Labile Cross Links in Low Unsaturation Elastomers. II. Effect of Chain and Cross-Link Structure on Thermal and Oxidative Stability

Peter F. Lyons[ab]; Timothy C. P. Lee[ac]; Arthur V. Tobolsky[a]

[a] Department of Chemistry, Frick Chemical Laboratory, Princeton University, Princeton, New Jersey [b] Pioneering Research Laboratory, E. I. du Pont de Nemours & Company, Wilmington, Delaware [c] Dunlop Rubber Company, Birmingham, England

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PETER F. LYONS,* TIMOTHY C. P. LEE,†
and ARTHUR V. TOBOLSKY

Department of Chemistry
Frick Chemical Laboratory
Princeton University
Princeton, New Jersey

SUMMARY

The thermal and oxidative stability of low unsaturation elastomers has been studied as a function of chain and cross-link structure by stress relaxation and oxygen absorption techniques. An ethylene-propylene terpolymer, a propylene oxide copolymer, and an ethylene sulfide-propylene sulfide terpolymer were used.

The thermally labile polysulfide cross link that results from sulfur cures is a potent antioxidant. The thermal lability is ascribed to an interchange mechanism, with an activation energy of 24 kcal/mole between 100 and 150°C.

The presence of an atom of oxygen in the chain results in an increased susceptibility to oxidative degradation compared with a hydrocarbon chain. The presence of a sulfur atom in the polymer chain confers a sensitivity to a destructive attack by the active ingredients and products of an accelerated sulfur-curing recipe.

* Present address: E. I. du Pont de Nemours & Company, Pioneering Research Laboratory, Experimental Station, Wilmington, Delaware.

† Present address: Dunlop Rubber Company, Birmingham, England.

INTRODUCTION

In a previous paper we reported on the thermal and oxidative stability of an ethylene-propylene terpolymer (EPT) cross-linked with a cumyl peroxide and also with a conventional accelerated sulfur-curing system [1(a, b)]. Stress relaxation measurements in air and nitrogen vividly contrasted the thermal stability and oxidative susceptibility of the hydrocarbon chain at 130°C. In the peroxide cure, which has carbon-to-carbon cross links, the stress remained constant in nitrogen, whereas in air the stress decayed to zero in an hour. The accelerated sulfur vulcanizates, on the other hand, were found to be thermally labile and oxidatively stable. Initially the stress decayed rapidly in both air and nitrogen to about one-half of the original value and then slowed to a small rate. The initially rapid stress relaxation was attributed to a thermal interchange of polysulfide cross linkages. The fact that the stress did not decay to zero indicated that thermally stable mono- and disulfide cross links were also present. Longer curing times caused this distribution between labile and stable cross links to shift in favor of the thermally stable linkages. The inhibition of oxidation was obviously due to the sulfur-curing system, but the exact nature of the inhibiting species was unknown. Consequently, the inhibition was assigned to the presence of unextractable sulfur moieties, which may or may not have been combined with the rubber network.

In the present work we investigated two additional curing recipes for the EPT system—a sulfur donor and a pure sulfur cure. The latter cure provided an especially attractive system to study in that the only species present in the network were the sulfur cross links and the hydrocarbon backbone chain. The myriad of products usually resulting from accelerated sulfur vulcanizations were absent. In addition, the low unsaturation content severely restricted the formation of cyclic sulfides and other non-cross-linking side reactions that occur when highly unsaturated rubbers are cured with sulfur alone.

We also investigated the effect on stability of changing the backbone chain structure. As shown below, the presence of a heteroatom (oxygen or sulfur) in the chain caused the cured elastomer to react quite differently to the influences of heat and oxygen than the hydrocarbon chain of EPT. The response is a direct function of the chemical nature of the heteroatom. A propylene oxide copolymer (POC) and an ethylene sulfide propylene sulfide terpolymer (ESPST) were used. Both contained a few per cent of pendant unsaturation to permit cross linking with sulfur.

EXPERIMENTAL

The raw rubbers were cold milled with curing ingredients as shown in Table 1, which also gives times, temperatures, and methods of curing. Thin sheets (6-12 mils) of the milled polymer were pressed under 40,000 psi in a Pasadena hydraulic press at the curing temperature. All samples were extracted with benzene in a continuous Soxhlet extractor for 12 hr and dried in vacuo.

The stress relaxation balance and the oxygen absorption apparatus are described elsewhere [2, 3]. For stress relaxation studies in an inert atmosphere the balance was enclosed in a nitrogen-filled dry box.

RESULTS AND DISCUSSION

Sulfur Donor Cure for EPT

When raw rubbers are vulcanized with a primary accelerator and the metal oxide and fatty acid activators but without the presence of free sulfur, the curing system is known as a sulfur donor. The sulfur to form the cross links comes from the primary accelerator, an organic sulfur compound. The tetramethylthiuram-disulfide (TMTD)-sulfurless system has been fairly well characterized in studies of natural rubber (NR) [4]. When the vulcanization reaction is taken to completion, mono- and disulfide cross links are formed along with an extremely potent antioxidant, zinc dimethyldithiocarbamate (ZnDMDC), which is extractable. In the absence of complete reaction, the TMTD groups, which attach themselves to the backbone (as a first step in the vulcanization) and are therefore not extractable, can go on to provide oxidative protection in subsequent aging tests [4].

In our first attempt to cure EPT with this sulfur donor system we were apparently unsuccessful in driving the vulcanization reaction to completion. This was evident from the lack of oxidative degradation and the presence of some residual thermal lability with a sample that was cured for over 20 hr in the press [1(b)]. By a change in the curing cycle which involved removing the sample from the press after a short time, extracting it, and then postcuring in a vacuum oven for a day, the vulcanization reaction was completed. The simplest explanation is that some species was vaporized, driving the reaction to completion. One possibility is the formation of the relatively volatile tetramethylthiourea (b.p. 245°C) and carbon disulfide from the TMTD [5]. This reaction is known to occur on pyrolysis of TMTD [6].

The stress relaxation curves measured at 130°C are shown in

Table 1. Cure Recipes of Low Unsaturation Elastomers

Cure type	Peroxide	Accelerated sulfur	Sulfur donor	Pure sulfur	H_2S
Polymer[a]	100	100	100	100	100
Benzoyl peroxide[b]	2				
Zinc oxide		5	5		
Stearic acid		2	1		
Sulfur		2		7	
Tetramethylthiuram-disulfide		1	3.5		
Mercaptobenzothiazole		1			
Dithiocarbamate salt					5
Cure temp., °C	120	150	150	150	150
Cure times	25 min	10-15 min	(1) 30 min (press) (2) Extracted (3) 20 hr (vacuum)	14 hr	15 min

[a]Weight per cent: EPT (Enjay 3509): ethylene, 55; propylene, 42; methylene norbornene, 2.6. POC (Dynogen XP-139): propylene oxide; unsaturated epoxide; composition unknown. ESPST (Dunlop XP): ethylene sulfide, 26; propylene sulfide, 68; allyloxymethyl thiirane, 6.2.
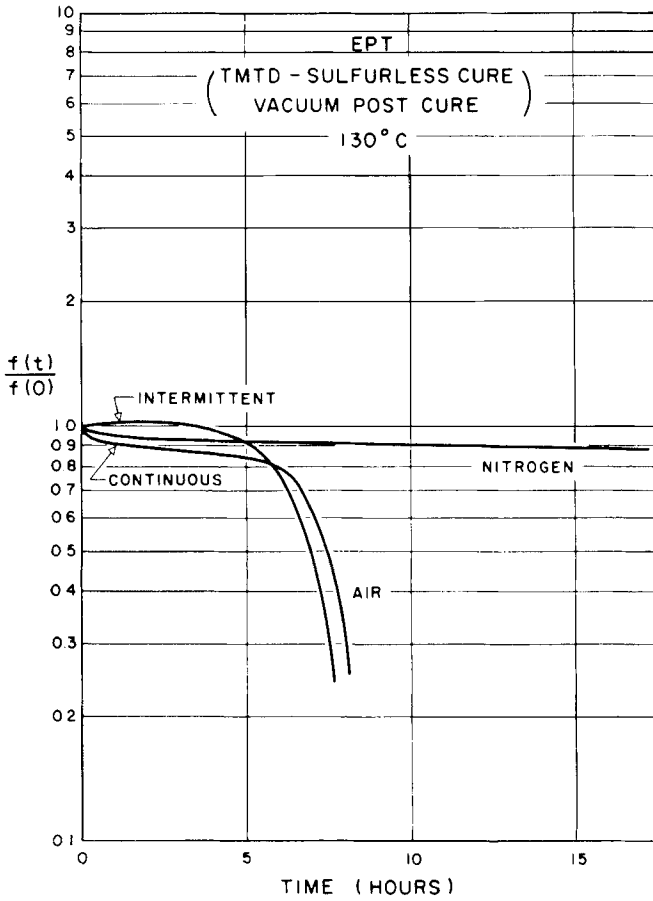[b]Temperature and time shown are for POC.

Fig. 1. Continuous and intermittent stress relaxation of sulfur donor cure of EPT in air and nitrogen at 130°C.

Fig. 1. The network is thermally stable as evidenced by the negli-
gible decay of stress in nitrogen. After a short induction period in
air the continuous and intermittent relaxations decay autocatalyti-
cally, indicating oxidative degradation. The final rate of decay is
the same as the peroxide cure of EPT [1]. The similar rapid rates
of oxygen absorption of the sulfur donor cure and the peroxide cure
are displayed in Fig. 2 (compare B and C).
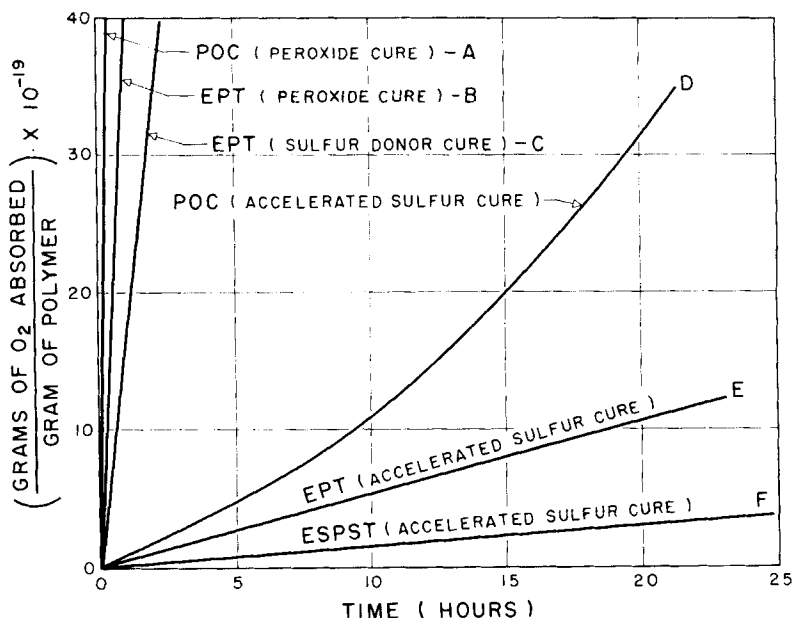
Fig. 2. Oxygen absorption of low unsaturation elastomers as a func-
tion of curing system.

    It is of interest to note that the mono- and disulfide cross links
present in this thermally stable vulcanizate are not effective as
inhibitors of oxidation. The aforementioned studies of NR indicate
that the mechanism of cross linking with the TMTD-sulfurless
system leaves the unsaturation intact, producing dialkenylsulfide
cross links [4]. Model-compound studies with dialkenylsulfides
have disclosed that these structures display little antioxidant ac-
tivity [7]. Thus it does not seem unreasonable to say that the stabi-
lity characteristics of the sulfur donor cure of EPT are indicative
of the presence of dialkenyl mono- and disulfide cross links.

Pure Sulfur Cure for EPT

A reasonably tight and simple network can be achieved in EPT with sulfur alone if higher concentrations of sulfur and longer curing times are utilized to compensate for the low rate of the cross-linking reaction in the absence of accelerators. This is possible because (1) EPT suffers very little reversion, i.e., irreversible breakdown of cross links, with long curing times; and (2) the non-cross-linking side reactions that lead to rearrangement of the backbone structure and formation of cyclic sulfides are minimized by the absence of a high unsaturation content.

As shown in Fig. 3, the stress relaxation curves at 130°C are the same in air and nitrogen and quite similar to those obtained for
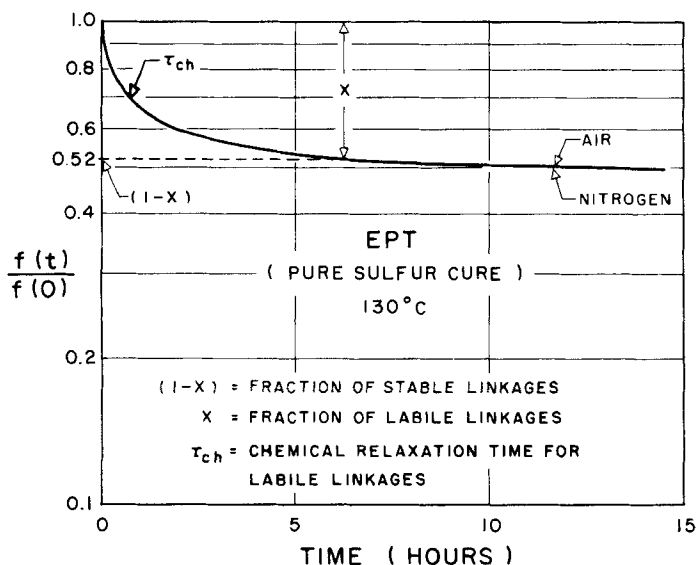
Fig. 3. Continuous stress relaxation of pure sulfur cure of EPT in air and nitrogen at 130°C; procedure for fitting Eq. (1) is illustrated.

short cures of accelerated sulfur recipes, i.e., an initially rapid decay slowing after a few hours to a small rate [1]. This result dramatically demonstrates that the polysulfide linkage by itself is an extremely effective inhibitor of oxidation. It is no longer necessary to speculate about the presence of attached accelerator fragments or other unextractable sulfur moieties and their roles in the cessation of oxidative breakdown.

As was mentioned in the previous paper, elemental sulfur swollen into peroxide cures of EPT is an effective, but short-lived, in-

hibitor of oxidation. The induction period increases with the free
sulfur content. Hawkins and Sautter attribute the antioxidant effect
of sulfur and its compounds to their ability to decompose hydro-
peroxides without the formation of radical products [8,9]. The hetero-
lytic decomposition occurs in two ways. The sulfur (or sulfide) first
effects a sacrificial decomposition of hydroperoxide, forming sul-
fur oxides which can then go on to decompose additional peroxides
catalytically. Elemental sulfur, which forms SO_2 by this mechanism,
is apparently a short-lived inhibitor because of the volatility of the
sulfur dioxide. The polysulfide cross links, on the other hand, act
as long-lived reservoirs and are therefore more effective as pro-
tective agents [10]. In effect, the antioxidant is built into and held
in the rubber network via primary chemical binding.

The pure sulfur cure of EPT provides an attractive kinetic sys-
tem to study because it is a clean system, free of accelerator resi-
dues that are potential catalysts for the cleavage of sulfur linkages.
Thus it should be possible to measure the rate of stress relaxation
in this system with some confidence that the kinetic parameter being
measured is closely related to the rate of bond cleavage (interchange)
of the polysulfide linkage. As before, we can fairly well represent
the stress relaxation curve of this sulfur vulcanizate by an exponen-
tial equation of the form [1].

$$f(t)/f(0) = X \exp(-t/\tau_{ch}) + (1 - X) \qquad (1)$$

where $f(t)/f(0)$ is the fraction of the initial stress at time t; X is the
fraction of the total number of linkages which is labile; and $(1 - X)$
is the fraction which is stable. τ_{ch} is the time taken for the stress
to relax to $1/e$ (0.368) of the total amount of labile relaxation. As
the stress $f(t)$ at any time t is proportional to the number of unbroken
linkages present at that time, the fraction of stable linkages $(1 - X)$
present in the network is taken as the final value of the relative
stress after relaxation has virtually ceased.

Equation (1) is actually just a sum of two exponentials, with the
second term on the right possessing an infinite relaxation time. The
assumption of an infinite relaxation time is not exactly correct, as
there is still a small rate of relaxation. But the relaxation time for
this process is many orders of magnitude greater than those we are
measuring. It is more accurate, however, to extrapolate the final
low rate of relaxation back to zero time and take this value for the
fraction of stable linkages. This is shown in Fig. 3 along with the
fraction of labile linkages (X) and the chemical relaxation time
(τ_{ch}).

The stress relaxation of the pure sulfur cure has been measured
at a number of different temperatures between 100 and 150°C.
Fresh samples were used at each temperature. The equation and
procedure described above were used to calculate the τ_{ch} at each

Table 2. τ_{ch} of Labile Cross Links in EPT and POC

EPT		POC	
		τ_{ch}, min	
Pure sulfur	Accelerated sulfur	Accelerated sulfur	Temperature, °C
	420		100
190			106
32	30	35	130
18			140
	15		145
8.0			150

temperature. These are listed in Table 2. A plot of log τ_{ch} vs. 1/T yields an Arhennius activation energy of 24 kcal/mole (Fig. 4). The agreement between this value and the value of 25.9 kcal/mole obtained for the activation energy for interchange in polysulfide networks of the Thiokol type is reasonably good [11].

We have also measured the τ_{ch} for the accelerated sulfur cure of EPT (12-min cure) at three different temperatures. They are listed in Table 2. As shown in Fig. 4, these data fit reasonably well on the Arhennius plot for the pure sulfur cure. This somewhat surprising result indicates that the polysulfide cross links in the accelerated sulfur cure are interchanging in the neat as it were, suffering no catalytic influences from accelerator fragments and such.

It should be mentioned that the stress relaxation of labile cross links can be more closely approximated by a sum of two exponential terms with finite relaxation times, i.e.,

$$f(t)/f(0) = A \exp(-t/\tau_1) + B \exp(-t/\tau_2) + (1 - X) \qquad (2)$$

where $A + B = X$, the fraction of labile linkages. The constants in this equation are evaluated by an exponential resolution technique known as procedure X [12]. As an example, the constants calculated from the stress relaxation curve of the pure sulfur cure at 130°C are

$A = 0.25 \qquad \tau_1 = 7$ min
$B = 0.23 \qquad \tau_2 = 85$ min
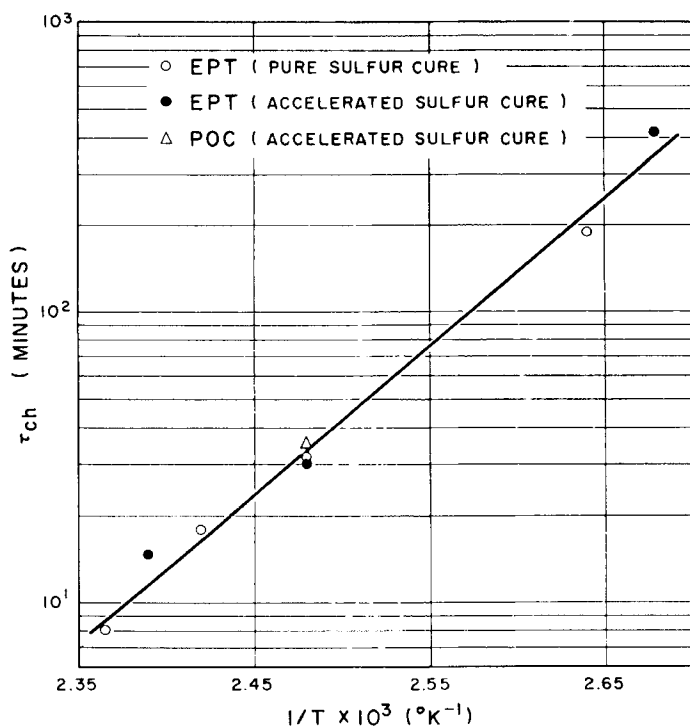
Fig. 4. Arhennius plot of chemical relaxation time (τ_{ch}) of labile polysulfide linkages.

It is of interest to note that the inability to closely fit the stress relaxation curves of rubbers containing polysulfide linkages by a simple exponential decay is a widespread phenomenon [13-16]. Some authors maintain that the initial curvature on plots of log stress vs. linear time is due to rheological or physical relaxation [13-15]. Scheele and Hillmer discount the rheological interpretation on the grounds that thermal pretreatment, which can eliminate the initial curvature, should have no effect on physical relaxation [16].

Our own studies of physical relaxation at room temperature and those of other authors at room temperature and as a function of temperature indicate that at 130°C the physical relaxation should occur in a matter of seconds [17, 18]. It is our contention that the stress relaxation curves measured at elevated temperatures are indicative of a chemical process, although it does not happen to follow a simple first-order rate law exactly.

The polysulfide linkage is usually represented by S_x, where $x \geq 3$. One possibility to be considered is that the sulfur-sulfur

bonds in the trisulfide and tetrasulfide are not of equivalent strength. It is tempting to speculate about the relationship between the two relaxation times (τ_1, τ_2) and the tetrasulfide and trisulfide linkages. But such speculation should be heavily tinged with skepticism until a much more intensive investigation is made on systems of this type.

An aspect of the vulcanization reaction that was apparent in the previous paper but was not emphasized is the fact that the overall vulcanization is actually composed of two main types of reactions [1]: (1) cross-linking reactions which are predominant during the early stages, and (2) conversion of the polysulfide cross links to mono- and disulfides. The important point here is that the maximum cross-link density is reached in about 1 hr at 150°C, while the reduction of the rank of the sulfur linkage takes many hours and the cross-link density remains essentially unchanged during this conversion. A recent study of the vulcanization chemistry of an ethylene propylene diene rubber by Frensdorff served to bring this point to our attention [5].

The persistence of the labile linkage in EPT is undoubtedly a direct consequence of the limited unsaturation content. It also seems reasonable that the interchange reaction plays a significant role in the mechanism of cross-link rank reduction. The fate of the sulfur that seemingly vanishes in this reduction process is somewhat puzzling. However, if some of the initial cross links were formed without destroying the unsaturation, further reaction of the labile linkages at these sites of unsaturation might result in the formation of lower-rank gem cross links without appreciably changing the cross-link density.

Effect of Oxygen in the Chain

Achieving a reasonable network with the peroxide cure of the propylene oxide copolymer (POC) was probably only possible because of the presence of the unsaturation in a branched structure. The abundance of tertiary hydrogens on the chain results in the formation of polymer radicals with weak coupling tendencies. Rowe and Thomas found that polypropylene glycol cured with cumyl peroxide in the absence of oxygen underwent extensive degradation rather than cross linking [19].

The results of the stress relaxation of the peroxide cure at 130°C are shown at the top of Fig. 5. In air the stress decays to zero in about 1 hr. The sample also exhibits the rapid oxygen absorption indicative of autocatalytic oxidation (Fig. 2, A). Of some surprise was the apparent lack of thermal stability of this network manifest by the appreciable decay of the stress in nitrogen. The carbon-oxygen bond in the polyether chain would be expected to be as stable as the carbon-carbon bond in EPT at this temperature.
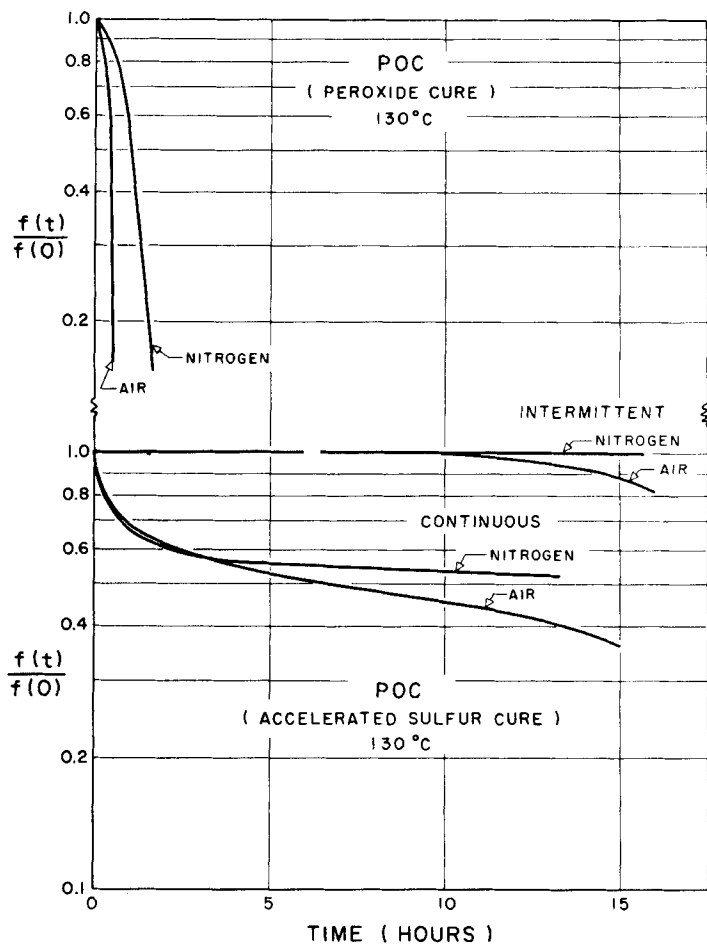
Fig. 5. Top: continuous stress relaxation of peroxide cure of POC in air and nitrogen at 130°C. Bottom: continuous and intermittent stress relaxation of accelerated sulfur cure of POC in air and nitrogen at 130°C.

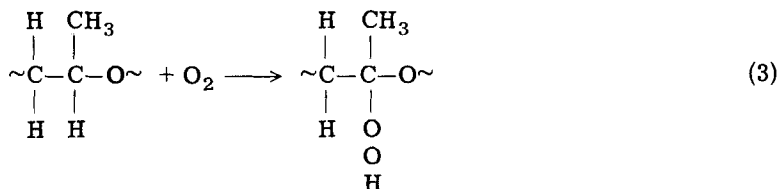The stress relaxation curves of a short (10 min) accelerated sulfur cure are at the bottom of Fig. 5. The sulfur vulcanizate of POC run in nitrogen exhibits almost an exact replica of the decay curve of the similarly cured EPT, which suggests that the polyether chain does not possess links that are inherently weak. If such links existed, the stress would presumably decay to zero. The τ_{ch} for the

initial rapid decay fits quite well on the Arhennius plot (Fig. 4), indicating that the polysulfide linkage in POC is the same as that found in EPT. The flat intermittent relaxation curve in nitrogen emphasizes the interchange nature of the thermal decay.
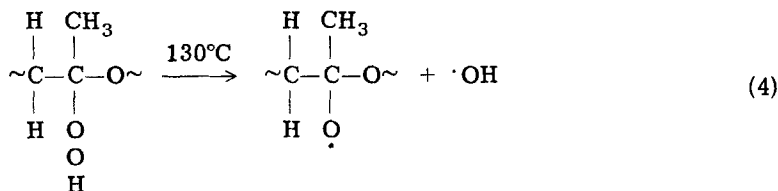
The sulfur cure run in air shows a continuing rate of relaxation after the rapid thermal interchange. This additional decay in air is evidenced in both the continuous and intermittent measurements. The moderate rate of oxygen absorption of this sample (Fig. 2, D) in conjunction with the stress relaxation data indicates that a retarded oxidative degradation is occurring.

It is well known that monomeric ethers readily form hydroperoxides in the presence of air at ambient temperatures. The mechanism of the hydroperoxide formation is presumably a molecule-induced homolysis of oxygen with the ether adduct [20]. In studies of the initiated oxidation of POC at elevated temperatures, Norling et al. showed that the presence of the oxygen atom alpha to the tertiary hydrogen greatly facilitated its abstraction and the subsequent formation of hydroperoxides [21]. In initiated oxidations the decomposition of these hydroperoxides into radicals causes branching of the kinetic chain, while in autoxidation the homolysis of the hydroperoxide is the initiation step.

In the preparation of the peroxide cure of POC, a large number of hydroperoxide groups evidently formed along the chain.

$$
\begin{array}{ccc}
\text{H} & \text{CH}_3 & \\
| & | & \\
{\sim}\text{C}-\text{C}-\text{O}{\sim} + \text{O}_2 \longrightarrow \\
| & | & \\
\text{H} & \text{H} &
\end{array}
\qquad
\begin{array}{cc}
\text{H} & \text{CH}_3 \\
| & | \\
{\sim}\text{C}-\text{C}-\text{O}{\sim} \\
| & | \\
\text{H} & \text{O} \\
& \text{O} \\
& \text{H}
\end{array}
\qquad (3)
$$

When the stress relaxation was measured in nitrogen at 130°C, such groups would decompose into tertiary alkoxy and hydroxyl radicals.

$$
\begin{array}{cc}
\text{H} & \text{CH}_3 \\
| & | \\
{\sim}\text{C}-\text{C}-\text{O}{\sim} \\
| & | \\
\text{H} & \text{O} \\
& \text{O} \\
& \text{H}
\end{array}
\xrightarrow{\;130°\text{C}\;}
\begin{array}{cc}
\text{H} & \text{CH}_3 \\
| & | \\
{\sim}\text{C}-\text{C}-\text{O}{\sim} + \cdot\text{OH} \\
| & | \\
\text{H} & \text{O} \\
& \overset{\bullet}{\phantom{\text{O}}}
\end{array}
\qquad (4)
$$

These tertiary alkoxy radicals are precursors of chain scission, undergoing fragmentation by a beta scission [21].

$$\begin{array}{ccc}
\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} \overset{\displaystyle CH_3}{\underset{\displaystyle O}{\overset{|}{\underset{|}{C}}}} \text{--O}\sim & \longrightarrow & \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} \overset{\displaystyle CH_3}{\underset{\displaystyle O}{\overset{|}{\underset{\|}{C}}}} \;+\; \cdot O\sim
\end{array} \qquad (5)$$
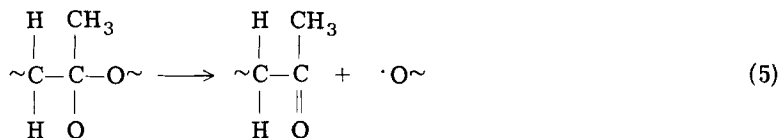
The primary alkoxy radical formed in reaction (5) together with the hydroxyl radical from reaction (4) are possible propagating radicals in a continuing degradation process. Further abstraction of tertiary hydrogens results in polymer radicals with a high preference for decay by scission [19]. The breakdown of POC in nitrogen is most likely due to the preoxidation during processing rather than to any inherent thermal instability of the polyether chain.

Curing with an accelerated sulfur recipe evidently restricts the formation of the hydroperoxide groups, since the relaxation in nitrogen appears to be due entirely to the thermal interchange of the labile cross links. Exposure of this cure to air at 130°C, however, undoubtedly results in a massive buildup of hydroperoxide groups that go on to initiate the oxidation reaction. Eventually this onslaught begins to swamp the inhibiting potential of sulfide linkages present, and oxidative scission of the main chain is manifest by the additional rate of relaxation observed.

It is apparent that the presence of an atom of oxygen in the chain confers increased susceptibility to the molecular variety.

Effect of Sulfur in the Chain

Various attempts to cure the ethylene sulfide propylene sulfide terpolymer (ESPST) with a peroxide recipe were unsuccessful. The visually observed polymer degradation that occurred in these attempts suggests that the polymer radicals formed by hydrogen abstraction on the chain have a strong preference for scission as in the polypropylene oxide system [19]. The presence of the branched unsaturation structure in ESPST appears to be ineffective in promoting network formation. It is possible that the sulfur atom in the chain decomposes the peroxide into nonradical products in a reaction akin to Hawkins and Sautter's mechanism of hydroperoxide decomposition [8, 9]. Exposure of ESPST to high-energy radiation also failed to effect cross linking.

The stress relaxation curves of the accelerated sulfur vulcanizate with a short cure (15 min) are shown at the top of Fig. 6. The lack of thermal stability of this sulfur-rich network is immediately apparent. In the continuous measurement at 130°C, the stress decays to zero in both air and nitrogen in about 1 hr. This sample showed a very low rate of oxygen absorption, underlining the nonoxidative nature of the degradation.
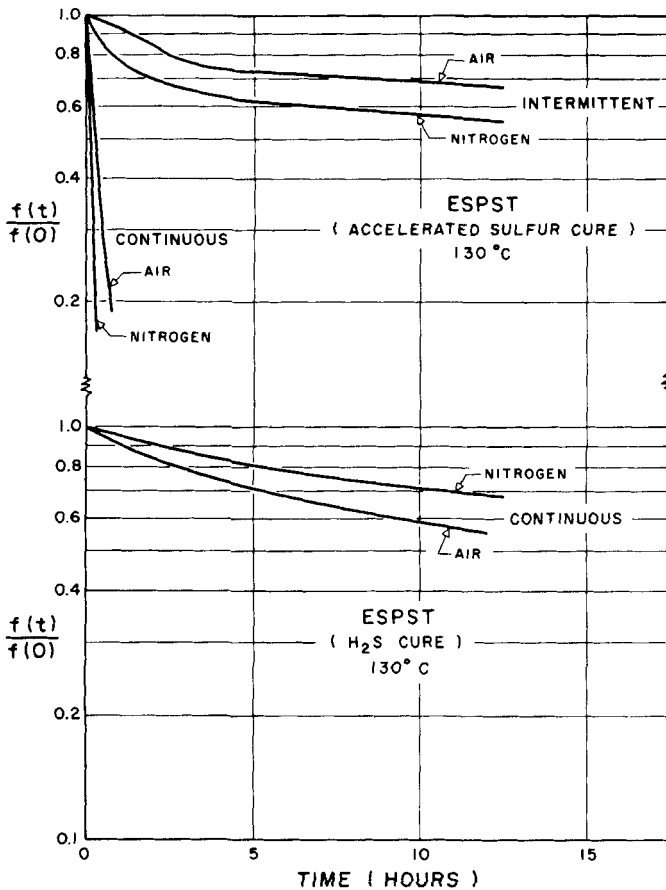
Fig. 6. Top: continuous and intermittent stress relaxation of accelerated sulfur cure of ESPST in air and nitrogen at 130°C. Bottom: continuous stress relaxation of H_2S cure of ESPST in air and nitrogen at 130°C.

On the other hand, the thermal decay is not solely due to an interchange reaction as in Thiokol elastomers [11]. The ESPST exhibits considerable stress relaxation when the measurements are made intermittently, indicating some irreversible destruction of the network. Since the stress at any given time in the intermittent experiment is larger than that in the continuous experiment, cross linking and scission are both occurring, with the latter predominating.

Since the curing recipe and conditions are the same as in EPT and POC, a similar distribution of cross-link structures—approximately equal amounts of stable and labile linkages—is expected. If this does obta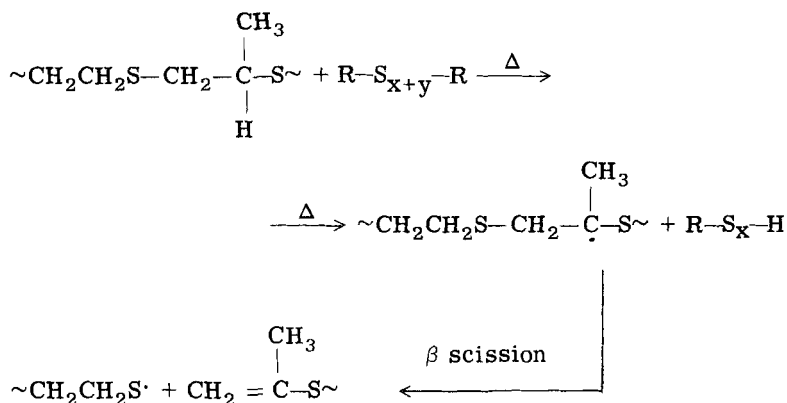in, then it becomes necessary to postulate irreversible cleavages of the "stable" sulfide cross links or the polythioether backbone in order to explain the stress relaxation results. There is no spectroscopic evidence (IR and NMR) for weak linkages in the chain [22].

In contrast to EPT, extending the curing cycle of ESPST causes extensive breakdown of the network. This reversion effect has also been observed by Lal with a propylene sulfide copolymer (PSC) cured with a sulfur recipe [23]. In his study of adduct rubber, which is polybutadiene in which 97% of the double bonds are saturated with methylmercaptan, Meyer found that curing it with an accelerated sulfur recipe promoted something equivalent to a reversal of the adduct reaction [24].

$$
\sim CH_2-CH-CH_2-CH_2\sim \;+\; \left[\begin{array}{l} \text{sulfur} \\ \text{acceler-} \\ \text{ator} \\ \text{zinc oxide} \\ \text{fatty acid} \end{array}\right] \xrightarrow{\;\Delta\;}
$$

with

$$
\begin{array}{c} | \\ \text{S} \\ | \\ CH_3 \end{array}
$$

$$
\xrightarrow{\;\Delta\;} CH_3SH \;+\; \sim CH_2-CH=CH-CH_2\sim
$$

Adduct rubber   Butadiene rubber

(6)
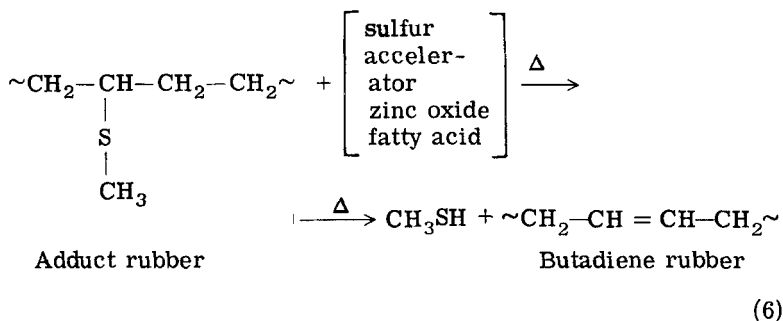
If this reaction occurs in ESPST, scission of the backbone chain would result. Considering the results of the length of the curing cycle on network formation, cross-linking reactions apparently predominate in the early stages of vulcanization. But as the unreacted sites of unsaturation decrease with time, the scission reaction becomes favored, causing the reversion in ESPST.

The stress relaxation results indicate that the scission reaction can be effected by the products of the vulcanization reaction as well as by the ingredients. Ideally the major potentially active product in an extracted network would be the labile polysulfide cross links. Dogadkin and Donstov have noted that the presence of a polar sulfur atom in a molecule can activate the adjacent carbon-hydrogen bond toward hydrogen abstraction by sulfur radicals [25]. The abundance of tertiary hydrogens alpha to a sulfur atom in ESPST may lead to the formation of polymer radicals that would fragment via a beta scission. A reasonable operational mechanism can be written for this sequence.

$$\sim CH_2CH_2S-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-S\sim \; + \; R-S_{x+y}-R \; \xrightarrow{\;\Delta\;}$$

$$\xrightarrow{\;\Delta\;} \; \sim CH_2CH_2S-CH_2-\underset{\underset{\cdot}{}}{\overset{\overset{CH_3}{|}}{C}}-S\sim \; + \; R-S_x-H$$

$$\sim CH_2CH_2S\cdot \; + \; CH_2 = \overset{\overset{CH_3}{|}}{C}-S\sim \quad \overset{\beta \; \text{scission}}{\longleftarrow}$$

A straightforward test of the proposed mechanism would be the demonstrated stability of the network in the absence of any abstracting (or more generally, any attacking) species. A possible way of introducing monosulfide cross links with a minimum of non-cross-linking side reactions is to cure with a dithiocarbamate salt

$$(CH_3NHC\overset{\overset{S}{|}}{S}^{\ominus} \; NH_3CH_3^{\oplus})$$ which decomposes at the curing temperature to form hydrogen sulfide (H_2S) [26]. H_2S is thought to be the actual cross-linking agent.

The stress relaxation curves for such a cure in air and nitrogen are displayed at the bottom of Fig. 6. The dramatic reduction in the rate of stress relaxation in a network purported to contain only monosulfide linkages lends support to the speculative mechanism of scission of the backbone chain induced by more labile sulfur species. It also confirms the spectroscopic evidence concerning the absence of "weak" links in the backbone chain [22]. It is of interest to note that a high level of oxidative resistance is retained in the H_2S cure.

The presence of a sulfur atom in the polymer chain seems to confer a sensitivity to destructive attack by the accelerated sulfur vulcanizing system and very probably by the labile polysulfide cross links formed in such a cure.

CONCLUSIONS

A sulfur donor cure of EPT resulted in a network with stability characteristics much like a peroxide cure—thermally stable, oxidatively unstable. The mono- and disulfide cross links possess little antioxidant activity and are thought to be dialkenyl sulfides. The interpretation of the immediate environment of the cross link is based on previous studies of natural rubber and model compounds.

Table 3. Effect of Chain and Cross-Link Structure on Stability—Summary

Increased susceptibility to oxidation		Increased sensitivity to nonoxidative destruction

←————————————————————————→

Cure (cross link) \ Polymer chain	Propylene-oxide copolymer, (POC)	Ethylene-propylene terpolymer (EPT)	Ethylene sulfide-propylene sulfide terpolymer, ESPST
Peroxide (carbon-carbon)	"Thermally" unstable (due to pre-oxidation)	Thermally stable	(Impossible to cure)
	Oxidatively unstable (autocatalytic	Oxidatively unstable (autocatalytic)	
H_2S (monosulfide)			Thermally stable
			Oxidatively stable
TMTD-sulfurless (mono-, disulfide)		Thermally Stable	
		Oxidatively Unstable (autocatalytic)	
Accelerated sulfur (mono-, di-, polysulfide)	Thermally labile	Thermally labile	Thermally unstable
	Oxidatively unstable (retarded)	Oxidatively stable	Oxidatively stable
Pure sulfur (mono-, di-, polysulfide)		Thermally labile	
		Oxidatively stable	

Increasing thermal lability and oxidative stability ↓

A pure sulfur cure of EPT produced a clean and structurally simple network. The outstanding oxidative stability of this cure dramatically demonstrated that the polysulfide linkage by itself is an extremely potent and long-lived inhibitor of oxidation. The calculation of the labile chemical relaxation times (τ_{ch}) of this cure as a function of temperature fitted an Arhennius plot with an activation energy of 24 kcal/mole. The agreement between this value and the value of 25.9 kcal/mole obtained for the activation energy for interchange in polysulfide networks of the Thiokol type is reasonably good [10]. It was also found that the τ_{ch}'s of the accelerated sulfur vulcanizate (short cure) fitted reasonably well on the same Arhennius plot.

EPT vulcanization is actually composed of two main types of reactions: (1) cross-linking reactions which are predominant in the early stages, and (2) conversion of the polysulfide cross links to mono- and disulfides. With accelerated sulfur recipes the maximum cross-link density is attained in about 1 hr at 150°C, while the reduction of the rank of the sulfur linkage takes many hours and the cross-link density remains essentially unchanged during this conversion. The persistence of the labile linkage in EPT is undoubtedly a direct consequence of the limited unsaturation content.

The presence of an atom of oxygen in the chain results in an increased susceptibility to oxidative degradation. The presence of a sulfur atom in the polymer chain confers a sensitivity to a destructive attack by the active ingredients and products of an accelerated sulfur curing recipe.

The conclusions concerning the effect of the chain and cross-link structure on thermal and oxidative stability are summarized in Table 3.

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