Compounding Rubber for Radiation Resistance

HERBERT R. ANDERSON, JR.

Research and Development Department, Phillips Petroleum Company, Bartlesville, Oklahoma

I. INTRODUCTION

The need for elastomers which undergo relatively little change in physical properties upon exposure to ionizing radiation has stimulated a great deal of active research in recent years.[1-10] Approaches to the problem have included studies of the response of well-known elastomers to radiation, synthesis of new rubbers containing radiation-resistant groups, and the effect of additives. This paper presents results obtained with butadiene-styrene vulcanizates, one of the most resistant to radiation; the results show that by proper compounding techniques resistance to radiation may be increased. Swelling and stress relaxation techniques are applied to determine the effect of styrene content of rubber, oil extension, vulcanization recipe, conditions of cure, additives (antirads), and irradiation atmosphere on radiation damage to polymeric network and the dependent stress-strain properties.

II. EXPERIMENTAL

Vulcanizates were exposed to the gamma-rays from spent fuel elements at the canal facilities of the Materials Testing Reactor at Idaho Falls, Idaho. The cured compounds were separated by sheets of Holland cloth, packed into aluminum cans which were evacuated and purged three times with helium or air, and irradiated under a slight positive pressure. The irradiation was carried out under 16 ft. of water at the ambient canal temperature of ca 27°C. Comparisons of the radiation resistance of the different vulcanizates without complications introduced by flux variations resulting from decay in activity of the fuel elements can be made by this procedure. All irradiations were performed within three to thirty days after withdrawal of the fuel elements from the reactor. Since much of the lowest energy radiation is absorbed by the intervening water and container walls, the mean energy of the gamma-rays used in this work is estimated at 1.5 m.e.v.; more than 50% of the energy is derived from the barium-lanthanum 140 chain.

The radiation dosages were determined for each experiment by ceric/cerous sulfate dosimetry, and are expressed in roentgens equivalent physical (reps).

Polymers studied were Philprene 1500 (a trademark of Phillips Petroleum Co.), a 50 ML-4 butadiene-styrene copolymer containing 23% bound styrene, and a 47 ML-4 high-styrene analog containing 41% bound styrene. These synthetic rubbers are emulsion copolymers prepared at 5°C. The compounding recipes are shown in Appendix A. A glossary of compounding agents is shown in Appendix B.

Physical testing of the vulcanizates was carried out by well-known procedures. Degrees of crosslinking were estimated by the equilibrium swelling technique in n-heptane.[11,12] Estimates of the amount of scission during irradiation were determined by measurements of stress relaxation.[13-15] Strips of the vulcanizates were stretched to 100% elongation on an aluminum rack and were allowed to relax 24 hr. before measurement of the initial stress. The strips were returned to the rack, placed in an aluminum can, and irradiated in an atmosphere of helium or air; the final tension was determined after removal from the radiation field.

III. GENERAL PRINCIPLES

Irradiation of organic high polymers with ionizing radiation causes both crosslinking and scission. Crosslinking predominates in the butadiene rubbers.[16-21] Estimates of radiation-induced changes in the polymeric network are made by application of the kinetic theory of rubber elasticity.

From statistical theory,[22-25] the equilibrium stress f in a strip of rubber is given by

$$f = \nu kT[\alpha - (1/\alpha^2)] \qquad (1)$$

where α is the ratio of the extended to the initial length and ν is the number of elastically effective network chains. Equation (1) is useful in a semi-

quantitative way even when nonequilibrium modulus values are employed, provided the elongation is kept low ($\alpha < 2$). Furthermore, modulus has been found to be related linearly to the number of network chains in carbon black-loaded rubbers for the range of values associated with rubbery vulcanizates.[12] One would expect this same linear dependence when a vulcanizate is exposed to radiation. As the change in number of network chains represents the difference of crosslinking and scission, the absolute value of crosslinking and scission is relatively unimportant in determining modulus.

Separate estimates of scission and crosslinking during irradiation are obtained by the measurement of both stress relaxation[13−15] and equilibrium swelling.[11] This scheme has been employed by Arnold, Kraus, and Anderson[26] to estimate the ratio of crosslinking to scission during gamma-vulcanization. More recently, Kraus[27] has shown that deviations of carbon black-loaded vulcanizates from ideal elastic behavior are minimized by measuring the initial (ν_0) and final (ν) number of network chains from equilibrium swelling[11,12] and relying on measurements of stress only to determine the stress ratio f/f_0, where f and f_0 are the final and initial equilibrium stresses in the stress relaxation experiment, respectively. The calculation of the number of scissions s, following the theories of Bueche[28] and Berry and Watson[29] yields for scission at crosslinks:

$$s = \nu_0(1 - f/f_0) \qquad (2)$$

and for first-order random scission in the main chain:

$$s = \nu_0(f_0/f - 1) \qquad (3)$$

The extent of crosslinking r is then

$$r = \nu - \nu_0 + s \qquad (4)$$

IV. RESULTS AND DISCUSSION

The results of this work will be divided into two parts. Part I is concerned with the radiation resistance (changes in 100% modulus) of common butadiene-styrene (77/23) rubber tread stocks, which were used to explore the action of vulcanization system, cure temperature, state of cure, irradiation atmosphere, and additives. The useful life of the high-styrene cold-rubber tread stocks which were found to resist radiation in a gamma-ray field was determined by the techniques used in Part I. These results and measurements of swelling and stress relaxation of these vulcanizates to relate network damage to changes in stress-strain properties are presented in Part II.

A complete tabulation of all stress-strain and swelling results of all these vulcanizates are included in Appendix C for possible engineering information.

Part I. Radiation Resistance of Butadiene-Styrene (77/23) Tread Stocks

A. Effect of State of Cure

Born and associates[1,2] have emphasized that an evaluation of radiation retarders must be made with vulcanizates at equivalent states of cure, i.e., with optimum physical properties. A similar observation was made independently in our laboratories, where it was found that completeness of cure is, generally, highly desirable for the evaluation of additives. These materials can affect the rate of vulcanization and the yield of crosslinks obtainable from a given recipe. Figure 1 shows a typical change in density of network chains during vulcanization. Once the plateau region of the cure rate curve has been reached there is little change in the 100% modulus [consistent with eq. (1)], tensile strength, and elongation. The amount of curing agent determines the height of the plateau, and, consequently the network chain density with a given compounding recipe. Additives should, preferably, be compared in fully cured stocks, because incomplete vulcanization improves radiation resistance. Born et al.[1,2] explained that this improvement was due to the initial expenditure of radiation to overcome the deficiency in crosslink density. Figure 2 shows the results of a study made with vulcanizates containing two different levels of sulfur to determine if the effect of undercure on radiation resistance is due to the initial
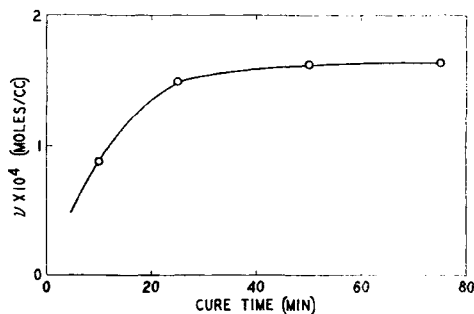

Fig. 1. Number of network chains vs. cure time at 307°F. for a butadiene-styrene (59/41) tread stock (50 phr HAF black) vulcanized with an accelerated sulfur system. For vulcanization recipe see Table I.
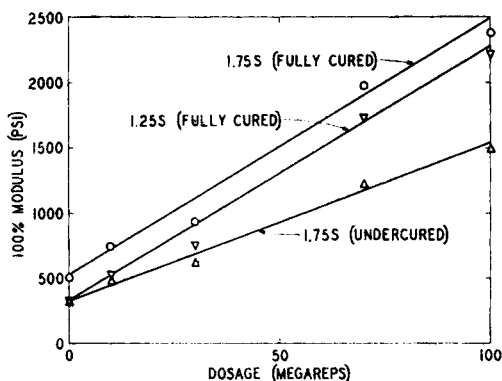
Fig. 2. Effect of state of cure on the radiation resistance of butadiene–styrene (77/23) tread stocks (50 phr HAF black) in a helium atmosphere. For vulcanization recipe see Appendix A, Table I.

crosslink density. These results indicate that curing short of the plateau region (undercuring) produces residual vulcanization intermediates which serve to modify and lessen radiation damage to sulfur-vulcanized rubbers. Such an effect is similar to the results observed by Kraus[27] and Ossefort[30] in their studies of the thermal and oxidative degradation of vulcanizates.

B. Effect of Sulfur Utilization During Vulcanization

Since undercuring of sulfur vulcanizates apparently produces residual intermediates capable of functioning as radiation retarders (antirads), it was

of interest to determine the impact of sulfur utilization during vulcanization on radiation resistance. Variations in sulfur utilization were obtained by varying the ratio of sulfur to accelerator at a fixed cure temperature and by curing at different temperatures. The data in Table I reveal that the radiation resistance of a sulfur vulcanizate is greatest when it is undercured at 307°F. with a high ratio of accelerator to sulfur, and that it is affected by cure temperature but not by variations in sulfur/accelerator ratios at full cure. Detailed explanation of these results is not possible. The radiation resistance of sulfur vulcanizates appears to be associated intimately with the relative amount and characteristics of crosslinks and with the amount of combined sulfur postulated to be in the form of five- and six-membered heterocyclic rings.[31]

C. Effect of Crosslink Type

Since the mode of preparation of sulfur vulcanizates plays an important role in their radiation resistance, it was of interest to compare the response to radiation of vulcanizates containing carbon-carbon crosslinks with those containing sulfur linkages. The data in Table II show that no sig-

TABLE I
Effect of Sulfur Utilization during Vulcanization on the Radiation Resistance of Butadiene–Styrene (77/23) Tread Stocks in a Helium Atmosphere[a]

Sulfur, phr	Santocure, phr	Cure temperature, °F.	Change in 100% modulus, psi, after indicated dosage	
			50 Mrep	100 Mrep
Undercured				
1.25	2.0	307	500	1130
1.75	1.0	307	670	1300
2.25	0.7	307	610	1260
1.75	1.0	280	740	1430
1.75	1.0	330	830	1680
Fully cured				
1.25	2.0	307	970	2020
1.75	1.0	307	1040	2000
2.25	0.7	307	1030	1950
1.75	1.0	280	740	1540
1.75	1.0	330	730	1460

[a] For vulcanization recipe see Appendix A.

TABLE II
Effect of Vulcanization System on Radiation Resistance of Butadiene–Styrene (77/23) Tread Stocks in a Helium Atmosphere[a]

Curing agents	Change in 100% modulus, psi, after indicated dosage	
	50 Mrep	100 Mrep
Undercured		
Gamma-rays	970	—
Sulfur (1.75 phr)/Altax (1.8 phr)	530	1070
GMF (5 phr)	730	1420
Fully cured		
Gamma-rays	670	1470
Sulfur (1.75 phr)/Altax (1.8 phr)	760	1460
GMF (5 phr)	770	1500

[a] For vulcanization recipe see Appendix A.

nificant benefit is obtained by undercuring vulcanizates with carbon-carbon crosslinks, viz., those cured with gamma-rays and p-quinone dioxime. These data are added support for the conclusion that radiation resistance obtained by undercuring sulfur vulcanizates is caused by residual sulfur vulcanization intermediates.

D. Combined Effect of Antirads and Undercuring

Born et al.[1,2] and Turner[6] have discovered a number of compounds which when added to rubber in minor amounts will retard radiation-induced changes in the polymeric network. Some of these compounds and other antirads discovered in this laboratory were incorporated into butadiene–styrene (77/23) tread stocks to determine their

TABLE III

Effect of Undercuring and Antirads on the Radiation Resistance of Butadiene–Styrene (77/23) Tread Stocks in Various Atmospheres[a]

| | Change in 100% modulus, psi, indicated dosage | | | |
| | Helium | | Air | |
Antirad (5 phr)	50 Mrep	100 Mrep	50 Mrep	100 Mrep
Undercured				
None	670	1300	600	1340
Akroflex C	420	870	320	830
Antiox 4010	580	1040	450	900
Thio-β-naphthol	470	820	400	790
2,5-Diphenyloxazole	480	910	290	820
α-Naphthylphenyloxazole	420	920	290	800
Fully cured				
None	1040	2000	820	2060
Akroflex C	570	1130	350	840
Antiox 4010	530	1080	460	1060
Thio-β-naphthol	490	1010	460	960
2,5-Diphenyloxazole	570	1140	500	1000
α-Naphthylphenyloxazole	640	1120	450	1010

[a]For vulcanization recipe see Appendix A.
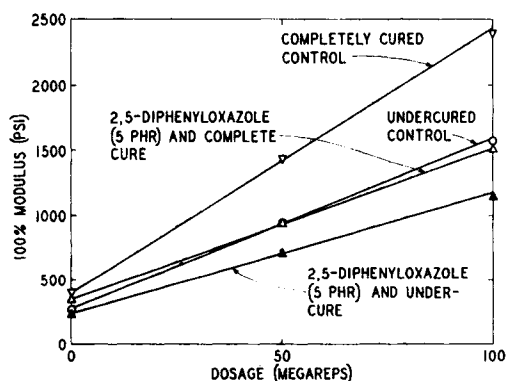
Fig. 3. Effect of undercuring and antirads on radiation resistance of butadiene–styrene (77/23) tread stocks (50 phr HAF black) in a helium atmosphere. For vulcanization recipe see Appendix A, Table III.

effectiveness in the presence and in the absence of undercuring.

Table III and Figure 3 show some of the results of this study. The magnitude of the protection afforded by undercuring is comparable with that obtained with the recommended antirads Akroflex C and Antiox 4010.[1,2] These retarders were effective in both fully cured and undercured stocks. Thio-β-naphthol, 2,5-diphenyloxazole, and α-naphthylphenyloxazole, which have not been reported previously as antirads, were equally effective.

An extensive screening program uncovered additional effective antirads for cold rubber, which with previously reported ones are listed in Appendix D. These additives are arranged according to their ability to resist changes in 100% modulus, which is related to the number of radiation-induced network chains. Akroflex C was used as a reference compound and is arbitrarily given a rating of 1.
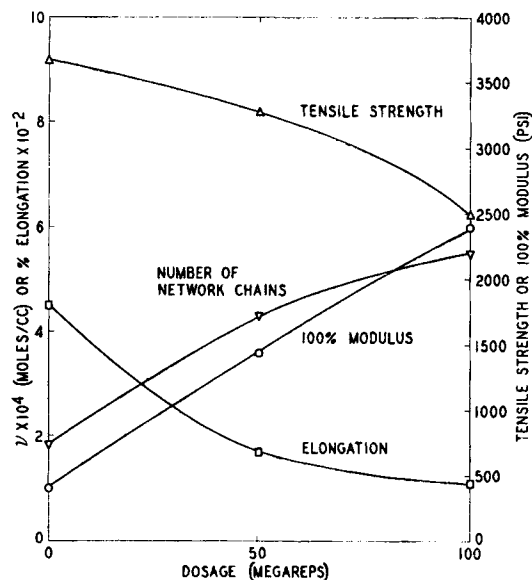
Fig. 4. Effect of gamma-rays on the physical properties of a completely cured butadiene–styrene (77/23) tread vulcanizate (50 phr HAF black) in a helium atmosphere. For vulcanization recipe see Appendix A, Table III.

Figure 4 shows typical changes in physical properties of these butadiene–styrene (77/23) tread stocks by exposure to gamma-rays. The apparent useful lifetime of these vulcanizates in the absence of radiation retarders is approximately 100 Mrep. Corresponding changes in crosslink density and nonequilibrium modulus values demonstrate experimentally the utility of these measurements to provide a fundamental basis for studying network damage to rubber by radiation.

The use of changes in tensile strength values to provide fundamental information about radiation damage to polymers is vitiated by the fact that this property does not depend simply on the number of radiation-induced network chains. Tensile strength also depends on the production of chain ends from scission and the accumulation of short network chains. Figure 4 shows that the over-compensation of radiation-induced scission by crosslinking serves to minimize changes in tensile strength, which would be drastically decreased in the absence of compensation.

E. Effect of Air

The radiation resistance of a vulcanizate depends also on the surrounding atmosphere. Previous work has shown that the presence of oxygen during irradiation of polymers tends to stabilize free radicals produced by scission and prevent their recombination.[32] The data in Table III show that the substitution of air for helium does not necessarily alter the change in 100% modulus, and hence does not affect the balance between crosslinking and scission. The lack of uniform change to the network with this substitution indicates that such changes depend on the interplay of polymer radicals, oxygen, and compounding ingredients during irradiation. Some aspects of this interplay will be discussed in Part II.

Part II. Radiation Resistance of High-Styrene Butadiene–Styrene (59/41) Tread Stocks

A. Effect of Increased Styrene Content and Oil Extension

Manion and Burton[33] show that aromatic groups can exert protective effects by intermolecular energy transfer. Alexander and Charlesby[34,35] were able to demonstrate intramolecular energy transfer with a copolymer of isobutylene and styrene. An increase in radiation resistance of butadiene–styrene rubbers would be expected with an increase in styrene content. Extension of the polymeric network with an aromatic oil would be another means of reducing radiation damage by intermolecular energy transfer. Crosslinking would be diminished also by the increase in distance between adjacent polymer chains caused by oil extension. Data in Figure 5 show that the radiation resistance of butadiene–styrene tread stocks increases moderately with styrene content and dramatically with oil extension.

B. Effect of Oil Extension, Undercure, Antirads, and Irradiation Atmosphere

The radiation resistances (changes in 100% modulus) of a number of butadiene–styrene tread vulcanizates with high styrene content are shown in Table IV. Typical changes with radiation exposure are shown in Figures 6 and 7. These data
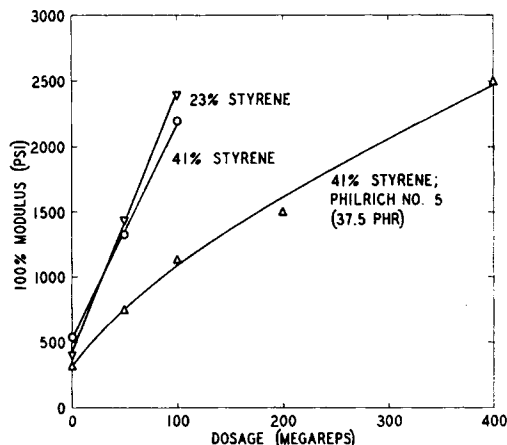
Fig. 5. Effect of styrene content and oil extension on the radiation resistance of butadiene–styrene tread stocks (50 phr HAF black) in a helium atmosphere. For vulcanization recipe see Appendix A, Table IV.
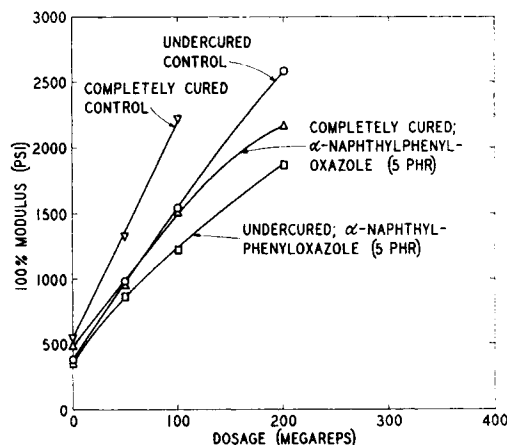
Fig. 6. Effect of undercure and antirad on the radiation resistance of high-styrene butadiene–styrene (59/41) tread vulcanizates (50 phr HAF black) in a helium atmosphere. For vulcanization recipe see Appendix A, Table IV.

show that undercuring and addition of antirads to the vulcanization recipe may be used to advantage to prolong the life of high-styrene cold rubber tread stocks, both in the presence and absence of oil extension. The presence of oil tends to lessen the protection afforded by undercuring and antirads;

TABLE IV
Effect of Oil Extension, Undercure, Antirads, and Irradiation Atmosphere on the Radiation
Resistance of High-Styrene Butadiene–Styrene (59/41) Tread Stocks[a]

	Change in 100% modulus, psi, after the indicated dosage											
	Not oil-extended						Oil-extended					
	Helium			Air			Helium			Air		
Antirad (5 phr)	100 Mrep	200 Mrep	400 Mrep	100 Mrep	200 Mrep	400 Mrep	100 Mrep	200 Mrep	400 Mrep	100 Mrep	200 Mrep	400 Mrep
Undercure												
None	1170	2210	—	950	2420	—	670	960	1890	540	1120	1740
Akroflex C	820	1380	2550	680	1620	2120	540	810	1360	470	970	1370
Antiox 4010	850	1460	2950	710	1620	2600	580	750	1370	470	900	1310
Thio-β-naphthol	810	1220	2690	680	1570	2590	490	740	1420	440	860	1490
2,5-Diphenyloxazole	920	1380	2710	720	1620	2690	520	780	1320	420	850	1310
α-Naphthylphenyloxazole	870	1520	—	730	1740	2550	590	860	1460	450	940	1370
Fully cured												
None	1680	—	—	1270	—	—	820	1190	—	720	1470	1850
Akroflex C	1230	1760	—	810	2050	—	600	880	1700	450	1140	1500
Antiox 4010	1110	1680	—	810	2070	—	600	850	1750	450	1090	1600
Thio-β-naphthol	1090	1560	—	730	1580	—	520	750	1590	450	910	1510
2,5-Diphenyloxazole	1030	1700	—	860	2070	—	640	1160	1860	520	1210	—
α-Naphthylphenyloxazole	1030	1690	—	740	2110	—	600	930	1740	570	1170	1540

[a]For vulcanization recipe see Appendix A, Table IV.

this result is consistent with the dilution of inhibitor in the rubber matrix. However, the stabilizing effect of oil more than compensates for this disadvantage.

Figures 8 and 9 show typical changes in swelling and stress–strain properties of vulcanizates compounded for radiation resistance. The lack of linearity in the changes in crosslink density and in the dependent modulus values with dosage is indicative of variations in the rate of crosslinking and scission after the vulcanizates have been exposed to a considerable amount of radiation. The apparent decrease in the ratio of crosslinking to scission with dosage serves to prolong the life of a vulcanizate in a radiation field. Comparison of these results with those in Table III and Figure 4 shows that the pro-
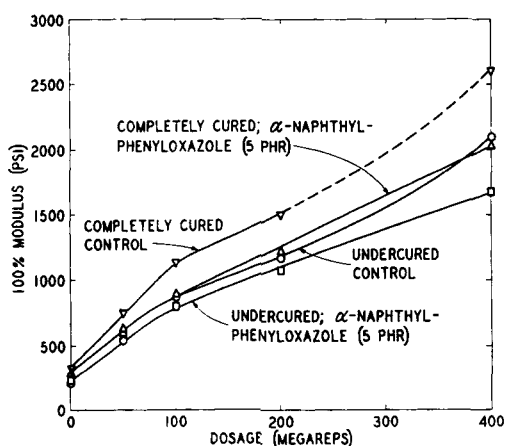
Fig. 7. Effect of undercure and antirad on the radiation resistance of Philrich-extended (37.5 phr) high-styrene butadiene–styrene (59/41) tread vulcanizates (50 phr HAF black) in a helium atmosphere. For vulcanization recipe see Appendix A, Table IV.

Fig. 8. Effect of gamma-rays on the physical properties of an undercured butadiene–styrene (59/41) tread vulcanizate (50 phr HAF black) in a helium atmosphere. For vulcanization recipe see Appendix A, Table IV.
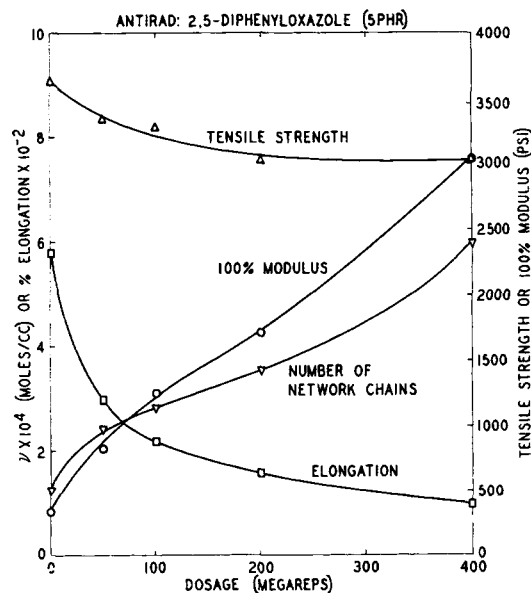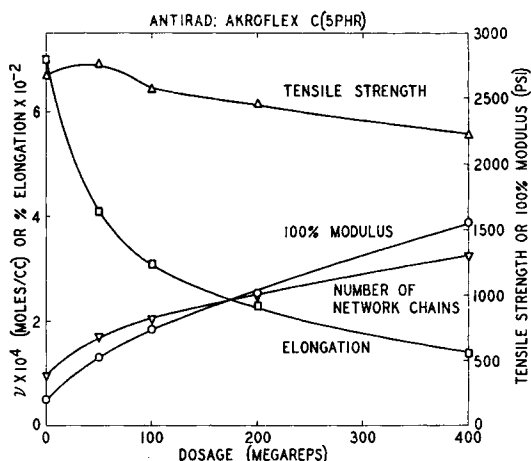
Fig. 9. Effect of gamma-rays on the physical properties of an undercured Philrich-extended (37.5 phr) butadiene–styrene (59/41) tread vulcanizate (50 phr HAF black) in a helium atmosphere. For vulcanization recipe see Appendix A, Table IV.

jected lifetime, i.e., when the elongation reaches 100%, of butadiene–styrene tread stocks has been increased by a factor of 5 to 6 by relatively simple and straightforward compounding techniques.

The data in Table IV show also that substitution of air for helium as an irradiation atmosphere generally causes a slight increase in the lifetime of these vulcanizates in a gamma-ray field; this result is similar to that described in Part I.

C. Network Damage During Irradiation

The net effect of radiation on vulcanizates can be surmised from changes in stress–strain properties.

Such changes can be explained qualitatively from a knowledge of the effect of crosslinking and scission on these properties. However, to obtain an understanding of radiation damage to vulcanizates, swelling and stress relaxation techniques must be used to obtain more quantitative estimates of changes in the polymeric network. The relative amounts of the concomitant crosslinking and scission that take place on a microscopic scale have a profound effect on the macroscopic properties.

Table V lists the combined results of swelling and stress relaxation results obtained with high-styrene butadiene–styrene tread stocks. Some assumption must be made about the locus of scission to determine the extent of scission. The most consistent results were obtained when calculations were based on the *a priori* expectation of random scission of main chains [eq. (3)]. A perusal of the data in Table V indicates the following.

(1) Undercuring retards both crosslinking and scission; crosslinking is retarded to a much greater extent, to give a net decrease in the number of radiation-induced network chains.

(2) The number of radiation-induced network chains is retarded by the presence of antirads. With the exception of thio-β-naphthol, the antirads protect by retarding crosslinking to a much greater extent than scission in both undercured and fully cured stocks. Thio-β-naphthol is unique in this group, since it retards crosslinking and scission about equally.

(3) Undercuring and antirads decrease the ratio of crosslinking to scission, r/s, during irradiation.

TABLE V
Radiation-Induced Crosslinking and Scission of Butadiene–Styrene (59/41)
Tread Stocks in a Helium Atmosphere[a]

Antirad (5 phr)	Dosage, Mrep	Undercured stocks				Fully cured stocks			
		$\nu \times 10^4$, moles/cc.	$s \times 10^4$, moles/cc.	$r \times 10^4$, moles/cc.	r/s	$\nu \times 10^4$, moles/cc.	$s \times 10^4$, moles/cc.	$r \times 10^4$, moles/cc.	r/s
None	50	1.18	1.09	2.27	2.08	1.66	1.18	2.84	2.40
	100	1.90	1.62	3.52	2.17	2.64	1.67	4.31	2.58
Akroflex C	50	1.18	1.07	2.25	2.10	1.10	1.32	2.42	1.83
	100	1.62	1.61	3.23	2.01	2.00	1.70	3.70	2.18
Antiox 4010	50	1.10	1.03	2.13	2.07	1.22	1.10	2.32	2.11
	100	1.58	1.58	3.16	2.00	1.88	1.61	3.49	2.17
Thio-β-naphthol	50	1.08	0.71	1.79	2.52	1.33	0.78	2.11	2.71
	100	1.48	1.16	2.64	2.28	2.33	1.16	3.49	3.01
2,5-Diphenyloxazole	50	1.20	0.96	2.16	2.27	1.12	1.14	2.26	1.98
	100	1.62	1.40	3.02	2.16	1.86	1.62	3.48	2.15
α-Naphthylphenyl- oxazole	50	0.99	1.09	2.08	1.91	1.17	1.06	2.23	2.10
	100	1.81	1.46	3.27	2.24	1.85	1.60	3.45	2.16

[a] For vulcanization recipe see Appendix A, Table IV.

These values are two to three times smaller than those obtained with similar systems without curing agents.[26,36] Most of the original network chains are lost by scission after a relatively small dosage compared to the lifetime of these vulcanizates in a radiation field. This indicates a rather dynamic making and breaking of network chains, which gradually accumulate because of the predominance of the crosslinking reaction. The accumulation of network chains causes the gradual and similar change in 100% modulus shown in Figure 8. Retardation of accumulation of network chains by undercuring and antirads increases the longevity of the vulcanizates in a radiation field. The relatively minor changes in tensile strength with dosage indicate that most of the scissions determined by stress relaxation must ultimately lead to crosslinking which compensates for this change.

Table VI lists the network damage results obtained with oil-extended vulcanizates. Comparison of these data with those in Table V show that the presence of an aromatic oil increases the amount of scission and decreases greatly the amount of crosslinking.

The results are consistent with stabilization of chain ends produced by scission by the aromatic oil and with a decrease in the possibility of crosslinking of adjacent polymer chains when in the swollen condition.

Undercuring of oil-extended vulcanizates promotes both crosslinking and scission. The residual vulcanization intermediates interact with oil to promote damage to the network. Little change in crosslink density takes place with dosage, because the promotion affects crosslinking and scission almost equally. This explains why undercuring does not provide as much protection in the presence as in the absence of oil.

The action of antirads in oil-extended stocks is different also. All of the antirads, tested with the exception of thio-β-naphthol, retarded both crosslinking and scission to about the same extent; thio-β-naphthol promoted crosslinking and scission to an equal extent. Both types of antirad activity resulted in little net change in crosslink density with increased irradiation to bring little change in macroscopic properties, e.g., 100% modulus. Apparently, the almost complete compensation of scission by crosslinking during irradiation in this more dynamic network preserves the tensile strength of the oil-extended vulcanizates.

Both undercuring and antirads in general do not greatly affect the ratio r/s of crosslinking to scission, in these oil-extended vulcanizates. Such values are lower in the presence than in the absence of oil. These measurements show that the relatively good radiation resistance of oil-extended stocks is due to a decrease in the predominance of crosslinking over scission.

Although quantitative data are not available, the substitution of air for helium as an irradiation atmosphere increased the amount of scission to such an extent that the test samples were completely relaxed after the exposures shown in Tables V and VI. This result is consistent with the findings of others,[37-40] who propose that the presence

TABLE VI

Radiation-Induced Crosslinking and Scission of Oil-Extended Butadiene–Styrene (59/41) Tread Stocks in a Helium Atmosphere[a]

Antirad (5 phr)	Dosage, Mrep	Undercured stocks				Fully cured stocks			
		$\nu \times 10^4$, moles/cc.	$s \times 10^4$ moles/cc.	$r \times 10^4$, moles/cc.	r/s	$\nu \times 10^4$, moles/cc.	$s \times 10^4$ moles/cc.	$r \times 10^4$, moles/cc.	r/s
None	10	0.24	0.40	0.64	1.60	0.26	0.43	0.69	1.60
	30	0.62	1.82	2.44	1.34	0.51	1.12	1.63	1.45
Akroflex C	10	0.40	0.34	0.74	2.18	0.30	0.30	0.60	2.00
	30	0.73	0.91	1.64	1.80	0.55	0.97	1.52	1.57
Antiox 4010	10	0.33	0.41	0.74	1.81	0.38	0.27	0.65	2.40
	30	0.56	0.87	1.43	1.64	0.48	0.68	1.16	1.71
Thio-β-naphthol	10	0.27	0.52	0.79	1.52	0.33	0.63	0.96	1.52
	30	0.69	2.38	3.07	1.29	0.76	2.13	2.89	1.36
2,5-Diphenyloxazole	10	0.24	0.41	0.65	1.59	0.21	0.43	0.64	1.49
	30	0.61	1.95	2.56	1.31	0.53	1.30	1.83	1.41
α-Naphthylphenyl-oxazole	10	0.25	0.34	0.59	1.73	0.22	0.49	0.71	1.45
	30	0.58	1.53	2.11	1.38	0.55	1.07	1.62	1.51

[a] For vulcanization recipe see Appendix A, Table IV.

of oxygen serves to stabilize free radicals produced as a result of scission. These results combined with changes in 100% modulus shown in Table IV suggest that, even though there are apparent increases in crosslinking and scission, the number of radiation-induced effective network chains is not greatly altered when air is substituted for helium as the irradiation atmosphere.

V. CONCLUSIONS

The radiation resistance of butadiene–styrene cold rubber vulcanizates reinforced with carbon black can be increased materially by increasing the styrene content of the rubber, by extension of rubber with an aromatic oil, by incomplete curing with an accelerated sulfur vulcanization system, and by incorporation of retarders of radiation damage. Incomplete curing produces vulcanization intermediates which are affected by the ratio of sulfur to accelerator and by cure temperature to retard radiation damage.

Results of swelling and stress relaxation measurements indicate that extension of the polymeric network with an aromatic oil increases the amount of chain scission during irradiation and decreases the amount of crosslinking to produce a correspondingly more radiation-resistant material. These measurements also show that in the absence of oil the decrease in radiation damage obtained by incomplete curing and with antirads is primarily the result of retardation of crosslinking. However, in the presence of oil, incomplete curing promotes and antirads retard radiation-induced crosslinking and scission about equally. Substitution of air for helium as an irradiation atmosphere accentuates the scission reaction to diminish moderately the changes in stress–strain properties.

The author would like to thank Dr. G. Kraus for many helpful suggestions and discussions during the course of this work.

APPENDIX A

VULCANIZATION RECIPES FOR RADIATION RESISTANCE STUDIES

Compounding recipes for gamma vulcanizates consisted of rubber, reinforcing filler (50 phr HAF Black), and the antioxidant Flexamine. The compounding recipes used to produce the other chemically vulcanized stocks are given in Appendix Tables I–IV.

APPENDIX TABLE I
Recipe for Stocks of Table I

	Parts
Butadiene-styrene (77/23)[a]	100
Philblack-O (HAF black)	50
Zinc oxide	3
Stearic acid	1
Sulfur	Variable
Santocure	Variable
Flexamine	1

[a] Philprene 1500.

APPENDIX TABLE II
Receipe for Stocks of Table II

	Parts
Butadiene-styrene (77/23)[a]	100
Philblack-O (HAF black)	50
Zinc oxide	3
Stearic acid	1
Sulfur	1.75 or 0
Altax	1.8 or 0
G.M.F.	0 or 5
Flexamine	1

[a] Philprene 1500.

APPENDIX TABLE III
Recipe for Stocks of Table III and Appendix D

	Parts
Butadiene-styrene (77/23)[a]	100
Philblack-O (HAF black)	50
Zinc oxide	3
Stearic acid	1
Sulfur	1.75
Santocure	1
Flexamine	1
Antirad (variable)	5

[a] Philprene 1500.

APPENDIX TABLE IV
Recipe for Stocks of Tables IV, V, and VI

	Parts
Butadiene-styrene (77/23)[a]	100 or 0
Butadiene-styrene (59/41)	100 or 0
Philrich #5 (highly aromatic)	37.5 or 0
Philblack-O (HAF black)	50
Zinc oxide	3
Stearic acid	1
Sulfur	1.75
Santocure	1
Flexamine	1
Antirad (variable)	5

[a] Philprene 1500.

APPENDIX B

A Glossary of Compounding Agents

Altax:	Benzothiazyldisulfide	Flexamine:	Reaction product of a diarylamine ketone aldehyde with N,N'-diphenyl-p-phenylenediamine
Akroflex C:	Phenyl-1-naphthylamine (65%) and N,N'-diphenyl-p-phenylenediamine (35%)	GMF:	p-Quinonedioxime
Antiox 4010:	N'-Cyclohexyl-N'-phenyl-p-phenylenediamine	Santocure:	N - Cyclohexyl - 2 - benzothiazole sulfenamide

APPENDIX C-1

Physical Properties of Butadiene–Styrene (77/23) Tread Stocks after Various Exposures to Gamma-Rays in Various Atmospheres[a]

Antirad (5 phr)	Cure time at 307°F., min.	Dosage, Mrep	Helium				Air			
			100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.	100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.
None	23	0	270	2740	550	0.93	250	2630	590	0.85
		50	940	2660	190	3.35	850	2990	250	2.80
		100	1570	2890	170	4.80	1590	3270	160	4.40
	45	0	400	3670	450	1.83	420	3780	460	1.75
		50	1440	3270	170	4.31	1240	3330	190	4.00
		100	2400	2490	110	5.50	2480	2750	110	6.10
Akroflex C	13	0	230	2490	660	0.85	240	2600	610	0.91
		50	650	3310	320	2.50	560	3880	420	2.15
		100	1100	2770	200	3.30	1070	3400	240	3.80
	45	0	380	3760	530	1.75	390	4120	520	1.77
		50	950	3310	240	3.80	740	3550	300	2.95
		100	1510	2750	150	4.60	1230	3490	210	4.50
Antiox 4010	18	0	300	3450	570	1.42	290	3210	590	1.18
		50	880	3220	270	3.40	740	3440	310	2.55
		100	1340	2950	180	4.50	1190	3150	200	3.60
	70	0	370	3780	510	1.70	370	3770	560	1.58
		50	900	3380	250	3.80	830	3590	280	3.05
		100	1450	2890	160	4.70	1430	2720	160	4.15
Thio-β-naphthol	20	0	250	2680	590	1.14	240	2990	680	1.12
		50	720	3500	310	2.95	640	3410	350	2.65
		100	1070	3030	210	4.00	1030	3370	240	3.40
	45	0	270	3200	610	1.36	270	3250	630	1.41
		50	760	3710	300	3.25	730	3970	340	2.95
		100	1280	3290	180	4.40	1230	3490	210	4.50
2,5-Diphenyloxazole	12.5	0	240	2990	650	1.01	230	2460	630	0.72
		50	720	3740	330	2.65	520	3740	440	1.95
		100	1150	3190	210	3.50	1050	3220	220	3.20
	45	0	370	3900	480	1.85	390	3650	460	1.75
		50	940	3440	240	4.05	890	3160	230	3.05
		100	1510	2860	150	4.60	1390	2940	170	4.60
α-Naphthylphenyloxazole	13	0	240	2890	630	1.02	220	2330	610	0.80
		50	660	3580	350	2.55	510	3340	380	2.15
		100	1160	2960	200	3.50	1020	3290	230	3.50
	45	0	370	4270	500	1.80	370	3980	510	1.60
		50	1010	3310	230	3.65	820	3400	260	3.05
		100	1490	2630	150	4.50	1380	3200	180	4.50

[a]For vulcanization recipe see Appendix A, Table III or IV.

APPENDIX C-2

Physical Properties of High-Styrene Butadiene–Styrene (59/41) Tread
Stocks After Various Exposures to Gamma-Rays in Various Atmospheres[a]

Antirad (5 phr)	Cure time at 307°F., min.	Dosage, Mrep	Helium				Air			
			100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.	100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.
None	13	0	380	3760	550	1.30	380	3760	550	1.30
		50	940	3920	320	2.16	980	3990	310	2.48
		100	1330	3480	230	2.84	1550	3640	210	3.20
		200	2800	3160	110	4.70	2590	3390	130	3.84
		400	—	3110	75	7.3	—	3120	75	8.0
	45	0	540	4020	440	1.60	540	4020	440	1.60
		50	1220	3880	250	2.88	1330	3530	210	3.26
		100	1810	3410	170	3.48	2220	3030	130	4.24
		200	—	2910	80	6.50	ca. 3380	2690	85	5.64
		400	—	2740	50	12.9	—	2510	40	14.3
Akroflex C	12	0	380	3670	530	1.30	380	3670	530	1.30
		50	750	3610	340	2.32	860	3660	320	2.48
		100	1060	2850	220	2.70	1200	3370	230	2.92
		200	2000	3360	150	3.94	1760	3200	170	3.46
		400	2500	2900	115	5.9	2930	2930	100	6.12
	45	0	500	4290	480	1.60	500	4290	480	1.60
		50	930	3740	290	2.62	1060	3480	250	2.70
		100	1310	3330	220	3.16	1730	3360	170	3.60
		200	2550	3360	130	5.24	2260	3270	135	4.38
		400	—	2650	70	8.5	—	3240	80	8.6
Antiox 4010	12	0	360	3830	580	1.36	360	3830	580	1.36
		50	830	3730	340	2.26	840	3640	330	2.46
		100	1070	3380	270	2.76	1210	3470	240	2.94
		200	1980	3200	160	3.74	1820	3530	180	3.56
		400	2960	3070	105	5.8	3310	3310	100	5.94
	45	0	460	4100	510	1.48	460	4100	510	1.48
		50	950	4030	320	2.60	990	3830	300	2.70
		100	1270	3520	240	3.05	1570	3550	200	3.36
		200	2530	3380	130	4.86	2140	3100	135	4.22
		400	—	3260	90	7.5	—	2650	70	8.1
Thio-β-naphthol	31	0	330	3480	600	1.32	330	3480	600	1.32
		50	740	3920	360	2.26	750	3660	340	2.40
		100	1010	3590	270	2.84	1140	3430	230	2.80
		200	1900	3010	145	3.56	1550	2470	145	3.36
		400	2920	3200	110	6.3	3020	3020	100	6.00
	75	0	390	3780	580	1.35	390	3780	580	1.35
		50	890	4140	320	2.64	890	3930	310	2.68
		100	1120	3600	240	3.06	1480	3450	190	3.68
		200	1970	3170	145	4.70	1950	3490	170	4.28
		400	—	2600	80	7.5	—	2860	80	7.7
2,5-Diphenyl-oxazole	12	0	330	3630	580	1.22	330	3630	580	1.22
		50	780	3770	350	2.22	830	3340	300	2.42
		100	1050	3470	260	2.80	1250	3280	220	2.84
		200	1950	3260	160	3.60	1710	3030	160	3.56
		400	3020	3020	100	5.80	3040	3040	100	6.01
	45	0	460	4050	460	1.52	460	4050	460	1.52
		50	950	3920	300	2.64	950	4010	290	2.64
		100	1320	3580	220	3.00	1490	3040	170	3.38
		200	2530	3040	115	5.00	2160	3910	170	4.56
		400	—	2580	80	8.1	—	2820	70	8.8

APPENDIX C-2 (*continued*)

Antirad (5 phr)	Cure time at 307°F., min.	Dosage, Mrep	Helium				Air			
			100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.	100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.
α-Naphthyl-phenyloxazole	13	0	350	4010	580	1.25	350	4010	580	1.25
		50	760	3580	320	2.18	860	3380	290	2.24
		100	1080	3220	240	2.76	1220	3220	220	3.06
		200	2090	2770	125	3.70	1870	3230	160	3.58
		400	2900	3150	110	5.7	—	3050	90	5.82
	45	0	450	3890	450	1.53	480	3890	450	1.53
		50	950	3840	280	2.46	960	3410	250	2.70
		100	1220	3370	210	3.04	1510	3070	170	3.38
		200	2590	3040	115	5.02	2170	3040	130	4.40
		400	—	3200	80	6.4	—	2750	70	8.2

[a]For vulcanization recipe see Appendix A, Table IV.

APPENDIX C-3

Physical Properties of Oil-Extended; High-Styrene Butadiene–Styrene (59/41)
Tread Stocks After Various Exposures to Gamma-Rays in Various Atmospheres[a]

Antirad (5 phr)	Cure time at 307°F., min.	Dosage, Mrep	Helium				Air			
			100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.	100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.
None	15	0	210	2700	670	1.04	210	2700	670	1.04
		50	550	2700	380	1.56	540	2690	390	1.58
		100	880	2510	260	1.96	750	2730	320	2.16
		200	1170	2310	180	2.50	1330	2380	170	2.52
		400	2100	2100	100	3.68	1950	2180	105	3.60
	45	0	320	2640	480	1.44	320	2640	480	1.44
		50	750	2600	270	2.02	720	2720	300	1.99
		100	1140	2690	210	2.65	1040	2400	200	2.42
		200	1510	2410	150	3.10	1790	2210	120	3.14
		400	ca. 2500	2430	95	4.60	2170	2240	105	4.50
Akroflex C	15	0	200	2680	700	0.96	200	2680	700	0.96
		50	530	2770	410	1.70	520	2730	410	1.63
		100	740	2580	310	2.04	670	2710	350	2.10
		200	1010	2460	230	2.52	1170	2370	190	2.48
		400	1560	2230	140	3.26	1570	2220	130	3.41
	45	0	330	2940	520	1.45	330	2940	520	1.45
		50	660	2850	340	1.95	590	2830	360	1.99
		100	930	2480	230	2.84	780	2680	280	2.46
		200	1210	2430	185	2.95	1470	2300	150	2.94
		400	2030	2550	120	3.98	1830	2350	120	3.66
Antiox 4010	14	0	220	2830	660	1.10	220	2830	660	1.10
		50	550	2590	370	1.70	560	2860	410	1.68
		100	800	2400	260	2.22	690	2740	350	1.94
		200	970	2270	210	2.35	1120	2340	190	2.50
		400	1590	2250	140	3.26	1530	2240	140	3.36
	75	0	290	2810	550	1.32	290	2810	550	1.32
		50	650	2890	350	1.85	540	2680	370	1.86
		100	890	2480	240	2.44	740	2410	270	2.38
		200	1140	2500	210	2.76	1380	2380	160	2.92
		400	2040	2520	120	3.68	1890	2320	120	3.62

APPENDIX C-3 *(continued)*

Antirad (5 phr)	Cure time at 307°F., min.	Dosage, Mrep	Helium				Air			
			100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.	100% Modulus, psi	Tensile strength, psi	Elongation, %	$\nu \times 10^4$, moles/cc.
Thio-β-naphthol	45	0	180	2350	730	1.23	180	2350	730	1.23
		50	480	2850	440	1.80	480	2860	420	1.80
		100	670	2690	320	2.24	620	2690	360	2.18
		200	920	2520	240	2.50	1040	2330	200	2.82
		400	1600	2280	140	3.60	1670	2090	120	3.78
	75	0	220	2280	670	1.24	220	2280	670	1.24
		50	570	2910	390	1.92	500	2750	390	1.90
		100	740	2600	280	2.46	670	2260	260	2.42
		200	970	2670	230	2.90	1130	2350	180	2.98
		400	1810	2290	120	3.94	1730	2170	125	4.30
2,5-Diphenyl-oxazole	14	0	200	2530	610	1.15	200	2530	610	1.15
		50	540	2240	300	1.58	520	2630	360	1.58
		100	720	2400	270	1.98	620	2220	270	1.90
		200	980	2190	195	2.30	1050	2210	180	2.42
		400	1520	1950	120	3.32	1510	1910	125	3.42
	75	0	260	2720	520	1.40	260	2720	520	1.40
		50	630	2490	290	1.86	580	2470	290	1.80
		100	900	2100	190	2.38	780	2080	210	2.36
		200	1300	1990	140	2.78	1470	2170	130	2.98
		400	2120	2120	100	4.02	—	1900	95	3.66
α-Naphthyl-phenyloxazole	16	0	220	2570	620	1.11	220	2570	620	1.11
		50	600	2910	390	1.64	560	2670	360	1.66
		100	810	2750	290	2.02	670	2550	330	2.02
		200	1080	2450	210	2.30	1160	2540	200	2.60
		400	1680	2050	130	3.48	1590	2070	125	3.62
	45	0	300	2960	540	1.40	300	2960	540	1.40
		50	640	2750	320	1.91	610	2910	360	1.96
		100	900	2680	240	2.36	870	2770	270	2.42
		200	1230	2600	190	2.76	1470	2310	150	2.92
		400	2040	2520	120	3.94	1840	2110	110	3.64

[a]For vulcanization recipe see Appendix A, Table IV.

APPENDIX D

Retarders of Radiation Damage to Butadiene–Styrene (77/23) Tread Stocks in a Helium Atmosphere[a]

Antirad	Rating[b]
Azobenzene	1.16
Thio-β-naphthol	1.13
Di-*tert*-butylhydroquinone	1.10
2,5-Diphenyloxazole	1.06
Azoxybenzene	1.06
trans-Stilbene	1.02
Antiox 4010	1.02
α-Naphthylphenyloxazole	1.02
Akroflex C	1
Hydrazobenzene	1
2,6-Dinitrophenol	0.99
2-Phenylbenzothiazole	0.98
Diphenylacetylene	0.97

[a]For vulcanization recipe see Appendix A, Table III.
[b]Rating = (change in 100% modulus with additive after 100 Mrep)/(change in 100% modulus with Akroflex C after 100 Mrep).

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Synopsis

Compounding techniques to improve the radiation resistance of butadiene-styrene tread vulcanizates in a radiation field are described. These include extension of rubber with an aromatic oil, incomplete curing of stocks containing sulfur vulcanization agents, and incorporation of additives. Incomplete curing produces vulcanization intermediates, which are affected by the ratio of sulfur to accelerator and by cure temperature and which are resistant to radiation. A combination of all these factors improved the lifetime of cold-rubber tread vulcanizates by a factor of 5 to 6. Swelling and stress-relaxation techniques are applied to follow quantitatively changes in the polymeric network, which are used to explain changes in stress–strain properties. These techniques indicate that much of the scission that occurs is more than compensated for by crosslinking. Dilution of the polymer network with an aromatic oil decreases the ratio of crosslinking to scission to produce a more radiation-resistant material. In the absence of oil, the decrease in radiation damage obtained by incomplete curing and with antirads is primarily the retardation of the crosslinking reaction. However, in the presence of oil, incomplete curing promotes and antirads retard radiation-induced crosslinking and scission about equally. Substitution of air for helium as an irradiation atmosphere serves to accentuate the scission reaction and to lessen radiation-induced changes in physical properties. A number of previously unreported retarders of radiation damage (antirads) are described.

Résumé

On décrit des techniques de mélange destinées à éprouver la résistance aux radiations des chapes butadiène–styrène vulcanisé dans un champ de radiation. Celles-ci comprennent l'extension de la gomme dans une huile aromatique, le traitement incomplet d'échantillons contenant des agents de vulcanisation sulfurés et incorporation d'additifs. Le traitement incomplet produit des intermédiaires de vulcanisation qui sont affectés par le rapport du soufre à l'accélérateur et par la température de traitement et qui sont résistants aux radiations. Une combinaison de tous ces facteurs a prolongé par 5–6 fois la durée de chapes de cauotchouc vulcanisé Les techniques de gonflement et de relaxation de tension sont appliquées pour suivre quantitativement les changements dans le réseau polymérique; on utilise ces données pour expliquer les changements dans les propriétés de tension interne et de contrainte. Ces techniques indiquent que la majeure partie des scissions qui se produisent est plus que compensée par du pontage. La dilution du réseau polymérique par une huile aromatique diminue le rapport du pontage à la scission et produit un matériau plus résistant aux radiations. En l'absence d'huile, la diminution à la détérioration par la radiation obtenue par le traitement incomplet et par les antiradieaux est surtout due à la réaction de pontage. Cependant, en présence d'huile, le traitement incomplet favorise également le pontage induit par les radiations et la scission tandis que l'action des antiradicaux retarde. Si l'on substitue l'hélium à l'air comme atmosphère d'irradiation, on accentue la réaction de scission et l'on diminue les changements de propriétés physiques induits par les radiations. On décrit un certain nombre de retardateurs à l'action destructrice des radiations qui n'avaient pas encore été décrits jusqu'à présent.

Zusammenfassung

Mischungsverfahren zur Verbesserung der Strahlungsbeständigkeit von Butadien–Styrol-Laufflächenvulkanisaten in einem Strahlungsfeld werden beschrieben. Dazu gehören Einbringen eines aromatischen Öls in den Kautschuk, unvollständige Vulkanisation von Kautschuk, der Vulkanisierungsmittel auf Schwefelbasis enthält, und Zusatz von Additiven. Unvollständige Vulkanisation führt zur Bildung von Vulkanisationszwischenprodukten, die von Verhältnis von

Schwefel zu Beschleuniger und von der Vulkanisationstemperatur abhängig und gegen Strahlung widerstandsfähig sind. Eine Kombination aller dieser Faktoren führte zu einer Verbesserung der Lebensdauer von Laufflächenvulkanisaten aus Tieftemperatur-Kautschuk um einen Faktor von 5 bis 6. Zur quantitativen Verfolgung der Veränderungen im Polymernetzwerk, die zur Erklärung der Änderung der Spannungs-Dehnungseigenschaften herangezogen werden, finden Quellungs- und Spannungsrelaxationsmessungen Anwendung. Diese Messungen lassen erkennen, dass ein Grossteil der auftretenden Kettenspaltung durch Vernetzung überkompensiert wird. Verdünnung des Polymernetzwerkes mit einem aromatischen Öl setzt das Verhältnis von Vernetzung zu Kettenspaltung unter Bildung eines gegen Strahlung widerstandsfähigeren Materials herab. In Abwesenheit von Öl ist die Abnahme der Strahlungsschädigung bei unvollständiger Vulkanisation und bei Zusatz von Strahlungsschutzstoffen primär auf die Verzögerung der Vernetzungsreaktion zurückzuführen. In Gegenwart von Öl fördert jedoch unvollständige Vulkanisation die strahlungsinduzierte Vernetzung und Kettenspaltung in etwa gleicher Weise, während Strahlungsschutzstoffe beide verzögern. Bei Bestrahlung in Luft anstatt in einer Heliumatmosphäre tritt die Spaltungsreaktion mehr in den Vordergrund und die strahlungsinduzierten Veränderungen der physilischen Eigenschaften werden geringer. Eine Anzahl von bisher noch nicht bekannten Verzögerern für Strahlungsschädigung (Antirads) werden beschrieben.