

Oxidative Stress Relaxation of Blends of *cis*-1,4-Polybutadiene and Natural Rubber

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Synopsis

Blends of *cis*-1,4-polybutadiene and natural rubber were vulcanized with dicumyl peroxide and a CBS (*N*-cyclohexylbenzothiazole-2-sulfenamide) accelerated sulfur system. For the peroxide-cured systems, soft vulcanizates had the natural rubber component only very lightly crosslinked and showed pronounced flow at room temperature. The oxidative stress relaxation of the hard vulcanizates at 80°C. in air was intermediate between that of the pure polymers. Intermittent stress relaxation measurements on these vulcanizates showed pronounced crosslinking during the aging of the pure polybutadiene and the 50/50 blend. Soft blends prepared by the accelerated sulfur system also showed flow due to the lightly crosslinked polybutadiene component. The unextracted hard blends resembled the pure polybutadiene vulcanizate in oxidative stress relaxation behavior at 80°C. in air, whereas after extraction to remove residual antioxidant and vulcanization products, etc., the blends were similar to natural rubber at all levels.

INTRODUCTION

The aging of blends of *cis*-1,4-polybutadiene and natural rubber have been studied by using the techniques of continuous and, to a lesser extent, intermittent stress relaxation. Continuous stress relaxation can be due to either main-chain or crosslink breakage. The ratio of stress after aging to the initial stress (F/F_0) is a direct measure of the network breakdown, whereas intermittent stress relaxation, where the strip is aged in the unstrained state, is influenced by any new crosslinks which may be formed during aging. A more detailed analysis of the data, which is not entirely satisfactory in the case of pure polymers, has not been attempted here. Instead we have been content to present our qualitative conclusions.

EXPERIMENTAL

The natural rubber (NR) used was taken from the middle portion of a bale of highly purified rubber (U.S. Rubber Company) and, after sheeting and light milling to break down any gel, extracted for 24 hr. with hot acetone. The Phillips Petroleum Company's *cis*-1,4-polybutadiene (BR) was also extracted with hot acetone; this material flowed considerably, making extraction rather difficult.

TABLE I
Natural Rubber-*cis*-1,4-Polybutadiene Blends Vulcanized with
Dicumyl Peroxide at 140°C.

	NR, wt.-%	BR, wt.-%	Dicumyl peroxide, %	Cure time, min.	V_r
Soft					
vulcanizates	100	0	3.0	40	0.180
	75	25	2.25	40	0.215
	50	50	1.5	25	0.218
	25	75	0.75	25	0.195
	0	100	0.75	15	0.194
Medium					
vulcanizates	100	0	4.5	40	0.290
	75	25	3.0	40	0.296
	50	50	1.5	40	0.261
	25	75	0.75	40	0.260
Hard					
vulcanizates	100	0	6.0	40	0.320
	75	25	4.5	40	0.327
	50	50	2.0	40	0.333
	25	75	1.25	40	0.334
	0	0	0.75	40	0.311

TABLE II
CBS-Cured Natural Rubber-*cis*-1,4-Polybutadiene Blends

	NR, wt.-%	BR, wt.-%	ZnO phr	Sulfur, phr	CBS, phr	Lauric acid, phr	Cure time at 140°C., min.
Soft							
vulcanizates	100	0	5	1.0	0.8	1.0	40
	75	25	5	1.0	0.8	1.0	50
	50	50	5	0.75	0.6	1.0	60
	25	75	5	0.75	0.6	1.0	60
	0	100	5	0.75	0.6	1.0	60
Hard							
vulcanizates	100	0	5	1.3	1.0	1.0	40
	75	25	5	1.3	1.0	1.0	50
	50	50	5	1.0	0.8	1.0	60
	25	75	5	1.0	0.8	1.0	60
	0	100	5	1.0	0.8	1.0	60

The rubbers were blended by sheeting out both polymers thinly on an open mill, wrapping one inside the other, and passing them through the nip at 100°C. Immediately a crumb was produced which was fed through the nip until it banded; the temperature was then slowly reduced to approximately 50°C., and if no further crumbing occurred the polymers were deemed to have blended.

Peroxide vulcanizates were prepared in a chromium-plated mold ($10 \times 10 \times 0.03$ cm.) at 140°C . with the use of varying amounts of recrystallized dicumyl peroxide. The blends were cured to one of three degrees of cross-linking as assessed by equilibrium volume swelling V_7 in decane, and designated hard, medium, and soft. Table I summarizes the vulcanization data for the peroxide systems. The vulcanizates were all extracted in hot chloroform-acetone-methanol azeotrope and stored *in vacuo*.

Accelerated sulfur vulcanizates were prepared under similar conditions, the cure time being varied as well as ingredient concentrations. For these vulcanizates two levels of cure, designated hard and soft, were aimed at, and these were characterized by values of C_1 and C_2 obtained from stress-strain measurements and equilibrium volume swelling V_7 . Table II summarizes the curing data for the CBS-accelerated vulcanizates.

Stress relaxation measurements were carried out on automatic stress relaxometers^{1,2} at 25% elongation at 80°C . in air. Antioxidant 2246, where used, was swollen in for 16 hr. as a 0.2% solution in ethyl acetate, the solvent being removed under reduced pressure (0.1 mm. Hg).

RESULTS AND DISCUSSION

Peroxide Vulcanizates

The medium and soft vulcanizates of the blends, with the exception of the medium 75% NR-25% BR blend, all showed very high initial stress relaxations indicative of flow. These vulcanizates also showed marked stress relaxation at 20°C . when oxidative degradation should be negligible

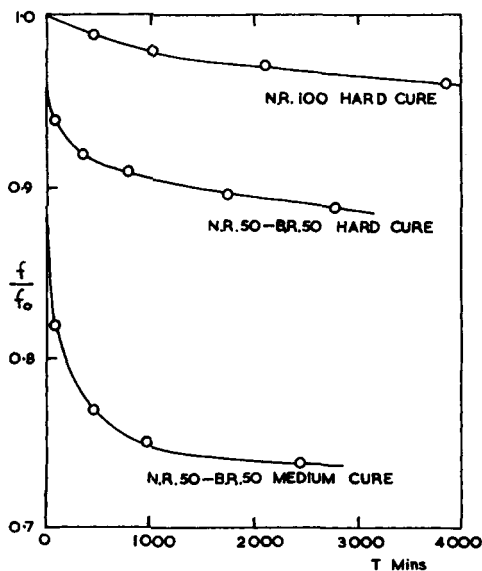


Fig. 1. Physical stress relaxation of dicumyl peroxide cured NR-BR blends at 20°C .

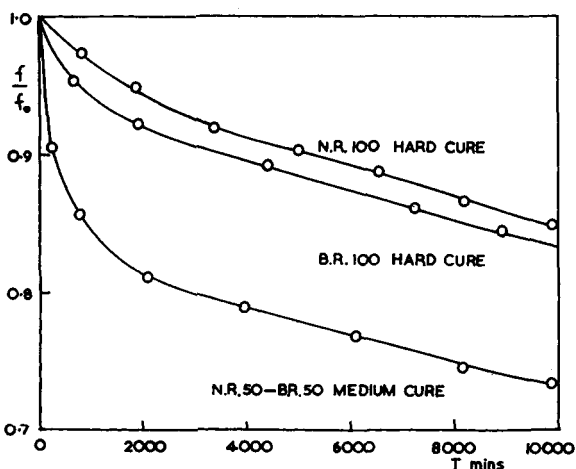


Fig. 2. Stress-relaxation at 80°C. of dicumyl peroxide-cured NR-BR blends containing 0.2% Antioxidant 2246.

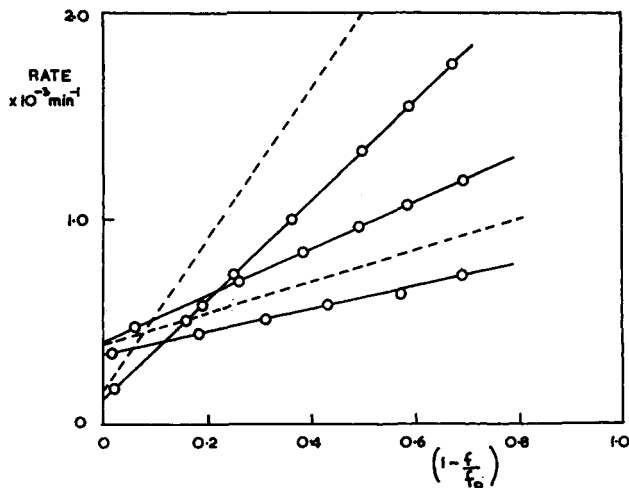


Fig. 3. Effect of composition on the stress relaxation at 80°C of dicumyl peroxide-cured NR-BR blends.

(Fig. 1), and at 80°C. Addition of 0.2% of Antioxidant 2246 [2,2'-methylene-bis(4-methyl-6-*tert*-butyl phenol)] afforded little protection, again showing that the changes were not oxidative (Fig. 2). For these vulcanizates plots of stress after aging to initial stress F/F_0 against log time were initially linear, behavior which is typical of a physical flow process.³ Prolonged extraction of these vulcanizates did not remove any soluble polymer, and it thus appears that one of the components is very lightly cross-linked.

The hard blends showed behavior similar to that of the pure polymers, giving typically autocatalytic plots, behavior which was inhibited by An-

TABLE III
Slope of $d(F/F_0)/dt$ versus $1 - (F/F_0)$ for Peroxide Vulcanizates

NR, wt.-%	BR, wt.-%	Slope $\times 10^4$, min. ⁻¹
100	0	35
75	25	24
50	50	11
25	75	7
0	100	10

tioxidant 2246. The plots of F/F_0 versus time tended to be rather irreproducible, a feature previously observed with peroxide vulcanizates of natural rubber which may be attributed to the variability of the initial hydroperoxidic content of the strips. However, if the rate $d(F/F_0)/dt$ is plotted against $(1 - F/F_0)$, straight lines are obtained whose slope is constant for a given rubber. This is typical of an autocatalytic reaction, where the rate is proportional to the extent of the reaction. This slope is a convenient means of characterizing the behavior of the various blends, and Figure 3 and Table III give the results obtained. The reproducibility of these slopes is of the order of 20%, and it can be seen that blends with 50% or more of *cis*-polybutadiene are virtually identical in behavior.

From Table I it is evident that the polybutadiene vulcanizes much more efficiently than does NR; thus, presumably, in the soft and medium cures the NR component is only very lightly crosslinked, and it is highly probable that even in the hard cures the NR component has a lower crosslink density than the polybutadiene component. This would result in most of the stress being borne by the polybutadiene component, and the stress relaxation behavior of this would, as observed, determine the overall behavior of the blend.

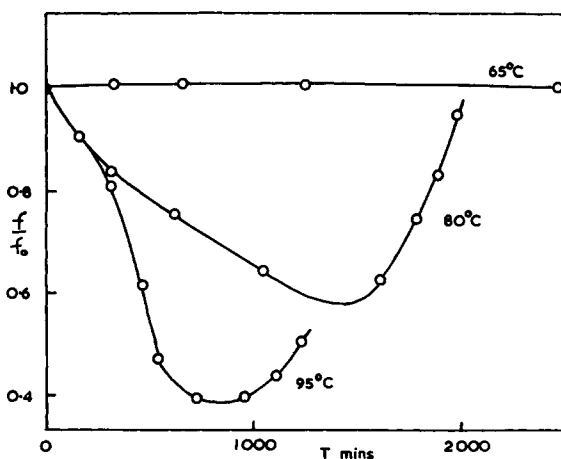


Fig. 4. Effect of temperature on the intermittent stress relaxation of dicumyl peroxide-cured polybutadiene.

Cis-1,4-Polybutadiene and its blends, unlike natural rubber alone, shows marked crosslinking on aging; the strips in the relaxometer harden considerably. Results of intermittent stress relaxation measurements on polybutadiene are shown in Figure 4 for three different temperatures. At the higher temperatures the degradation is initially autocatalytic, but after a while the crosslinking reaction becomes increasingly important, and the modulus begins to increase in some instances, almost reaching its original value before rupture occurs. This behavior is similar to that observed by Tobolsky and Mercurio at 130°C.⁴ At a temperature of 65°C. the crosslinking reaction seems exactly to counterbalance the degradation, and virtually no change in modulus occurs. Removal of oxygen or the presence of Antioxidant 2246 suppresses the degradation reaction and almost stops the crosslinking reaction also. Thus both reactions are oxygen-dependent but are separate, having different activation energies.

CBS-Accelerated Vulcanizates

Table IV gives values of C_1 , C_2 , and V_r obtained on vulcanizates accelerated with CBS (*N*-cyclohexylbenzothiazole 2-sulfenamide) and, in the case of the hard vulcanizates, includes a figure for the total combined sulfur, obtained after azeotrope extraction.

The solvent-polymer interaction coefficient μ for the blends was determined by using the relation

$$C_1 = -\dot{R}T[\ln(1 - V_r) + V_r - \mu V_r^2]/2 V_1 V_r^{1/4}$$

where V_r is the volume swelling, V_1 is the molar volume of solvent, and C_1 is obtained from the stress-strain curve.⁵

The values obtained are given in Table IV, and are consistent with the NR component being more highly crosslinked than the polybutadiene.

As in the case of the peroxide vulcanizates the soft rubbers showed very pronounced flow, making it impossible to interpret measurements in terms of oxidative stress relaxation. The hard rubbers did not show this flow, and plots of $\log(F/F_0)$ versus time are linear over a wide range (Fig. 6.) and their slopes give a ready method of comparing rates of relaxation (Table V).

TABLE IV
Physical Data of CBS Vulcanizates

NR, wt.-%	BR, wt.-%	Soft cures						Hard cures	
		C_1	C_2	C_1	C_2	V_r	μ	Combined sulfur, %	
100	0	0.93	0.65	1.13	0.58	0.258	0.46	1.3 ₁	
75	25	1.04	0.82	1.27	0.95	0.292	0.47	1.4 ₂	
50	50	0.99	0.84	1.29	0.95	0.297	0.48	1.0 ₁	
25	75	0.92	0.78	1.23	1.74	0.349	0.55	1.1 ₅	
0	100	1.00	2.10	1.40	2.24	0.395	0.59	1.1 ₁	

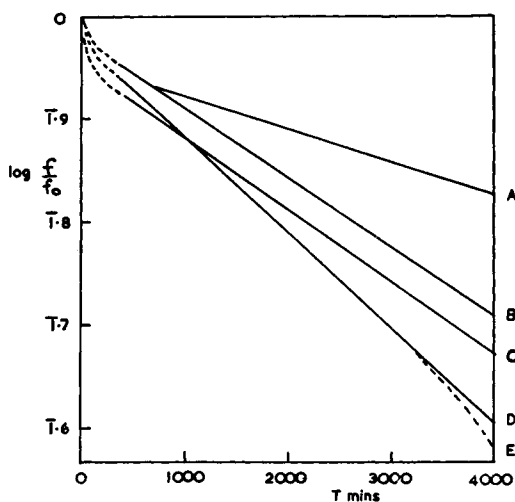


Fig. 5. Stress relaxation of unextracted CBS-cured NR-BR blends at 80°C.: (A) 100 NR; (B) 75 NR; (C) 50 NR; (D) 25 NR; (E) 0 NR.

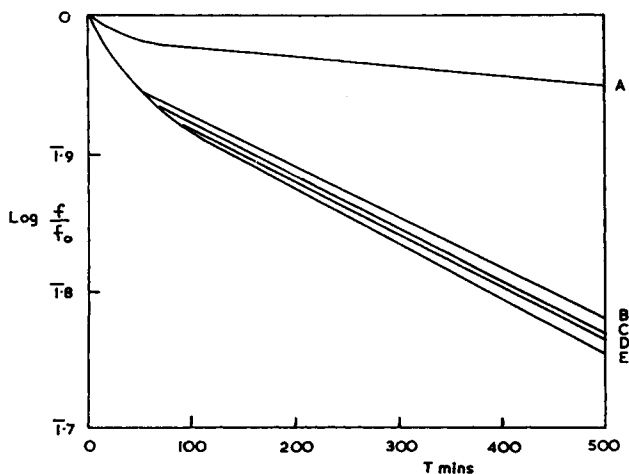


Fig. 6. Stress relaxation of extracted CBS-cured NR-BR blends at 80°C.: (A) 0 NR (B) 25 NR; (C) 50 NR; (D) 75 NR; (E) 100 NR.

The effect of extraction on the NR vulcanizate is considerable, indicating that the accelerator fragments and residues have marked antioxidant properties. Extraction seems to have little effect on the *cis*-polybutadiene vulcanizate (Fig. 5 and 6). The behavior of all of the extracted blends is clearly dominated by the NR component, confirming that this component is responsible for supporting most of the stress.

The effect of gross overcure (7 hr. at 140°C.) on the NR and BR is also quite different. With BR, extraction has no effect on the rate of stress relaxation; however, the rate is some four times faster than that obtained

TABLE V
Rate of Stress Relaxation of Hard CBS Vulcanizates

NR, wt.-%	BR, wt.-%	Slope of $\log(F/F_0)$ vs. time $\times 10^5$, min.	
		Extracted	Unextracted
100	0	45	3.3
75	25	45	6.4
50	50	45	7.1
25	75	46	8.9
0	100	9	8

after the optimum 1 hr. cure. With NR this overcure doubles the rate of aging of both extracted and unextracted vulcanizates. This may be due to the greater incorporation of sulfur groupings into the main chains.

CONCLUSION

Oxidative stress relaxation measurements of vulcanized blends of rubbers can be misleading if one of the components is only lightly crosslinked. Under these conditions pronounced flow occurs. Even if both components are sufficiently crosslinked to prevent this flow, the oxidative stress relaxation is still dominated by the more highly crosslinked component.

References

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Résumé

Des mélanges de *cis*-1,4-polybutadiène et de caoutchouc naturel ont été vulcanisés avec du peroxyde de dicumyle et un système sulfuré accélérateur au CBS (*N*-cyclohexyl-benzothiazole-2-sulphéné amide). Avec les systèmes peroxydiques de vulcanisation, les vulcanisats mous de caoutchouc naturel étaient très légèrement pontés, et présentaient un écoulement marqué à température de chambre. La force de relaxation oxydante de vulcanisats durs à 80°C sous air était intermédiaire à celle des polymères purs. Des mesures intermittentes de la force de relaxation sur ces vulcanisats montrent un pontage prononcé durant le vieillissement du polybutadiène pur et du mélange 50/50. Des mélanges mous, préparés par le système sulfuré accélérateur, montrent aussi un écoulement dû au faible pontage du polybutadiène. Les mélanges durs, non-extraits, ressemblent au vulcanisat du polybutadiène pur, pour ce qui est du comportement de la force de relaxation oxydante à 80°C sous air tandis qu'après extraction effectuée pour enlever l'antioxydant résiduel et les produits de vulcanisation, etc.; les mélanges sont semblables au caoutchouc naturel à tous les points de vue.

Zusammenfassung

Mischungen von *cis*-1,4-Polybutadien und Naturkautschuk wurden mit Dicumylperoxyd und einem CBS (*N*-Cyklohexyl-benzothiazol-2-sulphenamid)-beschleunigten

Schwefelsystem vulkanisiert. Bei den peroxydvulkanisierten Systemen hatten die weichen Vulkanisate nur sehr schwach vernetzte NR-Komponenten und zeigten bei Raumtemperatur ausgeprägtes Fließen. Die Oxydative Spannungsrelaxation der harten Vulkanisate bei 80°C in Luft lag zwischen denjenigen der reinen Polymeren. Intermittierende Spannungsrelaxationsmessungen an diesen Vulkanisaten zeigten ausgeprägte Vernetzung während der Alterung des reinen Polybutadiens und der 50/50-Mischungen. Auch bei weichen, mit dem beschleunigten Schwefelsystem dargestellten Mischungen trat wegen der schwachen Vernetzung der Polybutadienkomponente Fließen auf. Die nicht extrahierten harten Mischungen waren im oxydativen Spannungsrelaxationsverhalten bei 80°C in Luft dem reinen Polybutadienvulkanisat ähnlich, während sie nach Extraktion des restlichen Antioxydants' und der Vulkanisationsprodukte, etc., immer dem Naturkautschuk ähnlich waren.

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