

Effect of Cryoground Rubber on Properties of NR

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Synopsis

The influence of cryoground rubber (CGR) on the curing characteristics, physical properties, network structure, and failure behavior of natural rubber (NR) has been investigated. CGR was added at two different levels of curatives and in two different ways (i) in powder form and (ii) in mill-sheeted form (obtained by mechanical treatment of CGR in a two-roll mill). The form of CGR and level of curatives affect the processing characteristics and technical properties of CGR-NR blends. The acetone extractables in the CGR were found to affect the curing characteristics, but no significant effect on the physical properties was observed. Model mixes were prepared by adding partially vulcanized NR compound in the matrix of the same compound. A three-layer model was set up to study the diffusion of sulfur from the NR matrix phase to the CGR phase. Scanning electron microscope studies of the fractured surface revealed that the mechanical treatment of CGR effects improved adhesion of CGR to NR matrix and the compatibility between the two phases. CGR acts as an inert filler in NR.

INTRODUCTION

Addition of scrap rubber in the form of either ground vulcanized waste or reclaim in rubber compounds gives economic as well as processing advantages.^{1,2} In addition to lowering the cost of rubber compounds, the use of cross-linked rubber particles has beneficial effects such as faster extrusion rate, reduced die swell, and better mould flow.³

Different methods have been developed to upgrade scrap rubber. Yamashita and others⁴ have reclaimed powdered rubber using iron oxide-phenyl hydrazine catalyst. Okamoto and others⁵ have used compounding ingredients such as thiol-amine and dimethyl sulfoxide to plasticize and regenerate powdered rubber vulcanizates. In the cryogrinding process⁶ a fine mesh rubber powder is obtained by cooling the scrap in liquid nitrogen and then pulverizing it in a hammer mill.

Cryoground rubber (hereafter referred to as CGR) can be vulcanized with vulcanizing agents without the addition of fresh rubber, but the processability of such compounds is very poor.⁷ Processability of CGR compounds can be improved by blending them with fresh rubber. CGR can be used either as powder filler or as a milled sheet, obtained by mechanical treatment of CGR in a two-roll mill.

In this paper we have studied the effect of CGR on properties of natural rubber at two different curative levels. CGR was used as a filler and as a milled sheet. Model mixes using partially vulcanized NR gum compound in the NR matrix were prepared and its effects on physical properties of NR have also been reported.

EXPERIMENTAL

The CGR powder of -40 U.S. mesh size was procured from Air Products and Chemicals, Inc., Pennsylvania. The approximate percentage composition of CGR was the same as reported earlier:⁸ 55% rubber hydrocarbon, 14% acetone extractables, 25% carbon black, and 6% ash.

Formulations of the mixes are given in Table I. The mixes were prepared using different forms of CGR and curative levels. The ratio of sulfur to accelerator was the same at both curative levels. The mixes in series A contain 2.5 phr sulfur and 1.0 phr accelerator and CGR in the powder (filler) form. Mixes in series B and C contain a higher level of curatives (4.0 phr sulfur and 1.6 phr accelerator), but different forms of CGR. CGR in the powder (filler) form was added to natural rubber (NR) for the preparation of mixes in series B, while the milled sheet, obtained by milling CGR for 8 minutes in a two-roll mill, was used to prepare the mixes in series C.

The CGR contains about 14% acetone extractables, which may affect the processability and the properties of vulcanizates containing CGR. To understand the effect of acetone extractables, the acetone-extracted CGR was added to prepare the two mixes using the formulations of mixes B₄ and B₆ (Table I).

The macrogels, A₀' and A₀'', were prepared by curing the NR gum compound A₀ for 2.5 and 5 minutes, respectively. The model mixes X and Y, each containing a macrogel of known composition, were prepared by incorporating 60 phr of A₀' and A₀'', respectively.

A three-layer model, as shown in Figure 1, was set up to study the diffusion of sulfur from the zone of higher concentration to the zone of lower concentration. The three layers of the model were kept in mould of internal diameter of 4.5 cm and cured at a very low pressure on the mould cavity. The interface between each layer was separated and the volume fraction of rubber (V_r) was determined, as described earlier,⁹ cutting the samples from (a) the area in contact and (b) the area not in contact.

TABLE I
Formulations of the mixes^a

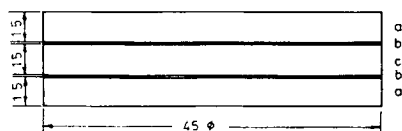
Mix	A ₀ /B ₀ /C ₀	A ₁ /B ₁ /C ₁	A ₂ /B ₂ /C ₂	A ₃ /B ₃ /C ₃	A ₄ /B ₄ /C ₄	A ₅ /B ₅ /C ₅	A ₆ /B ₆ /C ₆
NR ^b	100	100	100	100	100	100	100
CGR ^c	—	10	20	30	40	50	60
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
CBS ^d	1.0/1.6	1.0/1.6	1.0/1.6	1.0/1.6	1.0/1.6	1.0/1.6	1.0/1.6
Sulfur	2.5/4.0	2.5/4.0	2.5/4.0	2.5/4.0	2.5/4.0	2.5/4.0	2.5/4.0

^a Mixes in series A contain 1.0 phr CBS, 2.5 phr sulfur, and CGR in the powder (filler) form. Mixes in series B contain 1.6 phr CBS, 4.0 phr sulfur, and CGR in the powder (filler) form. Mixes in series C contain 1.6 phr CBS, 4.0 phr sulfur, and CGR in the mill-sheeted form.

^b Natural rubber, ISNR-5, obtained from Rubber Research Institute of India, Kottayam.

^c Cryoground rubber powder, -40 U.S. mesh, obtained from Air Products and Chemicals, Inc., Pennsylvania.

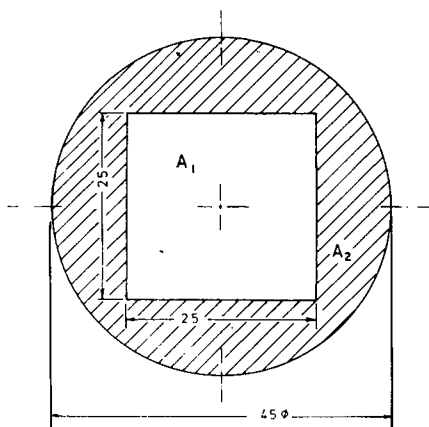
^d *N*-cyclohexyl-2-benzothiazylsulfenamide (Accicure HBS), obtained from Alkali and Chemical Corporation of India Limited, Rishra.

SCHEME I

- a : NR matrix (Mix A_0)
 b : Aluminium foil
 c : Cryo-ground rubber
 (milled sheet)

SCHEME II

- (a) Model Macrogel, A'_0
 (b) Aluminium foil
 (c) Model Macrogel, A''_0



- A_1 : Area in contact
 A_2 : Area not in contact

All dimensions are in mm
 Not to scale

Aluminium foil

Fig. 1. Three-layer model.

Details of vulcanization and determination of curing characteristics and physical properties were the same as reported earlier.^{10,11}

Scanning electron microscope (SEM) observations of failed test specimens were made using a Philips 500 Model Scanning Electron Microscope. After testing, the fractured surface was carefully cut out from one of the two pieces of the failed test specimen. The samples were stored in a desiccator to avoid contamination and then sputter coated with gold within 24 hours of testing.

RESULTS AND DISCUSSION

Figure 2 shows the rheographs of mixes in series A. The rheographs of mixes in other series (series B and C) show similar trends. It can be seen from Tables II, III, and IV, which list the curing characteristics of the mixes, that increasing CGR content causes (i) a small increase in the initial viscosity and (ii) a decrease in scorch time, optimum cure time, and maximum rheometric torque. Increasing CGR content does not affect the cure rate significantly. High viscosity is due to the presence of cross-linked rubber (CGR) and low scorch time is due to the presence of cross-linked precursors and/or unreacted curatives. In addition to the above, diffusion of sulfur from

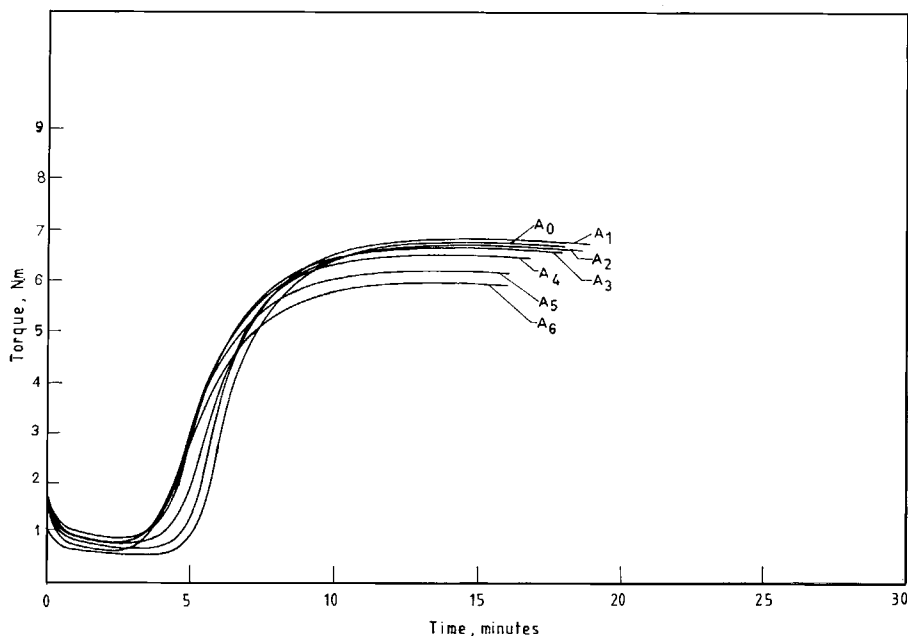


Fig. 2. Rheographs of mixes in series A at 150°C.

the rubber matrix phase to the CGR phase, which lowers the concentration of sulfur in the rubber matrix, may also be a reason for the lower cure time and the decrease in the values of maximum rheometric torque. Migration of acetone extractables from CGR phase to rubber matrix phase also contributes to the reduction in maximum rheometric torque. The rheographs given in Figure 3 show higher maximum rheometric torque for the mixes containing acetone-extracted CGR than the corresponding mixes in series B. The rheographs of the model mixes X and Y (Fig. 4) containing the macrogel of known composition and devoid of plasticizers (macrogel of mix A_0 in the matrix of the same mix) also show a decrease in the values of

TABLE II
Characteristics of the Mixes as Determined by Monsanto Rheometer (R-100)
Series A

Mix	A_0	A_1	A_2	A_3	A_4	A_5	A_6
Initial viscosity, N·m	1.07	1.38	1.56	1.69	1.61	1.58	1.58
Thermoplasticity, N·m	0.51	0.70	0.77	0.79	0.81	0.67	0.66
Scorch time at 150°C, min	4.7	4.5	4.0	3.7	3.5	3.5	3.5
Maximum rheometric torque, N·m	6.75	6.80	6.70	6.62	6.51	6.20	5.94
Optimum cure time at 150°C, min	9.0	8.75	8.5	8.2	8.2	8.2	8.2
Cure rate, %/min	22.22	23.50	22.22	22.22	21.05	21.05	21.05

TABLE III
Characteristics of the Mixes as Determined by Monsanto Rheometer (R-100)

Mix	B ₀	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆
Initial viscosity, N·m	1.13	1.30	1.39	1.56	1.41 (1.52) ^a	1.58	1.72 (1.81)
Thermoplasticity, N·m	0.45	0.62	0.71	0.79	0.68 (0.79)	0.74	0.87 (0.90)
Scorch time at 150°C, min	5.7	5.0	4.5	4.2	4.2 (4.5)	4.0	4.0 (4.2)
Maximum rheomet- ric torque, N·m	9.28	9.28	9.16	9.16	8.94 (9.28)	8.83	8.71 (8.99)
Optimum cure time at 150°C, min	9.4	8.4	8.0	7.9	7.5 (8.3)	7.5	7.5 (7.8)
Cure rate, %/min	27.58	29.62	28.57	27.58	30.76 (26.67)	28.57	28.57 (28.57)

^a Values in parentheses are the values of mixes B₄ and B₆ containing acetone-extracted CGR.

maximum rheometric torque and the reduction is proportional to the macrogel content in the mix.

This indicates that in addition to the migration of plasticizers, the diffusion of sulfur in the macrogel, as discussed later, also results in the reduction of maximum rheometric torque.

A comparison of the curing characteristics of the mixes in series B and C (Tables III and IV) shows that the scorch time, the maximum rheometric torque, and the cure time decrease on addition of the mechanically treated CGR (series C). Mechanical treatment of CGR causes size reduction and facilitates better interaction between the rubber molecules in CGR and NR matrix.¹² An improvement in the dispersion and compatibility of the mechanically treated vulcanized rubber powder in a rubber matrix has been reported.¹³ An increase in the surface area as a result of size reduction and improvement in the interaction between CGR and NR may lead to a higher extent of diffusion of sulfur and lower the concentration of sulfur in the rubber matrix phase. There is also a possibility that some compounding ingredients enter directly into the CGR phase under the shearing action of

TABLE IV
Characteristics of the Mixes as Determined by Monsanto Rheometer (R-100)

Mix	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
Initial viscosity, N·m	1.13	1.11	1.13	1.02	1.07	1.07	1.07
Thermoplasticity, N·m	0.45	0.57	0.57	0.53	0.54	0.57	0.57
Scorch time at 150°C, min.	5.7	4.7	4.0	3.7	3.5	3.2	3.2
Maximum rheomet- ric torque, N·m	9.28	9.28	9.16	8.94	8.60	8.37	8.20
Optimum cure time at 150°C, min	9.4	8.2	7.5	7.1	7.1	7.1	7.1
Cure rate, %/min	27.58	28.57	28.57	29.62	27.59	25.80	25.80

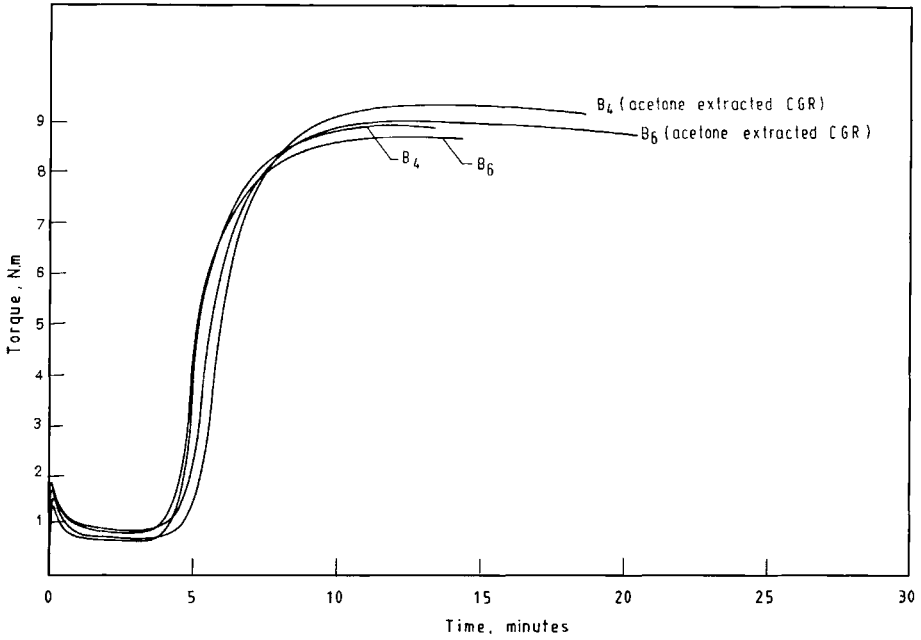


Fig. 3. Rheographs of mixes B_4 and B_6 , each containing untreated CGR and acetone-extracted CGR at 150°C .

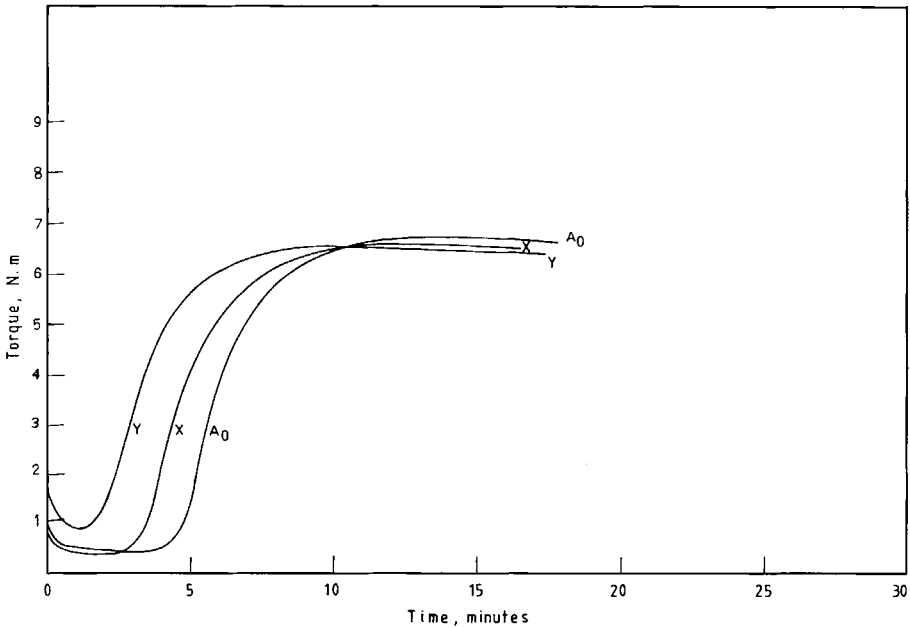


Fig. 4. Rheographs of the model mixes X and Y , containing macrogel A_0' and A_0'' , respectively, at 150°C .

the two rolls. This may be a plausible explanation for the differences in the curing characteristics of mixes in series B and C.

The results of the three-layer model to study the diffusion of sulfur from the rubber matrix phase to CGR phase are given in Figure 1. Scheme I consists of a layer of mill-sheeted CGR in between the layers of NR matrix (mix A_0). The volume fraction of rubber, V_r , (as given in Table V) of the samples from the "area not in contact" (area 2) is higher than that of the samples from the "area in contact" (area 1). This effect is more pronounced in Scheme I than in Scheme II. It can, therefore, be concluded that the migration of sulfur from NR matrix to CGR takes place during vulcanization. It has been reported¹⁴ that the rate of sulfur diffusion is proportional to the concentration gradient of free sulfur between the two phases. The tests revealed that CGR contains a very negligible amount of free sulfur, while it can be seen from the rheograph in Figure 2 that the mix A_0 , cured for 2.5 and 5.0 minutes (a little over scorch time at 150°C), contains a high amount of free (unreacted) sulfur. It is evident from the above that the concentration gradient between the two phases of Scheme I is higher than that between the two phases of Scheme II. The effect on the values of V_r is, therefore, more pronounced in Scheme I than in Scheme II.

Increasing loading of CGR in any form and at any curative level does not affect the volume fraction of rubber (V_r). Therefore, the ratio of the V_r of gum vulcanizate to that of the CGR-filled vulcanizate is found closer to unity in each of the three series. This may occur as a result of balancing the nonreinforcing effects of pockets or voids around the CGR particles by a local swelling of CGR particles, which contain reinforcing carbon black. This indicates that CGR is an inert filler.

The technical properties of the vulcanizates in different series are given in Tables VI, VII, and VIII. The loading of CGR, the form of CGR, and the amount of sulfur added affect the technical properties of the vulcanizates.

The vulcanizates in all the series show an increase in the modulus with increasing loading of CGR. The tensile strength and elongation at break of the vulcanizates in series A decrease with increasing CGR content, while these properties in the vulcanizates in series B and C fall sharply on addition of CGR, but improve considerably with increasing loading. The vulcanizates in series C (CGR in the mill-sheeted form) show higher tensile strength and elongation at break than do those in series B.

TABLE V
Volume Fraction of Rubber for Three-Layer Model

	Area in contact	Area not in contact
	Scheme I	
NR matrix (mix A_0 , top and bottom layer)	0.198	0.216
	Scheme II	
Macrogel A_0' (top and bottom layer)	0.207	0.215
Macrogel A_0''	0.216	0.214

TABLE VI
Characterization of Vulcanizates
Series A

Mix	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆
Modulus at 300% elongation, MPa	2.49	2.10	2.39	2.79	3.02	3.18	3.15
Tensile strength, MPa	27.63	19.39	16.84	15.24	13.65	13.03	10.78
Elongation at break, %	710	640	610	590	570	550	500
Tear strength, kN/m	32.3	41.6	39.3	38.9	35.6	33.3	32.5
Volume fraction of rubber, V_r	0.219	0.222	0.219	0.221	0.222	0.222	0.222
V_{ro}/V_{rf}	—	0.986	0.999	0.988	0.985	0.983	0.985

TABLE VII
Characterization of Vulcanizates
Series B

Mix	B ₀	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆
Modulus at 300% elongation, MPa	3.41	—	4.85	5.62	5.77 (5.39) ^a	6.00	6.26 (6.58)
Tensile strength, MPa	22.10	3.30	10.78	12.97	14.36 (12.02)	14.35	14.27 (14.45)
Elongation at break, %	560	230	430	450	450 (430)	450	450 (430)
Tear strength, kN/m	36.7	30.4	30.8	48.0	43.8 (40.1)	50.2	52.8 (45.8)
Volume fraction of rubber, V_r	0.262	0.265	0.267	0.267	0.269 (0.264)	0.271	0.272 (0.266)
V_{ro}/V_{rf}	—	0.989	0.979	0.974	0.974 (0.990)	0.965	0.962 (0.983)

^a Values in the parentheses are the values of mixes B₄ and B₆ containing acetone-extracted CGR.

TABLE VIII
Characterization of Vulcanizates
Series C

Mix	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
Modulus at 300% elongation, MPa	3.41	4.75	5.04	5.14	5.23	5.20	5.35
Tensile strength, MPa	22.10	10.36	15.15	18.84	20.55	19.98	20.82
Elongation at break, %	560	400	450	520	530	540	570
Tear strength, kN/m	36.7	46.8	46.2	54.6	54.5	54.1	49.8
Volume fraction of rubber, V_r	0.262	0.264	0.263	0.267	0.263	0.266	0.266
V_{ro}/V_{rf}	—	0.990	0.996	0.979	0.994	0.984	0.985

It has been reported¹⁶ that the addition of CGR in the powder (filler) form reduces the tensile strength and the elongation at break as a consequence of the poor adhesion between the two phases and the stress concentration around the CGR particles. Migration of sulfur from the rubber matrix phase to the CGR phase lowers the concentration of sulfur in the rubber matrix, resulting in an inhomogeneous distribution of cross-link density at the interface.²¹ This explains the reduction in these properties of the vulcanizates in series A with increasing CGR contents. Moreover, the stress-induced crystallization of natural rubber will presumably be retarded in the presence of the scrap rubber.

It is, therefore, necessary to increase the sulfur concentration in the rubber matrix with increasing CGR loading. This compensates for the worsening of the properties, which otherwise occurs on addition of CGR in the rubber matrix.¹⁵

The increase in the surface area at higher loading of CGR leads to a higher extent of diffusion of sulfur, which lowers the degree of discontinuity at the rubber matrix-CGR interface. The vulcanizates in series B and C, therefore, show an improvement in these properties at higher loadings of CGR. It is evident from the effects of mechanical treatment of CGR in a two-roll mill, as discussed earlier in this paper, that the vulcanizates in series C show higher tensile strength and elongation at break than those in series B.

The tear strength in series A increases at lower loading of CGR, but decreases with increasing loading of CGR (Table VI). In series B (4.0 phr sulfur and CGR as filler), the tear strength shows a trend opposite to that in series A. The tear strength decreases at lower loadings of CGR and then increases with increased loading of CGR. The tear strength of the mixes in series C increases consistently with increasing loading of CGR in the mill-sheeted form.

The tear resistance of vulcanizates containing CGR depends on the cross-link density of the rubber matrix, stress concentration around the CGR particles, and the adhesion of CGR to the rubber matrix.^{16,17} In series A, at higher loadings, the stress concentration around the CGR particles in a matrix of low cross-link density (a consequence of sulfur diffusion) causes reduction in the tear strength; on the other hand, in series B, the stress concentration around the CGR particles in a matrix of high cross-link density causes reduction in the tear strength at a lower loading of CGR. Mechanical treatment of CGR improves the adhesion of CGR to NR matrix, as shown later in this paper by scanning electron microscopy. The aggregates of CGR present in the tear path elongate to high strains and obstruct the tear, increasing the tear strength of vulcanizates.¹⁸

The vulcanizates of the mixes containing acetone-extracted CGR show that the acetone extractables in CGR do not affect the physical properties significantly. It is observed in the case of mixes X and Y, as shown in Table IX, that the tensile strength, the elongation at break, and the tear strength decrease with the addition of the partially cured NR compound (macrogel). The higher the cross-link density of the macrogel the higher is the reduction in the properties.

In order to understand the effect of mechanical treatment of CGR on

TABLE IX
Physical Properties of Model Mixes

Mix	A ₀	X	Y
Tensile strength, MPa	27.63	23.56	20.22
Elongation at break, %	710	700	680
Tear strength, kN/m	32.3	31.6	29.1

compatibility, adhesion and strength behavior of CGR-NR composites, the vulcanizates from mixes B₄ and C₄ (Table I) have been chosen for SEM studies of the fractured surfaces.

Figure 5 shows the tensile fractured surface of the vulcanizate of mix B₄. The fractograph shows separate CGR aggregates on the surface, and lack of adhesion of CGR to NR matrix. Figure 6 is a fractograph of a tensile-failed surface of the vulcanizate of mix C₄. The surface shows an improvement in compatibility and an improvement in the adhesion of CGR to NR matrix. The surface also shows no separate CGR particles.

Figures 7 and 8 are the SEM photomicrographs of tear-fractured surfaces of mixes B₄ and C₄, respectively. The rough surface consisting of weakly bound CGR particles and a large number of tear lines as in Figure 7 for the vulcanizate of mix B₄ is absent in Figure 8 (mix C₄). The torn surface of the vulcanizate of mix C₄ shows relatively shorter tear lines and improved adhesion.

CONCLUSIONS

Cryoground rubber affects the curing characteristics of the CGR-NR blends. It decreases the scorch time, optimum cure time, and maximum rheometric torque. This effect is more pronounced when CGR is added in the mill-sheeted form. Sulfur diffuses from the rubber matrix phase to the CGR phase during vulcanization, as shown by the studies of the three-layer model.

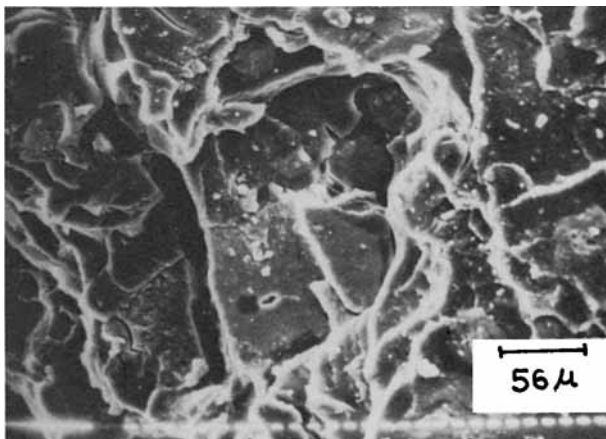


Fig. 5. SEM photomicrograph of tensile-fractured surface of the vulcanizate of mix B₄.

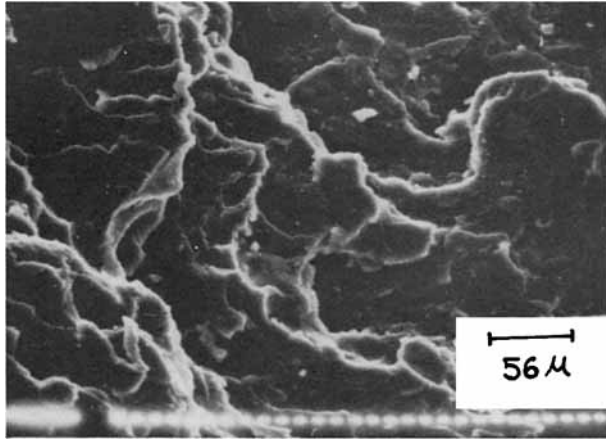


Fig. 6. SEM photomicrograph of tensile-fractured surface of the vulcanizate of mix C₄.

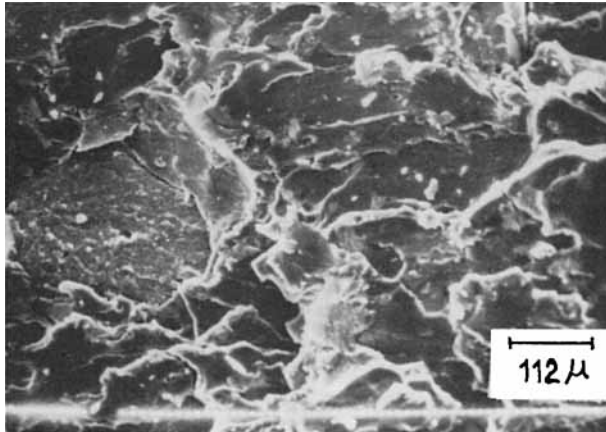


Fig. 7. SEM photomicrograph of tear-fractured surface of the vulcanizate of mix B₄.

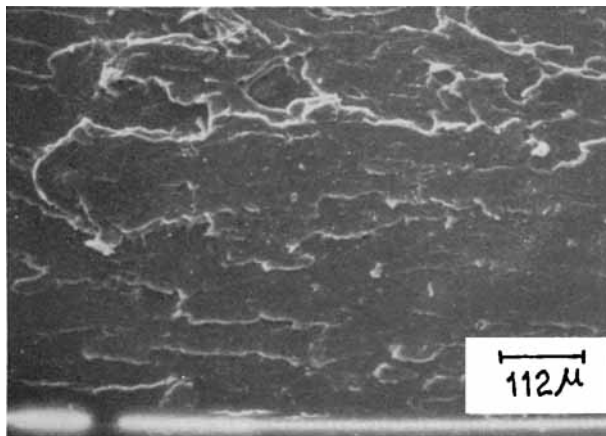


Fig. 8. SEM photomicrograph of tear-fractured surface of the vulcanizate of mix C₄.

Addition of CGR also changes the technical properties of the NR vulcanizates. The level of curatives and the form of CGR also influence the properties of the vulcanizate. Increasing level of curatives with increasing CGR loading compensates for the worsening of the technical properties of the vulcanizates. Mechanical treatment of CGR facilitates a better interaction between CGR and NR matrix as shown in the morphology of fractured surfaces. The network structure of the blends indicate that CGR acts as an "inert" filler.

Acetone extractables in the CGR contribute to the reduction in the curing characteristics. The model macrogel, prepared by partially vulcanizing the NR gum compound, also shows similar effects on the properties of NR.

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