Thermo-oxidative ageing and its effect on the network structure and fracture mode of natural rubber vulcanizates

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(*Received* 21 *June* 1982; *revised* 2 *December* 1982)

The changes in network structure and fracture mode of unfilled and filled natural rubber vulcanizates, during ageing at 100°C have been studied by chemical analyses and scanning electron microscopy. The fall in properties during ageing is caused mainly by chain scission. The increase in crosslink density during the initial periods of ageing causes an increase in modulus and tensile strength. Carbon black accelerates ageing, probably by surface catalysis. The simple network structure of efficiently vulcanized rubber results in better retention of properties during ageing. Antioxidant retards ageing. The extent of degradation of vulcanizates is reflected in the nature of the fracture surfaces. The roughness of the tensile fracture surface is affected to varying degrees depending upon the ageing resistance of the vulcanizates. However, in tear, the mode of fracture propagation is affected by ageing.

Keywords Ageing; natural rubber; network structure; fracture; scanning electron microscopy

The presence of a high level of unsaturation in a natural rubber (NR) molecule makes it highly susceptible to attack by oxygen. Several factors like heat, light, presence of pro-oxidants and mechanical strain accelerate the oxidation process. Among these, the effect of heat is the most significant. During service a number of rubber products are subjected to varying levels of heat, generated as a result of either cyclic mechanical strain as in the case of a running tyre or high ambient temperature. Prolonged exposure to heat causes thermo-oxidative degradation of rubber and results in the deterioration of its desirable properties, eventually leading to premature failure. A few recent reviews[1-3] have outlined most of the developments in the studies on ageing of rubber. Thermo-oxidative ageing of rubber is believed to occur in two ways[4], either via main chain scission or crosslink scission. Veith[5], Tobolsky[6] and Horikx[7] have suggested that only main chain scission occurs during ageing and a later study by Dunn and Scanlan[8] has confirmed this idea. But developments in the structural characterization of natural rubber vulcanizates[9] have led Colclough and coworkers[4] to study the oxidative ageing of rubber in more detail and they have reported the occurrence of crosslink scission during ageing. Blackman and McCall[10] have reported the structural changes in NR vulcanizates during thermal ageing and their effect on fatigue life. One of the objectives of the present study is to correlate the changes in tensile properties and tear resistance of NR vulcanizates during ageing with the changes in their network structure, including the extent of main chain scission.

In recent years fracture of rubber has been gaining attention and various studies on fracture have been reported[11-15]. These theoretical studies are now being supplemented by microscopic observations of the fracture surfaces[16-20]. Scanning electron microscopy (SEM) has been used to correlate the strength of the rubber with its fracture surface topography. It is well known that the weakening of the rubber matrix during ageing affects its failure properties. Hence the second objective of the present work is to study the effect of thermo-oxidative ageing on the fracture mode of rubber using SEM.

The parameters included in this study are: (1) the effect of vulcanizing system, (2) the effect of reinforcing carbon black, and (3) the effect of antioxidant.

EXPERIMENTAL

The various vulcanizates were prepared from a single bale of NR (ISNR-5) according to the formulations given in *Table 1*. Mixing was done in a two-roll laboratory mill and vulcanization to optimum cure was carried out in a hydraulic press having electrically heated platens. Optimum cure times of the mixes were determined using Monsanto rheometer R-100. Sheets of 2.2±0.1 mm thickness were moulded and, after a conditioning period of 24 h, tensile and tear test specimens were cut from the sheets along the grain direction. Ageing of the test specimens was done in a Blue M F.C 712 model hot air oven at 100°C. The test specimens were withdrawn from the oven at different intervals and, after conditioning for 24 h, were tested for tensile and tear properties. The samples were also subjected to chemical analyses. The tensile test was carried out as per ASTM designation D 412-51T using the C-type dumb-bells. Tear resistance was determined according to ASTM designation D 624-48 using the unnicked, 90° angle test specimen. A line drawing of the tensile and tear test specimens is given in *Figure 1*. Both the tensile and tear tests were carried out using a Zwick tensile testing machine at a pulling rate of 500 mm min^{-1} at room temperature (30°C).

0032-3861/83/081042-13$03.00
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Table 1 Formulations of the mixes

Ingredients	Mix number A	B	C	D	E	F	G	H
Natural rubber[a]	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
PBNA[b]	–	1	–	1	–	1	–	1
HAF black (N 330)	–	–	–	–	50	50	50	50
Naphthenic oil	–	–	–	–	5	5	5	5
CBS[c]	0.6	0.6	3.5	3.5	0.6	0.6	3.5	3.5
Sulphur	2.5	2.5	0.5	0.5	2.5	2.5	0.5	0.5
Optimum cure time at 150°C (min)[d]	11.0	12.0	18.0	17.0	10.5	12.0	9.0	8.0

[a] Crumb rubber, ISNR 5 grade, obtained from the Rubber Research Institute of India, Kottayam
[b] Phenyl-β-naphthylamine (Accinox DN), as supplied by the Alkali and Chemical Corporation of India Ltd, Rishra
[c] *N*-Cyclohexylbenzothiazyl sulphenamide (Accicure HBS), as supplied by the Alkali and Chemical Corporation of India Ltd, Rishra
[d] Obtained from Monsanto rheometer R-100

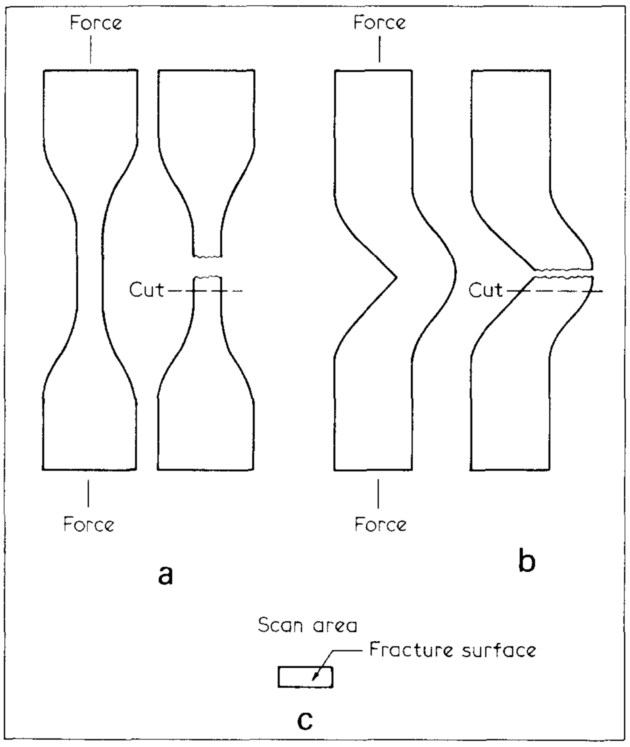

Figure 1 (a) Tensile test specimen before and after testing. (b) Tear test specimen before and after testing. (c) Fracture surface, cut from the failed test pieces

Chemical characterization

The test procedures used for the structural characterization of the vulcanizates were the same as those described by Saville and Watson[9] and later used in our earlier work[19].

The extent of main chain scission was assessed by measuring the sol content of the samples following the method used by Bristow[21]. The method consisted of extracting the specimen with cold acetone in the dark for 12 days. After drying *in vacuo* to constant weight, the specimens were extracted with cold benzene in the dark for 10 days. After this the samples were dried *in vacuo* at 60°C. The sol content was calculated from the weight loss due to benzene extraction.

Scanning electron microscopy

The fracture surfaces were carefully cut from the failed test pieces, as illustrated in *Figure 1*, without disturbing the surfaces and were sputter coated with gold within 24 h of testing. The SEM observations were made within one week after gold coating. A Philips 500 model scanning electron microscope was used for making the observations. The fracture specimens were stored in a desiccator both before and after gold coating till the SEM observations were made. From our preliminary studies we have found that storage of fracture specimens up to a period of one week before gold coating and up to a period of one month after gold coating does not alter the fracture surface topography as observed in SEM. *Figures 14* and *16–19* show micrographs taken near the edge of the fracture surface because it was near the edge of the unfilled vulcanizates (tensile fracture) that maximum changes were observed. However, in the case of the filled vulcanizates and in the case of the tear fracture surfaces of all vulcanizates the surface characteristics were uniform throughout.

RESULTS AND DISCUSSION

The changes in tensile strength of the unfilled and filled vulcanizates with respect to the period of ageing are given in *Figures 2* and *3* respectively. In the case of the unfilled conventional vulcanizate, there is a progressive drop in tensile strength after 6 h of ageing, whereas the addition of 1 phr (part per hundred rubber) of phenyl-β-naphthylamine (PBNA) to the same mix causes the tensile strength to increase up to a period of 12 h and then to drop. The rate of fall in tensile strength is almost the same in both cases, although the absolute values are always higher for the vulcanizate containing the antioxidant. In the case of the efficient vulcanizing (EV) mix, the tensile strength increases to a maximum and then drops, although the extent and rate of decrease are much less pronounced than in the conventional vulcanizates. The effect of antioxidant is more or less similar to that in the conventional vulcanizate, although the actual difference between the absolute values, caused by the presence of antioxidant, is different in the two cases. From *Figure 2* it appears that the antioxidant is almost twice as effective in the conventional system as in the EV system. The incorporation of carbon black affects the ageing behaviour appreciably, as is clearly shown in *Figure 3*. In

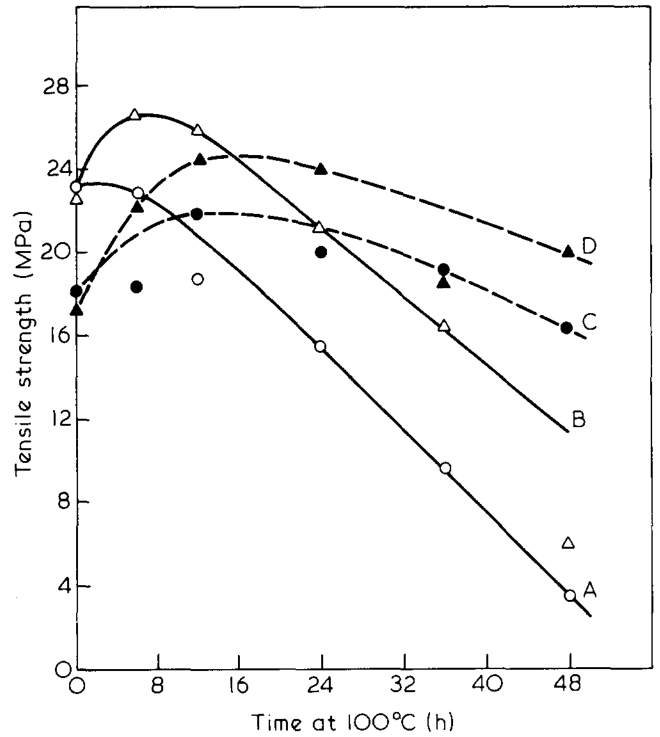

Figure 2 Changes in tensile strength of unfilled vulcanizates during ageing

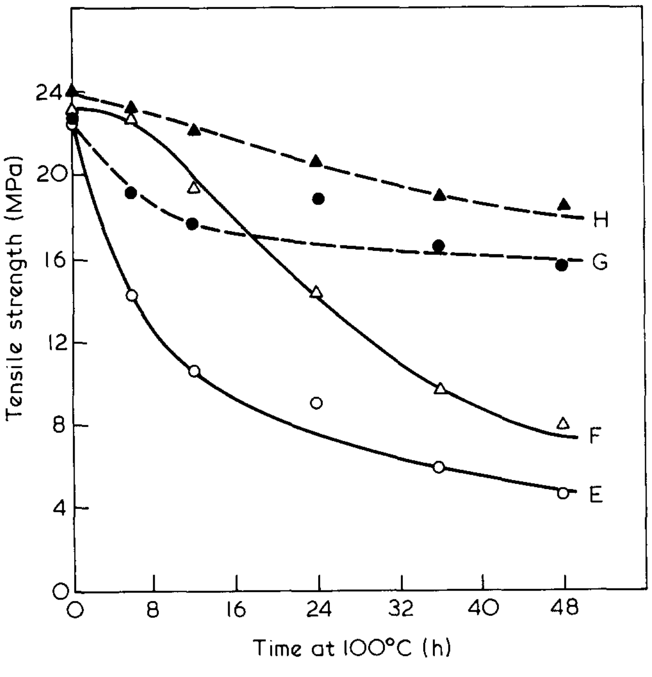

Figure 3 Changes in tensile strength of filled vulcanizates during ageing

all cases a drop in tensile strength occurs right from the beginning of ageing. The decrease is abrupt in the early stages of ageing for the conventional vulcanizates, which slows down as the ageing progresses. The antioxidant protects the vulcanizate initially, but the level of protection decreases as the ageing progresses. The EV system also shows the same type of behaviour. The vulcanizate without antioxidant shows a fairly rapid reduction in tensile strength, which levels off as the ageing is continued. As expected, the retention of tensile strength during ageing is much higher in the EV than in the conventional vulcanizates. Here also the level of protection obtained from the antioxidant is more pronounced during the initial period of ageing.

Figure 4 gives the chemical crosslink density of the unfilled vulcanizates, plotted against the period of ageing. As expected, the conventional system has a higher crosslink density and ageing causes an initial increase in its crosslink density, which decreases as the ageing is continued. The increase is much more pronounced when antioxidant is present in the system. It is also noted from *Figure 4* that the drop in crosslink density takes place only after a longer period of ageing, when antioxidant is present. Although the initial crosslink density of the EV vulcanizate is lower than that of the conventional vulcanizate, it increases steadily during ageing and at the end of the ageing period its crosslink density exceeds that of the conventional vulcanizate. The presence of antioxidant in the EV vulcanizate causes a higher level of crosslink density throughout the ageing period, although the difference is not as marked as in the case of the conventional vulcanizates. The changes in the crosslink density of the carbon-black-filled vulcanizates during ageing are given in *Figure 5*. The drop in crosslink density during ageing starts at a period earlier than that observed in the case of the unfilled vulcanizates. Here also the antioxidant helps in retaining the crosslink density at a higher level throughout the ageing period. In the filled EV vulcanizate the crosslink density remains almost constant, although the presence of antioxidant causes an increase.

A comparative study of *Figures 2* and *3* with *Figures 4* and *5* shows that changes in crosslink density alone cannot explain the fall in tensile strength of vulcanizates. Except in the conventional vulcanizate without antioxidant, in all the cases the crosslink density at the end of the ageing period of 48 h is either the same as or higher than the original value. But there is a definite decrease in tensile strength. This is especially true in the case of the carbon-black-filled vulcanizates. The sol content of a vulcanizate, as determined in our experiment, is a direct measure of the extent of main chain scission. *Figures 6* and

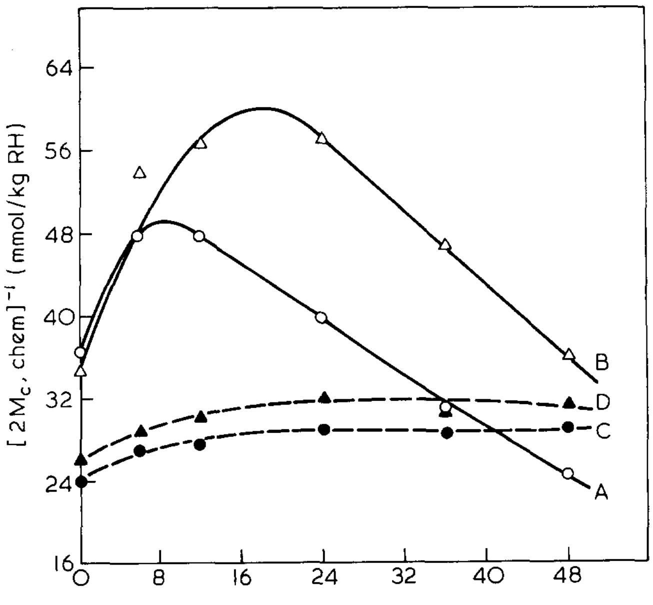

Figure 4 Changes in crosslink density of unfilled vulcanizates during ageing

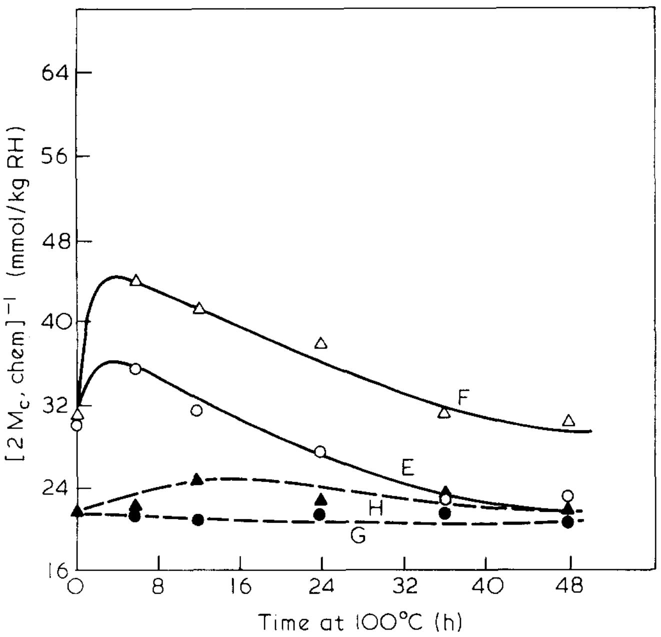

Figure 5 Changes in crosslink density of filled vulcanizates during ageing

7 are the plots of sol content as a function of ageing period in the case of the unfilled and filled vulcanizates respectively. The conventional vulcanizates undergo a higher level of chain scission. The rate of chain scission is slow initially, but increases rapidly as the ageing proceeds, thereby indicating the autocatalytic nature of the scission reaction. The presence of the antioxidant helps in minimizing chain scission during the early periods of ageing, but its activity is reduced as the ageing is continued. The EV vulcanizates show almost a linear increase in chain scission, but the absolute values of sol content are lower than the conventional vulcanizates. The effect of antioxidant is not significant in this system. With the addition of HAF carbon black there is almost a five-fold increase in main chain scission. The conventional vulcanizate shows a linear increase in sol content right from the beginning. It may be noted here that the initial sol contents of these vulcanizates are much higher than those in the unfilled ones. Hence it can be assumed that the radicals capable of catalysing the scission reaction are already present in the vulcanizate in sufficient quantity so that there is a steady increase in the sol content right from the beginning of ageing. But here again antioxidant is found to reduce the rate of chain scission during the initial periods of ageing. The filled EV vulcanizates show a much lower rate of chain scission throughout the ageing period. It is also found from *Figure 7* that the effect of antioxidant is not significant in the EV vulcanizates.

From the above results it is clear that the fall in tensile strength of the rubber vulcanizates during ageing is mainly due to main chain scission. The effect of changes in crosslink density is only marginal.

The modulus at 300% elongation can be considered to be an index of crosslink density of vulcanizates. Therefore, changes in crosslink density of vulcanizates during ageing are reflected more in their modulus values than in any other property. *Figures 8* and *9* are the plots of modulus against ageing period in the case of the unfilled and filled vulcanizates respectively. The conventional vulcanizates show broad maxima and their crosslink density values also show a similar trend. The EV vulcanizates show a continuous increase in modulus, which is supported by the changes in their crosslink density. The increase in modulus on ageing is observed in the carbon black-filled vulcanizates also. In the conventional vulcanizate 300% modulus values could not

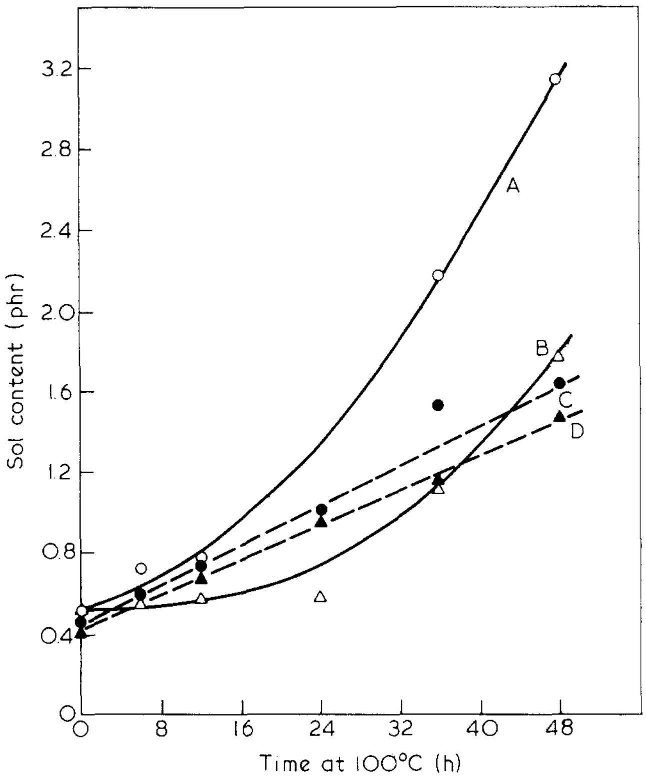

Figure 6 Sol content of the unfilled vulcanizates plotted against period of ageing

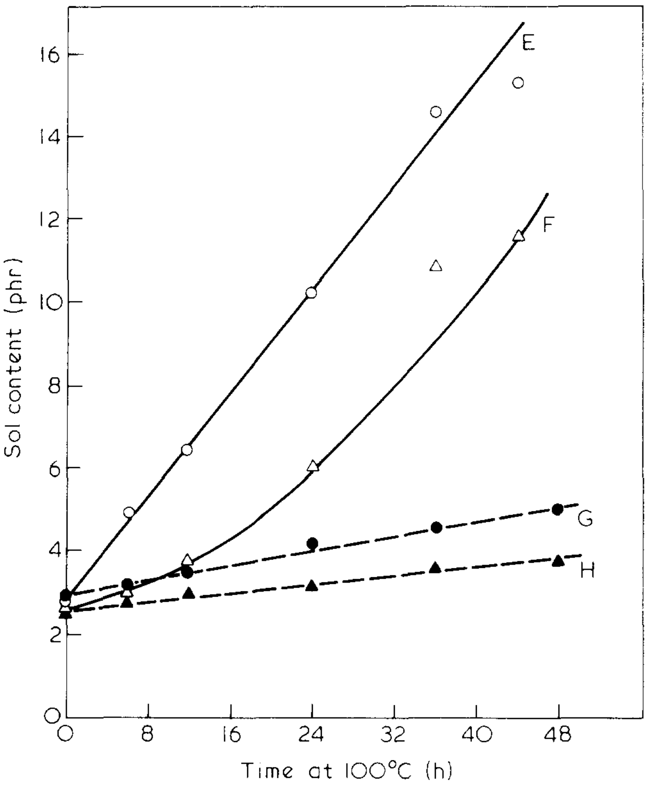

Figure 7 Sol content of the filled vulcanizates plotted against period of ageing

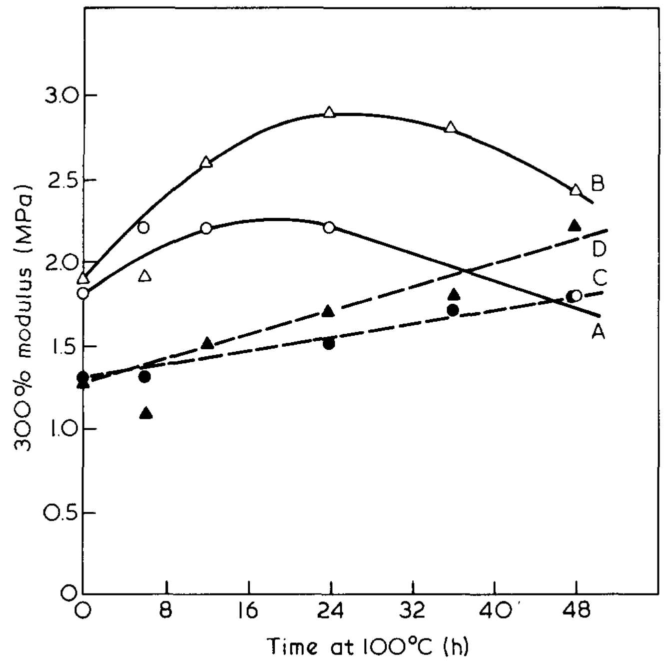

Figure 8 Variation in 300% modulus of the unfilled vulcanizates during ageing

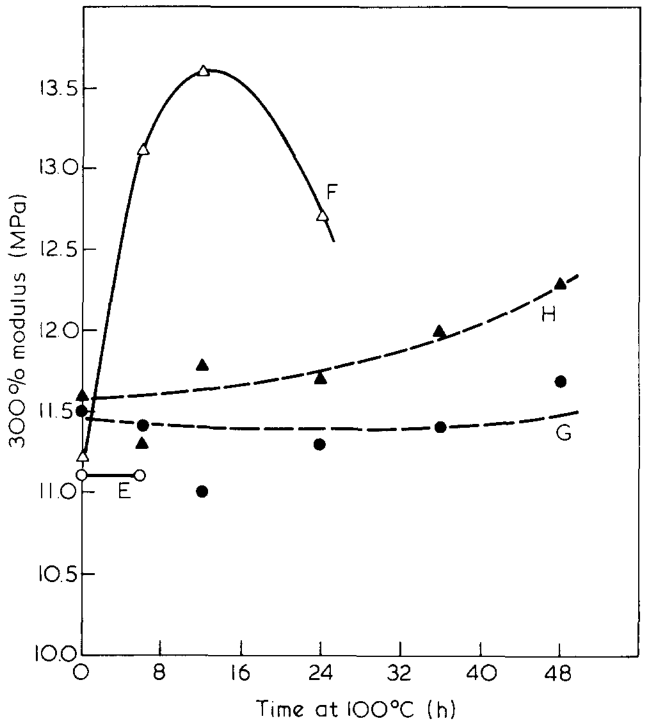

Figure 9 Variation in 300% modulus of the filled vulcanizates during ageing

Table 2 Chemical characterization of the vulcanizates before and after ageing at 100°C

Ageing period (h)	Parameter	Mix number							
		A	B	C	D	E	F	G	H
0	$[2M_c, \text{chem}]^{-1}$ (mmol/kg RH)	36.3	34.5	23.7	26.0	28.8	30.8	21.5	21.8
	Polysulphidic linkages (%)	73	70	15	21	58	62	25	27
	Combined sulphur (mmol/kg RH)	655	633	150	151	559	561	139	141
	Sulphide sulphur (mmol/kg RH)	46	55	1.4	1.4	46	48	5.2	6.3
6	$[2M_c, \text{chem}]^{-1}$ (mmol/kg RH)	43.8	50.1	26.9	28.6	35.2	43.8	21.2	22.0
	Polysulphidic linkages (%)	73	64	19	31	60	67	24	21
	Combined sulphur (mmol/kg RH)	718	714	150	150	690	683	138	142
	Sulphide sulphur (mmol/kg RH)	53	53	2.8	2.8	52	53	7.2	5.2
12	$[2M_c, \text{chem}]^{-1}$ (mmol/kg RH)	43.7	52.7	27.5	30.1	31.4	40.7	20.8	25.0
	Polysulphidic linkages (%)	65	62	15	18	49	57	22	30
	Combined sulphur (mmol/kg RH)	718	717	152	150	705	696	143	148
	Sulphide sulphur (mmol/kg RH)	51	54	1.4	1.4	54	54	7.2	5.2
24	$[2M_c, \text{chem}]^{-1}$ (mmol/kg RH)	39.5	53.0	29.0	32.4	27.4	38.0	21.3	22.4
	Polysulphidic linkages (%)	64	61	18	21	27	52	19	21
	Combined sulphur (mmol/kg RH)	710	718	149	149	707	709	142	140
	Sulphide sulphur (mmol/kg RH)	65	53	2.8	2.8	62	58	5.2	5.2
36	$[2M_c, \text{chem}]^{-1}$ (mmol/kg RH)	30.7	43.0	28.5	30.7	22.8	31.2	21.6	23.2
	Polysulphidic linkages (%)	36	55	14	15	*	38	18	22
	Combined sulphur (mmol/kg RH)	731	730	151	152	737	735	143	140
	Sulphide sulphur (mmol/kg RH)	64	64	4.2	2.0	56	60	5.2	5.2
48	$[2M_c, \text{chem}]^{-1}$ (mmol/kg RH)	24.8	36.1	29.3	31.5	23.3	30.2	20.3	21.7
	Polysulphidic linkages (%)	51	51	15	15	*	30	14	12
	Combined sulphur (mmol/kg RH)	718	740	150	139	737	746	142	143
	Sulphide sulphur (mmol/kg RH)	85	73	4.2	2.0	56	75	6.2	5.2

* Negligible

be obtained as its elongation at break was below 300% beyond the 6 h ageing period. But with the addition of antioxidant, the modulus curve shows a maximum and then drops. A comparison of *Figures 8* and *9* shows that the percentage increase in modulus during ageing is more in the unfilled vulcanizates. From *Figures 4* and *5* it is also seen that the increase in crosslink density is more pronounced in the unfilled vulcanizates, thereby confirming the idea that the increase in modulus during the early periods of ageing is due to the increase in the crosslink density. The increase in crosslink density during ageing is contributed by both oxidative crosslinking[8,22] and by the post-curing reactions. The large increase in crosslink density in the case of the conventional vulcanizates can be ascribed to: (i) the presence of a larger amount of free sulphur, which results in post-curing and which is evident from the increase in the value of combined sulphur, $[S_c]$, as shown in *Table 2*, and (ii) the

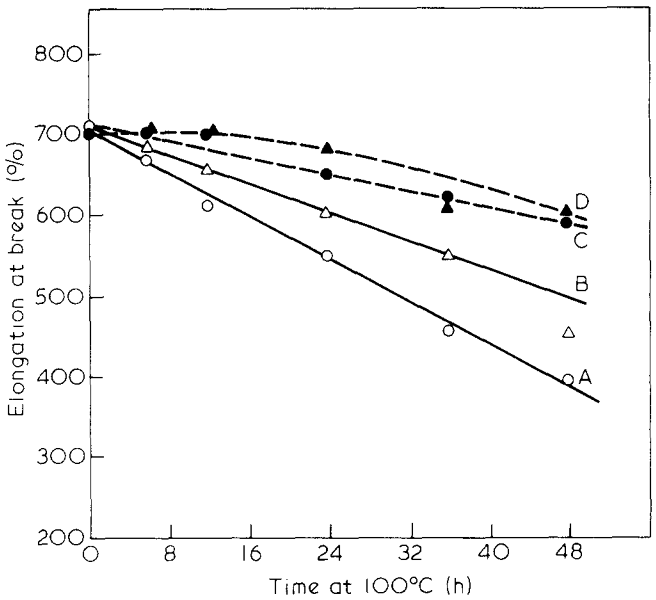

Figure 10 Changes in elongation at break of the unfilled vulcanizates during ageing

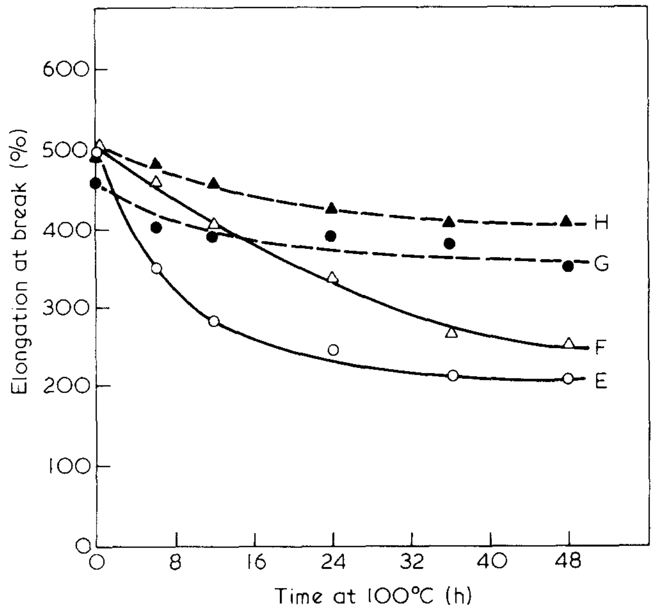

Figure 11 Changes in elongation at break of the filled vulcanizates during ageing

maturation of polysulphidic linkages which causes the formation of more crosslinks with a lower sulphur rank[23], which is evident from the changes in the percentage of the polysulphidic crosslinks and sulphide sulphur values during ageing, as shown in *Table 2*. The decrease in the modulus values during the latter part of the ageing period is due to the general weakening of the matrix resulting from the extensive main chain scission.

Elongation at break (EB) is a more sensitive measure of the extent of ageing as seen from *Figures 10* and *11*. *Figure 10*, where elongation at break of the unfilled vulcanizate is plotted as a function of the ageing period, shows a steady decrease in EB with ageing. Only the EV vulcanizate containing the antioxidant shows a certain level of retention of EB, but here also the EB drops as the ageing is continued. The superior ageing resistance of the EV vulcanizates and the more pronounced effect of antioxidant in the conventional vulcanizates are also evident from *Figure 10*. The drop in elongation on ageing is caused mainly by the weakening of the matrix as a result of the main chain scission. The crosslink maturation reactions, which result in the conversion of the flexible polysulphidic linkages into the less flexible di- and monosulphidic linkages, also might be contributing towards the decrease in elongation. The carbon black-filled vulcanizates show a more drastic reduction in EB during the early periods of ageing (*Figure 11*), which levels off as the ageing is continued. The better ageing resistance of the more stable network of the EV vulcanizates and the effect of antioxidant on ageing are evident from this figure also.

The changes in tear resistance during ageing are more or less similar to those in tensile strength. *Figure 12* is a plot of the tear resistance of the unfilled vulcanizates against ageing period. The conventional vulcanizate shows a steady decrease in tear resistance, although the rate of decrease is not as high as in the case of tensile strength. The antioxidant helps in retarding the fall in tear resistance during ageing. The EV vulcanizates do not show any change in tear resistance throughout the ageing period. Here the effect of antioxidant is not significant. In the case of the carbon black-filled vulcanizates there is a drastic decrease in tear resistance during the early periods of ageing (*Figure 13*), the change being more pronounced in the conventional vulcanizate. The rate of fall in tear resistance is found to decrease as the ageing is continued. The vulcanizates containing antioxidant show a higher retention of tear resistance throughout the ageing period. It appears that, during ageing, tear resistance is affected mostly by main chain scission rather than by changes in crosslink density.

From the above discussion it is clear that, during ageing, degradation of rubber results from two types of reactions: main chain scission and crosslink scission. The initial increase in tensile strength, modulus and tear resistance are caused by an increase in crosslink density whereas as the ageing proceeds, the effect of main chain scission overshadows the effect of an increased crosslink density. Moreover, the crosslink density also falls when the ageing is continued for a longer period. Antioxidant

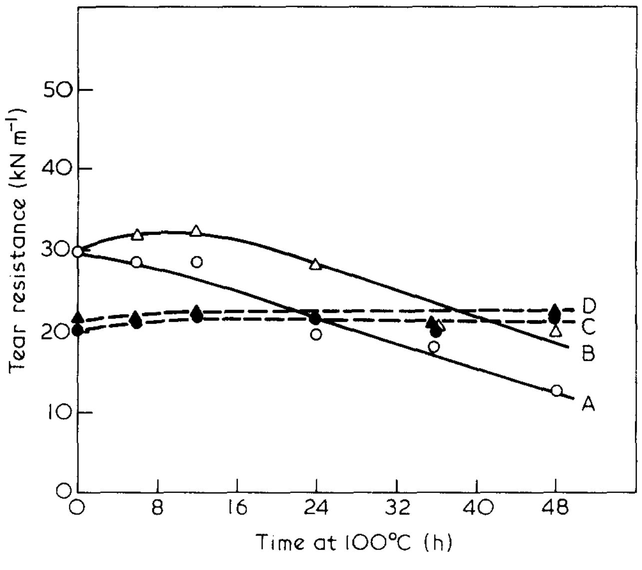

Figure 12 Changes in tear resistance of unfilled vulcanates during ageing

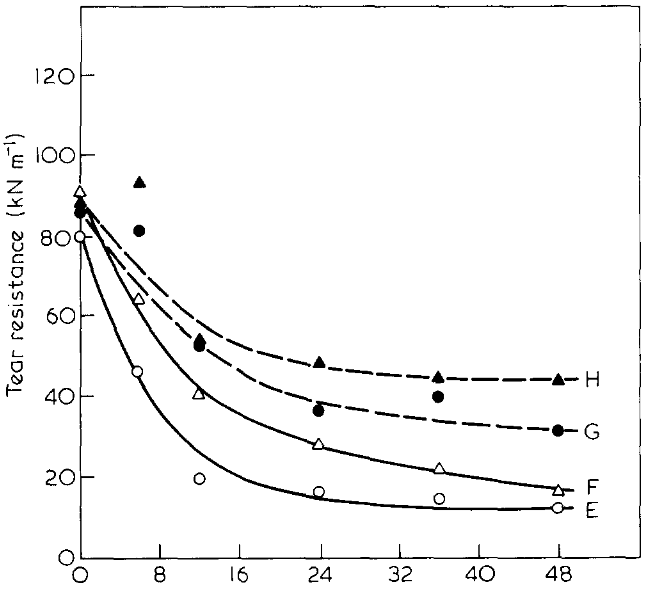

Figure 13 Changes in tear resistance of the filled vulcanizates during ageing

helps in retarding both crosslink scission and main chain scission. Carbon black causes an increase in the rate of main chain scission and crosslink scission. This is in agreement with the observations of Winn and coworkers[24] who found that carbon black accelerates the oxygen uptake of sulphur-cured rubber and that the reaction is accompanied by a rapid degradation of the polymer. These investigators have shown that the rate of oxidation of carbon black-loaded vulcanizates is directly proportional to the amount of carbon surface. Several possible mechanisms for the pro-oxidant behaviour of carbon black in rubber have been proposed[25-27]. The explanation by Shelton and Wickham[28] which involves surface catalysis of the reaction between the rubber and oxygen by carbon black seems to be the most probable one. In the present study it is also observed that the effect of carbon black is more pronounced in the conventional vulcanizates. Hence we believe that the catalysis of oxidation of rubber by carbon black involves the polysulphidic linkages and cyclic sulphides in the network, whose concentration is much higher in the conventional vulcanizates than in the EV. The decrease in the rate of fall of tensile strength, elongation at break and tear resistance and the crosslink density of the carbon black-filled vulcanizates as the ageing is continued is probably due to the decrease in the rate of penetration of oxygen into the inner layers of the vulcanizates. Because of the higher rate of oxygen uptake of carbon black-filled vulcanizates, penetration of oxygen to the inner layers of the vulcanizates will be slower in them. This causes the presence of a fairly undegraded inner layer of rubber in the vulcanizate. During the tensile and tear tests most of the applied stress is carried by this undegraded layer. As the size of this layer of rubber is reduced only slowly, a decrease in the rate of fall of these properties occurs during the latter part of the ageing period. The SEM studies reported later in this paper support this idea. In the case of the unfilled vulcanizates, the rate of oxygen uptake is much slower and hence the rate of penetration of oxygen to the inner layers is not hindered as in the case of the carbon black-filled vulcanizates. Hence chances for the presence of an undegraded inner layer are less and therefore during ageing no decrease in the rate of fall in properties was observed.

SCANNING ELECTRON MICROSCOPIC STUDIES

In some of our earlier studies we have tried to correlate the strength of rubber matrix with the fracture surface topography[20,29]. In the present study the main objective is to find out the effect, on the fracture surface topography, of the weakening of the matrix resulting from oxidative degradation. We have examined both tensile and tear fracture surfaces of the various vulcanizates both before and after ageing for 36 h, because the inherent differences in the ageing resistance of the various vulcanizates is reflected more after the 36 h period as seen from *Figures 2* to *13*. The various photomicrographs are shown in *Figures 14* to *39*.

Tensile fracture

Figures 14 and *15* are the photomicrographs of the fracture surfaces of the unfilled conventional vulcanizate. The surface shows a rough zone (*Figure 14*) followed by a comparatively smooth region (*Figure 15*). The other unfilled vulcanizates used in this study also show more or less the same surface characteristics. The presence of antioxidant or a change in the vulcanizing system do not

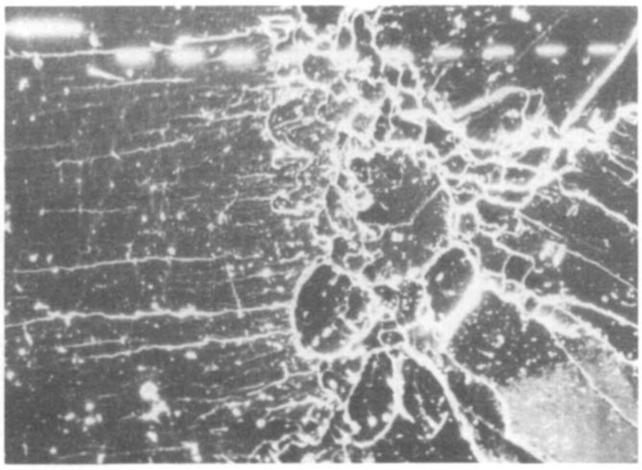

Figure 14 SEM of tensile fracture surface: rough zone, mix A before ageing (50x)

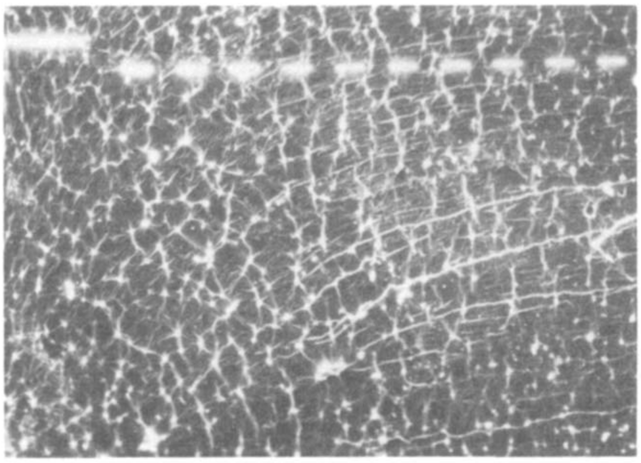

Figure 15 SEM of tensile fracture surface: general surface, mix A before ageing (50x)

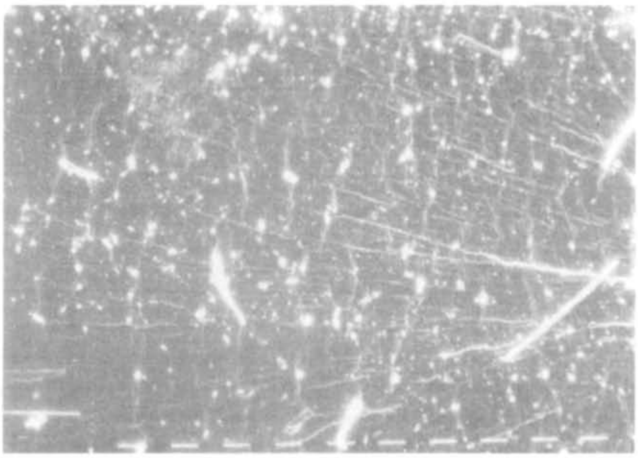

Figure 16 SEM of tensile fracture surface: smooth surface, mix A after ageing (50x)

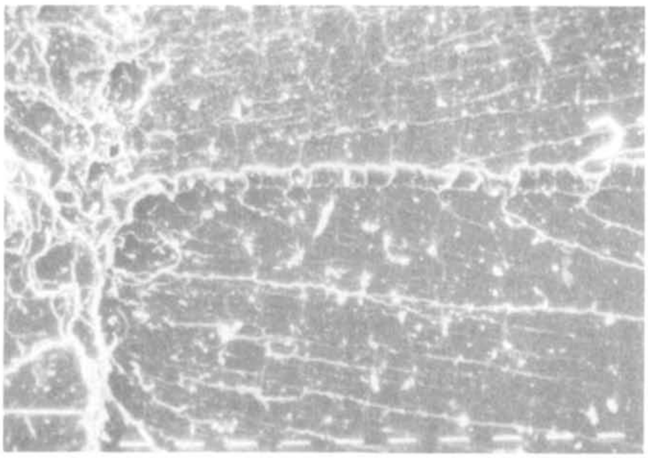

Figure 19 SEM of tensile fracture surface: rough surface, mix D after ageing (50x)

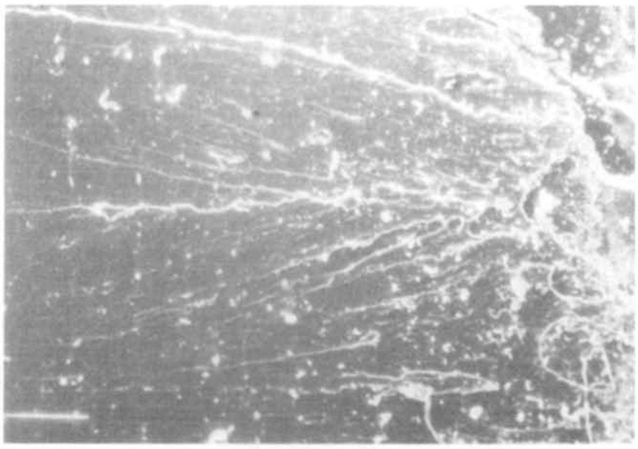

Figure 17 SEM of tensile fracture surface: rough zone, mix B after ageing (50x)

Figure 20 SEM of tensile fracture surface: rough surface with curved tear lines, mix E before ageing (50x)

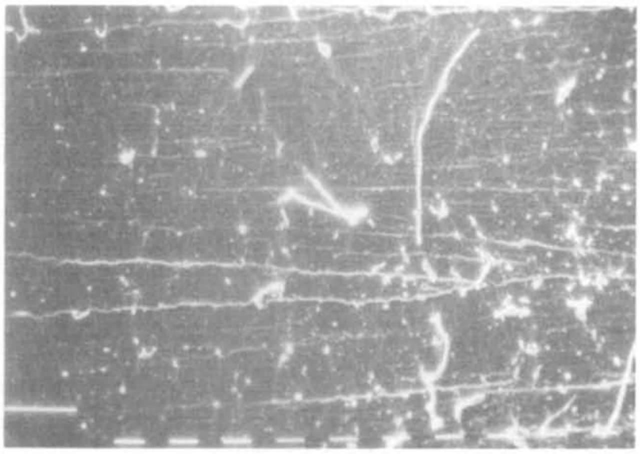

Figure 18 SEM of tensile fracture surface: tear lines on the surface, mix C after ageing (50x)

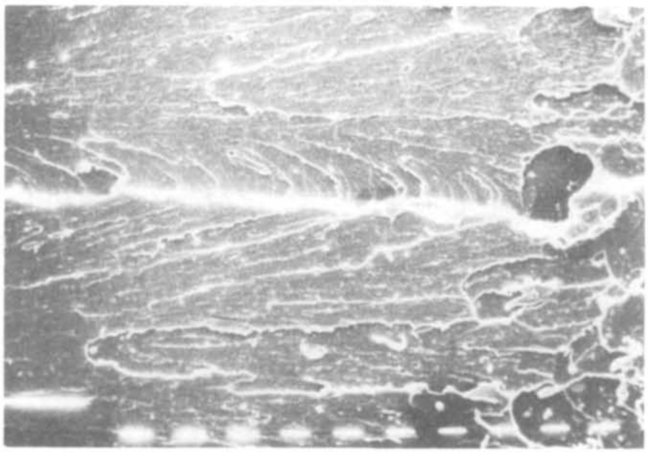

Figure 21 SEM of tensile fracture surface: rough fracture surface, mix G before ageing (50x)

cause any notable change in the mode of fracture as seen in SEM. Although the application of tensile force is considered to be uniform throughout the test specimen, the occurrence of natural flaws and edge nicks in the tensile test specimen, which are quite unavoidable, causes stress concentration in certain localized areas. Failure starts at these points, where the actual stress experienced is much higher than that in the bulk of the specimen. Because of the high stress-rupture and the complex stress distribution around the natural flaws, the fracture surface becomes rough at the point of initiation. Once the failure starts, it proceeds as a catastrophic tear, giving rise to a comparatively smooth surface with a number of tear lines. This type of tensile fracture surface has been reported by

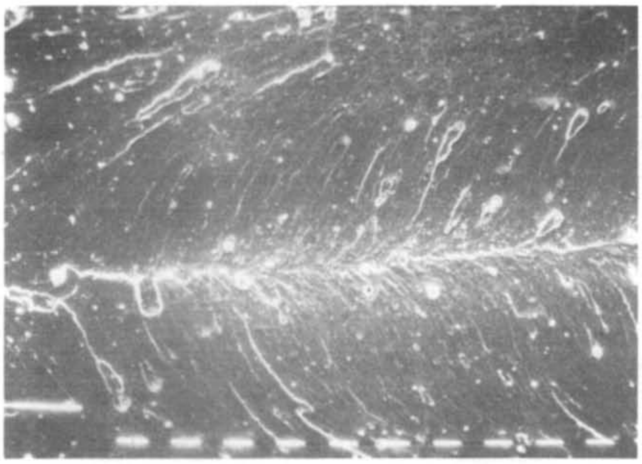

Figure 22 SEM of tensile fracture surface: tear path at the centre of the fracture surface, mix E after ageing (50x)

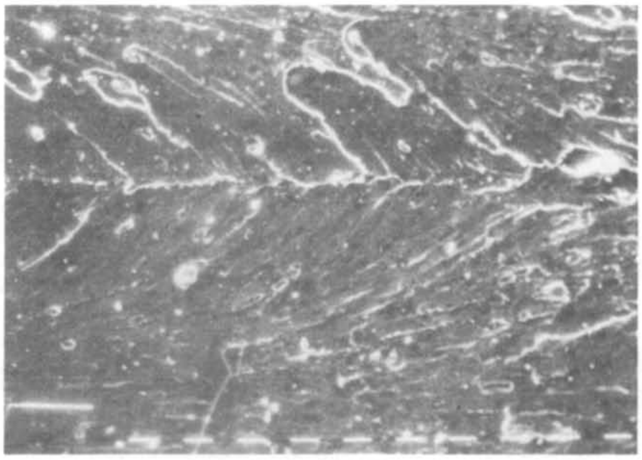

Figure 23 SEM of tensile fracture surface: general surface, mix F after ageing (50x)

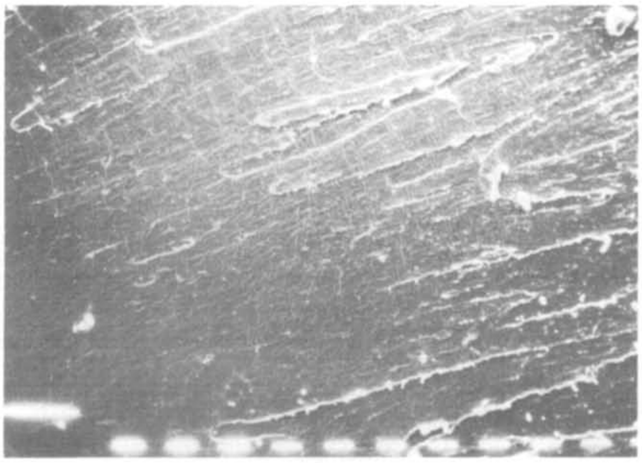

Figure 24 SEM of tensile fracture surface: general surface, mix G after ageing (50×)

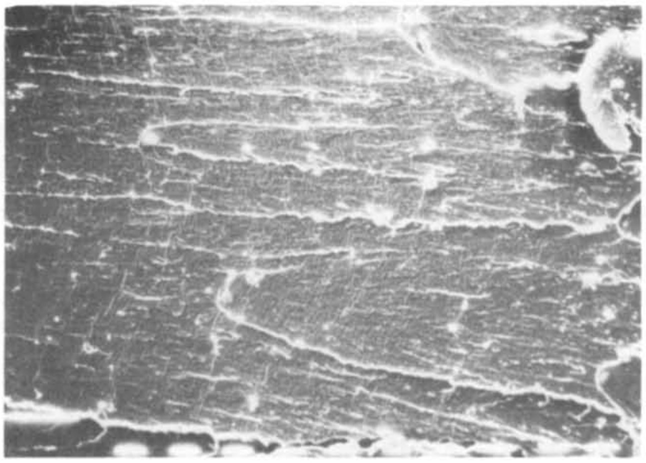

Figure 25 SEM of tensile fracture surface: rough surface, mix H after ageing (50x)

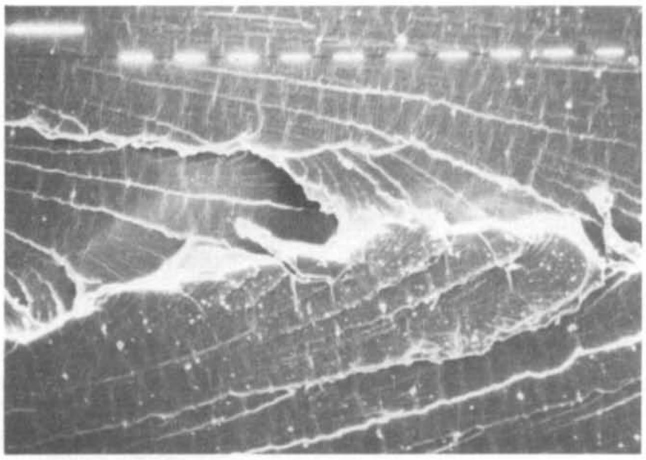

Figure 26 SEM of tear fracture surface: tear path and secondary tear lines, mix A before ageing (50x)

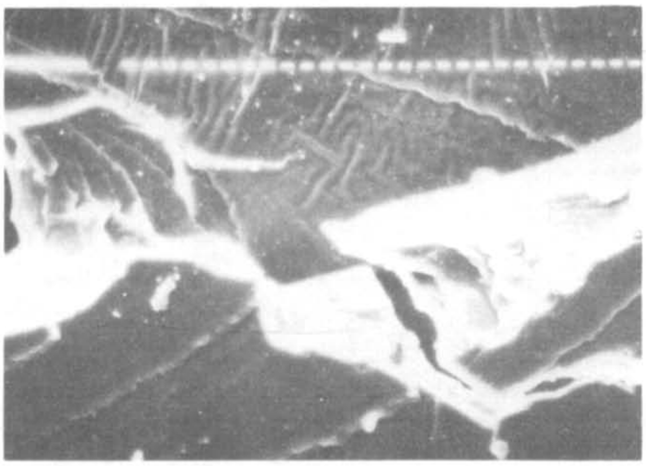

Figure 27 SEM of tear fracture surface: tear path magnified, mix A before ageing (200x)

us earlier[29]. The SEM tensile fractographs of the unfilled vulcanizates after ageing are shown in *Figures 16* to *19*. The low tensile strength of the conventional unfilled vulcanizate after ageing is reflected in its fracture surface (*Figure 16*). There is no rough zone. But the conventional vulcanizate containing antioxidant shows a rough zone, although the size of this zone appears to be less than that of the original vulcanizate (*Figure 17*). The fracture surface of the unfilled EV vulcanizate (*Figure 18*) shows a few tear lines without any rough zone, although its tensile strength after ageing is almost the same as that of the original sample. This behaviour appears unexpected. However, the unfilled EV vulcanizate containing PBNA, after ageing, shows on its fracture surface a rough zone

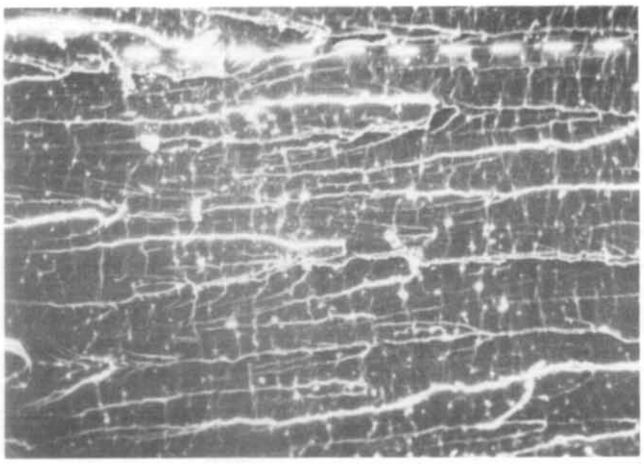

Figure 28 SEM of tear fracture surface: tear lines on the surface, mix C before ageing (50x)

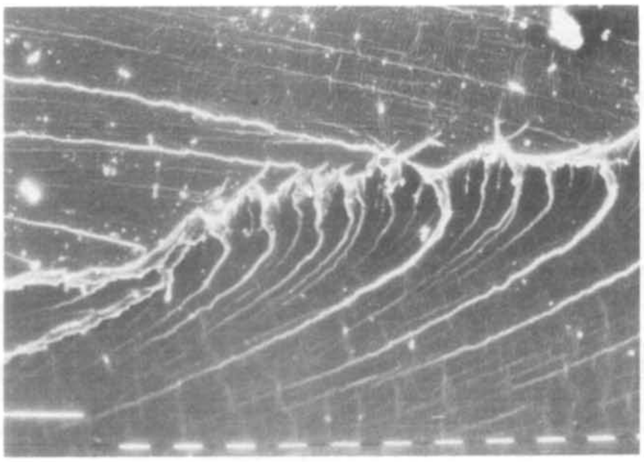

Figure 29 SEM of tear fracture surface: tear path and secondary tear lines, mix A after ageing (50x)

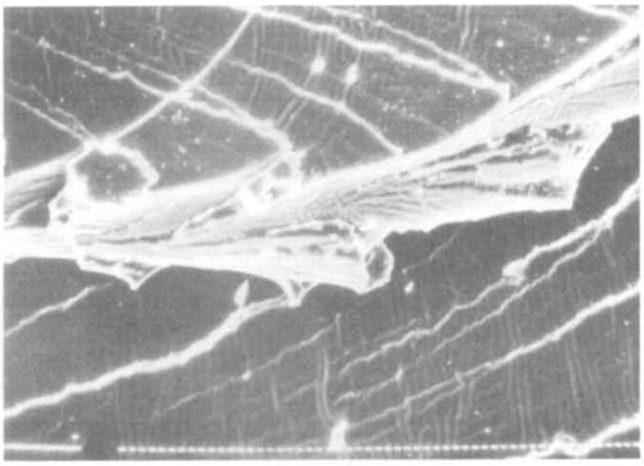

Figure 30 SEM of tear fracture surface: stick–slip tear, mix A after ageing (200x)

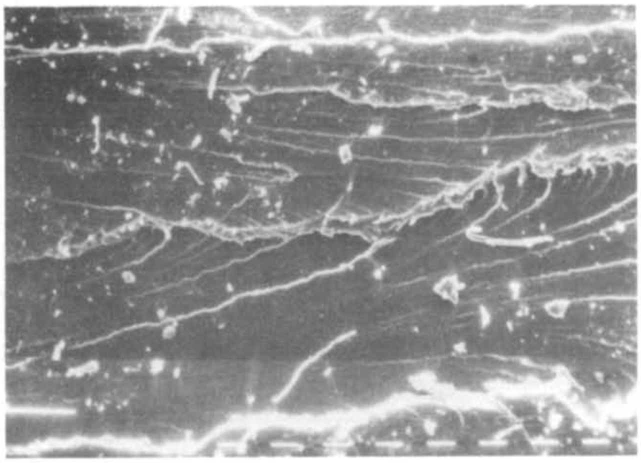

Figure 31 SEM of tear fracture surface: general surface, mix B after ageing (50x)

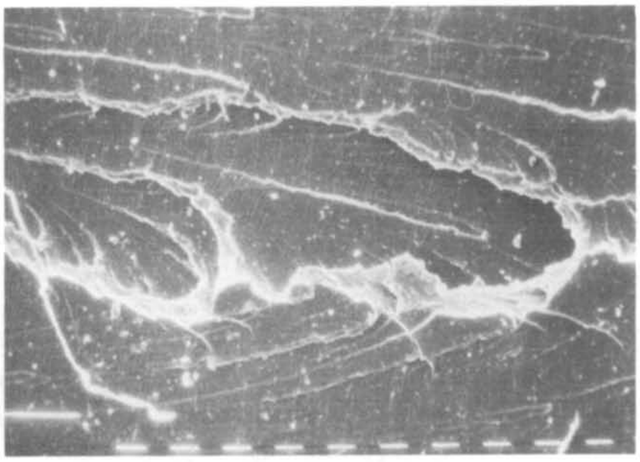

Figure 32 SEM of tear fracture surface: tear path, mix C after ageing (50x)

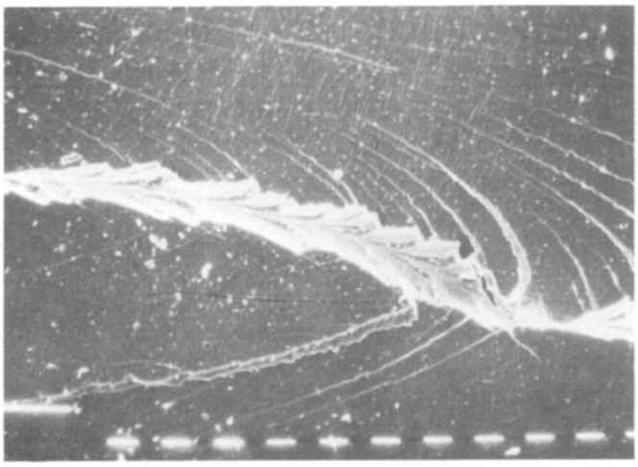

Figure 33 SEM of tear fracture surface: stick–slip tear, mix D after ageing (50x)

followed by a number of tear lines (*Figure 19*) and its tensile strength also is higher.

The addition of carbon black makes the matrix stiffer. In natural rubber, though the tensile strength is not improved significantly by carbon black, the mode of stress distribution during tensile testing is different from that in the unfilled vulcanizates. Hence the fracture surface shows a much different pattern. *Figure 20* is the SEM photograph of the tensile fracture surface of the carbon black-filled conventional vulcanizate. The whole surface appears rough, with a large number of curved tear lines. The regions of high strength, resulting from strong polymer–filler interaction, prevents the fracture from

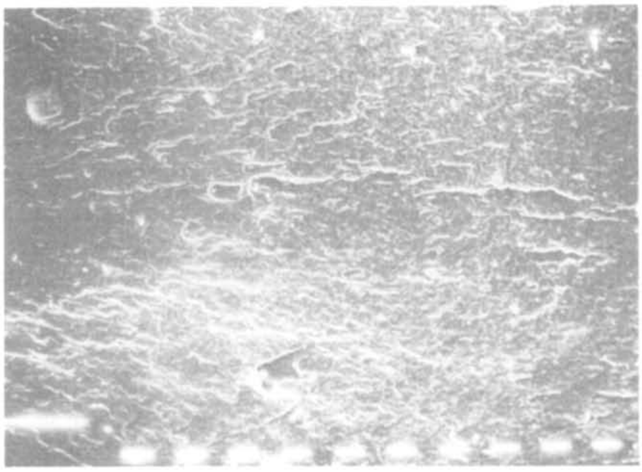

Figure 34 SEM of tear fracture surface: short curved tear lines, mix E before ageing (50x)

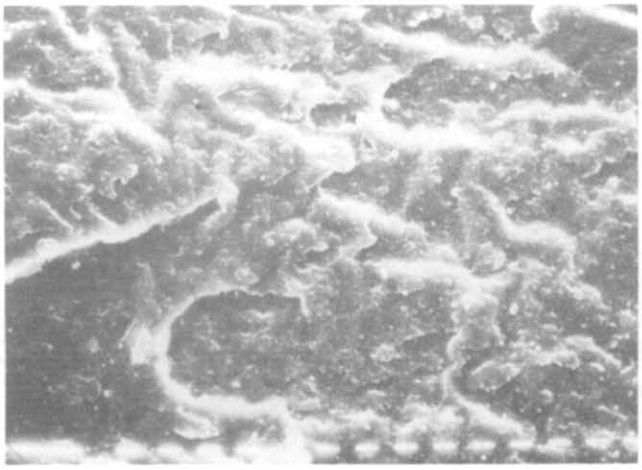

Figure 35 SEM of tear fracture surface: layered structure, mix E before ageing (400x)

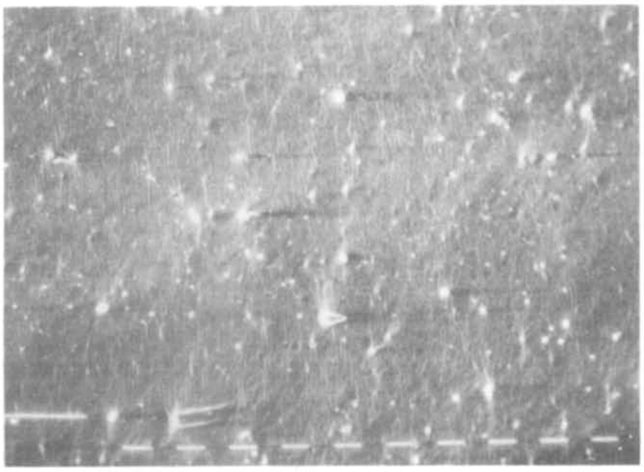

Figure 36 SEM of tear fracture surface: smooth tear surface, mix E after ageing (50x)

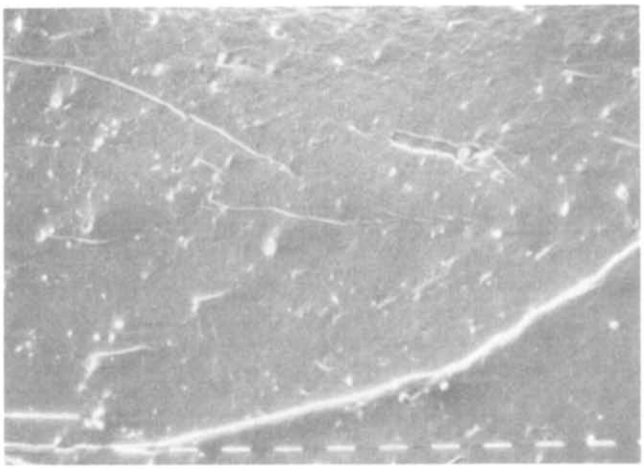

Figure 37 SEM of tear fracture surface: scattered tear lines, mix F after ageing (50x)

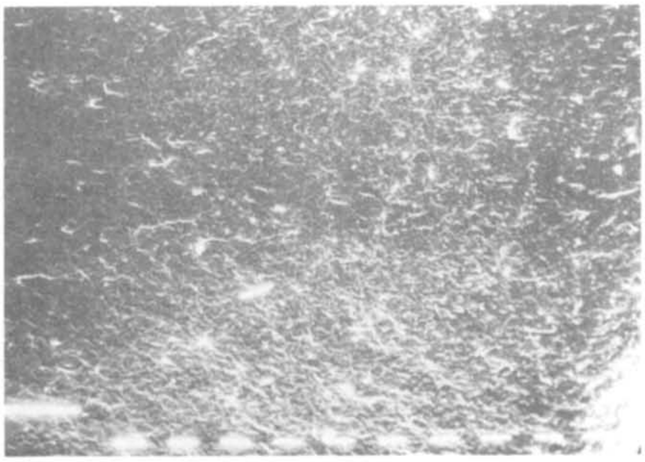

Figure 38 SEM of tear fracture surface: general surface, mix G after ageing (50x)

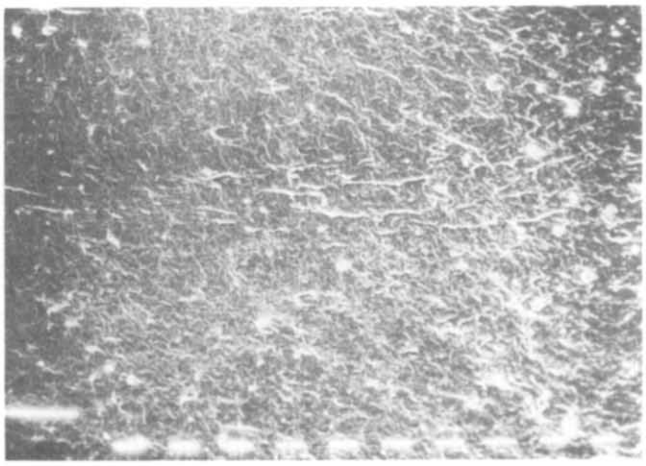

Figure 39 SEM of tear fracture surface: general surface, mix H after ageing (50x)

proceeding straight. This type of rough fracture surface in the case of carbon black-filled vulcanizates has been reported by us earlier[20,29]. The addition of antioxidant does not cause any notable change in the fracture surface. However, the fracture surface of the carbon black-filled EV vulcanizate (*Figure 21*) is slightly different from that of the conventional vulcanizate. The surface is generally rough, as in the case of the conventional vulcanizate, but it shows a prominent tear line. Here also addition of antioxidant does not cause any appreciable difference in the surface characteristics. *Figures 22* to *25* are the SEM photographs of the tensile fracture surfaces of the carbon black-filled vulcanizates, which underwent ageing for 36 h. The conventional carbon black-filled vulcanizate shows a much smoother surface showing a tear path with secondary tear lines near the centre of the specimen (*Figure 22*). It may be noted that in this specimen only the innermost layer is not affected much by ageing and hence this region, which is comparatively stronger, gives rise to a slightly rough surface. The major portion of the specimen, however, is weak and hence gives rise to a smooth fracture surface. The presence of antioxidant helps in retarding oxidative degradation and hence the conventional vulcanizate containing PBNA shows a slightly more rough surface (*Figure 23*). The EV vulcanizates containing carbon black show a higher level of retention of tensile strength during ageing, though the absolute values are lower. The fracture surface is rough (*Figure 24*), although not as rough as that of the same vulcanizate before ageing. Here the effect of antioxidant is not notable, as is evident from the SEM fractograph of the carbon black-filled EV vulcanizate containing PBNA (*Figure 25*).

Tear fracture

The dependence of tear fracture topography on the degree of ageing and hence on the strength of the matrix is not very clear. It is difficult to correlate the tear resistance of the vulcanizate with its fracture surface topography. However, we believe that the mechanism of fracture propagation is affected by the strength of the matrix and hence the extent of ageing will be reflected more in the mode of propagation of tear than in the other surface characteristics. *Figures 26* to *39* are the SEM photographs of the tear fracture surfaces of the various vulcanizates before and after ageing. The fractograph of the original unfilled conventional vulcanizate (*Figure 26*) shows a main tear path with secondary tear lines. The main tear path is the region of the highest stress concentration. During the fracture propagation, when the thin secondary tear lines reach the region of the main tear path, a very high stress concentration is experienced. Under this high stress, the matrix separates, giving rise to a tear path. *Figure 27* shows a magnified image of the tear path. The addition of antioxidant does not cause any appreciable change in tear fracture topography. However, when the vulcanizing system is changed to EV, the fracture surface also shows some difference. The SEM photograph of the tear fracture surface of the unfilled EV vulcanizate (*Figure 28*) does not show any large tear path. Instead, it shows a large number of thinner tear lines, showing the different nature of stress distribution in this vulcanizate. Here also the presence of antioxidant does not have any significant effect on the fracture surface characteristics. The tear fractograph of the unfilled conventional vulcanizate after ageing is shown in *Figure 29*. The size of the main tear path is smaller, but the number of secondary tear lines is greater. A magnified image of a portion of the tear path (*Figure 30*) shows that the tear proceeds in a stick–slip manner. The conventional vulcanizate with antioxidant shows a better retention of tear strength and its fracture surface shows more tear paths (*Figure 31*). The unfilled EV vulcanizate shows a slight improvement in tear resistance during ageing and its tear fracture surface, as shown in *Figure 32*, has become more or less similar to that of the original conventional vulcanizate. However, the secondary tear lines are fewer in number. The EV vulcanizate containing PBNA, after ageing, gives rise to a stick–slip type of tear, as shown in *Figure 33*. The secondary tear lines which join the main tear path are very feeble.

The addition of reinforcing carbon black causes the formation of a large number of small curved tear lines, as shown in *Figure 34*, which is the SEM tear fractograph of the carbon black-filled conventional vulcanizate. On closer examination, the surface was found to have a layered structure (*Figure 35*) with the layers aligned in the direction of tear. Addition of antioxidant or changing the vulcanization system to EV do not cause any change in these surface characteristics. But upon ageing, the strength of the carbon black-filled conventional vulcanizate decreases appreciably and this decrease is reflected in its fracture surface topography. The conventional vulcanizate containing no antioxidant gives rise to a smooth fracture surface as shown in *Figure 36*, whereas the one containing PBNA shows a few tear lines (*Figure 37*) and a slightly higher tear resistance. The carbon black-filled EV vulcanizates show better retention of tear resistance during ageing and their fracture surface (*Figures 38* and *39*) are also more or less similar to the original tear fracture surface.

CONCLUSIONS

The fall in physical properties during ageing is attributed mainly to chain scission. The increase in crosslink density during the initial periods of ageing causes an increase in modulus and tensile strength, but its effect is more than compensated for by main chain scission as the ageing is continued for a longer period. Carbon black accelerates main chain scission and crosslink scission, probably by surface catalysis. The simple network structure of efficiently vulcanized rubber causes better retention of properties during ageing. Antioxidant retards oxidative degradation.

The tensile fracture surface topography depends on the strength of the matrix. The extent of degradation of the vulcanizates during ageing is reflected in the nature of the fracture surfaces. The roughness of the tensile fracture surface is affected to varying degrees depending upon the ageing resistance of the vulcanizates. However, in tear fracture the mechanism of fracture propagation is affected more than the other surface characteristics.

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