Chemorheology of irradiation-cured natural rubbers: 3. Stress relaxation mechanisms in nitrogen at elevated temperature

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Chemorheological studies were carried out on three kinds of natural rubber vulcanizates, differing in the structure of their crosslinks, in nitrogen in the temperature range 100° to 230°C. The crosslinking site in these polymers consists of a carbon–carbon bond (sample 1), a carbon–sulphur–carbon bond (sample 2), and carbon–carbon and carbon–sulphur–carbon bonds (sample 3), respectively. The stress decay curve of all the samples was expressed by the sum of two exponential terms, that is, two different scission reactions took place in the polymer networks at the same time. Sample 1 underwent two different random scissions in the main chains above 180°C: one was the oxidative scission due to the oxygen molecules in the sample and the other was the thermal scission involving the peroxy and/or carbonyl groups on the polymer chains. The stress decay of sample 2 was based on the cleavages of two different types of crosslink which were mono- and disulphide linkages, whereas that of sample 3 was attributed to the scission both of crosslinkages and of the main chain. The scission of crosslinkages occurred at lower temperatures (above 120°C).

INTRODUCTION

In parts 1[1] and 2[2], stress relaxation mechanisms were investigated for various curing systems in natural rubbers, especially the complex crosslinking systems such as irradiation cures containing tetramethylthiuram disulphide (TMTD) or sulphur (S) in air at temperatures of 100° to 140°C. The main cause of the stress decays of these curing systems was due to the random oxidative scission on the main chain. We also concluded in part I that the stress relaxation in nitrogen was based on the thermal scission at crosslinkages. However, this conclusion was found to be incorrect, from the detailed study in the present paper.

Many studies of the thermal degradation of rubbers have been carried out at very high temperatures, above 500°C, by using other experimental techniques, e.g. pyrolysis–gas chromatography[3–5]. In this case, the low molecular weight compounds are produced during a short period of time. On the other hand, there are only a few studies[6–9] of thermal degradation of rubber vulcanizates in the range of comparatively lower temperatures from 100° to 250°C, which we call the intermediate temperature range. The volatile products of low molecular weight seem scarcely to be produced by the thermal degradation in this temperature range. The degradation mechanisms at the intermediate temperature will be significantly different from those at very high temperatures. The stress relaxation method is very convenient for investigating the initial stage of thermal degradation in the intermediate temperature range, because the other analytical methods, for example, i.r., n.m.r. etc., cannot detect the structural change in the initial stage of thermal degradation of rubber vulcanizates.

The purpose of the present paper is to reveal the stress relaxation mechanisms based on the thermal degradation of some irradiation-cured natural rubbers having different crosslinked structures, in the temperature range of 100° to ~230°C under the nitrogen.

EXPERIMENTAL

Natural rubber (NR-RSS-1) was cold milled with curing ingredients under the conditions described in *Table 1*. Sheets (about 0.5 mm) of milled polymer were pressed at 200 kg/cm^2 and 145°C. Samples 1 and 3 were prepared by γ-irradiation from a ^{60}Co source at room temperature. Sample 2 was tetrathiuram disulphide cured. Sample 3 was prepared by exposing sample 2 to γ rays. The crosslinking site in these samples consists of a carbon–carbon bond for sample 1, mono- and disulphide linkages for sample 2, and carbon–carbon bond and mono- and disulphide linkages for sample 3, respectively. All the samples were extracted with hot acetone for 48 h and dried *in vacuo*.

Details of stress relaxation methods were described in the part 1[1]. Continuous stress relaxation was measured at temperatures of 100° to 230°C under the nitrogen.

RESULTS AND DISCUSSION

Figure 1 shows the stress relaxation curves (the logarithm of relative stress, $\log f(t)/f(0)$, *versus* time, t) of sample 1 at

Table 1 Preparation of natural rubber vulcanizates

Sample	No. 1	No. 2	No. 3
Rubber	100	100	100
Tetramethylthiuram disulphide (TMTD)		3	3
Zinc oxide		5	5
Stearic acid		2	2
Hot press curing at 145°C min	10	10	10
Irradiation-curing	a		a

a Total dose: 12, 28.8 and 43.2 Mrad

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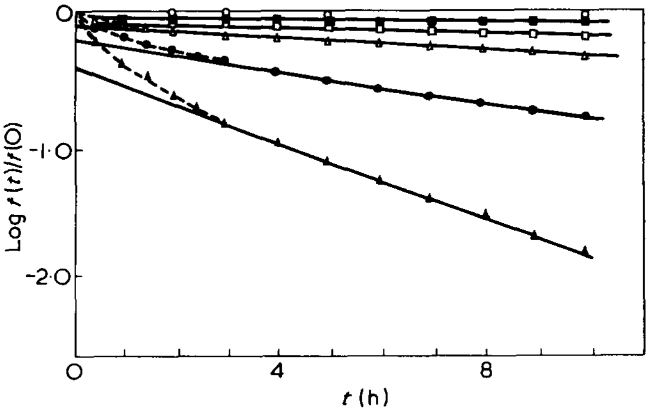

Figure 1 Temperature dependence of stress relaxation under nitrogen for sample 1 prepared by radiation of 28.8 Mrad: ○, 99.3°C; ■, 159°C; □, 180°C; △, 200°C; ●, 218°C; ▲, 233°C

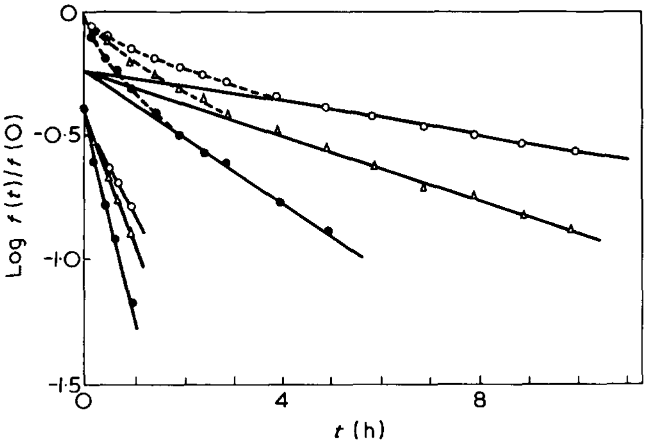

Figure 2 Stress relaxation of No. 1 samples of differing initial chain density at 233°C under nitrogen. ●, Irradiation dose = 12 Mrad, $N(0) = 0.64 \times 10^{-4}$ mol/ml; △, 28.8 Mrad, 1.28×10^{-4} mol/ml; ○, 43.2 Mrad, 1.54 mol/ml

temperatures of 100° to 233°C under nitrogen. It is found that the rate of stress relaxation is constant, independent of temperature, up to 180°C. Also, this did not significantly depend on the initial chain density, $N(0)$. Therefore, the slight stress decays in this temperature range are probably caused by the physical stress relaxation originating from chain entanglements. That is, the scission reaction of main chains and/or crosslinkages does not occur.

The stress relaxations above 180°C show a temperature dependence. This suggests that above this temperature, any scission reactions occur in the network of this vulcanizate. It can be seen from *Figure 1* that all stress relaxation curves at temperatures from 180° to 230°C decay rapidly in the short time region and then become linear. If we use the procedure described in the previous paper[1], these curves are divided into two straight lines expressed by:

$$f(t)/f(0) = A\exp(-k_A t) + B\exp(-k_B t) \qquad (1)$$

where k_A is the rate constant of stress relaxation in the long time region and k_B is the rate constant in the short time region. This is different from the stress relaxation behaviour in the air, i.e. the relaxation of sample number 1 was expressed by a exponential term, in the whole time scale region[1]. The stress relaxation of 3 number 1 samples having different initial chain densities was measured at 233°C. The results are given in *Figure 2*. In the both regions of short and long times, the rate of stress relaxations decreases with increasing $N(0)$. This is a typical case of main chain scission[2]. The slope of each relaxation curve in *Figure 1* gives the rate constant of the main chain scission reaction which is expressed by the Arrhenius equation. The temperature dependence for the sample 1 prepared by a γ radiation dose of 28.8 Mrad is plotted as log k_A (or log k_B) *versus* $1/T$ (K) in *Figure 3*.

From the slope of the straight line the apparent activation energy for the sample 1 was calculated to be about 27 kcal/mol either in the short or long time regions. These values are much lower than those obtained by Takahashi and Tobolsky[6]. They have reported that the activation energy of the stress relaxation, based on the thermal chain scission of natural rubber vulcanizates, is 55 kcal/mol independent of the chemical structure of the crosslinks. However, their calculation is not correct. We found from the recalculation of their data that the correct value of the activation energy was about 30 kcal/mol and similar to ours. This value of activation energy, however, does not seem to be appropriate as the energy for the 'thermal' scission of main chain. Generally, the energy for the network chain scission of the diene rubbers is said to be between 50 and 55 kcal/mol[10,11]. In fact, we have also obtained[12] a similar value for the isothermal degradation of polyisoprene vulcanizates in the temperature range 250° to 330°C, using thermogravimetric analysis. Now we need to investigate carefully the effects of the oxygen molecules dissolved in the samples, the peroxides formed in the polymer chain when the vulcanizates are prepared and a small quantity of oxygen molecules in the nitrogen gas. First, we carried out the stress relaxation measurements on sample 1 after different preheating times. Before the sample was extended to a certain ratio, it was held at the test temperature for the time taken to break down the network chain in the short time region in *Figure 1*, i.e. for 140 min at 200°C and for 210 min at 218°C. The result is shown in *Figure 4*. It is found that the relaxation is expressed by a straight line, that is:

$$f(t)/f(0) = A'\exp(-k'_A t) \qquad (2)$$

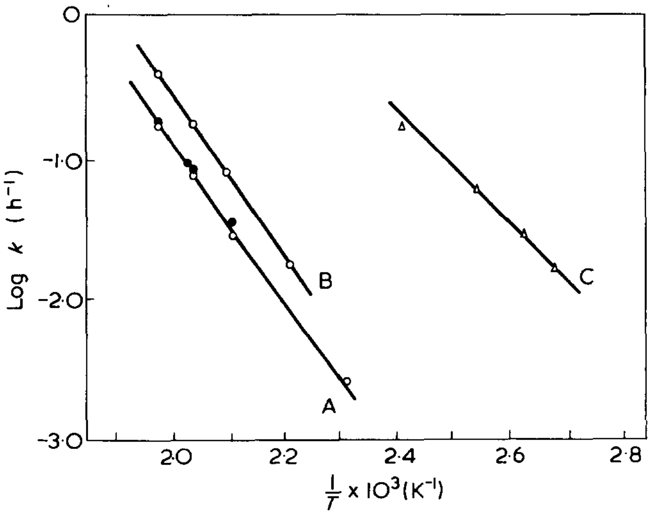

Figure 3 Relation between rate constant (log k) of stress relaxation and temperature ($1/T$) for sample 1 prepared by radiation of 28.8 Mrad. A, K_A, 27 kcal/mol; B, K_B, 26 kcal/mol; C, 20 kcal/mol. A and B in nitrogen; C, in air

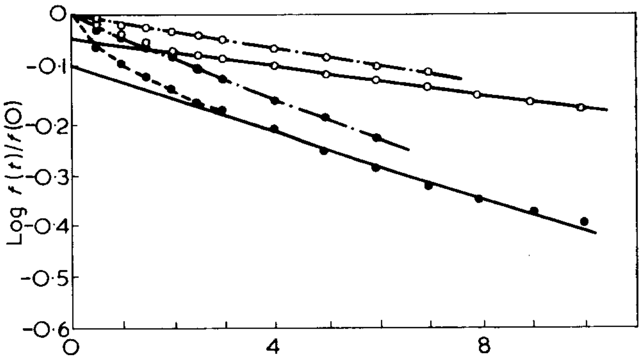

Figure 4 Effect of preheating time for stress relaxation of sample 1 prepared by radiation of 28.8 Mrad. ○, 200°C; ●, 218°C; ——, preheating time = 20 min; —·—·—; 140 min at 200°C and 210 min at 218°C

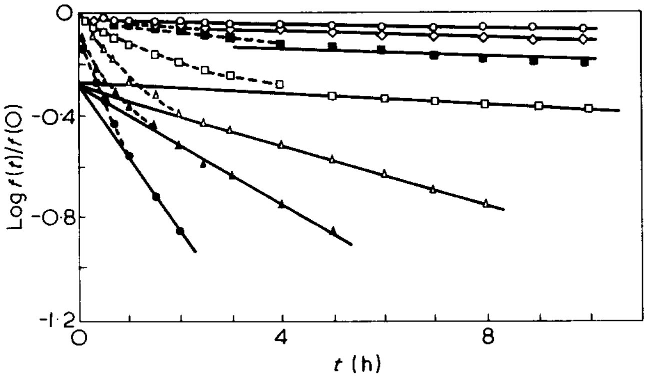

Figure 5 Temperature dependence of stress relaxation under nitrogen for sample 2: ○, 99°C; ◇,120°C; ■, 140°C; □, 160°C; △, 180°C; ▲, 200°C; ●, 230°C

Of course, the gradient (k'_A) of these straight lines is larger than that of the original stress relaxations (preheating time 20 min), because of the decrease of network chain density $N(0)$ from 1.28 x 10^{-4} mol/ml to 0.91 x 10^{-4} mol/ml based on the chain scission during preheating. However, the activation energy of the stress relaxations obtained here did not depend on the preheating time (see *Figure 3*). This means that two different scission reactions occur independently along the main chain.

Further, we investigated the effect of the film thickness for the stress relaxation of sample 1. The films of 0.03–0.14 cm thickness were moulded by pressing for 10 min at 200 kg/cm^2 and 145°C, and cured by γ irradiation of 28.8 Mrad. The initial network chain density of each sample was shown to be substantially the same (about 1.28 x 10^{-4} mol/ml) by stress–strain measurement. The stress relaxation decays at 200° and 233°C under the nitrogen atmosphere were not affected by the thickness. Recently, Ono *et al.*[13] have studied the effects of diffusion in the oxidative degradation of polyisoprene vulcanizates using the stress relaxation method. In these the oxidation of vulcanized rubber films is strongly controlled by the diffusion of oxygen. The above results suggest that the stress decay shown in *Figure 1* is not based on the oxidative cleavages of the network chain by the oxygen molecules in the nitrogen. The stress relaxation in the longer time region may be caused by any 'thermal' scission occurring through the peroxy and/or carbonyl groups on the polymer chains. Therefore, the apparent activation energy of the thermal network scission will be lower compared with that estimated by the other methods. In the short time region the faster stress decay may be based on the oxidative degradation of polymer networks by the oxygen molecules contained in the polymers. We cannot give definite evidence for the above description using analytical methods such as i.r., n.m.r. etc., since the concentration of the peroxy and carbonyl groups on the main chain is too low to be detected by these instruments.

The stress relaxation curves for sample 2 at various temperatures are shown in *Figure 5*. The stress decay of this sample is also expressed by the sum of two exponential terms as is the case for sample 1. The faster stress relaxation in the short time region, however, appears at the lower temperature compared with that of sample[1]. As shown in *Figure 6*, the stress relaxations of 2 number 2 samples having different initial chain densities $N(0)$, were in agreement with each other over the whole time scale. This suggests that the stress relaxation of this sample in nitrogen is based on the scission of crosslinks, contrary to that of sample 1. In the longer time region, the rate of stress relaxation of sample 2 is almost the same at temperatures of 100° to 160°C. That is, any scission reaction in the polymer network does not occur in this temperature range. In part 1 of this series, we suggested that the stress decay of sample 2 at 100°C was due to the thermal scission of the crosslinks. We must now correct the hypothesis in the part 1. At this temperature, the stress decay in the nitrogen is caused only by the physical relaxation. The rate of the stress relaxation in the longer time region increases with an increase in temperature above 160°C, that is, the scission reaction of crosslinks occurs.

The relation of the rate constant log k_A (or log k_B) (h^{-1}) *versus* $1/T$ (K^{-1}) is shown in *Figure 7*. The values of the activation energies are about 17 and 24 kcal/mol for the stress relaxations in the short (k_B) and the longer time (k_A) regions, respectively. As described above, the crosslinking site of sample 2 consists of mono- and di-sulphide. The monosulphide linkages are thermally more stable compared with disulphide. Therefore, it may be presumed that the value of 17 kcal/mol is the value of the activation energy of the stress relaxation based on the scission of disulphide linkages and 24 kcal/mol is that of monosulphide linkages. These activation energies are also considerably lower than the bond energies of C–S (54 kcal/mol) and S–S (27 kcal/mol) which were obtained by Ossefort[10]. This may therefore be attributed to the occurrence of a few oxidative scissions together with the thermal reaction of the crosslinks.

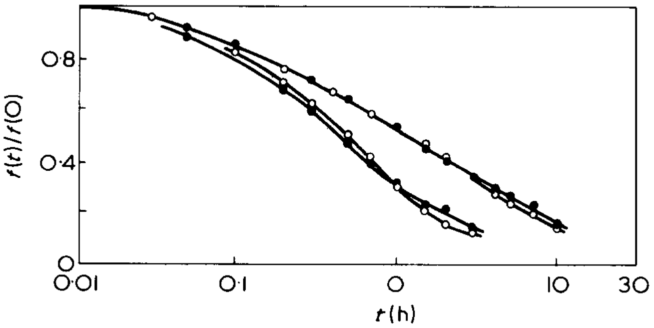

Figure 6 Stress relaxation of No. 2 samples having different initial chain densities: ●, curing time 10 min at 145°C, $N(0)$ = 1.03 X 10^{-4} mol/ml; ○, curing time 30 min at 145°C, $N(0)$ = 1.24 X 10^{-4} mol/ml

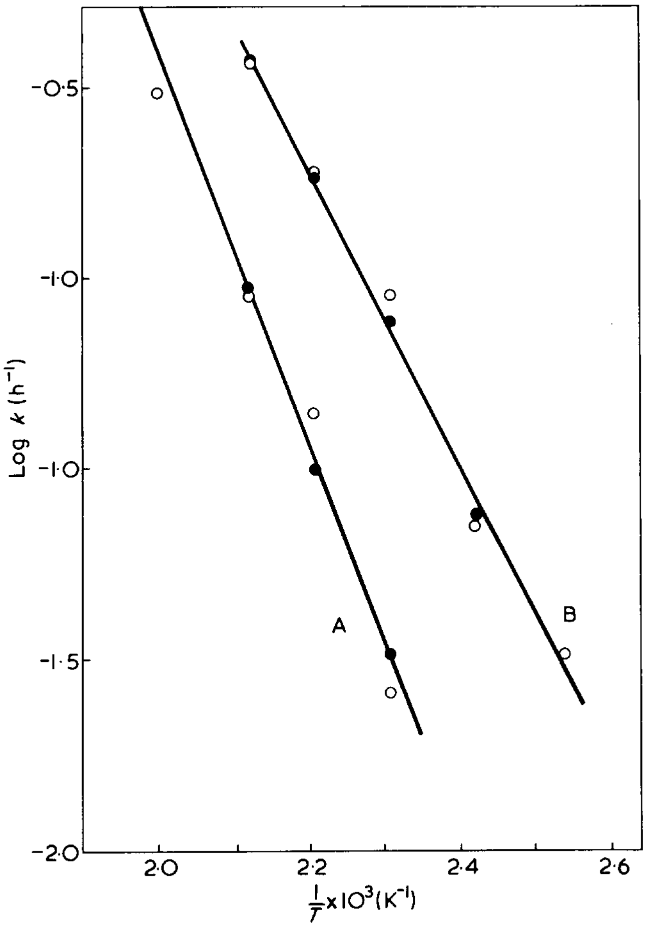

Figure 7 Relation between rate constant (log *k*) of stress relaxation and temperature (1/*T*) of No. 2 samples: ●, curing time 10 min at 145°C; ○, curing time 30 min at 145°C. A, k_A, 24 kcal/mol; B, k_B, 17 kcal/mol

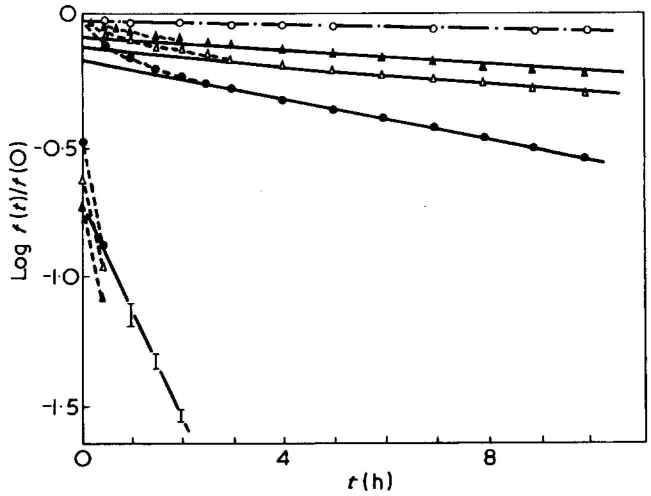

Figure 8 Stress relaxation of No. 3 samples differing initial chain density at 200°C under nitrogen. ○, for all the samples at 100°C; ●, irradiation dose = 12 Mrad, *N*(0) = 1.47 mol/ml; △, 28.8 Mrad, 1.72 mol/ml; ▲, 43.2 Mrad, 2.10 mol/ml

Figure 8 shows the stress relaxation curves at both 100° and 200°C for 3 number 3 samples having different initial chain densities *N*(0). The stress relaxation at 100°C is represented by a straight line independent of *N*(0), whereas that at 200°C is expressed by the sum of two exponential terms in the same way as in the case of the other samples. The stress decay in the short time region does not seem to be significantly dependent on *N*(0). On the other hand, the stress decay in the longer time region depends on *N*(0). This suggests that in the case of sample 3 in which the crosslinking sites consist of carbon–carbon bonds and mono- and disulphide linkages, the stress decay in the short time region is based on the cleavage of the crosslinks and that in the longer time region originates from the random scission of the main chains. The temperature dependence of stress decay for sample 3, which was prepared by a γ irradiation dose of 28.8 Mrad is shown as the rate constant log k (h^{-1}) *versus* $1/T(K^{-1})$ in *Figure 9*. The apparent activation energy is 14 kcal/mol for the crosslink scission and 25 kcal/mol for the main chain scission. These values are a little lower than the ones obtained for samples 1 and 2.

In conclusion, we suggest that the stress relaxation in nitrogen for all the crosslinking systems used here is attributed to two different scission reactions occurring in the polymer network at the same time. The site of the scission is dependent on the crosslinking structure. For the network with carbon–carbon crosslinks (sample 1), two different random scissions occur along the main chain: one is the oxidative cleavage of polymer networks due to the oxygen molecules which is a cause of faster stress decay in the short time region, and the other is the 'thermal' scission occurring under the influence of carbonyl and hydroperoxy groups on the main chain, which originates the stress decay in the longer time

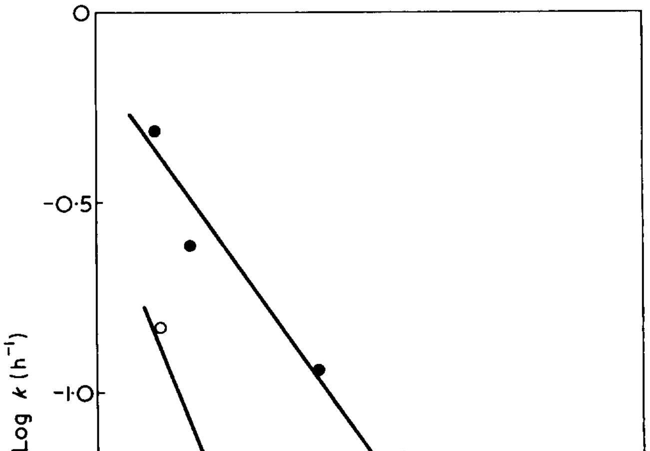

Figure 9 Relation between rate constant (log *k*) of stress relaxation and temperature (1/*T*) for sample 3 prepared by radiation of 28.8 Mrad. A, k_A, 25 kcal/mol; B, k_B, 14 kcal/mol

Table 2 Stress relaxation mechanisms in nitrogen of natural rubber vulcanizates

		Origin of stress relaxation					
		Temperature (°)					
Curing systems	Structure of crosslinks	$T < 80$	$T < 120$	$T < 180$	$T > 180$	Activation energy (kcal/mol)	Bond energy[10,11] (kcal/mol)
Irradiation cure (Sample 1)	C–C	Physical	Physical	Physical	Random scission on the main chain	26 27	50~65
Sulphur cure	$C–S_x–C$ $C–S_2–C$ $C–S_1–C$		Interchange of polysulphide	Interchange of polysulphide Scission of crosslinks	Interchange of polysulphide Scission of crosslinks	13[7] 18[7]	27
TMTD cure (Sample 2)	$C–S_2–C$ $C–S_1–C$	Physical	Physical	Scission of crosslinks	Scission of crosslinks	17 24	27 54
Irradiation–TMTD cure (Sample 2)	C–C $C–S_2–C$ $C–S_1–C$	Physical	Physical	Scission of crosslinks	Both scission of the main chain and of crosslinks	25 14	

region. It can be expected that such functional groups, through very low concentration, will affect the thermal scission of networks. Therefore, lower apparent activation energies for the thermal degradation seem to be obtained. The scission for the network with carbon–sulphur–carbon crosslinks (sample 2) take place at the crosslinks. The case of the network with carbon–sulphur–carbon and carbon–carbon crosslinks (sample 3) undergoes both scissions at the crosslinks and along the main chains. The stress decay of samples 2 and 3 is also subject to the effect of oxygen molecules and carbonyl and hydroperoxy groups in the polymer. These influences for the thermal degradation of diene rubber vulcanizates will be investigated in some detail elsewhere, using the other analytical methods[12].

Finally the degradation mechanisms in nitrogen of natural rubber vulcanizates differeing in their crosslinking structures are summarized in *Table 2* with the apparent activation energy of stress relaxation.

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