

Aging of SBR

E. M. BEVILACQUA and W. J. WENISCH,*

United States Rubber Company Research Center, Wayne, New Jersey

Synopsis

Changes in properties of vulcanized SBR during aging at 130°C. in air are the result of reactions involving both the hydrocarbon and the crosslinks. Hydrocarbon oxidation is related to the overall rate of oxidation; it leads to both scission and crosslinking. Sulfur crosslinks are broken and new crosslinks formed in reactions which are affected by oxygen but relatively independent of the overall rate of oxidation. The excess of crosslinking over scission decreases progressively with increasing cure.

The effect of aging on the properties of an unsaturated elastomer depends on its molecular structure.¹ Air aging of fully vulcanized isoprene polymers is characterized by a fall in modulus and tensile strength. In contrast, the modulus of SBR vulcanized with sulfur in conventional compositions rises during aging. At the same time the tensile strength and the elongation at break fall. In ordinary vulcanizates some of this modulus rise may be attributable to incomplete vulcanization at the end of press cure. However, even fully cured vulcanizates undergo substantial increase in modulus when heated in air. It can be demonstrated easily that this increase depends on the presence of oxygen in the atmosphere.

The fall in modulus of natural rubber vulcanizates is attributed primarily to scission resulting from hydrocarbon oxidation. Comparison of the rates of stress relaxation of SBR and of natural rubber and of the efficiency of oxidation of the two polymers leads to the conclusion that scission occurs with approximately equal facility in both.² The modulus rise of SBR must, therefore, be the result of crosslinking in excess of scission.

The nature of the reactions leading to scission and to crosslinking in butadiene polymers is not known. It can be inferred that both occur during oxidation of the unvulcanized polymer. In oxygen or in air the soluble fraction of SBR approaches a limiting amount independent of its original value. If it is assumed that scission and crosslinking are proportional to each other, the limiting solubility is a measure of their relative amounts.³

This simple interpretation cannot be made for SBR vulcanized with sulfur, for which solubility is a more complicated function of extent of oxidation. This report describes evidence that other reactions occur during aging of the vulcanized rubber in addition to those which take place in the raw polymer.

* Present address: Newark College of Engineering, Newark, New Jersey.

Experimental

Commercial polymers and compounding ingredients were used in this work. Masterbatches were mixed in a laboratory Banbury mixer. The curatives were added separately on a cool mill. Samples were cured in a press in molds $6 \times 6 \times 0.04$ in. The sample thickness was chosen after a preliminary investigation of the rate of oxidation of a fast oxidizing composition. From this comparison it appeared that 0.04 in. stock could be used without the danger of severe limitation of oxidation because of diffusion control. Subsequent experimental results showed that oxygen supply was unlikely to be a factor limiting the modulus changes during aging under the conditions used in this work.

In early experiments oxygen absorbed was measured by displacement of gas from burets with oil. A simple apparatus was used built around a commercial aluminum aging block.³ A manifold with appropriate connections permitted evacuation and refilling of cells containing the samples and subsequent measurement of the volume changes in the system. As the investigation proceeded and it appeared that the effect of oxygen pressure on the rate of deterioration was small, measurement of oxygen absorption was used less frequently. Samples were then aged in air individually or in small groups in test tubes in an aluminum aging block.

All aging experiments described in this report were made at 130°C. Substantial changes in properties occur in one day at this temperature.

Stress-strain properties were measured on an autographic apparatus used in these laboratories.⁴ A ring test piece is used, which can be conveniently died out from the 2×2 in. samples which were aged.

In early experiments, the solubility and swelling in benzene were measured after various periods of aging. These proved to be insensitive to the changes occurring during the short aging periods involved in this work and none of the data are reported here.

The basic vulcanizate composition consisted of rubber 100 parts, carbon black (FEF) 40 phr, zinc oxide 10 phr, stearic acid 1 phr, cyclohexylbenzothiazyl sulfenamide (CBS) 0.8 phr, and sulfur 2.5 phr. Variations from this composition are indicated in the discussion of specific experiments.

Results and Discussion

Although it can be inferred from results in the literature that oxygen is required for the increase in modulus of SBR vulcanizates,¹ it seemed desirable to establish this fact explicitly as a starting point for the present work. Press cures of conventional vulcanizates reach a limiting crosslink density fairly rapidly. Once this limit has been reached, further reaction in the press or in vacuum over a wide temperature range has no apparent effect even after periods of heating several times the initial period of vulcanization, when crosslink density is estimated from stress-strain properties. Figure 1 shows the effect of time of press cure on the modulus of a simple reinforced SBR vulcanizate. If the temperature in the press is

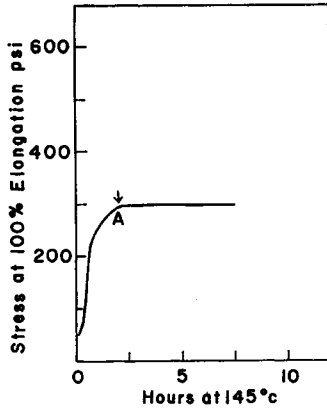


Fig. 1. Modulus as a function of time of cure: CBS-accelerated SBR vulcanizate (standard composition except 30 phr FEF).

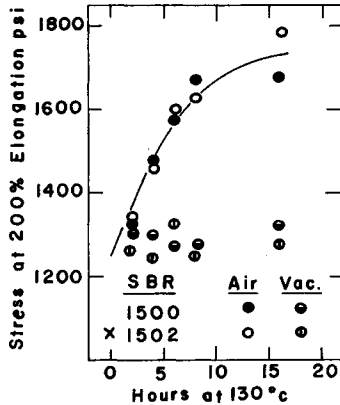


Fig. 2. Comparison of effects of aging in air and in vacuum. (Data for this figure only were obtained with 0.10 in. thick samples instead of 0.04 in.)

changed after point A of Figure 1 is reached, further heating at temperatures between 100 and 160°C. has little effect on the limiting modulus reached after up to 20 hr.

A sample removed from the press at a time corresponding to point A of Figure 1 will begin to rise in modulus if subsequently heated in an atmosphere containing oxygen. In Figure 2 the effect of heating in air is compared with that of heating the same vulcanizate in vacuum. The modulus of the control in this figure corresponds to a time of vulcanization of 1 hr., so that some further rise in modulus takes place on heating in a vacuum. However, a limiting value is soon reached in the vacuum, while the modulus in air increases steadily. It will be noted that according to Figure 2 the rate of modulus increase is not affected by the nature of the stabilizer initially present in the elastomer. Since vulcanizates made from polymers stabilized with amines and with phenol derivatives would be ex-

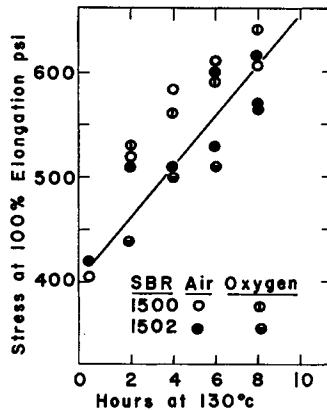


Fig. 3. Comparison of aging in air and in oxygen.

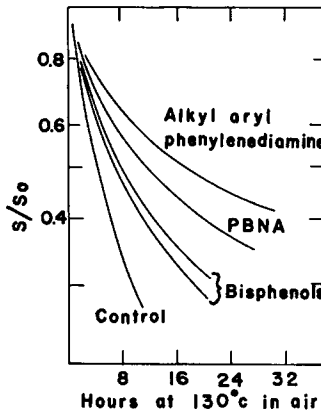


Fig. 4. Effects of antioxidants on stress relaxation (50% extension). Antioxidant levels 2 phr. Composition SBR 1502 100 parts, HAF 50 phr, zinc oxide 3 phr, stearic acid 1 phr, MBT 0.6 phr, DPG 0.2 phr, sulfur 1.75 phr. Vulcanized 45 min. at 145°C.

pected to absorb oxygen at different rates, this was investigated further. The apparent insensitivity of the rate of modulus change to the rate of oxidation has been confirmed in several experiments. In Figure 3 aging of two stocks in air and in oxygen is compared. A fivefold range of oxidation rates can be obtained in this way. However, the rates of modulus change are similar, oxygen pressure having no detectable effect outside of experimental error.

This indicates that the net crosslinking yield is relatively independent of rate of oxidation. At the same time the rate of scission is a function of the overall rate of oxygen absorption. This may be seen in Figures 4 and 5, in which the effect of typical amine and phenolic antioxidants on scission and crosslinking is compared. Scission is measured by stress relaxation, net crosslinking by modulus increase.

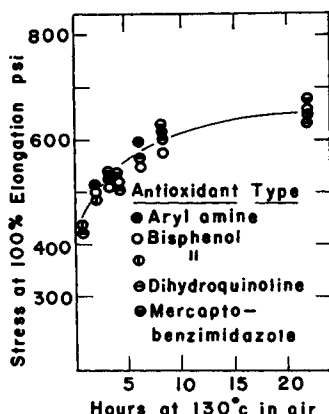


Fig. 5. Effect of antioxidants on modulus rise during aging. Standard compound.

It follows from the evidence thus far that there is a crosslinking reaction during the aging of SBR which requires oxygen but which proceeds at a rate relatively independent of the overall rate of oxidation.

Obvious factors which might influence this reaction have been investigated. The temperature and time of vulcanization, up to full development of modulus, do not radically change subsequent aging, nor does substitution of a sulfur donor as a source of sulfur or of one thiazole derivative for another have much effect. The modulus rise during aging is strongly dependent on the initial modulus, whether this is adjusted by sulfur level, accelerator level, or filler content. The higher the original modulus, the larger the gain in modulus during aging in air.

Most important from the point of view of the mechanism of the effect is the effect of heating in the absence of oxygen before aging in the presence of oxygen. The curve in Figure 1 shows that this has little effect on total crosslink density as measured by modulus, but it has a considerable effect on the behavior during aging in air. This is illustrated in Figure 6. The simple comparison in this figure leads to the suggestion that a particular structure resulting from the conventional vulcanization procedure is required for the modulus rise to occur. The three samples compared in Figure 6 were chosen to have initially the same modulus (although not the same chemical crosslink density. The carbon black level was 30 phr in B161 and B162 and 40 in B171A). The curve labelled B162 refers to the standard vulcanizate cured 60 min. at 145°C. The curve labelled B161 applies to a similar vulcanizate aged in a press for 17 hr. at 130°C. The third curve (B171A) refers to a cumyl peroxide vulcanizate. The modulus of sample B162 increased continuously during the period of the experiment. Sample B161, differing from B162 principally in the time of cure in an inert atmosphere, maintained nearly a constant modulus during aging. The modulus of the cumyl peroxide vulcanizate B171A fell slightly during the same period. Although the data have not been given here, there is a change

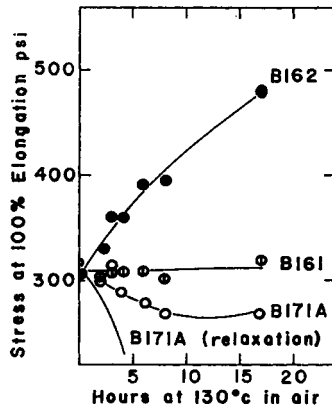


Fig. 6. Effect of vulcanization method on modulus increase during aging. Samples described in text.

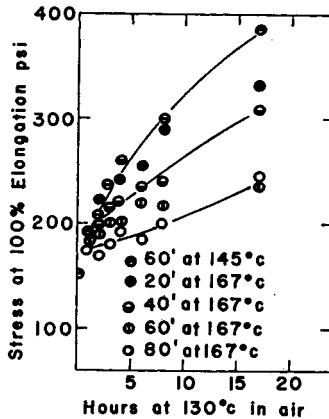


Fig. 7. Effect of time of cure on aging in air (SBR 1707 137.5, HAF 50, sulfur 3.0).

in elongation at break which parallels the change in modulus. The larger the increase in modulus, the greater the fall in elongation at break. Corresponding to the curves of Figure 6, the breaking elongation changes slowest for B171A and fastest for B162.

The crosslink structure in the peroxide vulcanizate is chemically relatively simple. The vulcanizate was cured to full development of modulus before being subjected to aging in air. No obvious possibilities exist for scission or crosslinking in addition to those reactions which lead to scission or crosslinking of the unvulcanized elastomer. No residual crosslinking potential remains in the vulcanizing ingredient after the maximum modulus is developed during press cure. The balance between scission and crosslinking results in the slow decrease in modulus during aging, the two having about equal and opposite effects. The extent of scission and crosslinking may be estimated by comparing the two curves in Figure 6 repre-

senting modulus and stress relaxation for B171A. The excess modulus developed by B162 is a measure of the excess of crosslinking over that due to the hydrocarbon oxidation. Heating the conventional vulcanizate for a period several times that required to reach maximum modulus converts it to a material which ages very much like the peroxide vulcanizate. The length of time required for this change is illustrated by the data of Figure 7, which show the effect of heating for various lengths of time on the rate of modulus increase in air.

The second conclusion follows, then, that the entity in sulfur vulcanizates responsible for the further crosslinking during aging in air involves the existing crosslinks and that heating the vulcanizate in the absence of oxygen slowly converts them to a stable form which does not lead to further crosslinking during oxidation.

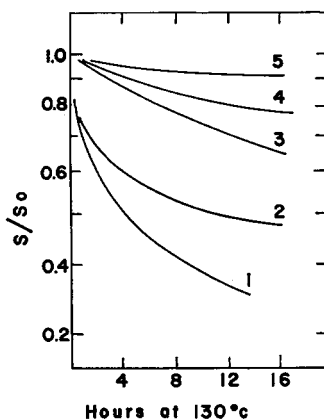


Fig. 8. Effect of time of cure on stress relaxation at 130°C.: (1) standard sulfur vulcanizate (60 min. at 145°C.) aged in air; (2) same, aged in argon; (3) same composition preheated 17 hr. in vacuum at 130°C. before aging in air; (4) same as 3 aged in argon; (5) peroxide vulcanizate aged in argon.

It should be noted in connection with this conclusion that the effect of heating in the absence of oxygen is not to produce an increase in the scission rate. Such an increase could also account for the changes on heating shown in Figures 6 and 7. Actually, as shown by stress relaxation, the overall rate of scission is decreased by prolonged cure. The effect of heating on relaxation is illustrated in Figure 8. This change occurs with only a small decrease in the overall rate of oxygen absorption.

Although there is no direct evidence as to the nature of the change in the crosslinking system which occurs when the sample is heated for a long time, it is tempting to speculate that it consists of the conversion of polysulfide crosslinks to mono- or disulfides. Not much is known about the structure of vulcanizates of SBR, but the experimental results of Studebaker and Nabors⁵ and of Bateman, Moore, and co-workers^{6,7} on vulcanization of natural rubber show that the average crosslink length decreases during

prolonged cure. It appears reasonable to infer that a similar change takes place in SBR.

It can also be inferred that the change in crosslink structure during heating involves the breaking of existing crosslinks and the creation of new ones. Vulcanizates of isoprene polymers relax in the absence of oxygen,⁸⁻¹¹ SBR vulcanizates do the same. The rate of relaxation in an atmosphere of argon at 130°C. is a large fraction of the rate of relaxation in air (Fig. 8). At lower temperatures it may exceed the rate of relaxation in air.^{8,11} As Figure 8 also shows, the relaxation of a peroxide vulcanizate in argon is very slow. It probably results from residual peroxidized groups in the hydrocarbon. At the worst, it represents the maximum rate of relaxation caused by traces of oxygen in the argon atmosphere. Since the rate of relaxation decreases steadily with argon flowing continuously through the system, this is considered an unlikely explanation. The faster relaxation of the conventional sulfur vulcanizate in argon can, therefore, be attributed to scission associated with the crosslinks. Scission is considered to involve sulfur-to-sulfur bonds rather than sulfur-to-carbon bonds because the vulcanizate modified by prolonged heating relaxes much more slowly in argon than the conventional composition, although sulfur-to-carbon bonds persist in its crosslinks.

According to the two-network hypothesis advanced by Tobolsky,¹² the assumption of a permanent set after stress relaxation is evidence for the formation during relaxation of new crosslinks which are in equilibrium at the extended length. Since the modulus of samples heated in a press does not change during long cure periods, it may be assumed that the total crosslink density is unchanged in the relaxation experiment. Then the ratio of new crosslinks formed to total crosslinks can be calculated from the dimensions of a test piece before, during, and after relaxation. If the original length is l_0 , the length during relaxation is l_x and the final length is l_s

$$\frac{\nu_e}{\nu_0 - \nu_e} = \frac{\alpha - (1/\alpha^2)}{(1/\alpha_1^2) - \alpha_1} \quad (1)$$

where ν_0 is total crosslink density, ν_e is density of broken (newly formed) crosslinks, $\alpha = l_0/l_s$ and $\alpha_1 = l_x/l_s$.

The ratio of crosslinks has been calculated from permanent set for samples aged two days at an extension ratio of 1.5 in vacuum at 130°C. Set was measured after two days further heating unrestrained at the same temperature. The ratio of new crosslinks to original crosslinks calculated according to eq. (1) was 0.6 to 0.8 depending on the sulfur level in the vulcanizate.

This calculation requires the assumption that the crosslinks lost are unstable under the conditions of aging and the new crosslinks stable. In a vulcanizate containing polysulfide crosslinks, the possibility of an exchange reaction^{12,13} represented by



cannot be ignored. If free exchange of this kind were responsible for a large fraction of the relaxation at the temperature of aging but were slow at room temperature, it might be detectable by comparing the set immediately after relaxation at elevated temperature with the set after a long further period of heating without restraint. This comparison has been made for a few samples. As shown in Table I, the evidence does not indicate that reversible exchange is an important factor. The differences between the crosslink ratios before and after the second period of heating are small and within the experimental error of this rather crude measurement.

Two mechanisms for the interaction of polysulfides with olefins in the absence of oxygen based on ionic dissociation of the polysulfide have been

TABLE I
Calculated Extent of Exchange

Carbon black, phr	Sulfur, phr	$(v_e/v_0)_1^a$	$(v_e/v_0)_2^b$
30	2.5	0.73	0.65
20	1.0	0.88	0.74

^a After relaxation at 130°C.

^b After heating unrestrained.

discussed by Bateman, Moore, and co-workers.^{6,7} One of these, a chain reaction involving the sulfenyl cation, could explain consistently the evidence on the effects of long cure on SBR vulcanizates. According to this mechanism, there is a stepwise decrease in chain length of the crosslink with each crosslink broken leading to the formation of one new crosslink with no other change in the network. It is unlikely that the second mechanism, which emphasizes the anion, applies to the changes in SBR vulcanizates during prolonged press cure since it requires the formation of inorganic sulfide to accompany the crosslink shortening. In SBR vulcanizates sulfide sulfur is formed in small amount, not readily related to the course of vulcanization. Typical analyses of two samples are given in Table II.

Only a qualitative interpretation of the effects reported here can be made with the available evidence. More detailed information about the chemistry of the aging process will require the study of reactions of low molecular weight model compounds. It can be concluded on the basis of the foregoing discussion that two sets of reactions are responsible for the changes in properties of SBR vulcanizates on aging. One includes the hydrocarbon oxidation, which proceeds as it did in the unvulcanized polymer. This results in both scission and crosslinking in amounts which are determined by the overall extent of oxidation. The other involves the crosslinks, proceeding at a rate relatively independent of the overall rate of oxidation. This involves the breaking of existing crosslinks and the

TABLE II
Effect of Heating on Sulfur Analyses^a

Sulfur taken, phr	Sulfur content, %							
	After cure (60 min at 145°C.)				After post cure (17 hr. at 145°C.)			
	Free	Sulfide	TCS ^b	Total	Free	Sulfide	TCS ^b	Total
1.73	0.19	0.005	1.58	2.04	0.015	0.08	1.69	2.04
1.73	0.04	0.11	1.80	2.07	0.007	1.74	1.74	2.07

^a Determined as described by Burger.¹⁴

^b TCS is "true combined" organically bound sulfur.

creation of new ones, the total formed being greater than the number broken in the presence of oxygen.

However, Mooney, Wolstenholme, and Villars⁸ reported that sulfur vulcanizates of natural rubber relax more slowly in air than in vacuum initially and showed there could be marked retardation in air at low temperatures. We have confirmed that this occurs with the SBR sulfur vulcanizates used in the present study. Gent¹¹ interpreted this to reflect weak crosslink structures, which are stabilized in the presence of oxygen. Both crosslink breaking and new crosslink formation may therefore involve oxygen (or a species formed during oxidation), but there is not yet a quantitative correlation with the overall rate of oxidation.

The participation of extra-network material other than antioxidants in the changes during aging is still not clear. Samples leached with cold acetone increase in modulus in air as fast or faster than unleached samples. If samples extracted for a week at room temperature are heated *in vacuo* after the extraction, they still increase in modulus in air at the same rate as

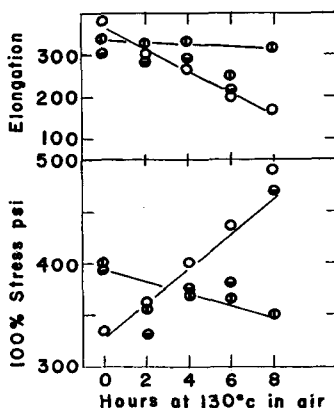


Fig. 9. Effect of acetone extraction on post cure and aging: (O) extracted with acetone one week at room temperature; (⊖) extracted, then heated 17 hr. at 130°C. in vacuum; (⊙) heated without extraction. Upper curves represent elongation at break.

before (Fig. 9). This would suggest that some soluble constituent of the vulcanizate is required for the stabilization of the crosslinks. (Separate experiments confirmed that if samples are acetone-extracted after the prolonged heating the modulus change during air aging is slow.) However, extracted samples relaxed in an argon atmosphere will acquire permanent set just as unextracted samples do. Further work will be required to define more precisely the effect of curatives on the aging process.

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Résumé

Les modifications dans les propriétés du SBR vulcanisé au cours du vieillissement à l'air à 130° résultent de réactions impliquant l'hydrocarbure et des pontages. L'oxydation de l'hydrocarbure est reliée à la vitesse globale de l'oxydation; ceci conduit à la fois à la scission et au pontage. Les ponts sulfures sont rompus et les nouveaux ponts formés au cours des réactions sont influencées par l'oxygène mais sont relativement indépendantes de la vitesse globale d'oxydation. L'excès de pontage par rapport à la scission diminue progressivement lorsqu'on augmente la durée du traitement.

Zusammenfassung

Veränderungen der Eigenschaften von vulkanisiertem SBR während Alterung bei 130° in Luft sind das Ergebnis von Reaktionen des Kohlenwasserstoffs und der Vernetzungsstellen. Die Kohlenwasserstoffoxydation wird zu der Oxydationsbruttogeschwindigkeit in Beziehung gesetzt; sie führt sowohl zur Spaltung als auch zur Vernetzung. Die Schwefelvernetzungen werden gespalten, und bei den durch Sauerstoff beeinflussten Reaktionen, die jedoch von der Oxydationsbruttogeschwindigkeit relativ unabhängig sind, werden neue Vernetzungen gebildet. Der Überschuss der Vernetzungen über die Spaltung nimmt mit zunehmender Vulkanisation ab.

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