

The Influence of Fillers and Degree of Vulcanization on the Mechanical Properties of Hard Rubber Polyblends

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Synopsis

Hard rubber polyblends, made from SBR-butyl rubber mixtures vulcanized with sulfur, show several consistent patterns of behavior in response to recipe modifications or changes in degree of vulcanization. T_g increases with degree of vulcanization, reinforcing fillers raise the modulus, and reversion is encountered upon overcure as in SBR hard rubber. The dual or stepwise transition from glassy to rubbery modulus behavior which characterizes polyblends is clearly distinguishable in all of the mixtures. The level of the polyblend modulus plateau between glassy and rubbery behavior is dependent on the proportion of butyl in the blend. The range of temperatures spanned by the polyblend modulus plateau is dependent on the degree of vulcanization of the hard rubber portion of the blend. Hard rubber dust suppresses the characteristic stepwise transition of the polyblend in proportion to the amount of dust added. The changes in the other mechanical properties investigated are consistent with the changes in modulus. The impact resistance of the polyblend appears to be effectively limited by the impact resistance of the hard rubber portion at all degrees of vulcanization.

Background

Polyblends of a resinous phase, made from sulfur-vulcanized SBR hard rubber, blended with a rubbery phase of butyl rubber, can be obtained by blending the polymers and then vulcanizing the SBR to hard rubber under suitable conditions.¹

These polyblends are characterized by two distinct stepwise transitions between glassy and rubbery behavior. The two transitions take place at temperatures corresponding respectively to T_g of the butyl and T_g of the vulcanized SBR hard rubber. Between the two transition temperatures the modulus of the polyblend is maintained at a nearly constant intermediate level, the magnitude of which is determined by the relative proportions of SBR hard rubber to butyl rubber in the blend.

When hard rubber polyblends are modified by the addition of fillers or by changing the sulfur to rubber ratio, significant changes in the properties of the vulcanized products result, just as they do in non-polyblend hard rubber mixtures. Modulus-temperature curves obtained from Clash-

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Berg torsion stiffness measurements² are a convenient means for following these changes and estimating their effects on other physical properties, such as the tensile strength and impact resistance of the original polyblend mixture.

Experimental

Hard rubber recipes containing respectively 22 and 34 wt.-% sulfur were prepared from SBR-1000, a general-purpose butadiene-styrene copolymer rubber, accelerated with 4 phr of butyraldehyde-amine accelerator (du Pont Accelerator No. 808), as in the previous work.^{1,3} Each of the hard rubber recipes was next blended with Butyl 365 (registered trade name of Enjay Chemical Co. for isobutylene-isoprene copolymer containing 2.0-2.5 mole-% unsaturation) to obtain polyblends containing respectively 30 and 40 wt.-% butyl rubber of the resulting batch.

The four polyblend combinations which resulted from this blending procedure were then further modified by adding hydrated lime, compounding oil, and a mold release agent according to the following recipe to facilitate further mixing and molding: polyblend, 90.0 parts (by weight); hydrated lime, 2.5 parts; Califlux GP (registered trade name for an unsaturated petroleum oil manufactured by Golden Bear Oil Co.), 7.0 parts; Armeen 18D (registered trade name for a technical grade of octadecylamine manufactured by Armour Industrial Chemical Co.), 0.5 parts. Fillers were then added to the modified mixtures to obtain a series of molding compounds containing between 30 and 50 parts by volume of filler.

Hard rubber dust, prepared by grinding scrap industrial battery jars to 100-250 μ particle size, was the only filler material examined at more than one level of loading, i.e., 30 and 50 vol.-% of the mixture. The maximum of hydrated lime (calcium hydroxide, 50-150 μ particle size) that could be incorporated into 22% sulfur blends without encountering scorching of the batch during mixing or lack of flow during molding was 40 vol.-%. The corresponding quantity for the 34% sulfur mixtures was 37.5 vol.-%. This difference was undoubtedly due to the additive effect of the sulfur and filler contributing to increase the friction within the batches during mixing in proportion to the total volume of sulfur and filler in the mixture. For similar reasons the 40% butyl mixtures were more plastic and easier to handle during mixing and molding than the lower polymer content (30% butyl) mixtures at both of the sulfur levels investigated.

The limit of loading used for the calcium carbonate mixtures was determined empirically as the maximum amount of the finer particle size Purecal U precipitated whiting (registered trade name for precipitated calcium carbonate, 0.03-0.04 μ particle size, manufactured by Wyandotte Chemicals Corp.) which could be incorporated without destroying the workability of the mixtures. Gamaco ground limestone (registered trade name for wet ground limestone, 5-40 μ particle size, prepared by Georgia Marble Co.), which could have been added in considerably higher proportions, was used at the same level of loading as precipitated whiting to give a

direct comparison of the two materials on the basis of particle size and surface area. The batches containing ground limestone were considerably more plastic than those containing precipitated whiting. This is the usual effect found in comparisons of high area, small particle-size fillers with low area, large particle size fillers.

Slabs of each of the mixtures were vulcanized at 180°C. and the following physical properties were determined: apparent modulus of elasticity

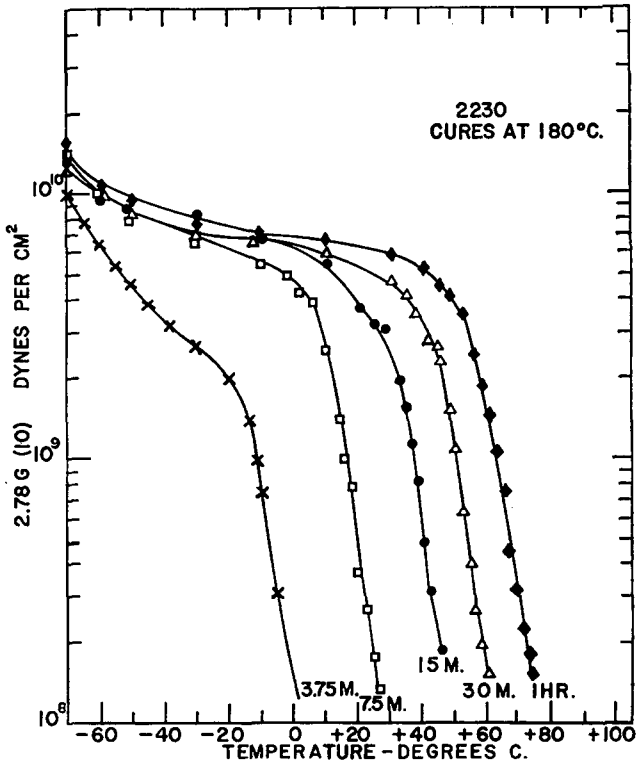


Fig. 1. 22% Sulfur hard rubber polyblend containing 30 wt.-% of Butyl 365.

(Clash-Berg procedure²) from $-70^{\circ}\text{C}.$ to above the glass transition temperature of the material; tensile strength and elongation at break, ASTM-D530;⁴ Durometer D hardness, ASTM-D1484;⁵ and tensile impact strength, ASTM-D1822.⁶ Ball drop impact strength⁴ was also determined by using a 2 lb. ball on the 2230 polyblend at two levels of vulcanization and three different test temperatures for comparison with the room temperature tensile impact values. Specimens were molded $\frac{1}{8}$ in. thick for all of the tests except the ball drop impact, which requires $\frac{1}{4}$ in. thickness. In each test the full thickness of the molded slab was used, and the profiles for the specimens were obtained by machining the edges of blanks cut from the molded sheet by means of a bench router equipped with a Carboloy cutter.

Figures 1 through 13 show the modulus-temperature relationships which are developed by these polyblends after vulcanization. In all of the figures $2.78G$ at 10 sec. stress is plotted as an approximation of Young's modulus. (This assumes a value of 0.39 for Poisson's ratio in all of the mixtures.) T_i has been taken as the temperature at which $2.78G(10) = 10^9$ dynes/cm.².

Modulus

Figure 1 shows a characteristic progressive increase of T_g and T_i as the time of vulcanization is increased up to 1 hr. at 180°C . at which point the combination of the available sulfur with the rubber is essentially complete.³ It therefore provides a frame of reference for the degree of vulcanization of the materials vulcanized for shorter fractional periods of time which are compared both in Figure 1 and by comparison of Figure 1 with the following figures.

The data in Figure 1 indicate that the transition temperature above which a hard rubber polyblend goes into rubbery behavior may be increased or decreased within the limits set by the maximum degree of vulcanization possible for the resinous or hard rubber component of the blend. The upper temperature limit for the level of the polyblend modulus

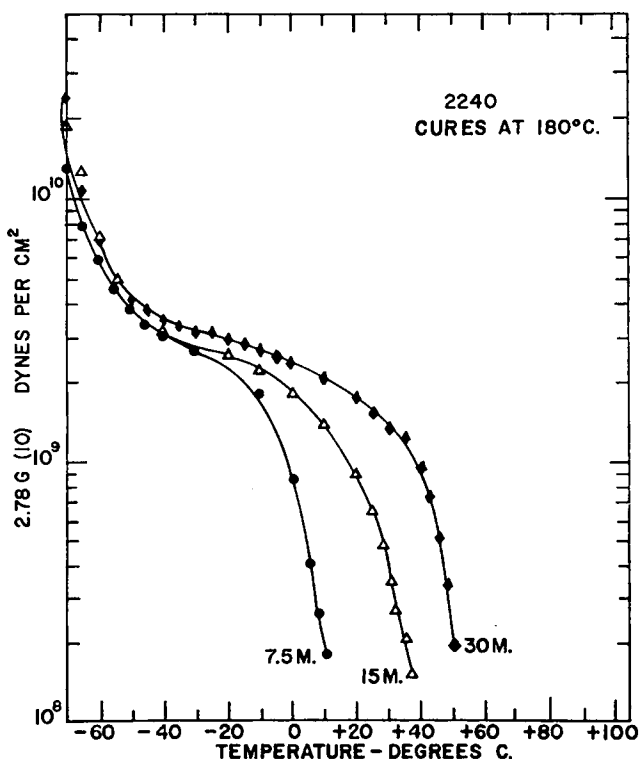


Fig. 2. 22% Sulfur hard rubber polyblend containing 40 wt.-% of Butyl 365.

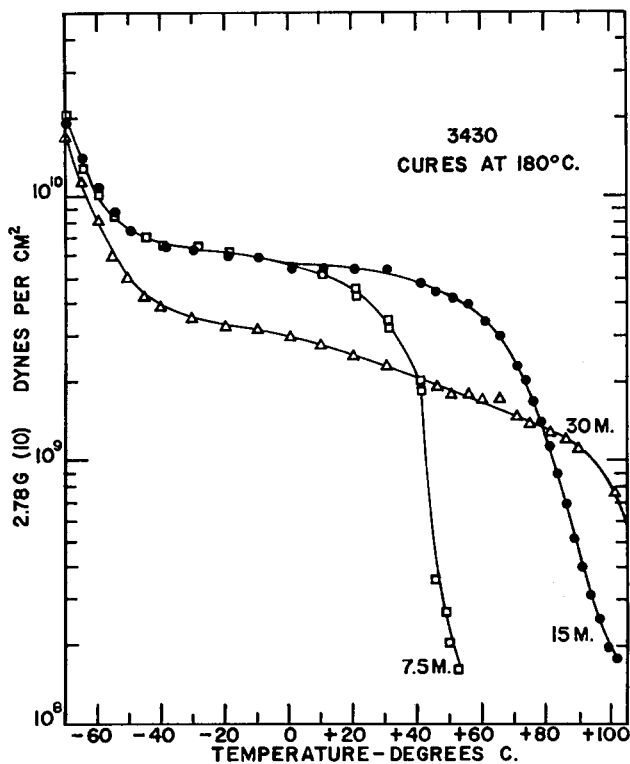


Fig. 3. 34% Sulfur hard rubber polyblend containing 30 wt.-% of Butyl 365.

plateau intermediate between glassy and rubbery behavior has been found to coincide with the glass transition temperature of the hard rubber portion of the blend in all of the recipes investigated.

Both the 1-hr. and the $\frac{1}{2}$ hr. cures at 180°C. shown in Figure 1 retain a modulus level of above 5.0×10^9 at ambient temperatures up to 25°C. This is equivalent to stating that at normal room temperatures and below they will behave as truly rigid materials. The $\frac{1}{2}$ hr. cure at 180°C. is therefore the shortest interval which will give a completely rigid product from a blend of this composition. The material cured $\frac{1}{4}$ hr. shows evidences of leathery behavior at room temperature, and the material cured $\frac{1}{8}$ hr. is below a modulus of 10^9 dynes at 20°C. and is therefore definitely soft and rubbery.

The effects of an increase of butyl rubber content in a polyblend are shown by a comparison between Figures 1 and 2. The higher amount of butyl in the 2240 mixture has caused a decided drop in the level of the polyblend plateau modulus and a more gradual change in modulus at both stages of the transition between glassy and rubbery behavior at each of the degrees of vulcanization shown. The glass transition temperature of the hard rubber, and therefore transition temperature to rubbery behavior for

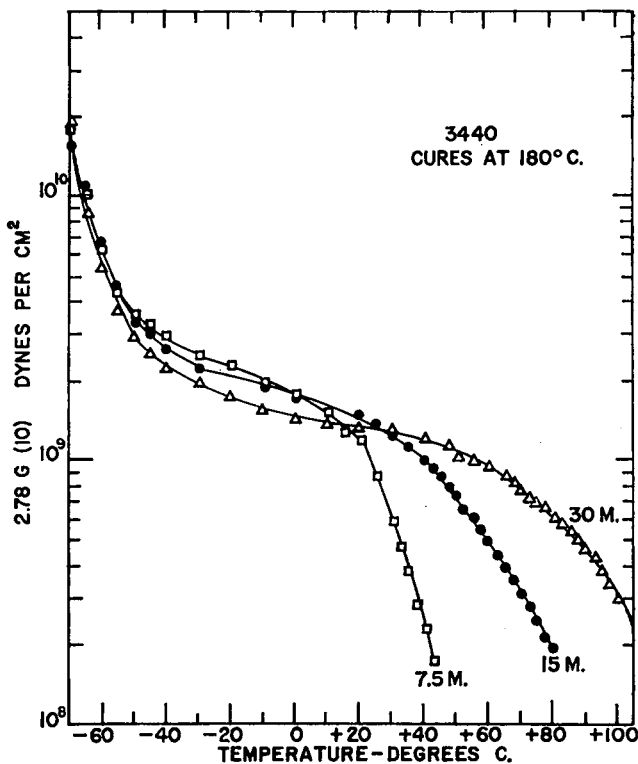


Fig. 4. 34% Sulfur hard rubber polyblend containing 40 wt.-% of Butyl 365.

the polyblend, is seen to have been only insignificantly reduced by the additional amount of butyl.

The effects compared in Figures 1 and 2 are even more pronounced when Figures 3 and 4 are compared. The higher sulfur content of the latter mixtures results in a faster increase of T_g and T_i during vulcanization. It also sets a higher limit on the values they can attain, thus effectively lengthening the temperature span of the polyblend modulus plateau. The differences in rate of transition and the reduction of the temperature of transition to rubbery behavior which are caused by the higher proportion of butyl are more highly accentuated than in the lower sulfur mixtures. The $\frac{1}{2}$ hr. cures for the 3430 and 3440 high sulfur mixtures show a drop in plateau modulus indicating reversion caused by the combined effect of high temperature and high sulfur content during the latter stages of cure. The comparatively lesser degree of reversion of the 3440 may reasonably be ascribed to the diluting effect of the higher amount of butyl both during and after vulcanization.

Effects of Fillers

The effects of adding hard rubber dust to both low and high sulfur polyblend mixtures are compared in Figures 5 and 6 and in Figures 7 and 8.

In both high sulfur and low sulfur mixtures at all degrees of cure the effect of the dust is to suppress the stepwise transition which characterizes polyblends. As the amount of dust is increased, the properties of the vulcanized product approach more closely to hard rubber rather than polyblend behavior. It is interesting to note that although 30 vol.-% of dust is not enough to prevent reversion, at 50% dilution the mixture shows no evidence of reversion.

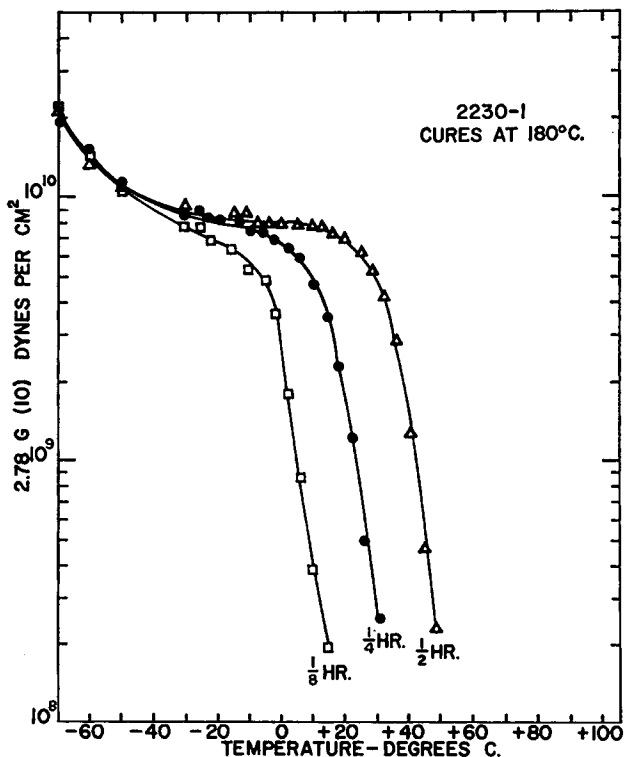


Fig. 5. 22% Sulfur hard rubber, 30% butyl polyblend containing 30 parts by volume of hard rubber dust.

Figures 9-11 show the reinforcing effects produced in high sulfur mixtures by the three inorganic fillers examined. Notable in all three figures are the increase in the level of the plateau modulus of the polyblend, the more gradual transition to rubbery behavior, and the effectively higher transition range which results from the combined effects of these two changes. The surface area, as well as the amount of filler used, appears to relate to the effectiveness of the filler in suppressing reversion as well as in providing mechanical reinforcement because the mixture made from fine particle size calcium carbonate shows no evidence of reversion, whereas the mixture containing ground limestone in identical proportions shows the effects of reversion sufficient to be clearly distinguishable from the effects

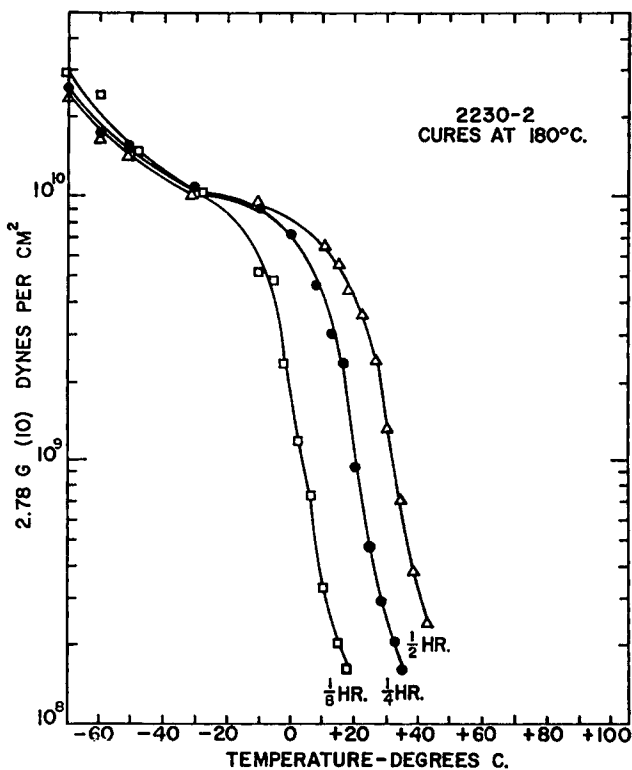


Fig. 6. 22% Sulfur hard rubber, 30% butyl polyblend containing 50 parts by volume of hard rubber dust.

of the lower degree of reinforcement afforded by the larger particle sizes of the ground limestone.

The remaining two figures compare high loadings of hard rubber dust in high butyl polyblends at both high and low sulfur levels. When compared with Figures 6 and 8, Figures 12 and 13 show the same types of relationships noted for the corresponding unfilled mixtures shown in Figures 1-4.

Suppression of the characteristic stepwise polyblend transition is evident in all of the highly loaded mixtures but the drop in polyblend plateau modulus and more gradual transition with increased butyl are still distinguishable. The longer polyblend modulus plateau and higher T_g with higher sulfur are also identifiable.

Other Physical Properties

Changes in the tensile strength, elongation at break, Durometer hardness, and tensile impact resistance at room temperature for the unfilled polyblends shown in Figures 1-4 are given in Table I. Table II corresponds to the modulus data in Figures 1, 6, and 7 and shows the changes produced by

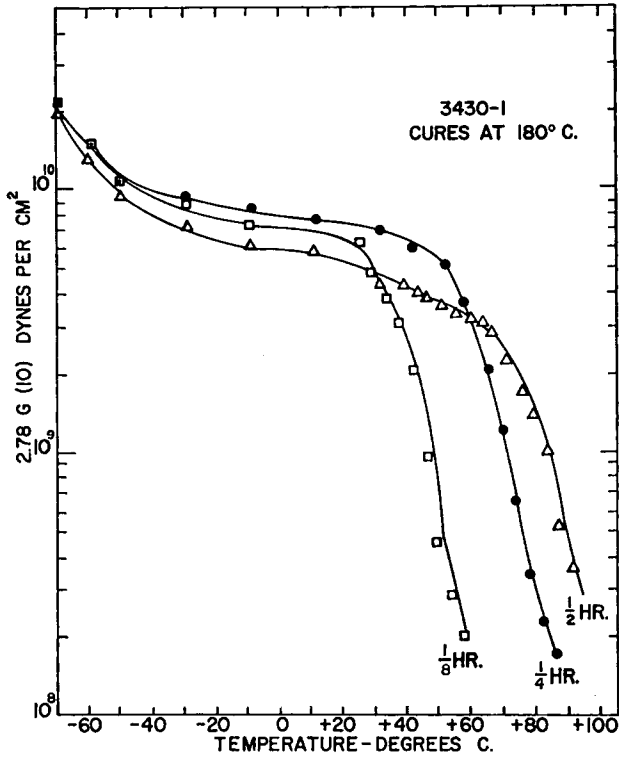


Fig. 7. 34% Sulfur hard rubber, 30% butyl polyblend containing 30 parts by volume of hard rubber dust.

TABLE I
Mechanical Properties of Unfilled Hard Rubber Polyblends

Mixture	Cure time at 180°C., min.	Ultimate tensile strength, lb./in. ²	Elongation at break, %	Durometer D hardness	Tensile impact strength, in./lb./in. ²
2230	3.75	—	—	20	1837 ^a
	7.5	568	52	38	320 ^a
	15	1149	20	53	189
	30	1777	3.3	55	152
2240	7.5	297	46	32	925 ^a
	15	555	3.5	50	202
	30	1340	4.3	50	139
3430	3.75	—	—	34	442 ^b
	7.5	1575	3.0	58	147
	15	1825	2.8	60	131
	30	847	1.2	59	177
3440	3.75	—	—	24	1008 ^b
	7.5	667	2.3	50	131
	15	416	1.5	51	177
	30	1300	2.3	50	127

^a Soft.

^b Soft, sulfur bloom.

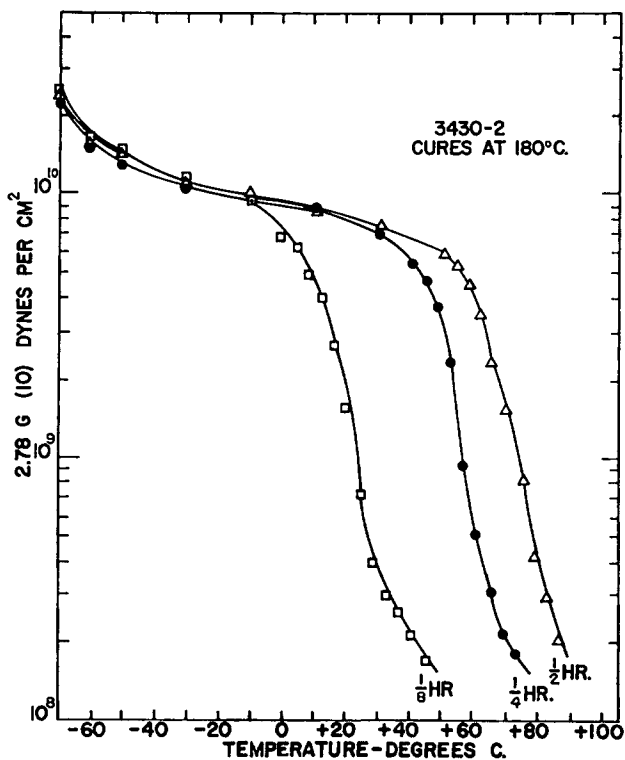


Fig. 8. 34% Sulfur hard rubber, 30% butyl polyblend containing 50 parts by volume of hard rubber dust.

TABLE II
Effects of Hard Rubber Dust Loading in a Typical Hard Rubber Polyblend

Mixture	Cure time at 180°C., min.	Ultimate tensile strength, lb./in. ²	Elongation at break, %	Durom- eter D hardness	Tensile impact strength, in.-lb./in. ²
2230, unloaded	7.5	568	52	38	320 ^a
mixture	15	1149	20	53	189
2230-1,	30	1777	3.3	55	152
7.5	614	56	32	275	
30 parts	15	1033	35	53	77
by volume	30	1560	5.3	61	75
of hard rubber dust					
2230-2,	7.5	479	41	33	175
50 parts	15	643	27	49	86
by volume	30	851	2.7	59	65
of hard rubber dust					

^a Soft.

TABLE III
Effects of Hard Rubber Dust and Inorganic Fillers in a
High Sulfur Hard Rubber Polyblend

Mixture	Cure time at 180°C., min.	Ultimate tensile strength, lb./in. ²	Elongation at break, %	Durom- eter D hardness	Tensile impact strength, in.-lb./in. ²
3430,	7.5	1575	3.0	58	147
unloaded	15	1825	2.8	60	131
mixture	30	847	1.2	59	177
3430-1,	7.5	1407	21	49	94
30 parts	15	2310	4.3	63	83
by volume	30	1555	1.2	58	69
of hard rubber dust					
3430-3,	7.5	702	32	48	76
50 parts	15	1768	3.7	62	53
by volume	30	1316	1.5	58	57
of hard rubber dust					
3430-3,	7.5	1131	1.8	69	64
37.5 parts	15	2633	2.2	73	64
by volume	30	2560	2.5	74	53
of hydrated lime					
3430-4,	7.5	1547	2.7	72	65
33.3 parts	15	2155	1.2	75	60
by volume	30	2553	2.2	76	56
of precipi- tated cal- cium car- bonate					
3430-5,	7.5	1065	12	61	85
33.3 parts	15	1652	1.8	67	67
by volume	30	1933	3.2	66	56
of ground limestone					

adding hard rubber dust to a low sulfur polyblend. Table III corresponds to Figures 4, 8, 9, 10, 11, and 12 and compares the effects of hard rubber dust and inorganic fillers in a high sulfur polyblend.

The tabular data were obtained from averages for three specimens for tensile strength, elongation, and hardness; five specimens were averaged for tensile impact resistance. Individual results differing from the mean by 2σ or more were discarded in arriving at averages. Where necessary, repeat tests were run to obtain a satisfactory average. There was more random scatter in the tensile and elongation values than in the values from the other tests. Durometer hardness gave the least scatter and the least discrimination between specimens. None of the other measurements was as highly reproducible as the modulus determinations.

Observations

Comparisons between the polyblend recipes show several consistent patterns of behavior similar to those found for conventional SBR hard rubber recipes which have not been modified by polyblending, among these are: faster cure rate and higher T_g and T_i at full cure for the high sulfur mixtures; progressive increase in tensile strength and durometer hardness as vulcanization progresses; corresponding decrease in elongation at break

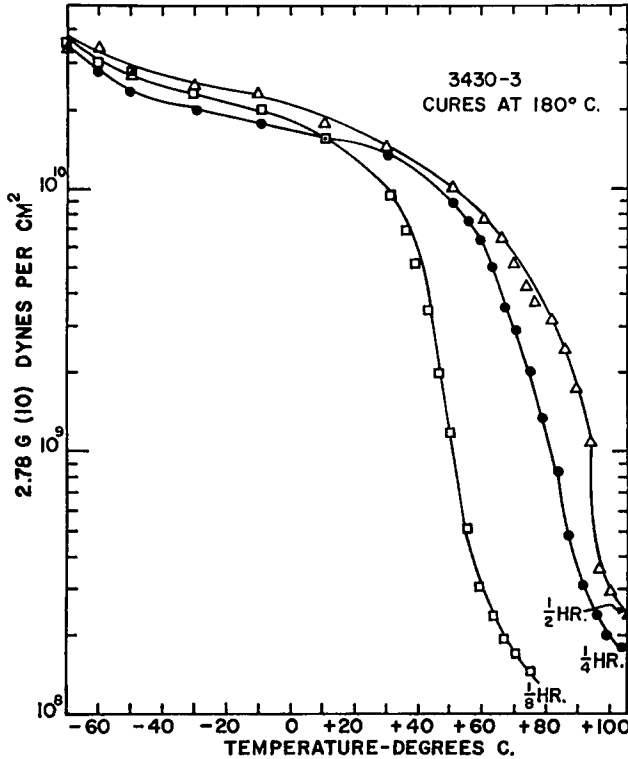


Fig. 9. 34% Sulfur hard rubber, 30% butyl polyblend containing 37.5 parts by volume of hydrated lime.

and impact strength as full cure is approached; higher hardness but lower tensile strength, elongation at break and impact resistance in highly filled recipes.

The highest impact strengths were measured for polyblends which were leathery or soft rather than rigid at room temperature. This type of behavior is also characteristic of hard rubber, but for hard rubber the terms "soft," "leathery," or "hard" are not definitive except as they are related to temperature. To identify hard rubber as "leathery" merely indicates that it has been measured at a temperature in the glass transition

range and that it will become either "soft" or "hard" as a result of a shift of only a few degrees up or down scale in temperature. This is not true for hard rubber polyblends. In these materials the hard rubber component is purposely vulcanized to a T_g well above room temperature. It is therefore in the glassy state for several degrees of temperature on both sides of

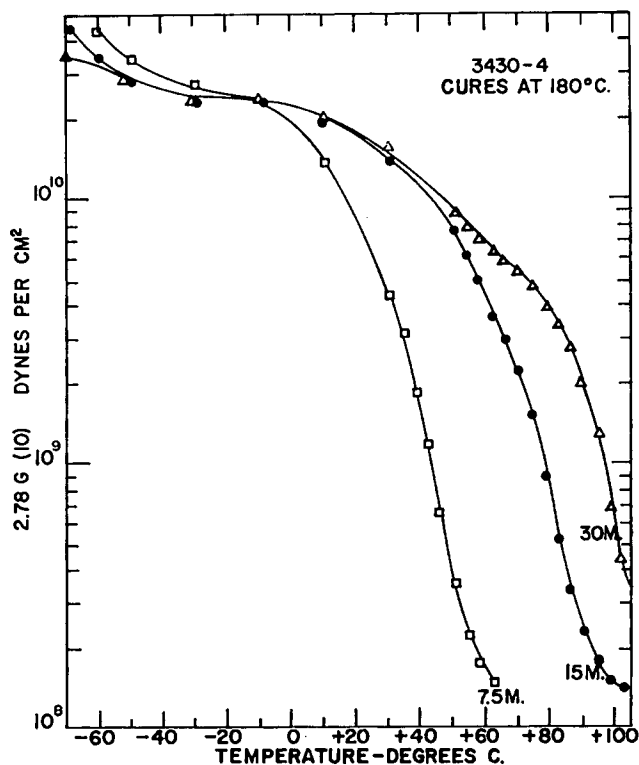


Fig. 10. 34% Sulfur hard rubber, 30% butyl polyblend containing 33.3 parts by volume of precipitated whiting.

the room temperature range and behaves accordingly. Leatheriness introduced into polyblends by additions of butyl rubber, rather than by reductions in sulfur content or degree of vulcanization, is retained over a wide range of temperatures corresponding to the length of the polyblend

TABLE IV
Ball Drop Impact Resistance of 2230 Hard Rubber Polyblend At
and Below Room Temperature

Cure	Impact resistance, in.-lb.		
	+20°C.	0°C.	-20°C.
7.5 min. at 180°C.	95	110	73
30 min. at 180°C.	26	33	18

modulus plateau. This is shown by the retention of room temperature impact resistance at colder temperatures for both degrees of vulcanization of the polyblend described in Table IV. The polyblend modulus plateau for this material is shown in Figure 1 to extend from about -40°C . to about $+40^{\circ}\text{C}$. for the 30-min. cure and to about $+5^{\circ}\text{C}$. for the 7.5-min. cure. The shorter cure therefore provides an interesting concurrence of leathery behavior at room temperature due in part to the amount of butyl in the blend and in part to the fact that the hard rubber moiety of the

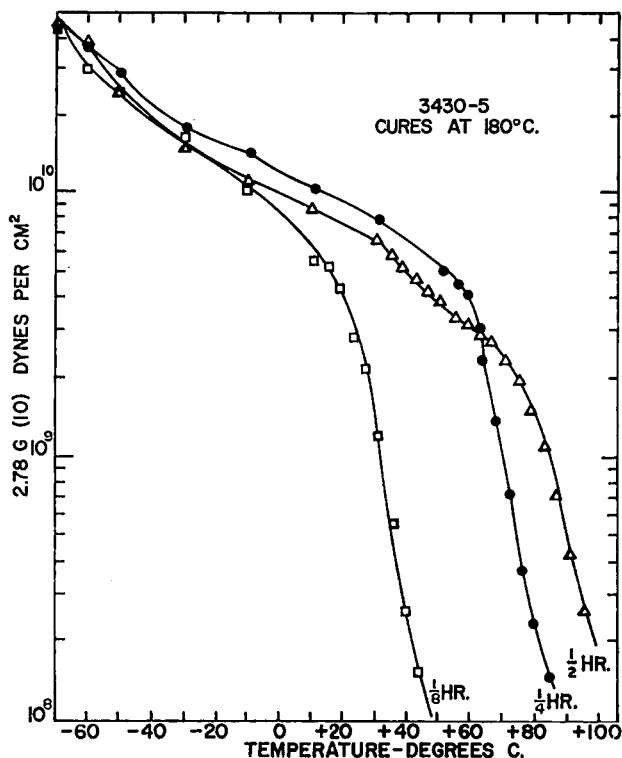


Fig. 11. 34% Sulfur hard rubber, 30% butyl polyblend containing 33.3 parts by volume of ground limestone.

mixture is approximately midway through its glass transition at 20°C . The fact that the impact resistance at room temperature does not differ greatly from that experienced at lower temperatures for either degree of cure suggests that this property is influenced to a greater extent by the level of the modulus plateau rather than the phenomena during transition.

In Table V we list the tensile impact results, modulus of 20°C ., and T_i values for SBR hard rubber containing 34% sulfur and vulcanized for various periods of time at 180°C . It is seen that the impact resistance remains at virtually the same level for all of the degrees of cure which

TABLE V
Properties of SBR Hard Rubber Containing 34% Sulfur

Cure time at 180°C., min.	Tensile impact resistance, in.-lb./in. ²	T_i 2.78(10) = 10, ³ °C.	2.78G(10) at 20°C. × 10 ⁹
3.75	268	31	3.8
7.5	114	69	21
15	143	100	21
30	109	116	25*
60	123	112	21

* The difference between this value and those above and below in the column represents a difference of 1° in the angle of rotation of the specimen. This is not regarded as significant.

undergo transition well above room temperature. Only the 3.75-min. cure which is part way through the glass transition at room temperature has a significantly higher impact resistance, reflecting the lower modulus at 20°C. The 100–150 in.-lb. tensile impact range for fully cured hard

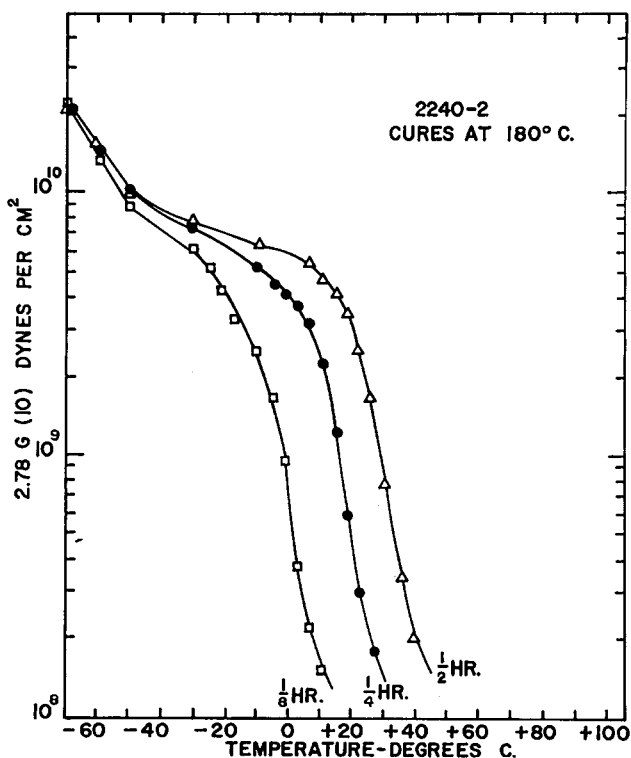


Fig. 12. 22% Sulfur hard rubber, 40% butyl polyblend containing 50 parts by volume of hard rubber dust.

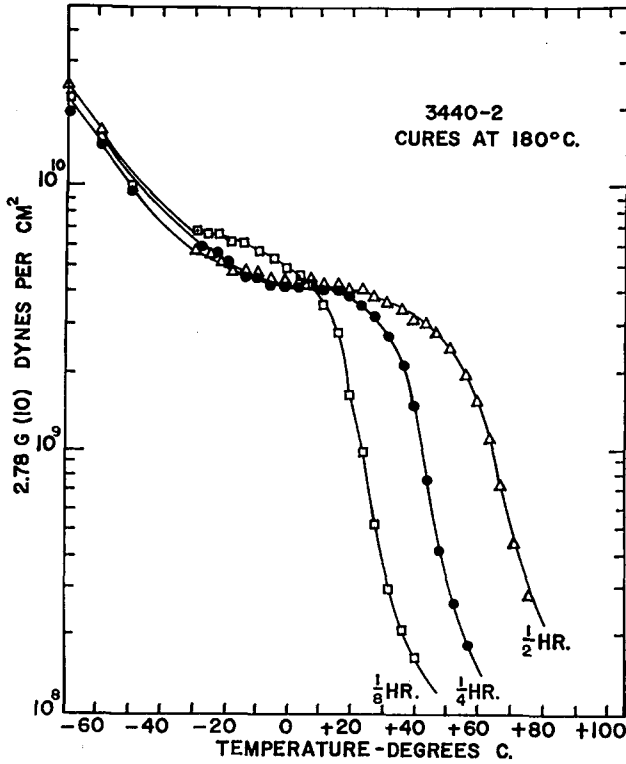


Fig. 13. 34% Sulfur hard rubber, 40% butyl polyblend containing 50 parts by volume of hard rubber dust.

rubber appears to approximate the upper limit for impact resistance in fully cured polyblends as shown in Table I.

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Résumé

Des polyblends de caoutchoucs durs, faits de mélanges de SBR-caoutchouc butylique vulcanisé au soufre montrent plusieurs régions consistantes de comportement quand on modifie le mode opératoire ou le degré de vulcanisation. T_g augmente avec le degré de vulcanisation, les charges renforçantes augmentent le module, et une inversion est rencontrée pour la survulcanisation comme pour le caoutchouc dur SBR. Le passage ou la transition graduelle du module vitreux ou module caoutchouteux, comportement qui caractérise les polyblends, est distingué très facilement dans tous les mélanges. Le niveau de plateau du module des polyblends entre le comportement vitreux et caoutchouteux dépend de la proportion de butyl dans la masse. La région de température pour laquelle le plateau du module du polyblend est valable dépend du degré de vulcanisation de la portion du caoutchouc dur. La poussière du caoutchouc dur supprime la transition caractéristique progressive de la masse et ceci proportionnellement à la quantité de poussière ajoutée. Le changement d'autres propriétés mécaniques est en accord avec le changement du module. La résistance au choc du polyblend est effectivement limitée par la résistance au choc de la quantité de caoutchouc dur à tous les degrés de vulcanisation.

Zusammenfassung

Hartgummi-Polymermischungen, die aus Schwefelvulkanisaten von SBR-Butylkautschukmischungen hergestellt wurden, zeigen mehrere gemeinsame Verhaltenszüge bei Änderung der Rezeptur oder des Vulkanisationsgrades. T_g nimmt mit dem Vulkanisationsgrad zu, verstärkende Füllstoffe erhöhen den Modul und eine Reversion tritt bei Übervulkanisation, wie beim SBR-Hartgummi, auf. Die duale oder stufenweise Umwandlung vom Glas- zum Kautschukverhalten, welche diese Mischungen charakterisiert, ist in allen Fällen klar zu erkennen. Das Niveau des Modul-Plateaus der Mischung zwischen Glas- und Kautschukverhalten hängt vom Butylanteil in der Mischung ab. Der vom Modul-Plateau der Mischung umfasste Temperaturbereich hängt vom Vulkanisationsgrad des Hartgummianteils der Mischung ab. Hartgummistaub unterdrückt die charakteristische stufenweise Umwandlung der Mischung im Verhältnis zur zugesetzten Staubmenge. Die Änderung der anderen untersuchten mechanischen Eigenschaften stimmt mit der Moduländerung überein. Die Grenze für die Stossfestigkeit der Mischung scheint bei allen Vulkanisationsgraden durch die Stossfestigkeit des Hartgummianteiles gegeben zu sein.

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