SBR and block SBR.

2. In the mill blend of random SBR and GP polystyrene resin, the firm continuous phase of the latter is easily formed as in the mill blend of low cis-BR with GP polystyrene resin, and the effect of the softening phenomenon by remilling is observed in the so-called phase inversion region.

3. On the other hand, in the mill blend of block SBR and GP polystyrene resin, such a firm continuous phase of the latter as was observed in random SBR is not easily formed, and the GP polystyrene resin easily turns into small and round, dispersed particles. As a result, the effect of the softening phenomenon by remilling is not observed in the so-called phase inversion region.

4. The difference in the polymerization methods (emulsion or solution polymerization) and the styrene contents of SBR's have little effect on the shapes of the physical properties-versus-blend ratio curves or on the state of dispersion of the polymers. But the structure of styrene unit of SBR have so much effect on them.

5. This large effect of the structure of the styrene unit of SBR may be attributed to the fact that the block SBR acts like a surface-active agent, because of a strong interaction between the polystyrene block of block SBR

and styrene homopolymer of GP polystyrene resin, thus forming the fine dispersed particles of GP polystyrene resin.

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