Studies on Polymer Blends.   II.   Butadiene–Styrene Copolymers and Polybutadiene–Polystyrene Blends

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Synopsis

The properties of butadiene–styrene copolymers and of polybutadiene–polystyrene blends were compared. Polybutadiene, polystyrene, and four copolymers having styrene contents of 20, 40, 60, and 80% were prepared. The copolymers were compared with blends having various styrene contents and prepared by means of latex blending and roll blending. Vulcanizates were prepared by three different curing methods, i.e., sulfur cure, peroxide cure, and radiation cure. The results of the benzene extraction of three vulcanizates showed that the polystyrene blended was not cured by any of the curing methods used. The properties of the vulcanizates of the copolymers were markedly different from those of the blends, i.e., in the case of the blends the properties showed a linear relationship with their blending ratio, while in the copolymers the properties showed a curvilinear relationship which had an inflection point at a styrene content of about 60%. From this phenomenon of the copolymers, it was proposed that the second-order transition point of styrene is the cause of the properties showing this peculiar point. From the results, it was found that the behavior of styrene in copolymers is essentially different from that in blends.

INTRODUCTION

Recently the consumption of butadiene–styrene rubber has increased rapidly, and in the rubber industry it has become an indispensable rubber.

It is well known that in butadiene–styrene rubber the properties of the copolymer are affected by the bonded styrene content. As the quantity of bonded styrene is increased, the copolymer becomes less rubbery and more leatherlike and resinlike. Many studies concerning the processing method and the properties of the copolymers have been reported for copolymers having a commercially practical bonded styrene content, i.e., SBR and high-styrene resin. However, copolymers containing styrene in amounts outside of the current practical range have not been studied extensively. There are a few studies on the relationship between the bonded styrene content and the properties of the copolymer.[1,2]

A study on the methods of blending natural rubber with butadiene–styrene rubber has been reported.[3]

In order to clarify the difference between the properties of copolymers and of blends of the butadiene and styrene, copolymers having various styrene contents and physically blended mixtures of polybutadiene (rubber) with polystyrene (resin) having styrene contents corresponding to those of the copolymers were studied.

The butadiene–styrene copolymers used were prepared on a pilot-plant scale for this study and had molecular weights of about 200,000. The blends were prepared by means of latex blending and roll blending. To study the differences in properties of the vulcanizates, both the copolymers and the blends were cured with sulfur, with peroxide, or by radiation.

Results of benzene extractions of these vulcanizates showed that the polystyrene blended was not cured by any of the curing systems.

Results on the vulcanizates indicate that the properties of the blends, showed a linear relationship with their blending ratio, while the properties of the copolymers showed a curvilinear relationship which had an inflection point at a styrene content of about 60%. The reason for this was thought to be that the second-order transition point of styrene causes the properties of the copolymers to show this peculiar point.

EXPERIMENTAL

Materials

The butadiene–styrene copolymers, polybutadiene, and polystyrene were prepared by emulsion polymerization at low temperatures in the pilot plant of the Yokkaichi Plant of the Japan Synthetic Rubber Co. Ltd.

Latex blending was carried out by mixing polybutadiene latex with polystyrene latex in various mixing ratios, coagulating and drying. The roll mill blending was carried out by mixing polybutadiene with polystyrene on a roll mill in various mixing ratios. 1.25 phr of an antioxidant (alkylaryl phosphate) was added to the coagulated polymers in order to avoid oxidation. Data on the polymers used are shown in Table I.

Properties of Copolymers and Latex Blends

The Mooney viscosity, specific gravity, refractive index, intrinsic viscosity, and infrared spectra of the copolymers and the latex blends were measured.

Mooney Viscosity. The specimens were preheated for 1 min., then their viscosities were measured after 4 min. at 100°C. by means of a large rotator.

Specific Gravity. The specimens were hot-pressed to make them uniform and smooth, then weighed in air and in ethanol at 20 ± 0.5°C. The specific gravities were calculated from the equation:

$$D = D_0 M / (M - M')$$ (1)

TABLE I
Polymers Used

Sample no.	Polymer	Mooney viscosity (ML 4)	Specific gravity	Refractive index	Intrinsic viscosity[a]	Styrene content, %	cis-1,4 content, %	trans-1,4 content, %	Vinyl-1,2 content, %	Styrene content (corrected)[f] %
1	Polybutadiene	50.5	0.910	1.5150	2.495	0	11.0	69.9	19.1	0
2	Butadiene-styrene copolymer	52.0	0.945	1.5340	2.074	23.2	8.3	55.4	13.1	24.6
3	Butadiene-styrene copolymer	51.0	0.970	1.5478	1.820	37.0	9.8	45.5	7.7	39.0
4	Butadiene-styrene copolymer	52.5	1.008	b	1.182	55.7	6.7	32.6	4.1	58.8
5	Butadiene-styrene copolymer	66.0	1.044	b	0.990	74.8	8.9	14.5	1.8	78.9
6	Polystyrene	—	1.056	b	0.448[c]	94.8	1.5	1.2	2.4	100.0
7	Latex blend[d]	81.0	0.934	e	2.078	20.1	9.1	58.4	12.5	21.4
8	Latex blend[d]	59.0	0.963	e	1.940	39.0	7.4	43.9	9.8	41.3
9	Latex blend[d]	—	0.998	e	0.599	56.2	6.1	30.9	6.8	59.4
10	Latex blend[d]	—	1.018	e	0.599	78.9	3.4	14.3	3.5	83.3

a Measured in toluene solution.
b Impossible to measure because off scale.
c Measured in benzene solution.
d Latex blends were prepared by blending polybutadiene (No. 1) with polystyrene (No. 6).
e Impossible to measure because of turbidity.

where D and D_0 are the specific gravities of the specimens and of ethanol, respectively, and M and M' are the weights of the specimens in air and in ethanol, respectively.

Refractive Index. The refractive index was measured by the usual method.

Intrinsic Viscosity. The polymers were purified by reprecipitation with methanol from toluene solution. The intrinsic viscosity of polystyrene was measured in benzene, that of other materials, in toluene.

Infrared Spectra. Infrared spectra of the purified samples were taken in carbon disulfide solutions. The instrument used was a Perkin-Elmer Model 21 double-beam recording infrared spectrophotometer.

Blending, Compounding, and Vulcanization

The blending of polybutadiene with polystyrene was carried out by latex blending and roll blending as described above. Roll blending was carried out by adding polybutadiene to polystyrene and milling on a roll at over 110°C.

The recipe for the compounding is shown in Table II. The compounding

TABLE II
Recipe

Compounding ingredients	Parts		
	Sulfur cure	Peroxide cure	Radiation cure
Polymer	100	100	100
Stearic acid	0.5	0.5	—
Zinc oxide (#1)	5	25	—
Sulfur	1.5	0.4	—
Accelerator (CZ)	1.5	—	—
Peroxide (DiCup 40C)	—	4.0	—
Calcium carbonate	—	—	100
Total	108.5	129.9	200

was carried out by using a roll mill. The temperature of the roll was varied for the various styrene contents.

The vulcanization was carried out with sulfur, peroxide and radiation cure. The sulfur and peroxide cure were carried out by using a hot press at 150°C. The radiation cure involved a dose of 10^8 rads radiation from a ^{60}Co source to the samples in air at room temperature.

Properties of Green Stocks and Vulcanizates

The Mooney viscosities, mill shrinkages, and torsional rigidities of the stocks, and the benzene extraction, hardness, tensile properties, rebound, compression set, tear resistance, and oil resistance of the vulcanizates were measured.

Mooney Viscosity. The specimens were preheated for 1 min., then the viscosity was measured after 4 min. by means of a large rotator at 100°C.

Mill Shrinkage. The shrinkage ratios of sheets of the stocks were measured. The per cent shrinkage is given by the equation:

$$\text{Mill shrinkage} = (150 - L)100/150 \tag{2}$$

where 150 cm. is the length between two lines marked on the surface of the sheet just after sheeting, and L is the length between the two lines after 1 hr. at room temperature.

Torsional Rigidity. Torsional rigidity was measured by the Gehman torsional testing method.

Rebound. The rebound elasticity was measured by a Lupke type apparatus.

Oil Resistance. The swelling of the samples immersed in ASTM #3 oil at 70°C. was measured.

Benzene Extraction. The extraction was carried out for about 60 hr. in a Soxhlet apparatus.

RESULTS AND DISCUSSION

Properties of Copolymers and Blends

The properties of polymers used are shown in Table I. The bonded styrene contents in Table I were determined from the infrared spectra and refractive indexes of the polymers.

The infrared spectra of the polymers used are shown in Figure 1. Hampton and Binder have presented a formula for determining the contents of the styrene, cis-1,4, trans-1,4, and 1,2 linkages in the polymers from the extinction coefficients of the infrared spectra.[4] From this equation the styrene contents were calculated; results are shown in Table I. The values of styrene contents, from Hampton's formula were smaller than those from the blending ratio of the blends prepared. This is because Hampton's formula is suitable for copolymers containing 20–25% styrene or 100% polybutadiene, but is not always suitable for copolymers containing such a wide range of styrene contents as the copolymers used in this study. The correction of the styrene contents was attempted, and the corrected styrene content values are also shown in Table I.

The viscosity-average molecular weights of the polybutadiene and the polystyrene were calculated from eqs. (3) and (4), respectively.[5,6]

$$[\eta] = 1.1 \times 10^{-3}M_v{}^{0.62} \tag{3}$$

$$[\eta] = 1.13 \times 10^{-4}M_s{}^{0.73} \tag{4}$$

The molecular weights of the polybutadiene and the polystyrene were found to be 2.58×10^5 and 8.54×10^4, respectively. The molecular weights of the copolymers cannot be calculated simply, but their estimated values, from a comparison of the molecular weights of the homopolymers and the intrinsic viscosities in Table I, were about 1.5×10^6–2.5×10^5.
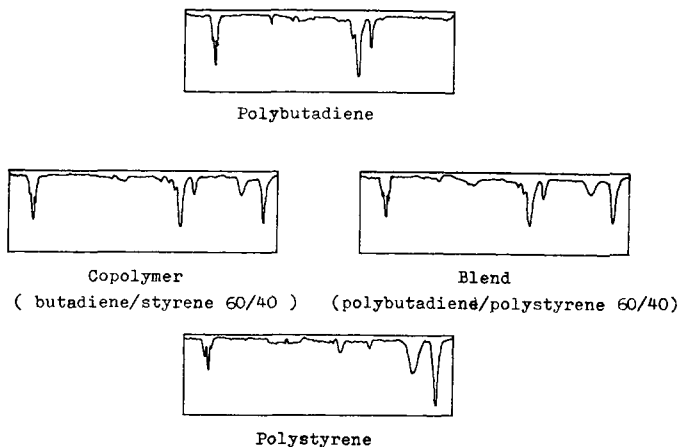
Fig. 1. Infrared spectra: (a) polybutadiene; (b) polystyrene; (c) butadiene–styrene (60/40) copolymer; (d) polybutadiene–polystyrene (60/40) blend.
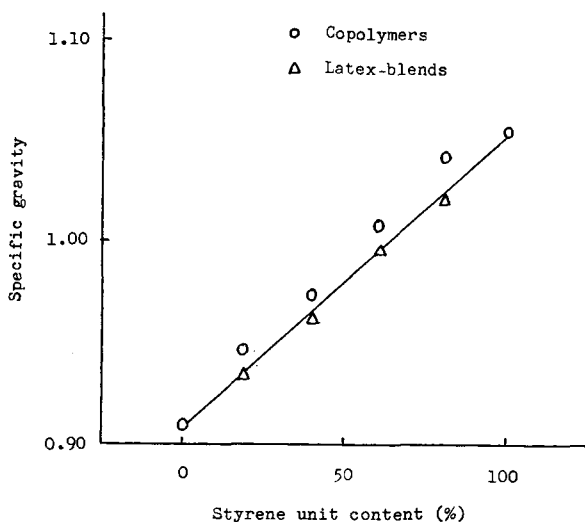

Fig. 2. Specific gravity vs. styrene content: (○) copolymers; (△) latex blends.

The specimens used for the specific gravity determinations were obtained by pressing the polymers at a high temperature. The copolymers became transparent on pressing, while the blends were opaque. This phenomenon suggests that the blends were not homogeneous, but only microheterogeneous.

The specific gravities of the copolymers and the blends are shown in Figure 2. For the blends, the specific gravities showed a linear relationship when plotted against the styrene content, while the copolymers showed instead a curvilinear relationship and their values were a little higher than those of the blends.

Properties of Green Stocks

The roll milling of the copolymers was easy and independent of the styrene content. In the cases of blends from both latex blending and roll blending, the roll temperature had to be adjusted, i.e., as the styrene contents of the blends increased to more than 40%, the roll temperature had to be adjusted to over 110°C. in order to carry out roll milling smoothly. Thus a difference between the copolymers and the blends was already found during the milling.

The mill shrinkages of the stocks are shown in Figure 3. The shrinkages of the copolymers were larger than those of the blends. A linear relationship was observed between the shrinkage and the styrene contents of the blends, while in the case of the copolymers, a straight-line relationship was not observed, but instead a curvilinear one having a maximum at a styrene content of about 60%.

It seems that the maximum shrinkage of the copolymers is due to the differences in the intra- and intermolecular forces which vary depending on the monomer ratio; in the case of the blends a linear relationship was obtained because of the microheterogeneous blending state.

The second-order transition points T_g of the stocks deduced from their torsional rigidities are shown in Figure 4. In the case of the copolymers the T_g varied continuously with the styrene content and showed an inflection point at a styrene content of about 40%, while in the case of the
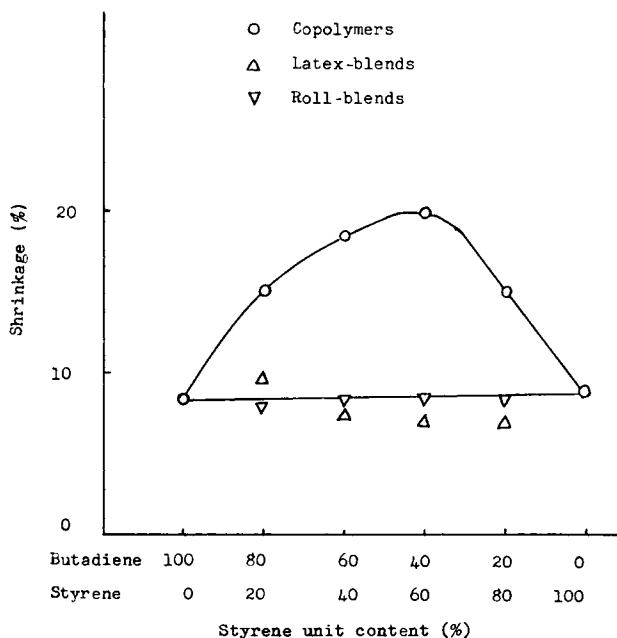

Fig. 3. Mill shrinkage of green stock of sulfur cure system: (O) copolymers; (△) latex blends; (▽) roll blends.
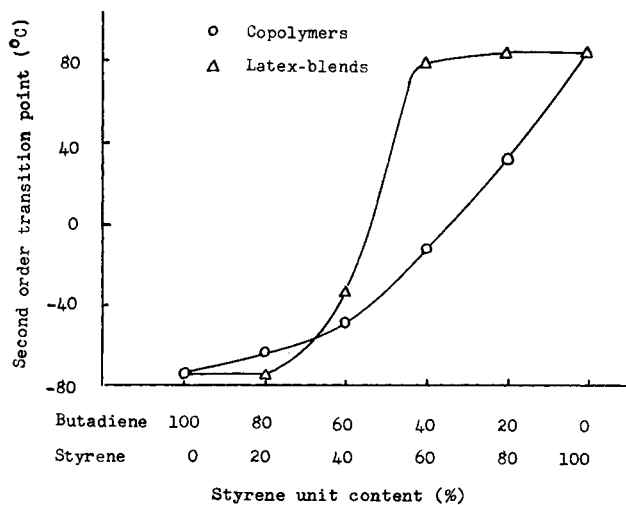
Fig. 4. Second-order transition temperature T_g vs. styrene content: (O) copolymers; (Δ) latex blends.
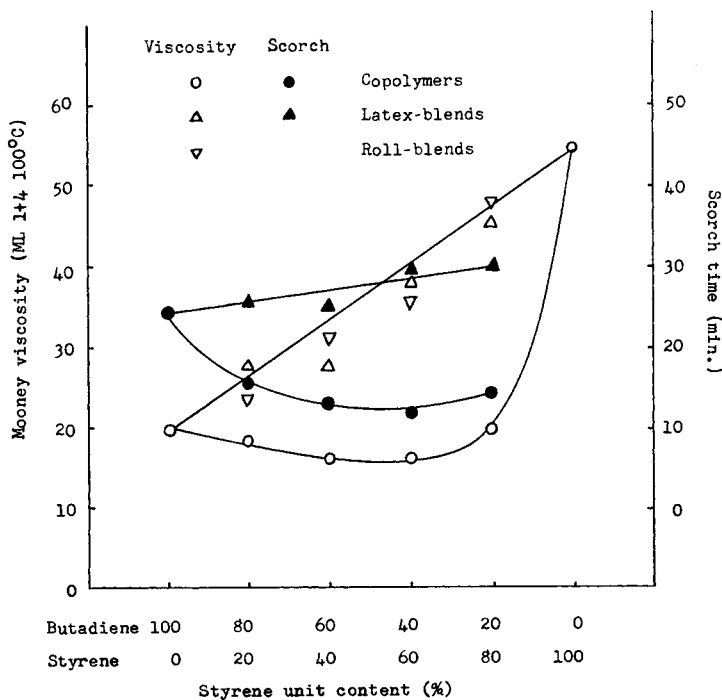

Fig. 5. Mooney viscosity and Mooney scorch of polymer of sulfur-cured stock: (O) viscosity, copolymers; (Δ) viscosity, latex blends; (▽) viscosity, roll blends; (●) scorch, copolymers; (▲) scorch, latex blends.

blends the T_g did not vary continuously, the values being divided into the domains of the T_g of polybutadiene or polystyrene. It appears that in polybutadiene-rich blends the phase of the blend is polystyrene in polybutadiene, while in polystyrene-rich blends the phase is polybutadiene in polystyrene, and at a blend ratio of 40–50% polystyrene inversion of those phases is occurring.

The Mooney viscosities and scorch times are shown in Figure 5. The Mooney viscosities of the copolymers are not so affected by the styrene content in the range below 60%, while in the cases of the blends the higher the styrene content, the higher the Mooney value.

The fact that the relationship between the Mooney values and the styrene contents of the copolymers shows an inflection point is thought to indicate intermolecular forces in the copolymer reach a minimum at a styrene content of about 60%, while the high T_g component such as styrene increases the intermolecular force, so that the viscosity of the copolymer increases at a styrene content of over 60%. In the cases of the blends, as both components are not dispersed molecularly but microheterogeneously, the intermolecular action does not change with variation in the blending ratio, so that the Mooney values of the blends appear to be arithmetic means of those of the two homopolymers.

The scorch times of the copolymers were shortened gradually with increasing styrene contents, because the crosslinking of the polymers was carried out efficiently and the viscosity of the stock increased with increasing styrene content. In the cases of the blends, as the polystyrene is not cured, the scorch value increases with increasing styrene content.

Properties of Vulcanizates

In order to determine whether the styrene polymer was cured, the samples were extracted with hot benzene. In the cases of the copolymers, a nearly constant amount of extract was obtained, independent of the styrene content. On the other hand, in the cases of the blends, the higher the styrene content, the larger the amount extracted, regardless of the curing method. The results are shown in Figure 6.

The extracts of the sulfur-cured blends were precipitated with methanol, and their components were determined by infrared spectra. The main components of the extracts were found to be polystyrene (polystyrene 91%, polybutadiene 3.4%, and unknown material 5.6%). The extracts of the cured copolymers were also treated with methanol, but there was no precipitation of polymer.

The results indicate that the polystyrene in blends of polybutadiene with polystyrene was not cured at all with sulfur, peroxide, or by radiation. In the following discussion on the vulcanizates, therefore, it is assumed that polystyrene in the blends is not cured.

The physical properties of the vulcanizates are shown in Figures 7–12. Characteristic behavior was observed for such properties as hardness and rebound. In the cases of the blended mixtures there was a linear relation-
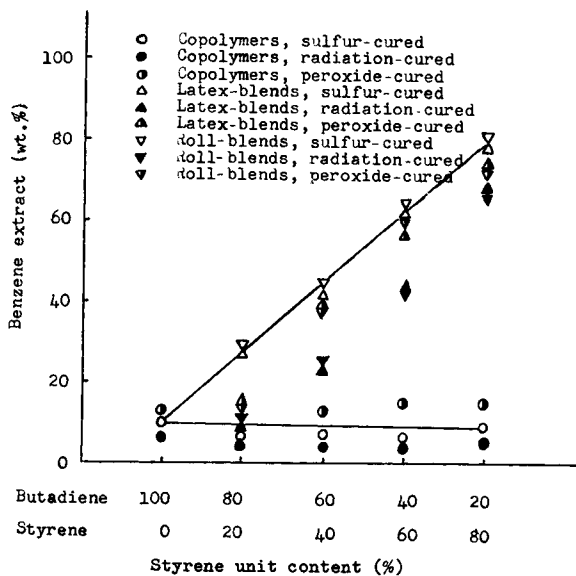
Fig. 6. Benzene extraction of vulcanizates obtained with sulfur, peroxide, and radiation cures; (O) copolymers, sulfur-cured; (●) copolymers, radiation-cured; (◐) copolymers, peroxide-cured; (△) latex blends, sulfur-cured; (▲) latex blends, radiation-cured; (▲) latex blends, peroxide-cured; (▽) roll blends, sulfur-cured; (▼) roll blends, radiation-cured; (▼) roll blends, peroxide-cured.

ship between the properties and the styrene contents, while in the cases of the copolymers a curvilinear relationship was observed. These results are shown in Figures 7 and 8.

The curvilinear relationship for the hardness of the copolymers is due to the variation of the intermolecular action which depends on the styrene content.

The rebounds for the blends showed a nearly linear relationship, in contrast to the copolymers, for which a curvilinear relationship having a minimum at a styrene content of 60% was observed. It seems that the intermolecular forces of the copolymers are minimized at a styrene content of about 60% and hence the rebound of the copolymers is minimized.

Figure 9 shows the results of the swelling tests. The swelling of blends on immersion in oil, decreased linearly as the styrene content increased, while in the cases of the copolymers, swelling did not decrease linearly. This may be explained by the decrease in the intermolecular forces of the copolymer in the middle range of styrene contents, and the resultant increasing affinity with oil.

The properties such as tensile strength and elongation, did not always show a regular relationship with the styrene contents. The results are shown in Figures 10 and 11.

The tensile strength of blends tended to increase with increasing in the styrene content but showed some scattering at low styrene contents, while

in the copolymers little change at styrene contents of less than 60% was observed, followed by a sudden increase at styrene contents of over 60%. The tensile strength behavior of the copolymers agreed with results presented by D'Lanni and co-workers.[1]
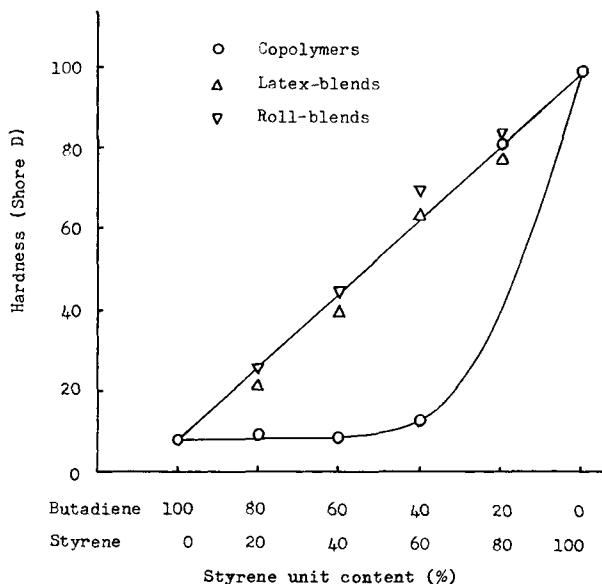

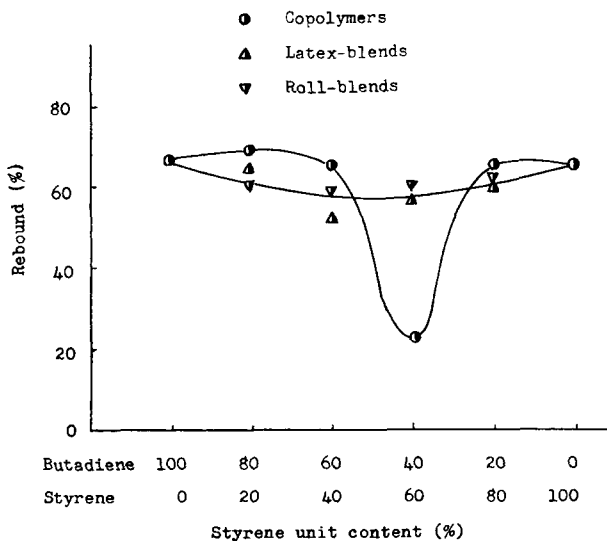Fig. 7. Hardness of sulfur vulcanizates: (O) copolymers; (△) latex blends; (▽) roll blends.

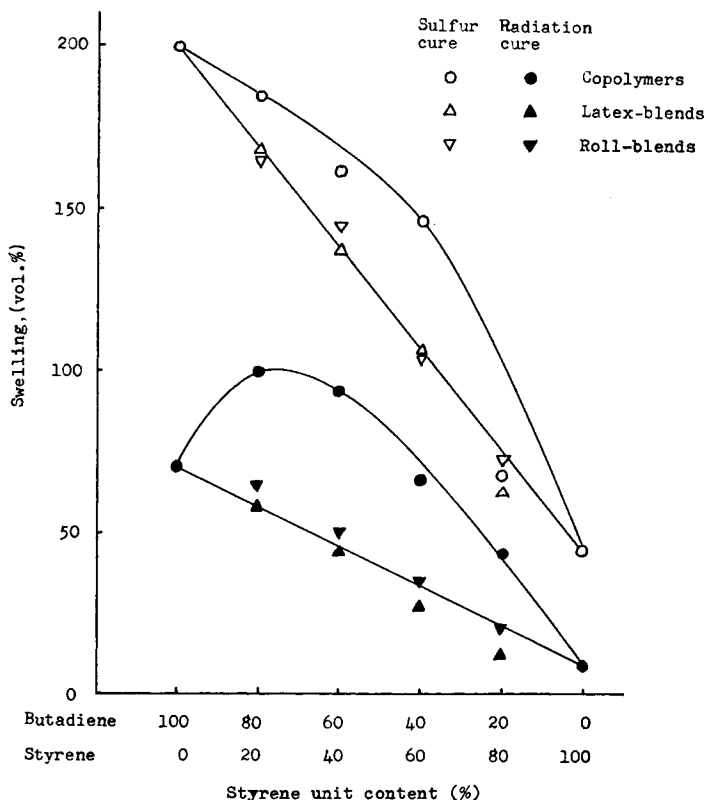Fig. 8. Rebound of peroxide vulcanizates: (◐) copolymers; (▲) latex blends; (▼) roll blends.

Fig. 9. Swelling of vulcanizates: (O) sulfur cure, copolymers; (●) radiation cure, co-polymers; (△) sulfur cure, latex blends; (▲) radiation cure, latex blends; (▽) sulfur cure, roll blends; (▼) radiation cure, roll blends.

The elongation showed a similar tendency to the tensile strength.   For blends, the elongation decreased linearly with increasing styrene content, while in the copolymers maxima at styrene contents of about 60% were observed.   These peculiarities of the copolymers may be explained by the fact that the butadiene–styrene copolymers show rubberlike properties with styrene contents less than about 60% and show resinlike properties with styrene contents higher than about 60%: at 60% styrene content, free rotation and flexibility of the molecules decrease, and intermolecular forces are minimized, thus facilitating deformation.   In the cases of the blends, such a peculiar point was not observed.

Compression set decreased appreciably for the blends and slightly for copolymers with increasing styrene contents.   The values of the compression sets for the copolymers were lower than those for the blends. These results are shown in Figure 12.

These phenomena may be explained as follows.   In the blends the cross-linking of polybutadiene is hindered by the polystyrene, and at the surfaces between the polybutadiene and polystyrene phases, which are mixed micro-

heterogeneously, flow easily takes place. On the other hand, in the copolymers, the polymer is effectively cured even when the styrene content is high, and therefore the compression sets are small.

As mentioned above, the properties of the vulcanizates vary depending on the styrene contents in both copolymers and blends. The tendency of the variation is different for the copolymers and the blends. It was found from
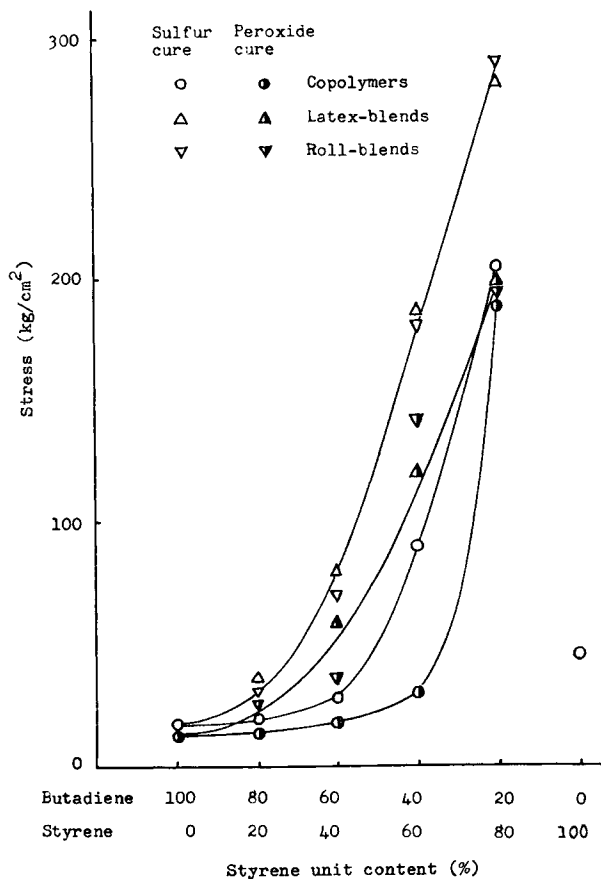

Fig. 10. Tensile strength of vulcanizates: (O) sulfur cure, copolymers; (◑) peroxide cure, copolymers; (△) sulfur cure, latex blends; (▲) peroxide cure, latex blends; (▽) sulfur cure, roll blends; (▼) peroxide cure, roll blends.

the results that the variation of the properties is independent of the quantity of styrene but dependent on the type of the styrene bond in the polymer. These tendencies were the same for all the curing systems, such as sulfur, peroxide or radiation.

In the cases of the blends, properties are affected by the microheterogeneous blending state. For example, the flow at surfaces between polybutadiene and polystyrene phases and phase inversion from polybutadiene
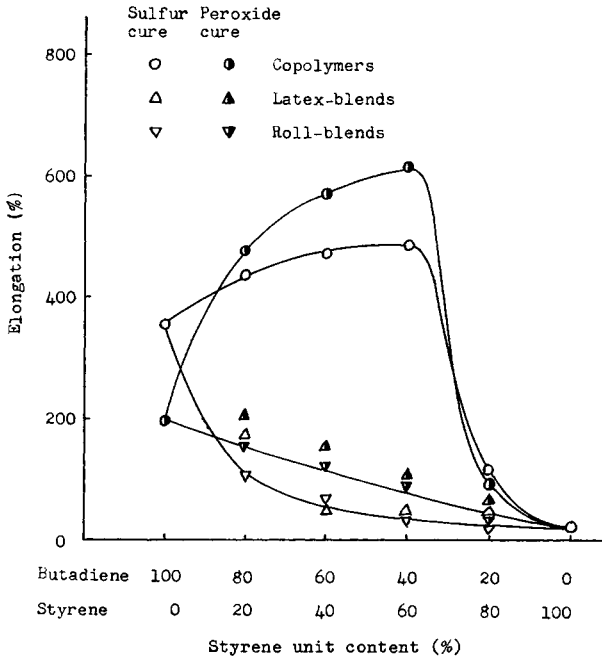
Fig. 11. Elongation of vulcanizates: (O) sulfur cure, copolymers; (◑) peroxide cure, copolymers; (△) sulfur cure, latex blends; (▲) peroxide cure, latex blends; (▽) sulfur cure, roll blends; (▼) peroxide cure, roll blends.
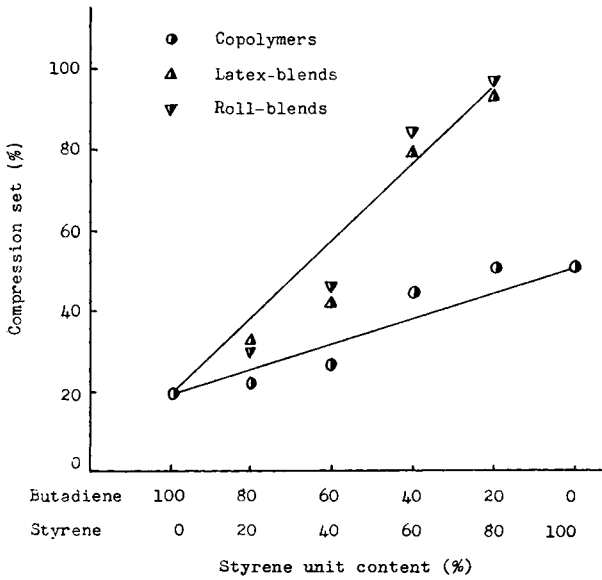

Fig. 12. Compression set of peroxide vulcanizates: (◑) copolymers; (▲) latex blends; (▼) roll blends.

in polystyrene to polystyrene in polybutadiene are necessary to explain the properties of the blends.

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