Influence of oxygen content in the atmosphere on chemical stress relaxation of natural rubber vulcanizates:
1. Relaxation mechanisms of sulphur-cured systems

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Stress relaxation of sulphur-cured natural rubbers of different crosslinked structures was investigated in an atmosphere containing variable amounts of oxygen. At high temperature, even very low contents of oxygen strongly affected the degradation of these vulcanizates. The stress relaxation of each vulcanizate was analysed in relation to the sol fraction and the swelling of sample degraded under the same condition. The scission mechanism of the vulcanizates depended on the quantity of oxygen in the atmosphere. Under nitrogen, the scission occured mainly near the crosslink site in all the samples. However, in the case of their being small amounts of oxygen present it took place near the crosslink site in the initial stages of degradation and then along the main chain at the later stages. In the atmosphere of comparative high oxygen content, the degradation seemed to result from the oxidative scission along the main chain. The degradation mechanisms of sulphur-cured natural rubbers were also discussed.

INTRODUCTION

Chemorheological studies of rubber vulcanizates have been carried out extensively[1-4]. The chemical stress relaxation method is thought to be useful for the investigation of initial degradation of rubber vulcanizates, because any change of the physical and/or chemical structures in the networks appear in the stress decay. However, the usual analytical techniques do not detect the initial stages of degradation. So far, most chemorheological studies have been carried out for the thermo-oxidative or thermal degradation of rubber vulcanizates. We have also discussed the degradation mechanisms of some rubber networks in air[5,6] and under nitrogen[7], in relation to the nature of the crosslinking.

Generally, the oxygen content in the atmosphere affects the degradation mechanisms of polymers. This effect has been scarcely studied for the degradation of rubber vulcanizates[8], although such studies may be important in the understanding of the degradation mechanisms of networks. In this series, the degradation of different types of natural rubber vulcanizates will be investigated at differing oxygen concentration and in the present paper, the scission mechanisms of networks will be studied.

EXPERIMENTAL

Sample

Natural rubber (Pale crepe-1) plus additives (*Table* 1) was milled at 50°C ± 1°C. Thin sheets (~0.25 mm) of milled polymer were pressed at 200 kg cm^{-2}, 145°C. The crosslinking structure of each sample is also given in the table. All the samples were extracted by a hot azeotrope mixture of acetone/methanol/chloroform (352/274/291 cc) under nitrogen for 48 h.

Stress relaxation measurement

Continuous and intermittent stress relaxations were measured under the condition of different oxygen concentration at 140°C for the sample 1 and 178°C for the samples 2 and 3. The stress relaxation apparatus used was constructed in our laboratory and included the usual strain guage system. The concentration of O_2 in the surrounding atmosphere was varied by changing the flow rate of oxygen and nitrogen (99.99% N_2) from storage tanks. The apparatus is illustrated in *Figure* 1. The oxygen concentration could be controlled to a precision of ~0.01% O_2. To minimize the oxidative degradation of

Table 1 Preparation of natural rubber vulcanizates

	Sample No. 1	No. 2	No. 3
Rubber	100	100	100
Sulphur	3		0.4
Tetramethylthiuram disulphide		3	
Mercaptobenzothiazol	1		
N-cyclohexylbenzothiazole 2-sulphenamide			6
Stearic acid	0.5	2	
Lauric acid			1
Zinc oxide	3	5	5
Hot press curing at 145°C min^{-1}	15; 30	30	193*
Initial chain density† (10^4 mol ml^{-1})	1.15; 1.48	1.10	1.39
Crosslinking structures	—S— —S_2— —S_x—	—S— —S_2—	—S—

* At 140°C
† Estimated using the statistical theory of rubber-like elasticity

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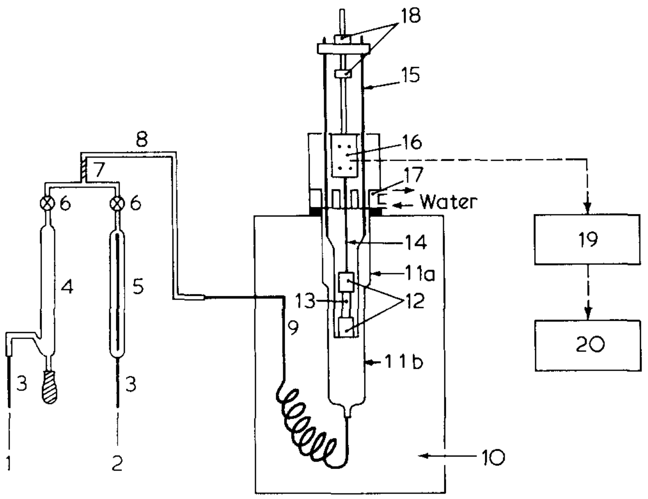


Figure 1 Apparatus for stress relaxation measurement; (1) from oxygen gas tank; (2) from nitrogen gas tank; (3) glass capillary to control flow rate of gas; (4), (5) flow meters; (6) ground-glass joint; (7) glass wool and drying agent; (8) glass tube; (9) copper tube; (10) thermostat; (11a) glass tube; (11b) glass tube; (12) clamps; (13) samples; (14) piano wire; (15) sliding bar; (16) strain gauge; (17) cooler; (18) stopper; (19) amplifier; (20) recorder

rubber networks during the preheating (20 min), the sample was held under nitrogen for 15 min and then under the fixed oxygen concentration for 5 min at the experimental temperature before any stress was applied.

In the intermittent stress relaxation, the stress at time t, $f_i(t)$ was measured by the recorder immediately after the sample was stretched to the fixed extention ratio, $\alpha \sim 1.2$ and then returned at once to the unstrained state.

Estimation of sol fraction

Sol fractions were determined as follows: a degraded sample was immersed in benzene for 24 h at room temperature, the soluble part of rubber (sol) removed, and the remaining gel weighed after drying in vacuo. The sol fraction was estimated from the weight loss during degradation. In order to adopt the same initial condition as for the mechanical measurement, the sample preheated for 20 min was taken as the undegraded one.

Measurement of swelling

The gel sample obtained by the above method was also used for the swelling measurement. The sample was swollen in n-decane for 48 h at 25°C. The effective network chain density was calculated using the Flory–Rehner equation.

Analysis of stress relaxation

When the rubber vulcanizates are stretched by the constant strain at high temperature, the stress decay results mainly from the scission of networks. The scission occurs along the main chain, at the crosslink and/or on the main chain near a crosslink site. Analysis of stress relaxation of these samples was carried out using the method proposed by Kaeriyama, Ono and Murakami[9]. They reported that a relative stress $f_i(t)/f_i(\mathrm{o})$ in the intermittent relaxation measurement was connected with sol fraction by the following equations:

(i) Random scission along the main chain:

$$f_i(t)/f_i(\mathrm{o}) \sim f_s(t)/f_s(\mathrm{o}) = \left[\frac{1-S(t)^{1/2}}{1-S(\mathrm{o})^{1/2}}\right]^2 \qquad (1)$$

(ii) Scission of crosslinks:

$$f_i(t)/f_i(\mathrm{o}) \sim f_s(t)/f_s(\mathrm{o}) = \frac{[S(\mathrm{o})+S(\mathrm{o})^{1/2}][1-S(t)^{1/2}]^2}{[1-S(\mathrm{o})^{1/2}]^2[S(t)+S(t)^{1/2}]} \qquad (2)$$

(iii) Selective scission near crosslink sites:

$$f_i(t)/f_i(\mathrm{o}) \sim f_s(t)/f_s(\mathrm{o}) = \left\{\frac{1-[2S(t)]^{1/2}}{1-S(\mathrm{o})^{1/2}}\right\}^2 \qquad (3)$$

where, $S(\mathrm{o})$ and $S(t)$ are sol fractions at the degradation time $t=0$ and $t=t$, respectively, and $f_s(t)/f_s(\mathrm{o})$ is a relative stress obtained from the sol fraction measurement.

RESULTS AND DISCUSSION

Analysis of stress relaxation for samples 1, 2 *and* 3

Continuous stress relaxation of sample 1 was measured in different oxygen atmospheres at 140°C. The results (*Figure* 2) show that the rate of stress relaxation is strongly influenced by the oxygen content of the atmosphere. The kinetic study of these results will be presented in a subsequent paper. Firstly it is necessary to investigate how the scission occurs in the network under the condition of different oxygen concentration. *Figure* 3 shows the continuous and intermittent stress relaxation curves of sample 1 at 140°C under nitrogen. Faster stress decay at the initial stage in the continuous relaxation measurement is thought to be due to the exchange reaction of polysulphide crosslinkages, as described in the previous paper[7]. The occurence of the exchange reaction does not influence the effective chain density of the sample (*Figure* 4). This means that this reaction does not result in the increase of sol fraction. Dashed lines in *Figure* 3 are the relaxation curves ($f_s(t)/f_s(\mathrm{o})$ *versus* t) obtained from the sol fraction measurements by assuming the independent occurrence of the

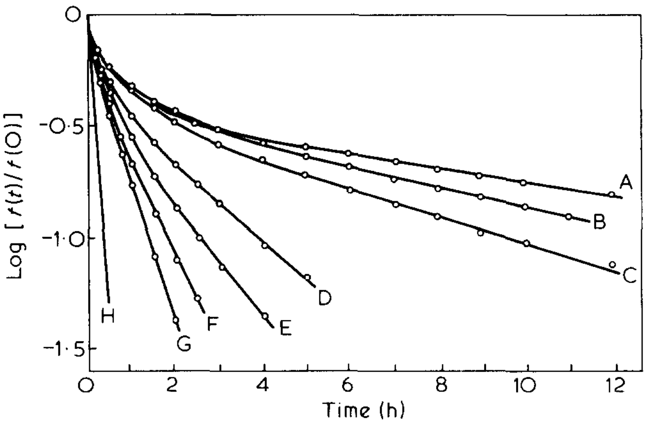


Figure 2 Continuous stress relaxation of sample 1 (curing time = 15 min, $n(\mathrm{o})$ = 1.15 x 10^{-4} mol ml^{-1}) in an atmosphere containing different amounts of oxygen at 140°C: A, under the nitrogen; B, 0.04 vol % O_2; C, 0.05 vol % O_2; D, 0.23 vol % O_2; E, 0.42 vol % O_2; F, 0.81 vol % O_2; G, 1.40 vol % O_2; H, in air

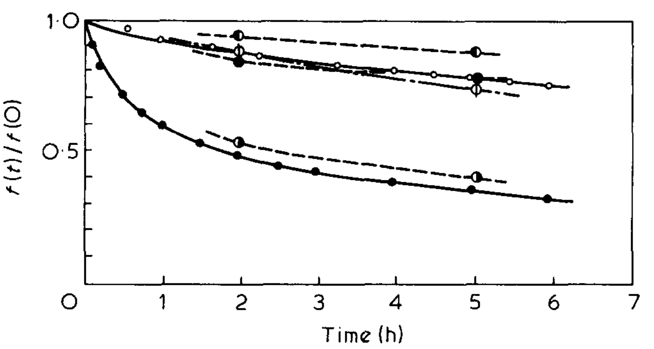


Figure 3 Analysis of stress relaxation for sample 1 (curing time = 30 min, n(o) = 1.48 10^{-4} mol $\min^{-1}$) under the nitrogen at 140°C. —●— Continuous stress relaxation; —○— intermittent stress relaxation ($f_i(t)/f_i(o)$). — — — — Relative stress ($f_s(t)/f_s(o)$) calculated from sol fraction; ◐, assuming random scission along the main chain (equation (1)); ◑, assuming scission at crosslink site (equation (2)); ●, assuming selective scission near crosslink site (equation (3)); — - -⊕- - — relative network chain density ($\nu(t)/\nu(o)$) estimated by swelling measurement.

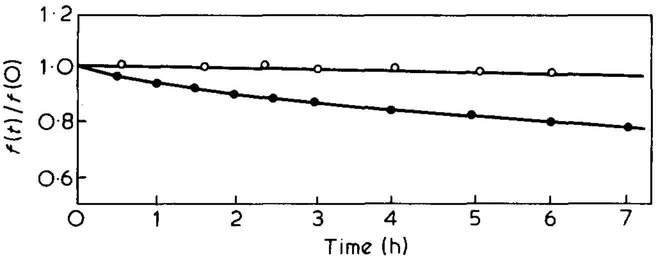


Figure 4 Continuous and intermittent stress relaxation of sample 1 under nitrogen at 100°C. —●— Continuous; —○— intermittent

scissions (i), (ii) and (iii). On the basis of the statistical theory of rubber-like elasticity, $f_1(t)/f_i(o)$ is equal to the ratio of effective network chain densities $\nu(t)$ and $\nu(o)$ which are estimated from the degree of swelling, viz.

$$f_i(t)/f_i(o) = n_i(t)/n_i(o) \sim \nu(t)/\nu(o) \qquad (4)$$

where, $n_i(o)$ and $n_i(t)$ are the chain densities at $t=0$ and $t=t$, respectively. In order to confirm equation (4), $f_i(t)/f_i(o)$ and $\nu(t)/\nu(o)$ were compared in *Figure* 3. The intermittent stress relaxation curve is in good agreement with $\nu(t)/\nu(o)$ and $f_s(t)/f_s(o)$ calculated on the assumption that scission of the polymer network occurred *near* the crosslink site. We have investigated the stress relaxation mechanisms of this curing system on the basis of the theory developed by Tobolsky[10], and concluded that the continuous stress decay in the nitrogen was caused by the scission at mono- and di-sulphide crosslinks and the exchange reaction of polysulphide linkages. Using Tobolsky's theory, we have not been able to distinguish between the scissions at and near crosslink. Later we will discuss why the scission in the nitrogen does not occur at the crosslink but on the main chain near the crosslink.

Under concentration up to ~0.30 vol.% oxygen (*Figure* 5(*a*)) the stress decay at the initial stage is attributed to the scission near the crosslink site, and then at the later stage it will be predominantely based on the random chain scission. However, in an atmosphere containing more than 1.0 vol.% oxygen the stress decay seems to be due to the random scission along the main chain over the time range studied, e.g. at 3.00 vol.% oxygen as shown in *Figure* 5(*b*). In the concentration from 0.30 to ~1.0 vol.% oxygen, the scission initially takes place near the crosslink site and along the main chain in the network at the same time, followed by the random chain scission at the later stage.

Figure 6 shows the continuous stress relaxation curves of sample 2 at several oxygen concentrations, 178°C. All the curves are represented by the sum of two exponential terms, as reported in the previous paper[7], that is, two different types of scission take place in the network. At such high temperatures the rate of stress relaxation in this

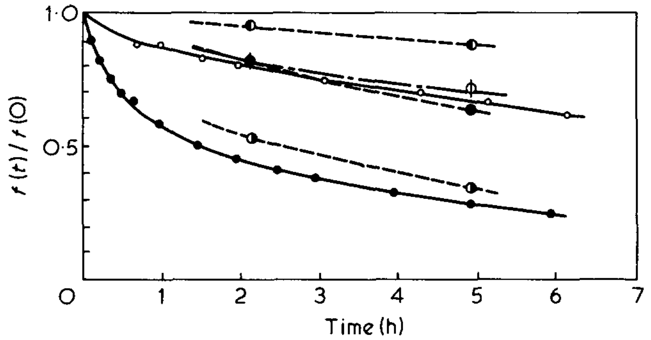


Figure 5(a) Analysis of stress relaxation for sample 1 in the atmosphere containing 0.28 vol % oxygen gas. Symbols as in *Figure 3*

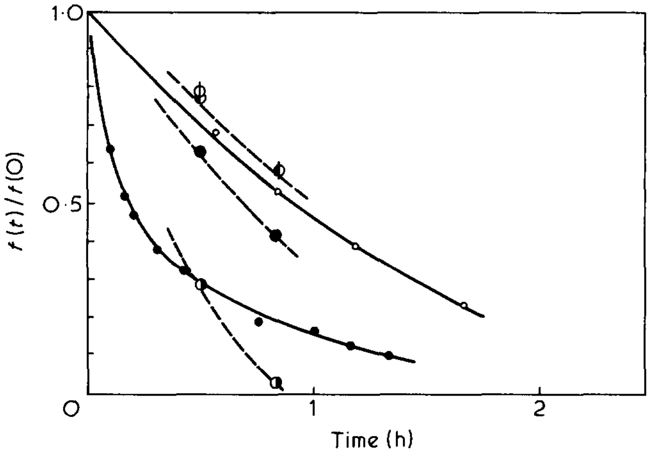


Figure 5(b) Analysis of stress relaxation for sample 1 in the atmosphere containing 3.00 vol % oxygen gas. Symbols as in *Figure 3*

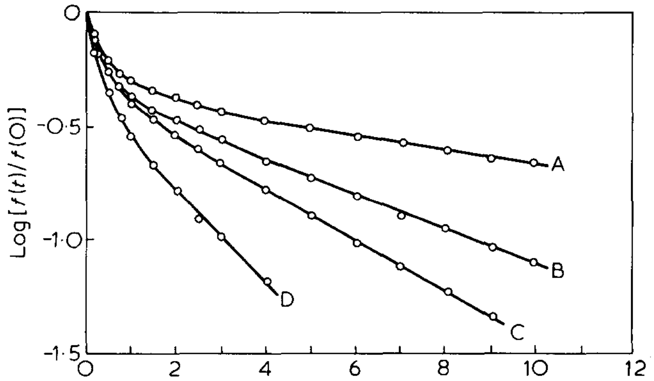


Figure 6 Continuous stress relaxation of sample 2 in the atmosphere containing different amounts of oxygen gas at 178°C.
A, Under nitrogen; B, 0.05 vol % O_2; C, 0.07 vol % O_2; D, 0.24 vol % O_2

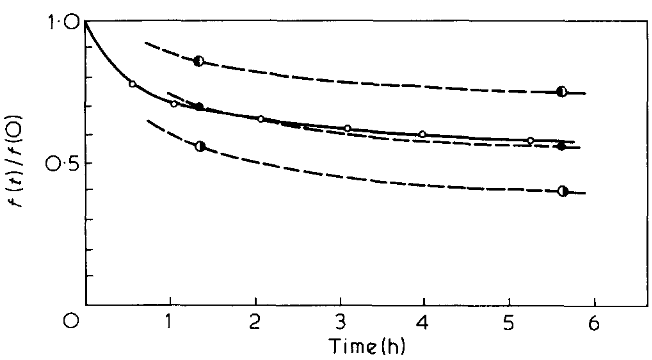


Figure 7(a) Analysis of stress relaxation for sample 2 under the nitrogen at 178°C. Symbols as in *Figure 3*

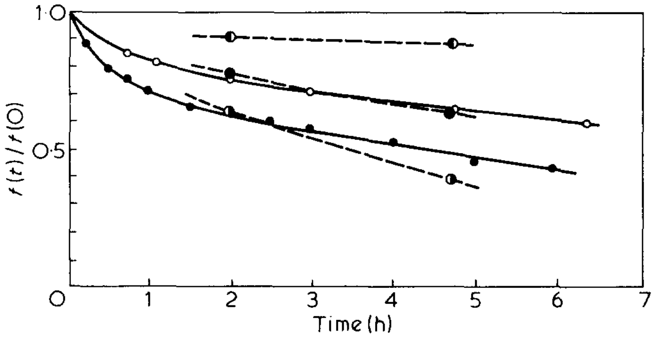


Figure 7(b) Analysis of stress relaxation for sample 3 under the nitrogen at 178°C. Symbols as in *Figure 3*

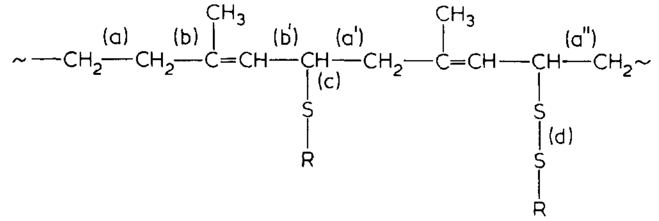
sample is greatly affected by a very small amount of oxygen gas in the atmosphere. The results of the analysis of intermittent stress relaxation of samples 2 and 3 in the nitrogen at 178°C (*Figure* 7(*a*) *and* (*b*)), show that the stress relaxation of both samples is caused by the scission near crosslinkages as with sample 1. However, the stress relaxation of sample 2 at the initial stage is faster than that of sample 3. This may be associated with the bond strength of main chain crosslinkages. The crosslinkage of sample 2 consists of the mono- and di-sulphide linkages, while that of sample 3 is mainly composed by the monosulphide linkage[11]. Probably, the carbon–carbon bond strength in the main chain near crosslinkages will be affected by the structure of crosslinkages. These considerations indicate that the faster stress decay of sample 2 at initial stage is due to the scission near disulphide crosslinks.

The results of the stress relaxation of sample 2 are shown in *Figure* 8(*a*) *and* (*b*). At oxygen gas concentrations below 0.03 vol.%, the stress decay of this sample at the initial stage is based mainly on the scission near crosslinks similar to that under nitrogen, whereas at the later stage it seems to be due to the oxidative scission along the main chain (*Figure* 8(*a*)). At concentrations of oxygen above 0.03 vol.%, the stress decay is preferentially based on the random scission along the main chain over the time range studied, although the rapid decay in the short time region may also be contributed to scission near crosslink sites. In the case of sample 3, the similar results were also obtained.

Mechansims of stress relaxation

Firstly, we consider why all the vulcanizates used undergo the thermal scission near crosslink sites in the nitrogen and at the early stage of degradation in the atmosphere containing a very small amount of oxygen gas. In the sample 1, mono- and di-sulphide linkages which are comparatively stable thermally, are formed by the exchange reaction of polysulphide crosslinks without any alteration in the number of effective network chain. The crosslink site of samples 2 and 3 originally consists of mono- and/or di-sulphide links and therefore, it can be considered that the intermittent stress relaxation in all the samples used here is due to the scission near mono- and/or di-sulphide crosslinks.

The bond dissociation energies of these vulcanizates are as follows;



$$\sim CH_2-CH_2-\overset{CH_3}{C}=CH-\underset{\underset{R}{|}}{\underset{S}{\underset{|}{CH}}}-CH_2-\overset{CH_3}{C}=CH-\underset{\underset{\underset{R}{|}}{\underset{S}{|}}}{\underset{S}{\underset{|}{CH}}}-CH_2\sim$$

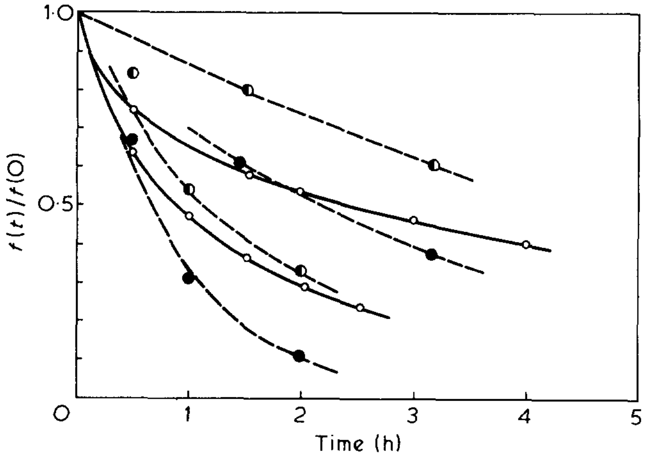


Figure 8(a) Analysis of stress relaxation for sample 2 in the atmosphere containing oxygen gas: a, 0.05 vol % O_2; b, 0.27 vol % O_2. Symbols as in *Figure 3*

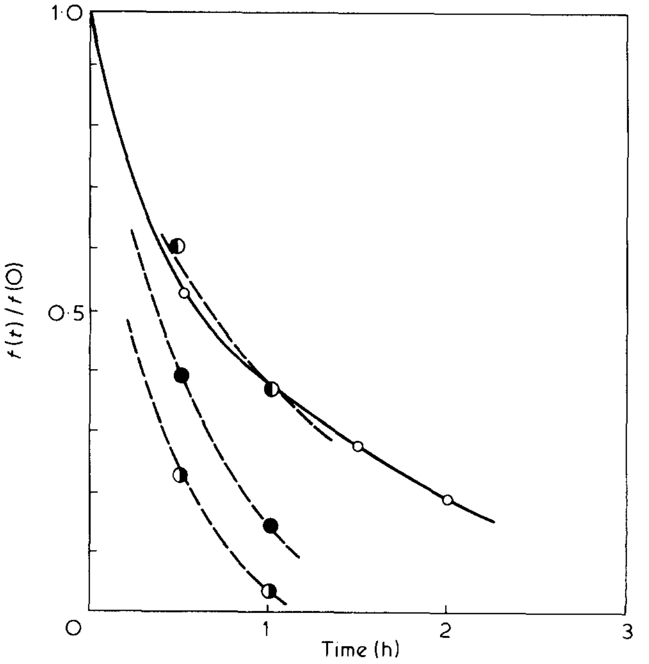
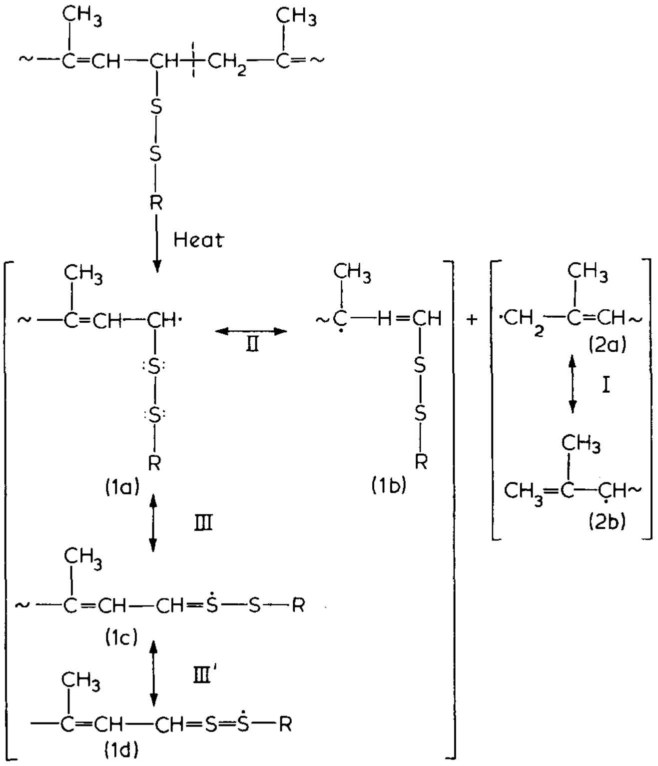


Figure 8(b) Analysis of stress relaxation for sample 2 in the atmosphere containing 0.45 vol % O_2. Symbols as in *Figure 3*

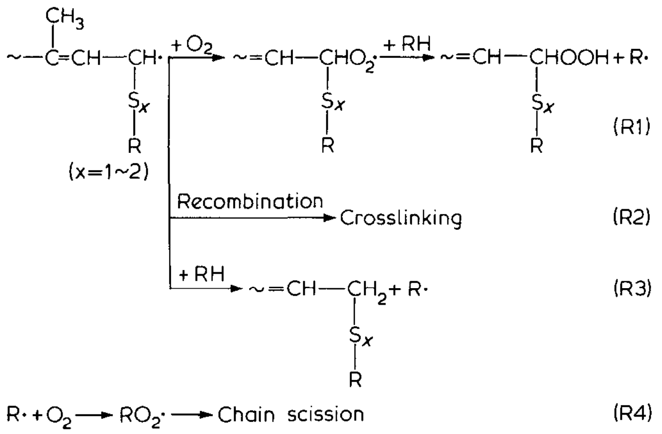
(a) 93 kcal/mol
(a′)unknown
(a″)unknown
(b), (b′) 90~93 kcal/mol
(c)50~60 kcal/mol[12]
(d)25~40 kcal/mol[13~15]

where R represents the polyisoprene chain. If these values only are considered, the scission should take place at the crosslink, which is contrary to the results observed. If the scission occurs on the main chain adjacent to a crosslink, the following radicals will be produced:



This corresponds to cleavage at the carbon–carbon bonds ((a′) and/or (a″)) in β position to the double bond. The radicals produced can resonate between the different structures, and accordingly the energy to break respective bonds ((a′) or (a″)) will be smaller than is normal for bond ((a)). However, if the scission occurs at mono- and disulphide crosslinks, such resonances cannot be depicted without the formation of allyl radicals, which will be produced by the scission of monosulphide linkages. Although the energies to break the carbon–carbon bonds [(a′) and (a″)] nearest to the crosslinks cannot be estimated accurately since the resonance energy of the radicals 1a, 1c and 1d are not known, these positions can be expected to become to somewhat weaker than the monosulphide (carbon–sulphur bond) and/or disulphide (sulphur–sulphur bond). Consequently, the results obtained in the present work seems to be reasonable. The rate of stress relaxation of sample 2 at the initial stage is faster than that of sample 3 (*Figures* 7(*a*) and 7(*b*)). This is attributable to the difference of crosslinking structures between the two samples. The number of resonance structures of the radicals is greater in the case of the scission near disulphide than monosulphide crosslinks. Therefore, the scission near the disulphide crosslink site will occur preferentially at the early stage. The faster stress relaxation of sample 2 results for this reason.

At high temperatures and very low oxygen concentration, except in the initial stage of degradation, these vulcanizates undergo random scission along the main chain (*Figures* 5(*b*) and 8(*b*)). The scission under such conditions should be thought to occur firstly near the crosslink site as in nitrogen, followed by the oxidative scission along the main chain. The degradation mechanism is:



Because of a very small amount of oxygen gas, the reactions (R1) and (R4) may be limited and further will be strongly controlled by the diffusion of oxygen[16]. Consequently at the later stage the stress relaxation curve (log f/f_0 *versus* t) of these samples is represented by a straight line as shown in *Figures* 2 and 6.

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