Studies on Blend Polymers. Mixing of *cis*- and *trans*-1,4-Polybutadiene

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Synopsis

cis-1,4-Polybutadiene and *trans*-1,4-polybutadiene were mixed at the ratio in weight of 100/0, 75/25, 50/50, 25/75 and 0/100, and various problems related to the mixing were studied. The mixing was carried out by the three methods, i.e., (*1*) by rolling, (*2*) by filler batch polymer, and (*3*) by coprecipitation of the solution. For the mixed compound and vulcanized rubber, such characteristics as the viscosity of the solution, the Mooney viscosity, x-ray diffraction, infrared spectra phase separation of the solution, tensile strength, and the swelling ratio in benzene were observed. No marked difference in the state of mixing was noted, regardless of the method of mixing. However, the mixing of filler batch polymer was accomplished more easily than by the rolling method. A 50/50 blend rubber was microheterogeneous and contained particles about 0.5 μ in length, but these did not affect the crystallization, as judged from the observation of the state of dispersion, by means of electron microscopy, x-ray diffraction, and infrared analysis. The *trans*-4 polymer, vulcanized at a much slower rate than Cis-4. This was revealed by comparing infrared spectra of extracts obtained from the unvulcanized portion after various vulcanization times. The Cis-4 vulcanizate did not show any crystalline pattern even at 550% elongation.

I. INTRODUCTION

In recent years, new polymers have been studied in rapid succession and have found increasing new applications. Depending on the end uses for these polymers, however, special qualities of polymers are often desired, and, especially, in the case of one homopolymer the desired properties are not necessarily attained. For this reason, copolymers, or graft or block copolymers have come to be used. Also, attempts to obtain the better quality materials by mixing more than two component polymers of superior qualities, have been made for many years.

Unfortunately, however, very little research has so far been carried out regarding the fundamental problems involved in such mixing of polymers, and the relation between the methods of blending and the properties of the resultant mix has not been fully clarified.

The rubber–melamine resin system, for example, is often mixed with polymers to be used as reinforcing filler. In most cases, however, the system is mixed to only apparent uniformity. In the present study, for the

purpose of clarifying polymer blending systems, we have undertaken to examine the blending of heterogeneous *cis-* and *trans-*polybutadiene rubbers of identical composition and properties by various methods: (*1*) polymer blending by rolling; (*2*) blending with filler batch polymer; (*3*) polymer blending by coprecipitation of the solution.

The differences in the condition of blending and the physical properties of the resultant rubber obtained by these three different methods have been examined.

The condition of blending was observed by means of x-ray diffraction, infrared absorption spectra and electron microscopy. Furthermore, the ratio of blend was varied, and its effect on the various properties of vulcanized rubber (modulus, tensile strength, elongation, resilience, and swelling rate in benzene) was measured.

The resulting *cis–trans* polymer blends seemed to be microheterogeneously dispersed and to have their physical properties modified in a straight line depending on the ratio of components in the blend. The differences in the method of blending were uniform, and dispersity decreased in the order: solution method, batch method, roll method.

Of the batch and roll methods, the former seemed to be easier and more likely to produce dispersed product. If, however, operation was carried out especially carefully, it was considered that both of these methods would lead to the same degree of blending.

II. EXPERIMENTAL

Polymers Used

While studies of polybutadiene rubber are being carried out extensively,[1-5] in the present experiment, a commercial *cis-*1,4-polybutadiene manufactured by the Philips Petroleum Co. (Cis-4, 94.5% *cis*, ML-4 at 212°F.

TABLE I
Recipe

Component	Expt. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5
Cis-4	100	75	50	25	0
Trans-4	0	25	50	75	100
Sulfur	1.75	1.75	1.75	1.75	1.75
Zinc oxide	3.0	3.0	3.0	3.0	3.0
Stearic acid	0.50	0.50	0.50	0.50	0.50
CaCO$_3$ (Hakuenka C.C.)	10.00	10.00	10.00	10.00	10.00
Suprex clay	50.00	50.00	50.00	50.00	50.00
Accelerator mix 2[a]	1.00	1.00	1.00	1.00	1.00
Accelerator TMDM	0.10	0.10	0.10	0.10	0.10
Total	166.35	166.35	166.35	166.35	166.35

[a] Equal amounts of mercaptobenzothiazole and hexamethylenetetramine.

40–50, volatility 0.7% max., ash 1.0% max., organic acid 2.5% max.) and a commercial *trans*-1,4-polybutadiene (Trans-4, 90% *trans*) were used.

Recipe and Conditions of Vulcanization

The recipe used in the present experiments is shown in Table I. All of the materials used were commercially available ones. Hakuenka C.C. $CaCO_3$ as colloidal calcium carbonate, was used as an internal standard for the measurement of x-ray diffraction intensity.

The conditions of vulcanization were as follows: press vulcanization at a temperature of 134°C. (steam pressure: 30 psi). The mold used was 1 × 250 × 150 mm., chrome-plated metal. The times of vulcanization were: 5, 10, 20, 30, 40, 50, and 60 min.

Various Methods of Blending

Blending on Roll

In the roll blending (R method) the roll used was 7 × 24 in.; the speed of revolution of the front roll was 16 rpm; the ratio of revolution was 1:1.09.

The conditions of blending of the polymers were as follows.

Making of Blend Rubber. In case of *cis* polymer alone, the temperature of the roll was kept at 22–28°C. Milling through a 0.4 mm. roll gauge was carried out five times (test specimen R-1). In case of test specimens R-2–R-5, the temperature of the roll was kept at 90°C., with 2.0 mm. spaces; the roll width was 30 cm. Blend or milling through a thin roll gauge was undertaken.

TABLE II

Expt. no.	Temperature, °C.	Roll gauge, mm.	Operation	Time, min.
1	18	0.6	Milling through a thin roll gauge 3 times	4.0
		1.0	Addition of accelerators and stearic acid	
		2.0	Addition of fillers	7.0
		2.0	Addition of sulfur	1.5
		1.0	Milling through a thin roll gauge 3 times	1.5
			Sheeting	1.0
2–5	90	0.6	Rolling up on the front roll	2–9
		1.0	Addition of accelerators and stearic acid	2.5–4.0
		2.0	Addition of fillers	6–8
		2.0	Addition of sulfur	1.5
		1.0	Milling through a thin roll gauge 3 times	1.5
			Sheeting	1.0

In operation, the Trans-4 was first reeled on the front roll, then Cis-4 was added in small amounts for blending, $^3/_4$ cut-back was effected, and, lastly, the roll was fastened up for milling through a thin roll gauge 3 times.

Compounding of Blend Rubber. The operation and the conditions are shown in Table II.

The total time required for blending increased in proportion to the content of Trans-4. This was because of reeling on the roll took considerable time. The effective time of blending was practically identical.

Blending of Filler Batch Polymer

In the filler batch blending method (B-method), to the basic recipes shown in Table I, filler batches of 3493.35 g. each in the blended quantity were prepared. The compounding conditions are shown in Table III. The

TABLE III

Roll tempera- ture, °C.	Roll gauge, mm.	Operation	Time, min.
		Cis-4 filler batch	
30	0.4	Milling through a thin roll gauge 5 times	
	2.0	Addition of accelerators and stearic acid	7.0
	2.0	Addition of fillers	15.0
	1.0	Milling through a thin roll gauge 3 times	4.0
		Trans-4 filler batch	
90	0.4	Rolling up on the front roll	16.0
	2.0	Addition of accelerators and stearic acid	4.0
	2.0	Addition of fillers	15.0
	1.0	Addition of sulfur milling through a thin roll gauge 3 times	9.0
		Sheeting	

TABLE IV

Roll temperature, °C.	Roll gauge, mm.	Operation	Time, min.
90	0.6	Rolling up on the roll	2–6.5[a]
	2.0	Blending	7.5–3.5[b]
	0.4	Milling through a thin gauge 3 times	3.0
	1.0	Sheeting	1.0

[a] This required time increased with increasing Trans-4 content.
[b] This required time increased with decreasing Trans-4 content.

Cis-4 filler masterbatch (test specimen B-1) and Trans-4 filler masterbatch (test specimen B15) prepared as described above were weighed and blended as shown in Table IV.

The *cis-trans* ratios of the batch-blended rubbers were 100/0, 75/25, 50/50, 25/75, and 0/100; the conditions of blending are shown in Table IV.

Blending by Coprecipitation from Solution

This method is designated the S method.

Preparation of Mono Solution. Cis-4 and Trans-4 were dissolved in benzene to make up a 10% solution; 20 kg. was prepared. The temperation of solution was room temperature for Cis-4, and 40–50°C. for Trans-4.

Preparation of Blended Rubber by Coprecipitation. The 10% Cis-4 solution and 10% Trans-4 solution were blended at the weight ratios of 6.0/2.0, 4.0/4.0, 2.0/6.0, and 0/7.7 and thoroughly agitated.

Five kg. of xylene were added to each of the blended solutions and diluted; the rubber was precipitated from the blended solution under agitation by addition of 20 kg. methanol. The precipitate thus obtained was cut into small pieces with scissors. The sample was then immersed in methanol for 5–6 hr., the methanol was removed, and, after being subjected to air-drying and drying under vacuum, it was completely dry. The yields are shown in Table V.

TABLE V

Sample	Yield of precipitate, wt. %
S-1	99.3
S-2	98.0
S-3	99.3
S-4	97.6
S-5	104.0

Compounding of Blend Rubber by Coprecipitation. The procedure for blending was similar to that for the R-method (Table II).

Physical Properties

With modified ratio and method of blending, the following properties of blend rubber, compounded rubber, and vulcanized rubber were measured in order to examine the condition of blend. The conditions of these tests were as shown below.

Mooney Viscosity

A Mooney viscometer manufactured by Shimazu Seisakusho, Ltd. was used. The ML-4 value was obtained with the after preheating for 1 min.

at 100°C. by the use of a large rotor, and 4 min. after commencement of measurement.

The Mooney scorch was shown by MS-5″ up and MS-35″ up at 121°C.

MS-5″ and MS-35″ denoted the time from the minimum Mooney value to 5″ and 35″ up, respectively.

Viscosity of Solution

Viscosity was measured with the use of an Ostwald viscometer at 25 ±0.05°C., and by the usual method, in the case of benzene solution and expressed in terms of $[\eta]$.

Infrared Absorption Spectra

A recording spectroscopic analyzer (manufactured by Leitz Co., West Germany) was used. The test specimens used consisted of blend rubber made in 10% CS_2 solution, coated on a NaCl plate, and dried. The extinction of the spectrum shows the ratio of the extinction area of cis and trans structures against the extinction area of −CH stretch.

The wavelengths assigned were as follows: −CH=CH— (trans), 10.4 μ; −CH=CH— (cis), 13.6 μ; −CH stretching, 3.35 μ.

X-Ray Diffraction

A recording x-ray diffraction instrument (manufactured by Seifert Co. West Germany) was used.

Measurements were carried out under the conditions of slit width 5 mm., 40 kv., 7.5 ma., and $1/3$ rpm. The diffraction intensity was calculated against colloidal calcium carbonate as the internal standard substance and in terms of area ratio.

The diffraction angles assigned were; 14.70° for calcium carbonate, 9–10° for −CH=CH— (cis) and 11.17° for −CH=CH— (trans). The rubber samples used in the test were unvulcanized rubber, and vulcanizate (test specimens S-1 and 2 vulcanized at 134°C. for 20 min., samples S-3 and 4 for 30 min., sample S-5 for 60 min.). The room temperature at the time of measurement was 18°C.

Electron Microscope Photographs

The electron microscope manufactured by Akashi Seisakusho, Ltd. was used. The test specimen consisted of thin films prepared from 1% benzene solution of each blended rubber by the collodion method.

The original magnifications were 3000. The photographs, were then further enlarged by 10,000 ×.

Rate of Mill Shrinkage

The rate of shrinkage in the direction of calendering of rubber subjected to sheeting against the circumference (56 cm.) of the front roll of the test roll, was calculated under the following conditions: roll temperature

100°C., roll gauge 0.5 mm., length of time the test specimen allowed to stand 20 min. on a glass plate.

Physical Properties of Vulcanized Rubber

Tensile strength, elongation, modulus, hardness, permanent set, and tear resistance were determined according to JIS 6301.

A Shobb's elasticity tester was used to determine elasticity, and a William's abrasion tester was used for determination of abrasion loss.

To assess flexibility and cracking, Dematia's testing machine was used; the ASTM Method was followed.

Rate of Swelling in Benzene at 50°C.

A test specimen of vulcanized rubber, 8 × 125 × 0.1 cm., was prepared. This was immersed in benzene, maintained with the use of a reflux condenser, at 50 ± 1°C., for 6 hr.; the specimen was then taken out, the benzene was thoroughly wiped away, and the sample volume measured.

III. RESULTS

Effect of Mastication of Raw Rubber

Table VI shows the result of comparison of the changes in the Mooney viscosity of *cis* and *trans* polymers caused by mastication. No change in the Mooney value due to the rolling operation was noted. The conditions of measurement were: roll gauge 0.8–1.0 mm., temperature of the rolls for Cis-4 30°C., for Trans-4 90°C.; the temperature of measurement of the Mooney value was 115°C.

TABLE VI
Mooney Value of Polymer after Mastication

Mastication time, min.	Mooney viscosity	
	Cis-4	Trans-4
0	25.9	11.9
10	25.8	13.0
20	24.9	12.6
30	24.9	12.9
40	24.9	13.0

Blended Rubber

Relation between Ratio of Blending and Viscosity of the Solution

As shown in Figure 1, the R method and the S method, in spite of slight differences, were found to be practically identical. In terms of the intrinsic viscosity $[\eta]$, Trans-4 showed a value which was nearly $1/3$ that of Cis-4. Because the weight of each rubber molecule was not known definitely, no
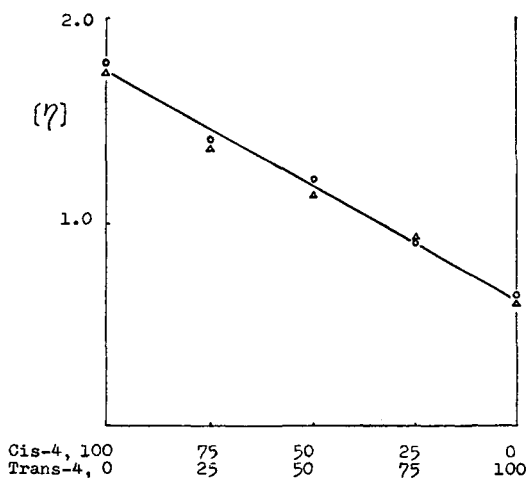
Fig. 1. Relation between the intrinsic viscosity and the blending ratio: (O) R method;
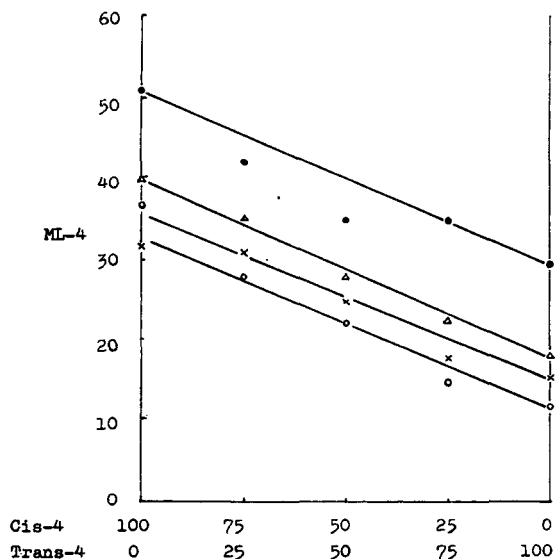(△) S method.

Fig. 2. Mooney viscosity vs. blending ratio of rubber by the solution method: (●)
105°C.; (△) 115°C.; (×) 125°C.; (O) 135°C.

details could be obtained, but, as judged from the Mooney viscosity shown
in Table II, Trans-4 was considered to have a rather low solid viscosity.

From the fact, as shown in Figure 1, that $[\eta]$ showed a linear relation to
the ratio of blending, the molding property due to the ratio in terms of
weight, was expressed as:

$$[\eta] = \alpha_{cis} \, [\eta]_{cis} + \beta_{trans} \, [\eta]_{trans}$$

where α_{cis} and β_{trans} are the weight fractions of Cis-4 and Trans-4,

Relation between Ratio of Blending and Mooney Viscosity

As in the case of the intrinsic viscosity $[\eta]$, a linear relationship was obtained also between the ratio of blending and Mooney viscosity. The
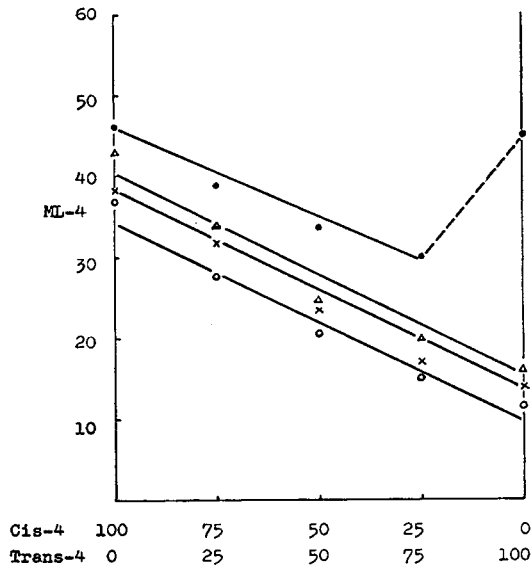
Fig. 3. Mooney viscosity vs. blending ratio of blend rubber by the roll method: (●) 105°C.; (△) 115°C.; (×) 125°C.; (O) 135°C.
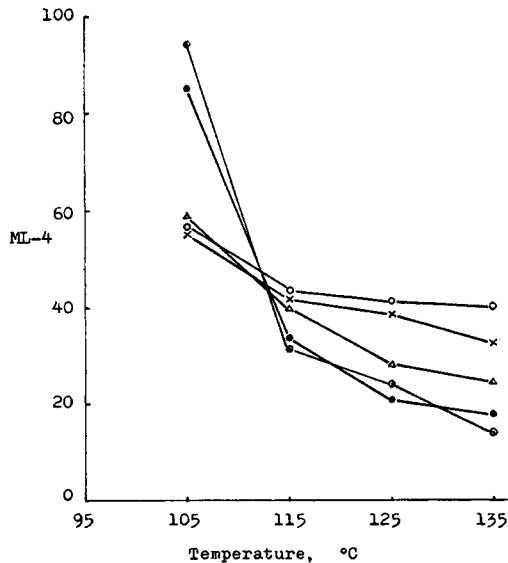
Fig. 4. Effect of temperature on the Mooney viscosity of blend rubbers by the solution method at various Cis-4/Trans-4/ratios: (O) 100/0; (×) 75/25; (△) 50/50; (●) 25/75; (⊙) 0/100.

measurement of Mooney viscosity was carried out at 105, 115, 125, and 135°C.; a maximum in the Mooney value due to the crystallization of Trans-4 was in the neighborhood of 115°C. in the case of ML-2 value, and 105°C. in the case of ML-4 value, but no differences due to the method of blending was seen. The results are shown in Figures 2–4.

Compound Rubber

Relation between Ratio of Blending and Method of Blending and Mooney Values

For the compound rubbers, as in the case of blended rubber no differences due to the method of blending of polymers was noted. A linear relationship between the changes in the ratio of blending and Mooney values was observed. The measurement temperature was 115°C. for all cases in order to avoid the crystallization effect of Trans-4. The results are shown in Table VII.

TABLE VII
Mooney Values of Compound Rubber at 115°C.

Ratio Cis-4/ Trans-4	Roll method		Batch method		Solution method	
	ML-2	ML-4	ML-2	ML-4	ML-2	ML-4
100/0	55.6	54.2	61.0	60.2	58.0	56.4
75/25	55.0	52.0	71.1	66.8	51.6	49.3
50/50	41.9	39.0	62.5	49.9	41.0	38.3
25/75	37.4	32.5	45.6	37.4	41.8	32.5
0/100	34.9	28.2	72.3	33.9	34.8	28.5

Mooney Scorch

When the two kinds of polymers vulcanized at different rates of vulcanization were blended, the rate of vulcanization of the blended rubber was found.

As shown in Figure 5, the method of blending did not cause a difference, it being noted only that the rate of vulcanization speed of Cis-4 and Trans-4 was proportional to the ratio of blending. The vulcanization rate of Cis-4 was about three times that of Trans-4.

Initial Vulcanizing Rate of Cis-4 and Trans-4 Polymers

The difference in the vulcanized rubber was determined and compared in infrared absorption spectra to the extracted Cis-4 and Trans-4 by the following method.

First, a specimen with a 50/50 blend ratio of roll-blended compound rubber, about 10 g. in weight, was prepared by being wrapped in cellophane, pressed for vulcanization at 134°C. for 45, 60, and 75 sec., then, suddenly cooled, and the cellophane removed.
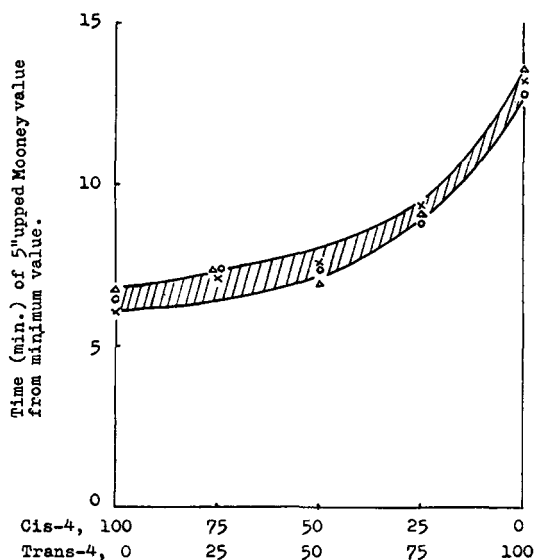
Fig. 5. Scorch time vs. blending ratio: (O) R method; (×) B method; (△) S method.

About 95 ml. of CS$_2$ was put in an Erlenmeyer flask, and pieces of the vulcanized rubber, cut to 5 g. each, were added.

Then, after reflex cooling, the blend was extracted for 15 min., was filtered, and dried. The gel fractions were removed, and the sol (colloidal solution) was used as test specimen for infrared spectroanalysis. The infrared spectroanalysis was indicated by the ratios of —CH stretch absorption against the absorption area of the *cis* structure.

The data shown in Table VIII, were obtained by assuming the amounts of *cis* and *trans* in the polymers to be as shown in Table IX, from which their

TABLE VIII
Quantities of *cis* and *trans* Isomers in the Extract of Vulcanized Rubber

Cure time, sec.	—CH intensity	*cis* intensity	*cis* CH	*cis* %	Total extract, g.	*cis* Rubber in extract, g.	*trans* Rubber in extract, g.
0	60	36	60	55	5.00	2.75	2.25
45	90	48	54	43	3.78	1.63	2.15
60	87	44	50	39	2.88	1.12	1.75
75	83	3	38	27	1.58	0.43	1.15

TABLE IX

	cis structure, %	*trans* structure, %
cis Polymer	95	5
trans Polymer	10	90

relation with the actually measured values of I_{cis} or I_{trans}/I—$_{CH}$ was established.

The actual values (Fig. 6) indicate that, at a time of 60–70 sec., the speed of vulcanization of Cis-4 is 2–3 times that of Trans-4. In this treat-
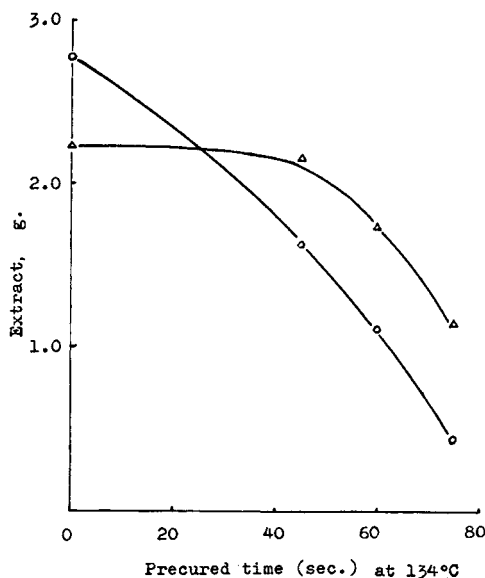
Fig. 6. Relation between the amount of uncured polymer extracted from 5 g. of a 50/50 *cis/trans* blend vulcanizate and vulcanization time.
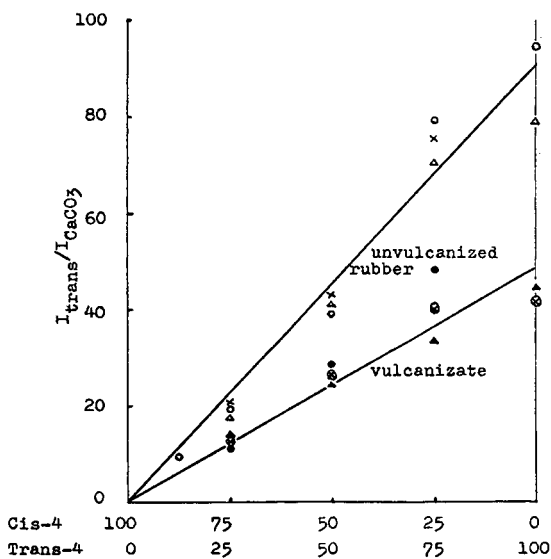

Fig. 7. Relationships of x-ray diffraction intensity and blending ratio by various methods: (O, ●) R method; (×, ⊗) B method; (△, ▲) S method.

ment, the interchange between *cis–cis*, *trans–trans* and *cis–trans* could not be taken into consideration.

Relation between Blending Ratio and X-Ray Diffraction Intensity

The study of the conditions of blending was effective because the crystallization of the *trans* polymer could be followed by means of x-ray diffraction. The result obtained by dividing the crystallinity of the *trans* structure by the area intensity was as shown in Figure 7. In this case, the *cis* structure was not affected by blending with the *trans* structure, and there was no broadening of the *trans* crystalline band as is often seen with natural rubber.

If the blending of two polymers is the molecular dispersion, the crystallization becomes too difficult by the interaction of polymers. But it was clearly distinct that a *trans* structure was noted even in the blending of a small *trans* polymer with *cis* polymer. These phenomena are assumed to be attributable to the fact that the coherent energy of Trans-4 is much higher than that of Cis-4, and the change of diffraction intensity of the vulcanized and unvulcanized rubbers was due to the reduction in crystallization accompanying vulcanization.

Next, to ascertain the presence or absence of crystallinity due to the elongation of Cis-4 the *cis* portion at 550% elongation was observed; the result thus obtained is shown in Figure 8. No crystallization of Cis-4 was observed, and the background of the non-crystalline portion appeared to have been somewhat rised.
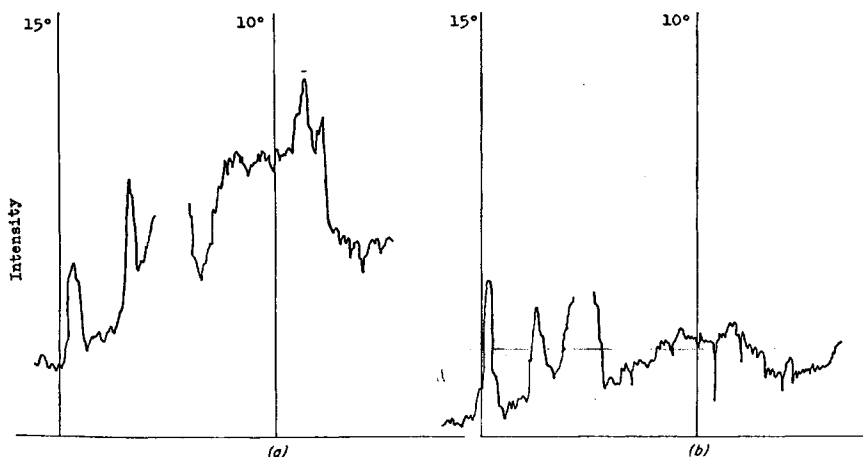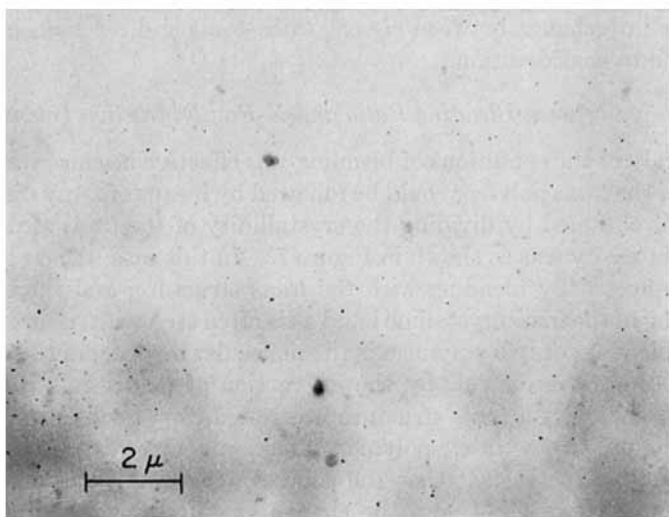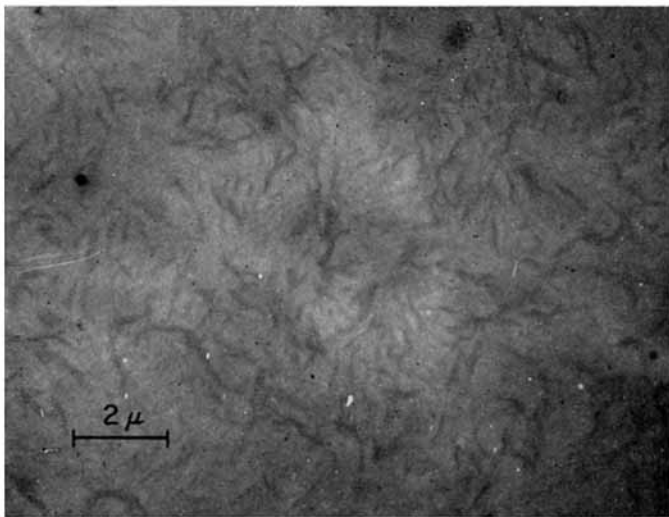

Fig. 8. X-ray diffraction of Cis-4 rubber vulcanizate: (*a*) 550% elongation; (*b*) no elongation.

Phase Separation of the Solution

Carbon tetrachloride and benzene were used as solvents. Cis-4 and Trans-4 polymer solutions of 15, 10, and 7.5% concentrations were prepared; equal weight quantities of Cis-4 and Trans-4 solutions were

(a)

(b)

blended in a test tube, which, after being thoroughly agitated, was tightly sealed.

The *trans* polymer was heated to 50–60°C. with benzene and dissolved. These blended solutions were allowed to stand at room temperature, for one week.   After this interval it was found that, in the case of the benzene solutions of more 7.5% polymer a tendency for phase separation was shown. In the case of the carbon tetrachloride solution, considerable phase separation was seen at concentrations of 15% and greater.
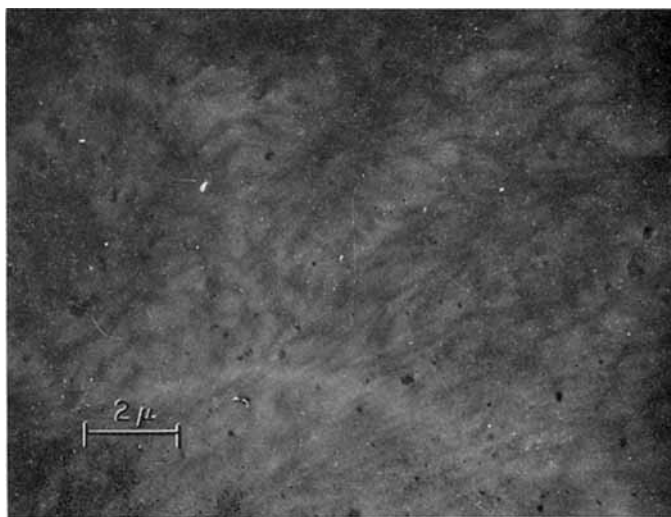
(c)

Fig. 9. Electron micrographs of blended rubbers: (a) Cis-4; (b) Cis-4/Trans-4, 50/50 blend; (c) Trans-4.

Observations with the Electron Microscope

As seen by the photographs (Fig. 9), the Cis-4 polymer, when existing independently, is transparent; the Trans-4 polymer on the other hand, gave the appearance of a network of high density crystalline elongated fibers.

In the case of film, prepared from a 50/50 blend of the polymer solutions, the appearance on the whole, was uniform, but some crystallized portions, evidently due to Trans-4, were seen.

The length of the crystals was in the range of 0.4–0.5 μ, and the width was 0.05–0.08 μ.

Relation between Blending Method and Rate of Mill Shrinkage

The rate of mill shrinkage was determined at various temperatures of each of the rolls.   The results thus obtained are shown in Table X.

The rubber blended with Trans-4 polymer became less suitable for sheeting as the temperature was reduced.   A comparison of the basis of the ratio of blend was carried out at 100 °C.   The results thus obtained, are shown in Figure 10.

In Table X, the rubber obtained by the batch method is shown to have a slightly higher value.   The difference, however, is so minor that this may well be considered as falling within the error of measurement.

However, in the comparison based on the blending ratio, a distinct linear trend was apparent.   In Figure 10, the Cis-4 polymer alone shows a high value.   This presumably is due to the fact that different conditions were used in the blending of the Cis-4 polymer.

TABLE X
Relation between Measured Temperature and Mill Shrinkage

Temp., °C.	Method	Mill shrinkage at various Cis-4/Trans-4 ratios				
		100/0	75/25	50/50	25/75	0/100
100	Roll	17.5	14.3	14.3	37.8	48.6
	Batch	21.4	20.0	29.3	42.0	53.0
	Solution	16.1	17.5	20.6	37.5	49.8
80	Roll	15.2	10.4	7.1[a]		
	Batch	17.5	10.7	5.0[a]		
	Solution	16.8	11.2	3.6[a]		
60	Roll	14.1	10.4			
	Batch	15.7	8.0			
	Solution	15.7	8.0			
40	Roll	19.3	11.2			
	Batch	26.8	9.8			
	Solution	26.8	9.5			
20	Roll	49.8	32.6			
	Batch	56.6	29.4			
	Solution	58.5	25.8			

[a] Because of slipping of rubber between rolls, the value is not accurate.
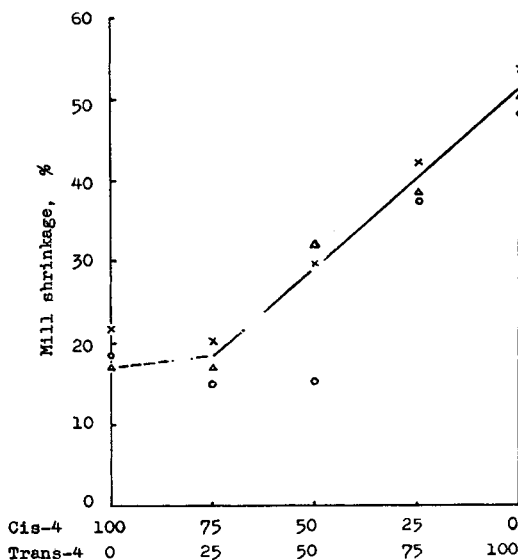
Fig. 10. Mill shrinkage vs. blending ratio (roll temperature 100°C.):   (O) R method; (×) B method;   (△) S method.

Physical Properties of Vulcanized Rubber

Relation between Blending Method and Various Physical Properties

The results of the experiment are shown in Figures 11–18.

In comparing the physical properties of two blended polymers, especially when the vulcanizing rate for each is different, it is a problem whether the
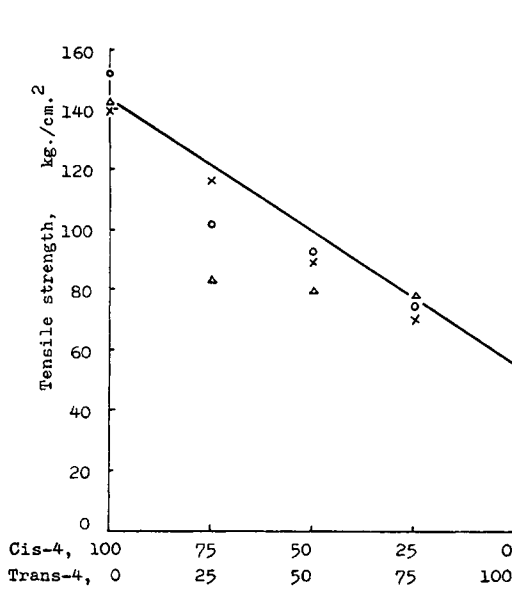
Fig 11. Tensile strength of blended vulcanizates vs. blending ratio: (O) R method; (X) B method; (△) S method.
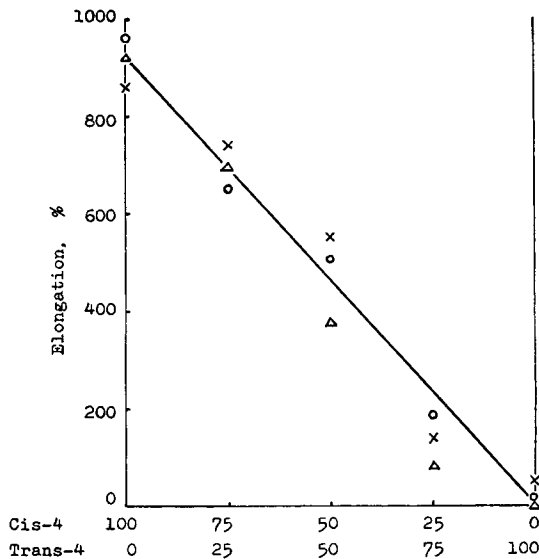

Fig. 12. Elongation of blended vulcanizates vs. blending ratio: (O) R method; (X) B method; (△) S method.

properties of the vulcanized rubber should be examined in a state of equal vulcanization time, or at the maximum strength for each blending ratio.

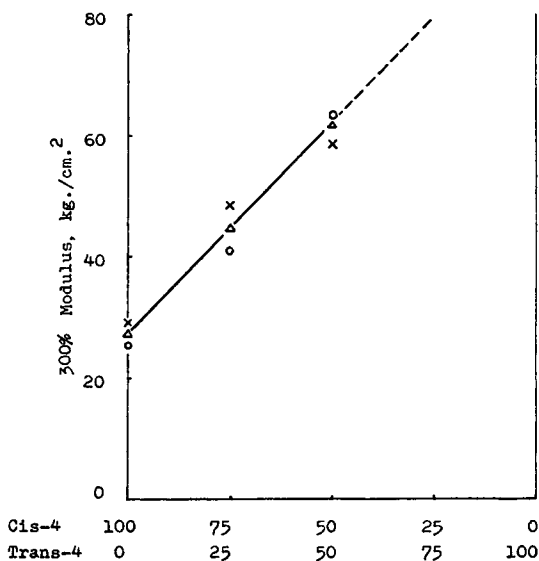Because it was our objective to compare the physical properties as a means of ascertaining the extent of blending, the former procedure was

Fig. 13. 300% Modulus of blended vulcanizates vs. blending ratio: (O) R method; (×) B method; (△) S method.
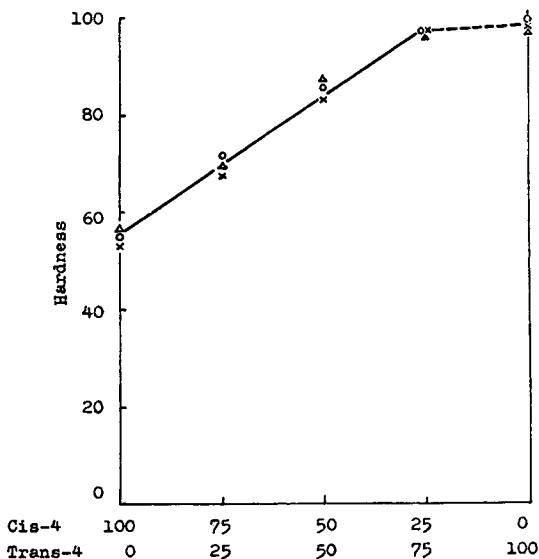
Fig. 14. Hardness of blended vulcanizates vs. blending ratio: (O) R method; (×) B method; (△) S method.

selected, and, thus, the values of the respective special properties at equal vulcanization time were examined; as a result a roughly linear relation was obtained.   Accordingly, the measured values contained some measurement errors, but, on the whole, a proportional relationship between the
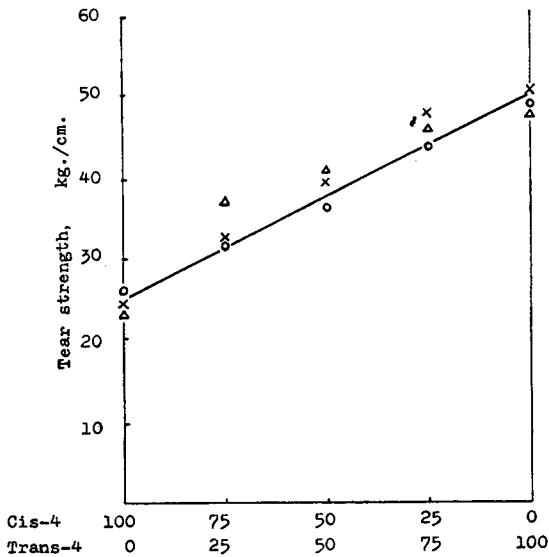
Fig. 15. Tear strength of blended vulcanizates vs. blending ratio: (O) R method; (X) B method; (△) S method.
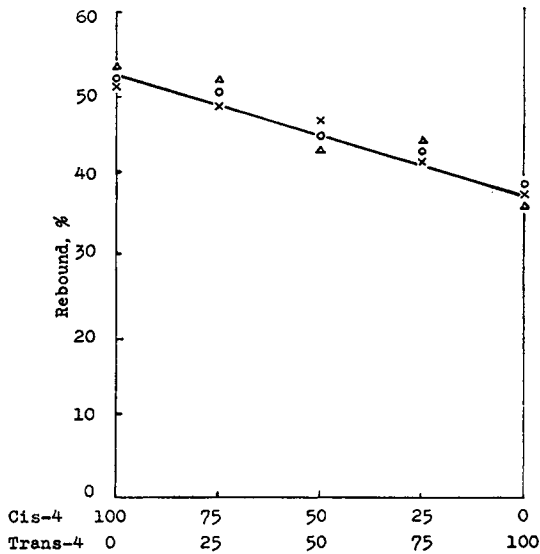

Fig. 16. Rebound of blended vulcanizates vs. blending ratio: (O) R method; (X) B method; (△) S method.

properties of vulcanization and the blend ratio was found. No differences in this relationship due to the blending method were observed.

In regard to the physical properties of polybutadiene in general, clay was used as a white-colored reinforcing agent, and, thus, as compared with the blend of carbon black, as in the case of most studies,[6-8] a low value was indi-
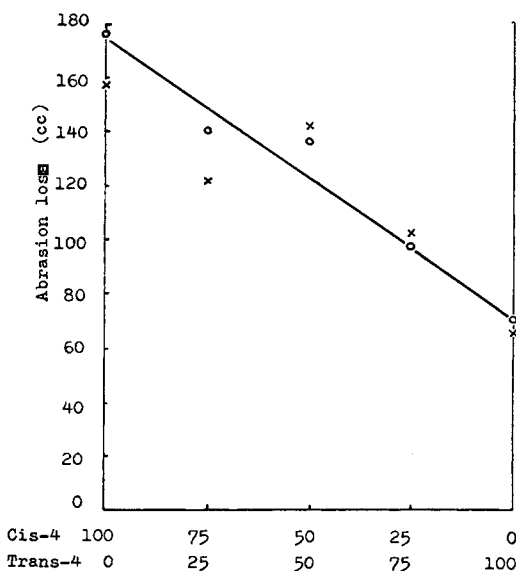
Fig. 17. Abrasion loss of blended vulcanizates vs. blending ratio: (O) R method; (×) B method; (△) S method.
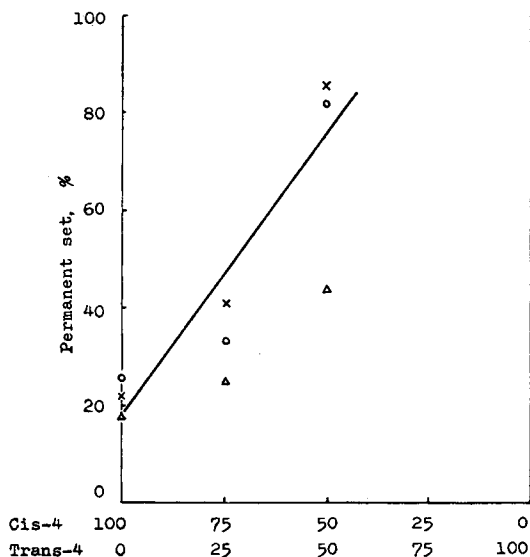

Fig. 18. Permanent set of blended vulcanizates vs. blending ratio: (O) R method; (×) B method; (△) S method.

cated. Of the dynamic characteristics, flex resistance, as measured by the ASTM method, was observed to be particularly striking, and the Trans-4 polymer was observed to have a still lower value. In this aspect, the results conform completely to those reported by Sarbach.[9]
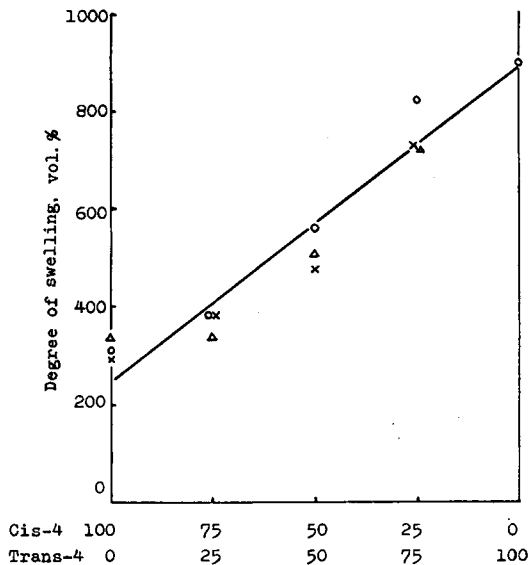
Fig. 19. Degree of swelling in benzene at 50°C. of blended vulcanizates vs. blending ratio: (O) R method; (×) B method; (△) S method.

Ratio of Swelling in Benzene

As shown in Figure 19, the *trans* polymer has a low density of crosslinking, and will swell to a remarkable extent in benzene at 50°C. In another experiment, in which Trans-4 polymer was immersed in toluene at room temperature, it swelled hardly at all. This was either because of the lower molecular weight in Trans-4 polymer, as compared with Cis-4 polymer, or because the crystallization of the *trans* structure became loose due to heating.

IV. CONCLUSIONS

In the blend of the *cis* and *trans* polybutadiene rubbers, the blending method and blending ratio were varied to permit the condition of their dispersion to be examined. The following findings were obtained.

In the blend of *cis-* and *trans*-polybutadiene no major difference was seen depending on the roll method, batch method, or solution method. The same degree of mixing is attained by any of these methods if operation is carried out thoroughly.

In all cases, the blend polymers were found to be microheterogeneous mixtures and not homogeneous.

As the extent of dispersion was examined at various blend ratios it was shown by x-ray diffraction, infrared spectroanalysis, and electron micrographs, that the *cis* and *trans* polymers, while being polymers of the same kind, were not blended perfectly. As one of the causes for this, the greater coherent power of the *trans* polymer molecule may be cited.

With the polybutadiene rubber, the roll blending conditions for *cis* and *trans* polymers are entirely different, and, then, the compounding of blend rubber on roll was very difficult. In the case of the S-method, the dispersion of the compounding agent was entirely similar to the roll method.

Cis-4 showed a rate of vulcanization about three times as fast as that of Trans-4, as shown by means of infrared spectroanalysis and Mooney scorch values.

The crystallinity of Trans-4 was confirmed by electron microscopy, and, in blends of equal amounts of Trans-4 with Cis-4 the formation of dispersion of the *trans* polymer of about 0.5 μ in length was observed.

The vulcanized rubber from Cis-4 was not observed to crystallize on elongation.

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Résumé

On a mélangé le *cis*-1,4-polybutadiène et le *trans*-1,4-polybutadiène dans des rapports en poids de 100/0, 75/25, 25/75 et 0/100, et on a étudié les différents problèmes en connexion avec ce mélange. On a utilisé trois processus de mélanges, à savoir: (*1*) le mélange de polymère par calendrage, (*2*) le mélange de polymère comme l'addition d'une charge, et (*3*) le mélange par coprécipitation des solutions. On a étudié les caractéristiques du mélange de caoutchoucs retravaillé et vulcanisé, telles que: la viscosité de la solution, la plasticité selon Moony, la diffraction aux rayons-X, le spectre infra-rouge, la séparation de phase de la solution, la force de rupture et le taux de gonflement dans le benzène, et avons ainsi fait les constatations suivantes. On n'a pas noté de différence dans l'état du mélange due aux différentes méthodes de mélange, mais l'introduction de polymère d'une manière analogue à la charge est plus facile que le mélange par calendrage. Le mélange 50/50 consiste en un mélange microhétérogène de particules d'environ 0.5 μ et cependant il ne se produit pas de cristallisation pour autant que l'on puisse en juger à partir d'observations sur l'état de dispersion grâce à la microscopie électronique, à la diffraction des rayons-X et à l'analyse infra-rouge. La vulcanisation du polymère *trans* et beaucoup plus lente que la vulcanisation du polymère *cis*. Ceci a été constaté lorsqu'on compare la vitesse de vulcanisation de l'extrait non-vulcanisé mesurée par spectroscopie infra-rouge. Le polymère *cis* vulcanisé ne montre aucune trace de cristallinité même étiré à 550%.

Zusammenfassung

cis-1,4-Polybutadien und *trans*-1,4-Polybutadien wurden im Verhältnis 100/0, 75/25, 50/50, 25/75 und 0/100 gemischt und verschiedene Mischungsprobleme untersucht. Das Mischen wurde nach drei Methoden ausgeführt, nämlich (*1*) Mischen der Polymeren durch Walzen, (*2*) Mischung von Füllstoff-Polymeransätzen und (*3*) Mischung durch gemeinsame Fällung der Lösung. Am gemischten, am komaundierten und am vulkanisierten Kautschuk wurden charakteristische Grössen, wie Lösungsviskosität, Moony-Plastizität, Röntgenbeugung, Infrarotspektrum, Phasentrennung der Lösung, Zugfestigkeit und Quellungsgrad in Benzol bestimmt und daraus folgende Schlüsse gezogen: Es wurde kein ausgeprägter Unterschied im Mischungszustand in Abhängigkeit von den verschiedenen Mischungsmethoden festgestellt. Mischung der Füllstoffpolymeransätze war leichter zu erreichen als diejenige durch Walzen des Polymeren. Der Mischkautschuk mit der Zusammensetzung 50/50 war mikroheterogen gemischt mit Teilchen von etwa 0,5 μ; wie die Beobachtung des Dispersionszustandes durch elektronenmikroskopische Aufnahme, Röntgenbeugung und Infrarotanalyse erwies, zeigten diese Teilchen jedoch keine Neigung zur Kristallisation. Im Vergleich zum *cis*-Polymeren war das *trans*-Polymere sehr vulkanisationsträge. Das wurde durch Vergleich der Vulcanisationsgeschwindigkeit durch Extraktion des unvulkanisierten Anteils mit Hilfe des Infrarotabsorptionsspektrums gezeigt. Das *cis*-Polymervulkanisat zeigt auch bei 550% Elongation keine Anzeichen von Kristallisation.