Time-dependent fracture in vulcanized elastomers*

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Various aspects of time-dependent crack growth are discussed, including effects of fillers on slow crack growth in non-crystallizing rubbers and the conditions under which such growth can occur in strain-crystallizing rubbers. The results suggest that the inhibition of time-dependent growth, in both types of rubber, is associated with the development of an anisotropic structure at the crack tip. Features of cyclic crack growth under non-zero strain cycle conditions that are again indicative of anisotropic structure formation are also discussed.

(Keywords: fracture; elastomer; crack growth; rubber)

INTRODUCTION

Slow, time-dependent crack growth under constant stress sometimes occurs in vulcanized elastomers. Such growth can be due to chemical attack, ozone being the commonest cause, but the present work is concerned with essentially mechanical failure. Compared with cyclic fatigue crack growth, time-dependent mechanical cracking appears to have been relatively little studied. It is normally associated with non-crystallizing elastomers but is seen, under some circumstances, in a strain-crystallizing elastomer. The phenomenon is of practical, as well as fundamental, interest in relation to certain load-bearing applications.

A review of early work on fracture in amorphous elastomers was given by Halpin[1], who was particularly concerned with tensile failure but also considered tearing and 'slow' crack growth. Much work on time-dependent crack growth has come under the heading of 'tearing' and has normally been concerned with relatively high rates of growth. The occurrence of 'steady' tearing, with relatively small fluctuations in force in constant-rate tests, is often indicative of a time-dependent process. The most clear-cut evidence, however, is provided by constant-force (or fixed-extension) tests in which the growth is steady, enabling the (time-dependent) rate to be measured.

The energetics approach used to analyse the results in the present work was first proposed in relation to the tearing of rubber by Rivlin and Thomas[2]. Their initial experiments were on crystallizing natural rubber, but experiments on non-crystallizing rubbers soon followed[3], and the strong influence of the viscoelastic behaviour on tearing in the latter materials was established[4,5], paralleling that observed in other aspects of fracture[1,6]. Most of the tear work was carried out at fairly high crack growth rates, but Lindley and one of the present authors[7] investigated much slower time-dependent growth in an unfilled styrene–butadiene rubber (SBR) vulcanizate and showed that this was relevant to fatigue failure under constant-load conditions. Subsequently Muller and Knauss[8] and Gent and coworkers[9–11] have investigated various, mainly unfilled, rubbers, to determine primarily the threshold energy for the onset of crack growth[12–14]; in order to expedite the measurements, the materials were often swollen, which alters the crack growth behaviour above the threshold. More extensive investigations of cyclic crack growth have been carried out and it has been shown that the energetics approach can also be used to analyse this, at least under conditions where the strain is fully relaxed for part of each cycle[7,15,16] and to establish the interrelation between crack growth and fatigue[7,16]. It was known at an early stage that there could be a large increase in the cyclic fatigue life for a crystallizing rubber if the strain did not fully relax and that this effect was largely absent for non-crystallizing SBR[17–19].

In view of the limitations of earlier work, the present study is concerned with various aspects of time-dependent crack growth, including effects of fillers on slow crack growth in non-crystallizing rubbers and the establishment of conditions under which such growth can occur in crystallizing rubbers. Closely related features of cyclic crack growth under 'non-relaxing' conditions are also discussed.

MATERIALS AND TEST PIECES

The vulcanizates used were prepared in the form of sheets, normally 9 inch × 9 inch × nominally 2 mm thick (23 cm × 23 cm × 2 mm), from which test pieces were cut. Details of the mix formulations and vulcanization conditions are given in *Table 1*.

The test pieces used for the crack growth measurements were either 'trousers' test pieces (*Figure 1a*), 'split' test pieces (*Figure 1b*) or tensile strip test pieces containing edge cracks (*Figure 1c*).

The strain energy release rate T—the strain energy released per unit area of crack growth (referred to the

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Table 1 Mix formulations (parts by weight) and vulcanization conditions

Vulcanizate reference letter	A	B	C	D	E	F	G	H	J
Acrylonitrile–butadiene copolymer (34% acrylonitrile; NBR34; Polysar Krynac 34/35)	100	100	100	–	–	–	–	–	–
Epoxidized natural rubber (50% epoxidation, ENR50)	–	–	–	100	–	–	100	–	–
Deproteinized natural rubber	–	–	–	–	100	–	–	–	–
Natural rubber (SMR5)	–	–	–	–	–	100	–	100	100
Zinc oxide	3	3	3	5	5	5	5	5	5
Stearic acid	1	1	1	2	–	2	2	2	2
Zinc-2-ethyl hexanoate	–	–	–	–	2	–	–	–	–
Sulphur	1.5[a]	1.5[a]	1.5[a]	1.3	0.6	1.2	1.2	2.5	2.5
t-Butylbenzthiazyl sulphenamide	0.7	0.7	0.7	–	–	–	–	–	–
Cyclohexylbenzthiazyl sulphenamide	–	–	–	1.3	–	–	–	–	0.6
Oxydiethylenebenzthiazyl sulphenamide	–	–	–	–	1.44	1.2	1.2	0.5	–
Tetrabutylthiuram disulphide	–	–	–	–	0.6	–	–	–	–
N-1,3-Dimethylbutyl-*N*′-phenyl-*p*-phenylenediamine (Santoflex 13)	1	1	1	2	–	–	–	–	1
Poly(trimethyldihydroquinoline) (Flectol H)	–	–	–	–	2	2	2	2	–
Medium thermal black	–	50	–	–	–	–	–	–	–
High-abrasion furnace (HAF) black (N330)	–	–	50	–	–	50	50	50	–
Semi-reinforcing furnace (SRF) black	–	–	–	–	50	–	–	–	–
Vulcanization time (min)	40	40	40	30	30	30	15	27	40
Vulcanization temperature (°C)	150	150	150	140	153	150	150	150	140

[a] Coated with magnesium carbonate

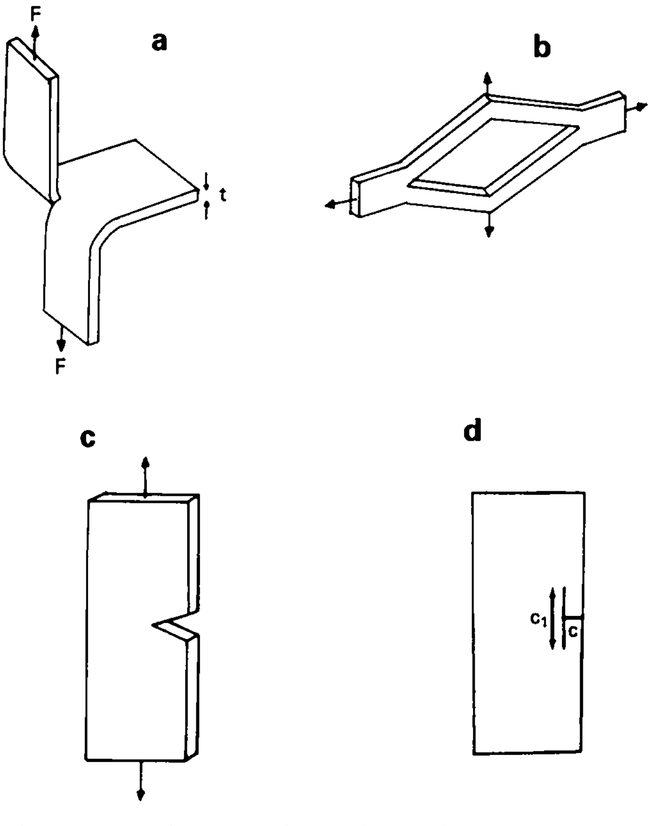

Figure 1 Test pieces used for crack growth measurements: (a) trousers; (b) 'split'; (c) tensile strip with an edge crack; (d) a model branched, 'hammer-head' crack of the type that sometimes develops

unstrained state)—is defined by

$$T = -\frac{1}{t}\left(\frac{\partial U}{\partial c}\right)_{\lambda} \tag{1}$$

where U is the total strain energy stored in a test piece of thickness t held at extension ratio λ and c is the crack length (considered uniform throughout the thickness). T can be calculated for each test piece[2], as follows.

For the 'trousers' test piece:

$$T = 2\lambda F/t - wW \tag{2}$$

where F is the force applied to each leg, w the test piece width and W the strain energy density in the legs. If extension of the legs is prevented, equation (2) simplifies to:

$$T = 2F/t \tag{2a}$$

since $\lambda = 1$ and $W = 0$.

For the 'split' test piece:

$$T = \{[F_A\lambda_A \sin\beta \times F_B(\lambda_A \cos\beta - \lambda_B)]/t\} - w(W_A - W_B) \tag{3}$$

where F_A, F_B are the forces applied to the respective pairs of legs, λ_A, λ_B and W_A, W_B the corresponding extension ratios and strain energy densities, 2β the angle of opening of the legs ($\tan\beta = F_A/F_B$), and w and t are as before.

For the tensile strip test piece with an edge crack:

$$T = 2KWc \simeq 2\pi Wc/\lambda^{1/2} \tag{4}$$

where W is the strain energy density in the bulk (remote from the crack), c the crack length and K a dimensionless parameter that approaches a value of about π at very small strains and decreases slowly with increasing strain. A reasonable approximation for K is given by $\pi/\lambda^{1/2}$, where λ is the extension ratio in the bulk[20], as above.

In some experiments to be discussed, an edge crack in a tensile strip test piece (*Figure 1c*) developed into a 'hammer-head' shape, as shown schematically in *Figure 1d*. In this case, if the crack length c_1 is relatively large compared with c, propagation in the direction of c_1 will simply transfer material from a state of simple extension to the unstrained state. For the 'hammer-head' type of crack, the corresponding strain energy release rate is given by:

$$T_1 = -\frac{1}{t}\left(\frac{\partial U}{\partial c_1}\right)_\lambda = W\dot{c} \qquad (5)$$

Comparison with equation (4) gives:

$$T_1/T \simeq \lambda^{1/2}/2\pi \qquad (6)$$

and thus the energy available for substantial crack propagation in the direction of extension is only about one-sixth of that for transverse propagation for values of λ not much greater than 1, the ratio increasing only slowly with λ for higher extension ratios.

The development of 'hammer-head' cracks is an extreme case, but there are many circumstances under which cracks growing in rubber tend to become blunted. Such blunting will alter the stress concentration at the crack tip according to the following relation[21]:

$$T = W_t d \qquad (7)$$

where W_t is a suitably averaged value of the strain energy density at the tip and d the effective unstrained tip diameter.

EXPERIMENTAL PROCEDURE

Experiments with 'trousers' test pieces were carried out either with a constant force applied to each leg, when the rate of crack growth was measured, or with the legs pulled apart at a constant rate, when the force was measured. In some experiments a flexible but inextensible backing was used to prevent extension of the 'trousers' test piece legs; similar results were obtained from unbacked or backed test pieces (calculated from equations (2) or (2a) respectively). For the 'split' test piece, the deformation in the length direction was normally applied as a fixed extension, although in a few cases it was a fixed force, while the transverse deformation was applied either at a constant rate, when the force was measured, or at a constant force, when the rate of crack growth was measured, as for the 'trousers' test piece. Special procedures, used for experiments in individual subsections only, are described in the section in which they arise.

Cyclic crack growth experiments were carried out using tensile strip test pieces containing edge cracks. The test machine provided an approximately sinusoidal waveform at a frequency of about 2 Hz and was operated with a fixed stroke throughout each test. The basic test procedure was as described previously[12]. For 'non-relaxing' tests, where the minimum strain was not zero, the maximum and minimum strains were measured at the start and finish of each test using a similar procedure to that used to measure the maximum strain in 'relaxing' tests. For the unfilled natural rubber vulcanizate used for these tests, the stress–strain behaviour was found to be almost unaltered throughout a test when allowance was made for the small amount of set occurring. The resulting stress–strain curve, integrated numerically, could thus be used to estimate the strain energy densities from the measured strains for each non-relaxing test.

RESULTS

Force–time traces and types of crack growth observed

In constant-rate experiments with 'trousers' test pieces the force *versus* time traces obtained fall typically into two categories, as illustrated in *Figure 2*. Certain materials show 'stick–slip' behaviour (full curve in *Figure 2*), in which the crack propagation or tearing occurs in sudden, rapid steps with corresponding decreases of the force, whereas others show 'steady' crack propagation with much smaller force fluctuations (broken curve). In constant-force tests, the latter materials usually show time-dependent crack growth whereas the former do not, showing virtually no growth (except possibly for a very slow contribution due to chemical attack by ozone) unless the force reaches a critical value, when very rapid, 'catastrophic' tearing occurs. For unfilled materials, stick slip behaviour is usually shown by crystallizing elastomers whereas steady, time-dependent mechanical crack growth occurs typically in non-crystallizing elastomers. Incorporation of carbon black or other filler may modify the behaviour, particularly for non-crystallizing elastomers.

Corresponding differences to the above are observed in the fracture paths and surface appearances. For steady crack growth, the fracture path is often essentially straight (*Figure 3a*) and the surfaces relatively smooth, while for stick–slip crack growth the path may show branches or much larger deviations, as in 'knotty' tearing (*Figure 3b*) with correspondingly rough fracture surfaces.

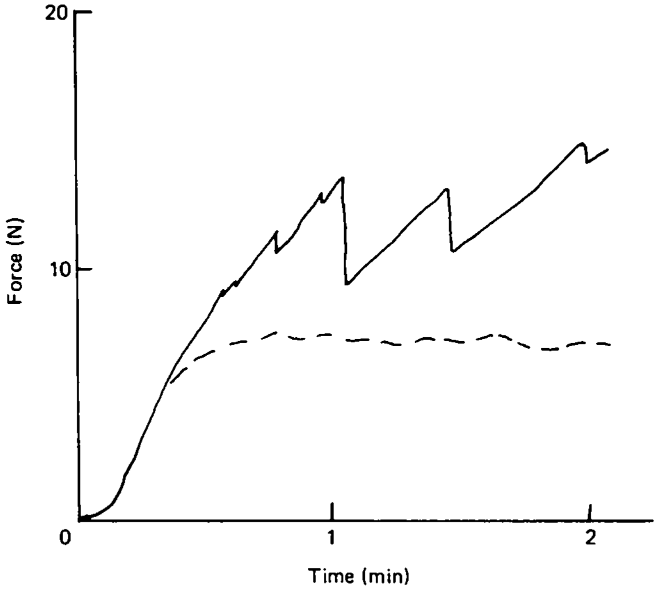

Figure 2 The graph shows force *versus* time traces obtained using 'trousers' test pieces of an unfilled natural rubber vulcanizate tested at a constant rate of extension (100 mm min^{-1}). The only difference between the two experiments was the test temperature; at 23°C the vulcanizate showed stick–slip behaviour (——), while at −40°C the crack growth was essentially steady (- - -)

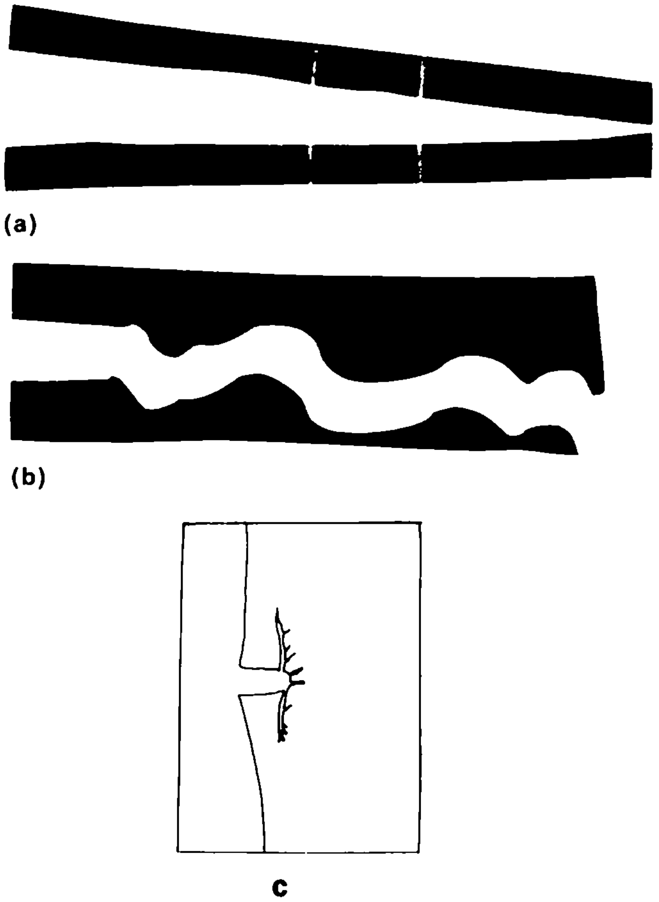

Figure 3 Crack profiles for (a) steady crack growth and (b) 'knotty' behaviour, which gives stick–slip traces; and (c) a 'hammer-head' crack formed during cyclic loading of a black-filled natural rubber vulcanizate under non-relaxing conditions

Time-dependent crack growth in a non-crystallizing elastomer

Results for vulcanizates of a random acrylonitrile–butadiene copolymer (34% acrylonitrile, NBR34), which is believed to be essentially non-crystallizing, are shown in *Figure 4*, where the time-dependent crack growth rate is plotted against the strain energy release rate (termed here the tearing energy) on logarithmic scales. The tests were carried out using 'trousers' test pieces, either at constant rate or at constant force, at an ambient temperature of either 23°C or 70°C. As can be seen, the two test methods give essentially the same results for either material, with the tearing energy for a given crack growth rate being rather higher for the vulcanizate containing the medium thermal black (vulcanizate B, *Table 1*) than for the unfilled vulcanizate (vulcanizate A). The effect of temperature in reducing the energy (at a given rate) is, at least qualitatively, as would be expected on the basis of changes in the viscoelastic behaviour. The present results extend down to rates in the vicinity of 10^{-6} cm s^{-1} and appear consistent with the existence of threshold energies for the onset of mechanical crack growth of somewhat less than 0.1 kJ m^{-2}, as would be expected from other observations[8–14].

Results for a similar acrylonitrile–butadiene rubber vulcanizate containing 50 phr (parts per hundred parts rubber by weight) of the fine-particle high-abrasion furnace (HAF) black (vulcanizate C) are shown in *Figure 5*. The results at high crack growth rates are broadly similar to those shown in *Figure 4* for the other NBR34 vulcanizates although the tearing energies are appreciably higher. Constant-rate and constant-force tests again give similar results at these high energies. In a constant-force test at a lower energy (the result at the lowest energy for the NBR34 vulcanizate in *Figure 5*) the initial rate of crack growth was much as expected from the higher-energy results. However, after propagating in this way for a millimetre or so, the crack turned away from the normal, straight-ahead path and the rate of growth became much lower, both trends continuing with the further passage of time. This behaviour is indicated in *Figure 5* by the broken line and arrows. Further tests at

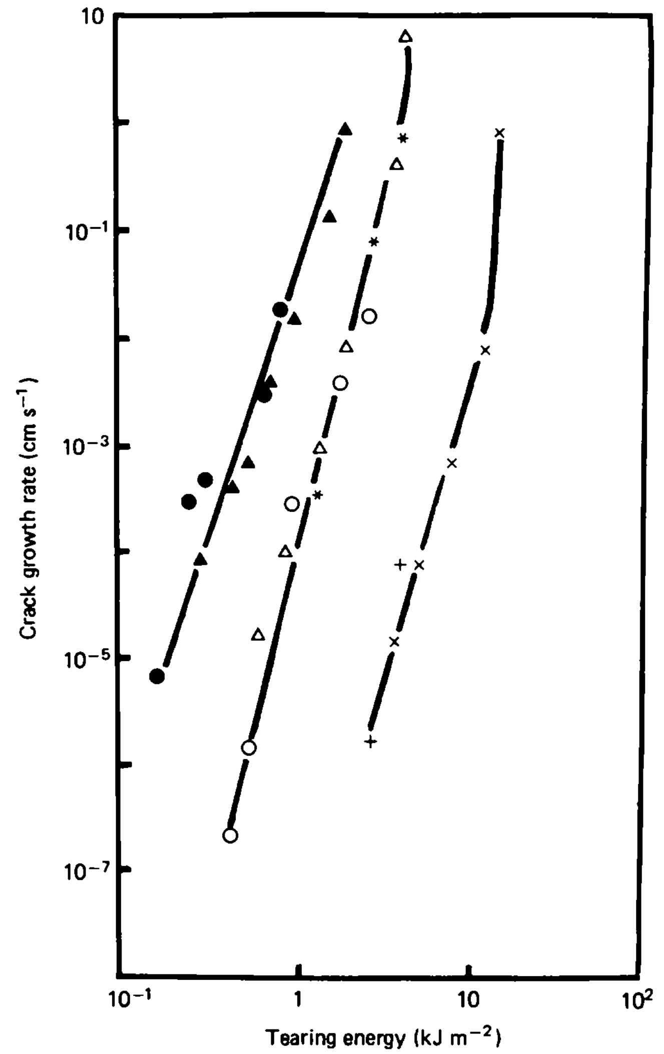

Figure 4 Time-dependent crack growth rate *versus* strain energy release rate (logarithmic scales) for a random acrylonitrile–butadiene copolymer (34% acrylonitrile by weight, NBR34)

	Test temperature (°C)	Constant-rate experiments[a]	Constant force experiments[a]
Unfilled vulcanizate	23	△	○
	70	▲	●
Filled vulcanizate containing 50 phr[b] of medium thermal black[c]	23	×	+
	70	*	

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[a] Using 'trousers' test pieces
[b] Parts per hundred parts rubber by weight
[c] A relatively large-particle carbon black

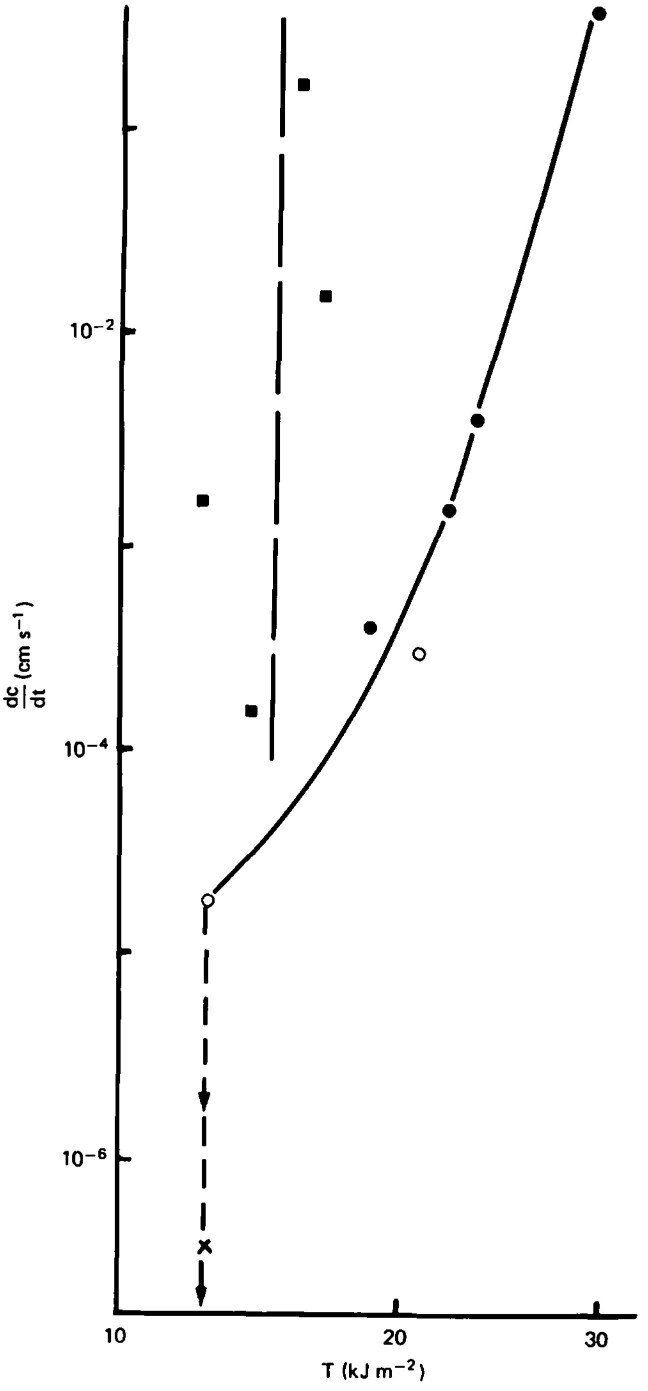

Figure 5 Time-dependent crack growth rate dc/dt *versus* strain energy release rate T for a non-crystallizing rubber (NBR34) containing a 'reinforcing' filler (a fine-particle carbon black) and a strain-crystallizing rubber (epoxidized natural rubber with about 50% epoxidation, ENR50, unfilled). The arrows for the NBR34 vulcanizate show results from a test where the crack deviated from the normal fracture plane and became 'knotty' (×), with accompanying reduction in the crack growth rate. This behaviour was not observed at higher energies and is shown in more detail subsequently

	Constant-rate experiments[a]	Constant-force experiments[a]
Vulcanizate of NBR with 50 phr high-abrasion furnace (HAF) black	●	○
Unfilled ENR50 vulcanizate	■	

[a] 'Trousers' test pieces, ca. 23°C

similar or lower energies revealed the same behaviour. This effect is shown more clearly in *Figure 6*, where the crack length is plotted against time for the lowest-energy test and also, for comparison, a higher-energy test (different scales are used to enable the results for markedly different rates (cf. *Figure 5*) and extents of crack growth to be shown).

Similar behaviour to the above was observed in tests on vulcanizate C at constant rate, a transition from steady to 'knotty' tearing occurring as the rate was reduced (*Table 2*). The rate at which the transition occurred was found to depend on temperature in accordance with the expected changes in viscoelastic behaviour, as illustrated by the results at −5°C and 70°C.

It appears that the above behaviour could be associated with the development, in a time-dependent manner, of an anisotropic structure in the high-stress region near the crack tip. At high tearing energies and rates of crack growth the structure would be unable to develop sufficiently rapidly so that time-dependent growth would continue unimpeded. At a certain rate of crack growth some structure might just be able to start to develop in the region ahead of the crack tip as the tip approached, producing initially only slight anisotropy and only a

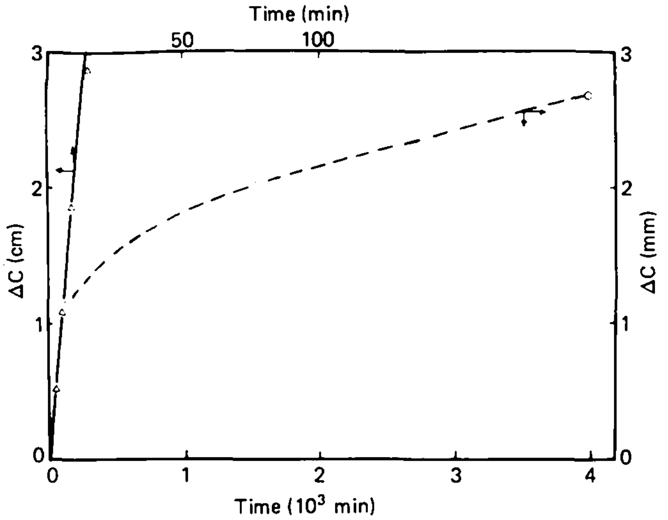

Figure 6 Increase in crack length Δc *versus* time under constant force for NBR34 containing 50 phr HAF black at two strain energy release rates T. With $T = 19$ kJ m^{-2} (triangles, left-hand and upper scales), the crack propagates in an essentially steady manner over many centimetres. With $T = 12$ kJ m^{-2} (circles, right-hand and lower scales), the crack propagates initially (for ca. 1 mm) at about the expected rate (see earlier graph) but then slows down progressively, eventually virtually stopping (not shown). The retardation accompanies deviation of the crack from the normal 'straight-ahead' direction, leading to the formation of a 'knot'

Table 2 Type of tearing observed with NBR34+50 phr HAF black as a function of rate and temperature (trousers tests at constant rate)

Temperature	Crosshead speed (mm min^{-1})				
(°C)	0.1	1	10	100	1000
70	K	K	K	K	K
23	K	V	S	S	S
−5	S		S	S	S

K = 'knotty' tearing
S = 'steady' tearing
V = variable tearing

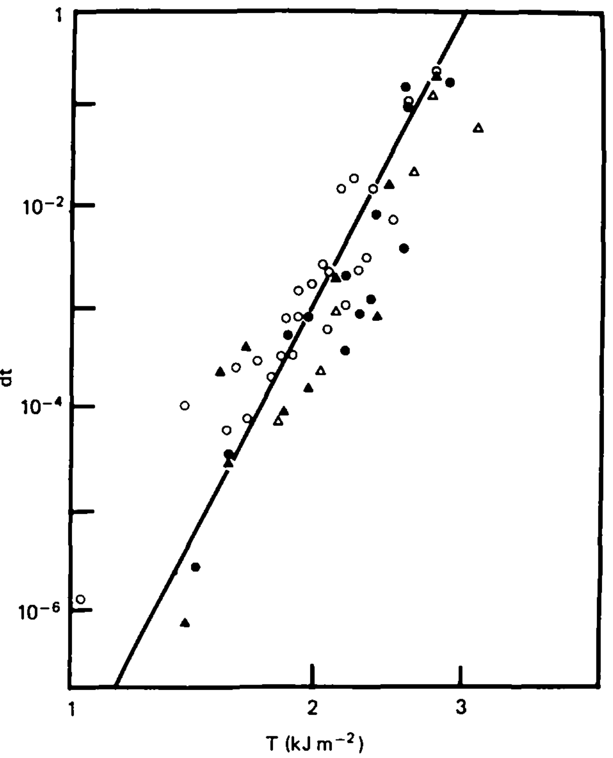

Figure 7 Time-dependent crack growth rate dc/dt *versus* strain energy release rate T, for a natural rubber vulcanizate containing 50 phr of 'semi-reinforcing' furnace black, obtained with 'split' test pieces subject to a pre-strain (of 200%) (○, ●) or a pre-stress (△, ▲), which was in the direction of crack growth and was maintained throughout the test. In the latter case, the pre-stress produced a strain of 170% (△) or 230% (▲) measured 15 min after the force was applied

small reduction in the rate of growth; however, this would allow more time for structural development so that, once begun, the process would become progressively more pronounced. The time required would be expected to increase with increasing viscosity of the rubber, in accord with the observed temperature dependence, and is given approximately by:

$$\tau \sim d/\dot{c}$$

where τ is the time required for significant structural development to occur, d the length (in the unstrained state) of the high-stress region in which orientation can take place and $\dot{c}$ the rate of growth; d is likely to be of the order of the effective unstrained tip diameter. For a value of d of 10^{-6} cm (the order of the distance between crosslinks), the results in *Figure 5*, where $\dot{c}$ is about 10^{-5} cm s^{-1} at the transition (cf. *Figure 5*), indicate a value for τ of about 0.1 s for the HAF black-filled nitrile rubber at 23°C, but this may be an underestimate since d may well be larger. The behaviour of the acrylonitrile–butadiene rubber containing HAF black may be explained by such a mechanism.

Crystallizing rubbers—'typical' behaviour

Also shown in *Figure 5* are results for an unfilled vulcanizate of epoxidized natural rubber (50% epoxidation, vulcanizate D), which, although crystallization is somewhat impeded by the epoxide groups, does exhibit strain-induced crystallization[22]. These results are typical of a crystallizing rubber in that, in constant-rate tests with 'trousers' test pieces, the tearing energy T is substantially independent of the rate. In constant-force tests, no (mechanical) crack growth is observed unless an energy similar to that observed in the constant-rate tests is attained, when large-scale, 'catastrophic' failure ensues immediately. Crystallization might be expected to produce similar anisotropy near the crack tip to that inferred for the HAF black-filled nitrile rubber but there is no indication of similar time-dependent effects from the results for ENR50. However, this point will be considered again below.

Effect of pre-strain. Although, as illustrated above, time-dependent crack growth does not normally occur in crystallizing rubbers, if a filled crystallizing rubber is subject to a large pre-strain, such crack growth may become possible in the direction of the pre-strain. *Figure 7* shows results obtained for a natural rubber vulcanizate containing 50 phr of 'semi-reinforcing' furnace (SRF) black (vulcanizate E, *Table 1*) obtained with pre-strained 'split' test pieces (*Figure 1b*). The results shown were obtained in two ways: with the test piece either pre-stretched to a fixed extended length in the length direction or subjected to a constant force in this direction, with the force chosen to give nominally the same pre-strain (200%). In either case when a transverse force was applied, crack growth was observed to occur in the longitudinal direction in a time-dependent manner (the rate of growth was determined by noting when the crack passed reference marks on the test piece surface made at measured separations in the unstrained state). As can be seen from *Figure 7*, the two methods of test give essentially the same results. The rate of growth shows a very strong dependence on the available energy, the line drawn in *Figure 7* having a slope of about 16, i.e. being of the form:

$$\mathrm{d}c/\mathrm{d}t = BT^{\beta} \qquad (8)$$

where B and β are constants, with $\beta \simeq 16$ in this case. Thus while the observed growth is intrinsically time-dependent, the slope of the rate vs. energy relation is very steep, so that the behaviour is not far removed from catastrophic failure (cf. *Figure 5*, for example). It appears that sufficient orientation was produced under the imposed pre-strain, by the combination of crystallization and alignment of the black filler, for the vulcanizate subsequently to be unable to develop sufficient structure in the perpendicular direction to prevent the time-dependent growth. In similar tests, an unfilled vulcanizate did not show time-dependent growth, presumably because the orientation was less, although the tear strength was still greatly reduced at high strains, as observed previously[23].

Effect of the magnitude of the pre-strain. The dependence of the time-dependent growth rate on the magnitude of the pre-strain is shown in *Figure 8a* for a natural rubber vulcanizate and in *Figure 8b* for a vulcanizate of epoxidized natural rubber (ENR50), both vulcanizates containing 50 phr HAF black. In either case, at least over the ranges covered, the energy required for a given rate of crack propagation tends to decrease with increasing pre-strain, while the slope of the relationship correspondingly increases. Values of the slope (the exponent β in equation (8)) are given in *Table 3* and can be seen to be similar for the two materials. The energies required

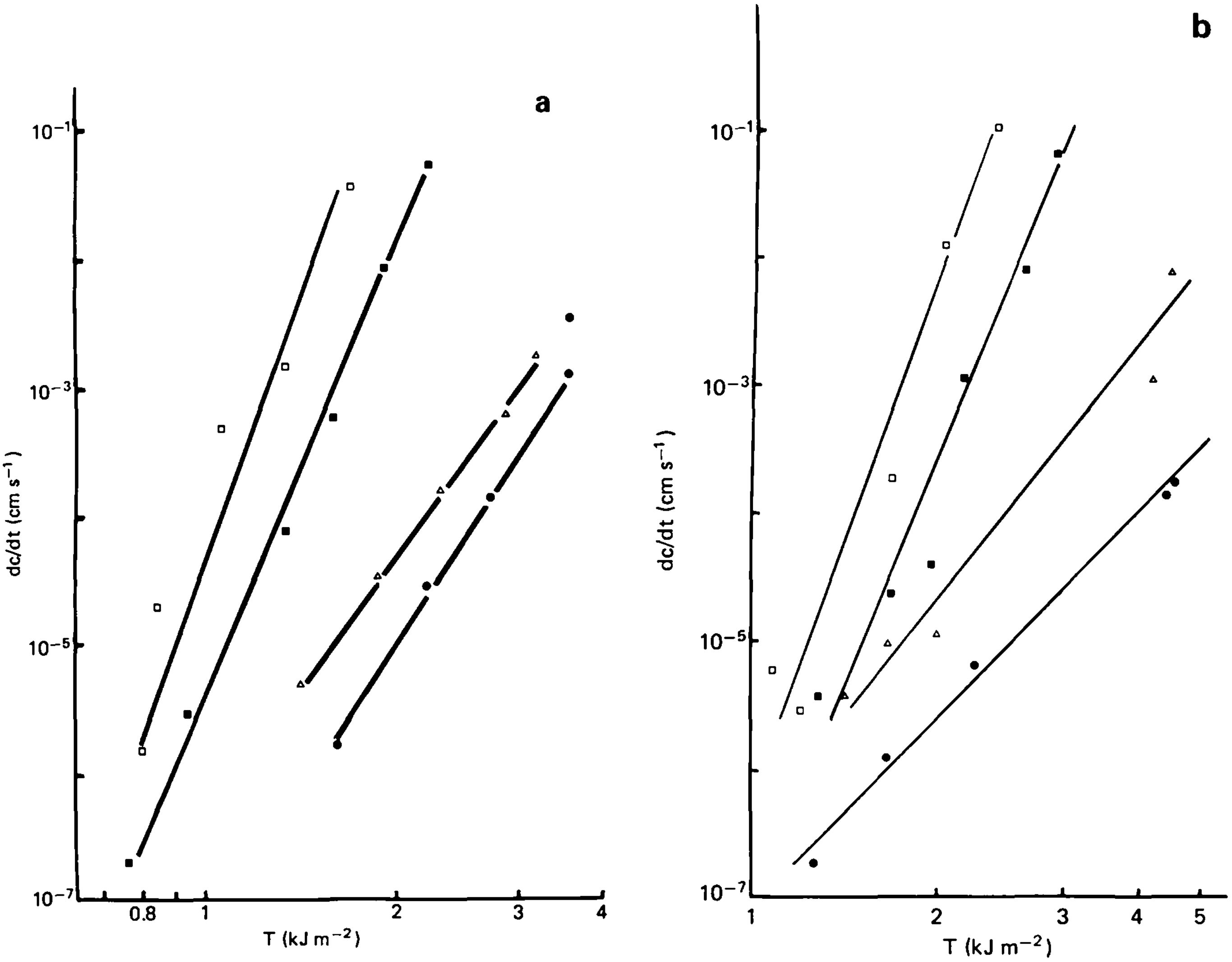

Figure 8 The relationship between the time-dependent growth rate dc/dt in a filled, crystallizing rubber and the strain energy release rate T depends on the magnitude of the pre-strain, as shown here for (a) natural rubber and (b) ENR50 vulcanizates containing 50 phr HAF black: (a) pre-strain 150% (●), 200% (△), 300% (■), 350% (□); (b) pre-strain 200% (●), 250% (△), 300% (■), 350% (□)

Table 3 Dependence of time-dependent crack growth exponent (β in equation (8)) on the magnitude of the pre-strain

	β	
Pre-strain (%)	NR + 50 HAF (vulcanizate F)	ENR50 + 50 HAF (vulcanizate G)
150	7.5	–
200	7	5
250	–	6.5
300	12	13
350	14	14

for propagation are rather higher, however, for the ENR50 vulcanizate, as might be expected in view of its lower crystallizability and higher transition temperature. For both materials, these energies are much lower than those found (for catastrophic tearing) in the absence of a pre-strain (about 50 kJ m^{-2} for natural rubber and about half that for ENR50) and the fracture surfaces are much smoother, as observed earlier by Gent and Kim[23] for natural rubber and, to a lesser extent, styrene-butadiene rubber using pre-strained pure shear test pieces.

Effect of a single pre-strain. For certain vulcanizates, time-dependent crack growth can occur not only in the presence of a previously applied strain but also after a single large pre-strain is applied and removed. *Figure 9* compares results for 'trousers' test pieces of natural rubber vulcanizate H that had been subjected to a single pre-strain of 450% (maintained for 1 min in the longitudinal direction) with those for test pieces that were not pre-strained at all. Tearing occurred in the longitudinal direction in both cases. The vulcanizate used for these experiments was a 'conventional' formulation having relatively high sulphur and low accelerator levels (cf. *Table 1*) and contained a high proportion of polysulphidic crosslinks. Such crosslinks are known to have the ability to re-form (in the strained state) after breaking under stress, so that some orientation (and anisotropy) may be retained after a pre-strain is removed[24]. A permanent set is developed, which provides a measure of the extent of crosslink breakdown and re-formation[25,26]. In order to distinguish the permanent set from any delayed recovery due to viscoelasticity, the pre-strained test pieces were swollen in solvent and then dried prior to testing.

Time-dependent crack growth under constant load is not normally observed in vulcanizate H in the absence of a pre-strain history. The results for the control test

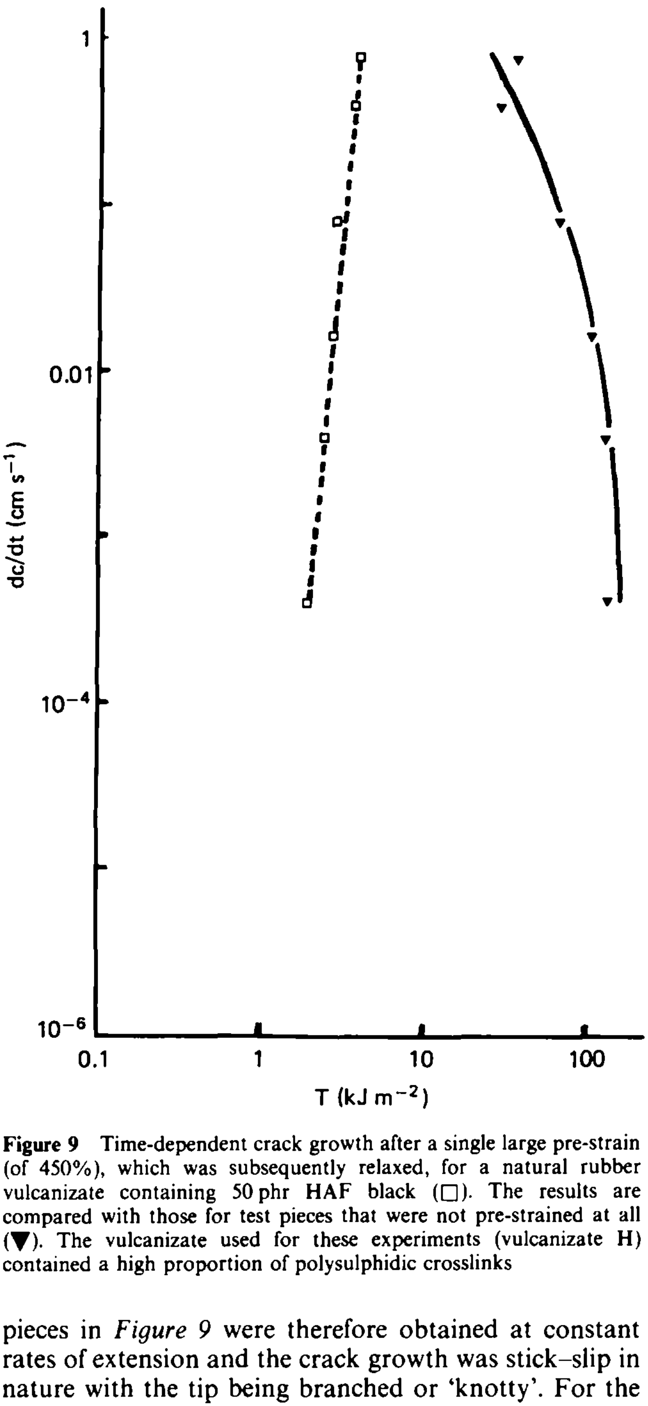

Figure 9 Time-dependent crack growth after a single large pre-strain (of 450%), which was subsequently relaxed, for a natural rubber vulcanizate containing 50 phr HAF black (□). The results are compared with those for test pieces that were not pre-strained at all (▼). The vulcanizate used for these experiments (vulcanizate H) contained a high proportion of polysulphidic crosslinks

pieces in *Figure 9* were therefore obtained at constant rates of extension and the crack growth was stick–slip in nature with the tip being branched or 'knotty'. For the pre-strained material, the crack growth was steady and time-dependent in nature. At the lowest rate of growth for which results are shown in *Figure 9*, the tearing energy for the pre-strained test piece is only about one-sixtieth of that for the control. If the pre-strain had been maintained during the test, the energy would have been about a further factor of 2 lower. Thus for this vulcanizate, by far the greater part of the anisotropy developed by a large pre-strain is retained after the strain is removed. Similar effects of the application a single pre-extension on tear strength have been observed by Hirakawa and Kida[27], who found an order-of-magnitude reduction with HAF black-filled natural rubber but smaller effects with styrene–butadiene rubber or butadiene rubber. These differences may well correlate with variations in crosslink breakdown and anisotropic structure development for the different rubbers[25,26]. It is of interest to compare the energy changes observed for natural rubber in the present experiments with those observed previously by Gent and Kim[23], who found about a 30-fold reduction for pure shear test pieces held at 250% strain in the direction of crack growth, and also, with a different experimental technique, by Lake and Yeoh[28], who found a 200-fold reduction in energy for the initial growth from a very sharp crack tip. In either case the basis of comparison was the 'normal' measurement (with no pre-strain or a blunted tip, respectively) when a much rougher fracture surface and blunter tip occurred. Thus much of the reduction in tearing energy observed for pre-strained test pieces in the present experiments may arise from suppression of crack branching rather than anisotropy of strength as such. Nevertheless, the magnitude of the observed energy reductions, especially in relation to the expected energy release rates for straight-ahead or transverse propagation (cf. equation (6)), suggests the possibility, perhaps probability, that crack branching will occur in 'normal' experiments.

After a pre-strain was relaxed, test pieces of vulcanizate H showed time-dependent growth under fixed load, the results being very similar to those illustrated in *Figure 9*; the slope is about 10, which is comparable with the slopes observed when a pre-strain was maintained (cf. *Figure 8* and *Table 3*). Time-dependent crack growth behaviour of the above type is not observed after removal of a large pre-strain for vulcanizates that contain mainly monosulphidic or carbon–carbon crosslinks; such crosslinks are believed not to be able to re-form if they are broken under stress.

Effect of temperature. The phenomenon described above for a 'conventional', accelerated-sulphur vulcanizate of natural rubber enables the temperature dependence of the time-dependent crack growth in natural rubber to be investigated in a convenient way. 'Trousers' test pieces of vulcanizate H were held at a pre-strain of about 430% for 1 min at room temperature and were then swollen and dried, as before, to remove any viscoelastic set. Crack growth measurements were subsequently carried out at various temperatures within the range 23 to 90°C using both constant-rate and constant-force methods. *Figure 10a* shows the results, which reveal an appreciable and systematic temperature dependence. This contrasts with the 'normal' behaviour of this vulcanizate, in the absence of a pre-strain history, where very little temperature dependence is found over the above range, consistent with the dominant role of crystallization as reported in earlier studies. The rate of crack growth in non-crystallizing rubbers commonly shows a strong dependence on temperature, particularly for unfilled materials, which accords with the variation of the viscoelastic properties with rate and temperature. The latter can be described for various elastomers by the well known Williams–Landel–Ferry (WLF) equation[29]. The usual form of the WLF equation is:

$$\log_{10} a_\theta = \frac{-8.86(\theta-\theta_s)}{101.6+\theta-\theta_s} \tag{9}$$

where θ is the temperature, θ_s a reference temperature and a_θ a shift factor by which the rate must be multiplied; θ_s is usually taken to be $\theta_g + 50°C$, where θ_g is the glass transition temperature for the elastomer. For vulcanizate H, θ_g was measured (by differential scanning calorimetry) to be about $-68°C$, enabling θ_s and a_θ to be calculated

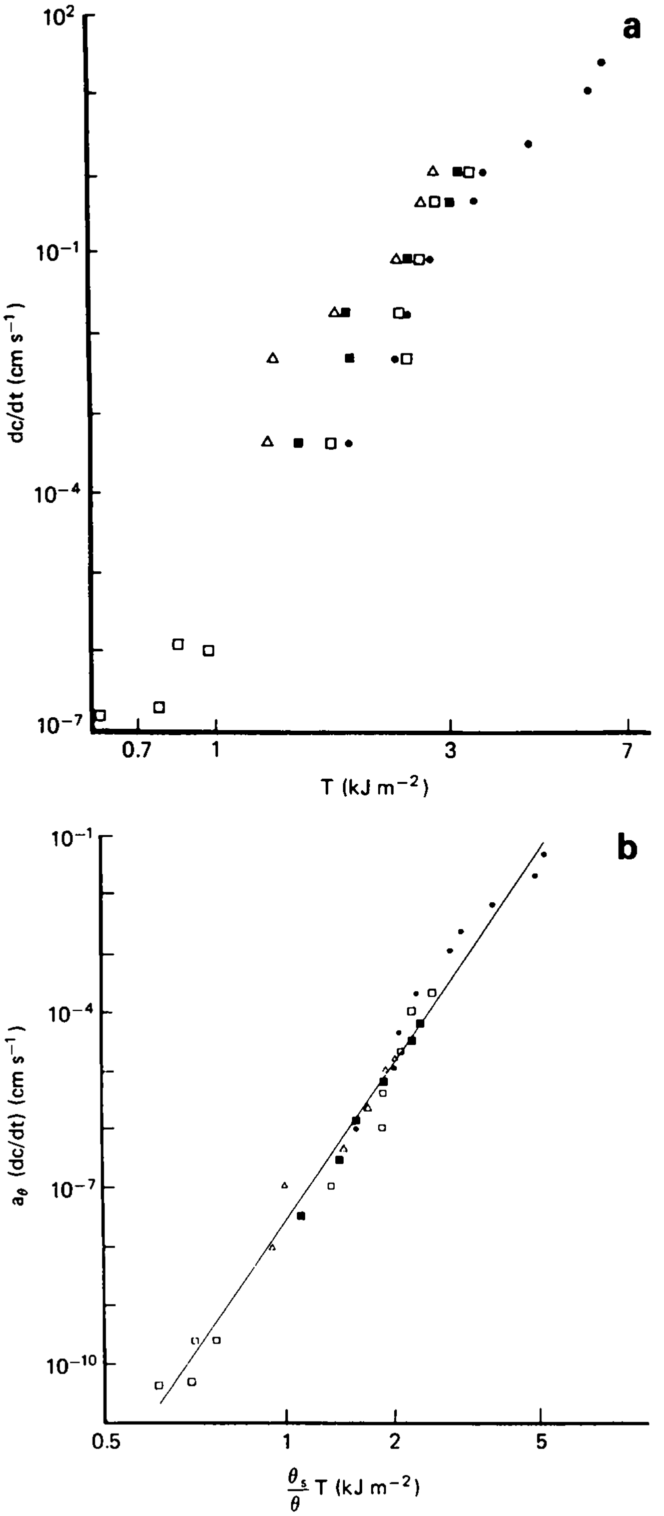

Figure 10 (a) Time-dependent crack growth rate dc/dt in the direction of pre-strain plotted against strain energy release rate T for a 'conventional' natural rubber vulcanizate containing 50 phr HAF black (vulcanizate H) after a single pre-strain (of 430% maintained for 1 min and subsequently removed) at various temperatures: 23°C (●), 50°C (□), 70°C (■), 90°C (△). (b) Results of (a) replotted with the rate multiplied by the viscoelastic shift factor a_θ from the WLF equation (cf. equation (9)) and the energy release rate multiplied by the reference temperature θ_s divided by the test temperature θ

for the various temperatures used. *Figure 10b* shows the crack growth results replotted as $a_\theta(\mathrm{d}c/\mathrm{d}t)$. In this figure, T is multiplied by the factor θ_s/θ, paralleling the temperature adjustment normally applied to the stress in viscoelasticity measurements (following the statistical theory of rubber elasticity). The application of such a 'correction' to a strength measurement is of uncertain validity but the effect is relatively small. As can be seen, the results for different temperatures are substantially brought together by the above means, suggesting that the temperature effect arises primarily from the changes in viscoelasticity. This crack growth behaviour for natural rubber thus parallels that found typically for non-crystallizing rubbers (at least unfilled ones), suggesting that crystallization does not affect the observed growth in the pre-strained natural rubber.

Inverse correlation between strength and set after various pre-treatments. In addition to the effect of a single large pre-strain on the crack growth behaviour, experiments were also carried out on 'conventional' vulcanizates containing mainly polysulphidic crosslinks to investigate the effect of repeated cycling to lower strains. For vulcanizates containing few polysulphidic crosslinks, the set produced by the above treatments is small; greater set, arising from network formation in the strained rate, can be introduced by using a two-stage cure, with the rubber held in the strained state for the second stage. *Figure 11* shows the strain energy release rate required for crack growth at a standard rate (100 mm min^{-1}) in the direction of the strain applied during the pre-treatment, plotted against the permanent set remaining after the various pre-treatments. As can be seen, the results all fall approximately on a single curve. Furthermore the nature of the crack growth varied in a systematic way, being 'knotty' when there was little or no set, steady when the set was large and a mixture of the two at intermediate values. The results thus suggest that there is no intrinsic strength difference between the vulcanizates used, other than that arising from their ability to form a second network in the strained state.

Time-dependent growth in the absence of pre-strain. Although well defined time-dependent crack growth is not usually observed in crystallizing rubbers in the absence of large pre-strain effects, there are circumstances under which it is seen. Thus in ordinary tear measurements at room temperature, time-dependent crack growth is sometimes observed when the energy release rate is very close to the catastrophic tear strength; this growth is, inevitably, quite rapid, although much less so than the 'catastrophic' tearing that normally follows. In an earlier study it was observed that high-speed tearing in natural rubber, at a rate of about 10 m s^{-1}, occurred in a steady manner with smooth fracture surfaces, and it was concluded that, at the very high strain rates produced at the tip, crystallization could not occur[30]. The observations reported earlier in the present paper on HAF black-filled nitrile rubber (cf. *Figure 5* and *Table 2*) show a qualitatively similar effect of rate on the nature of the growth. In this case, the transition to steady tearing occurs at a much lower rate (about 10^{-5} cm s^{-1} at 23°C) but the material has a much higher glass transition temperature than natural rubber (ca. −27°C compared with −68°C).

These observations suggested the possibility that slow, time-dependent crack growth might be observed in natural rubber if the internal viscosity were made sufficiently high. Accordingly, experiments were carried out on natural rubber at temperatures low enough to

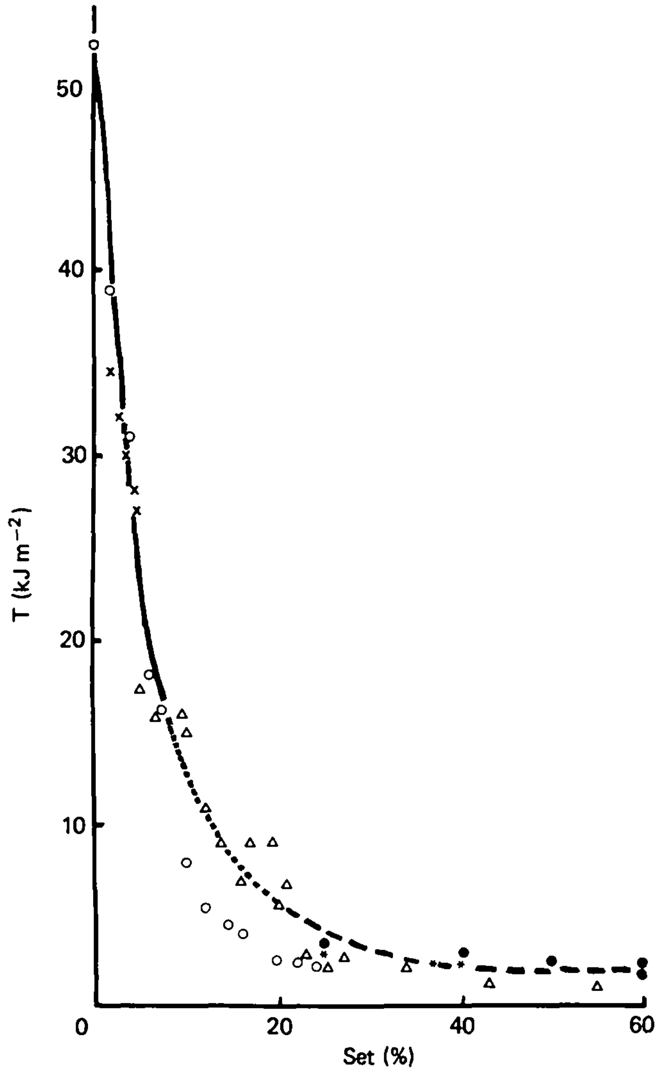

Figure 11 The strain energy release rate T for crack growth at a standard rate (100 mm min^{-1}) in the direction of pre-strain plotted against the permanent set remaining after various pre-treatments. Natural rubber vulcanizates containing 50 phr HAF black. Vulcanizate containing mainly polysulphidic crosslinks after: a single pre-strain (subsequently relaxed) of various magnitude (○); repeated (cyclic) pre-strains of various magnitude (△); two-stage vulcanization with the sheet deformed in simple extension prior to the second stage (●). Vulcanizate containing few polysulphidic crosslinks after: single pre-strains of various magnitude (×); two-stage vulcanization (✱). Type of crack growth: 'knotty' (——), steady (- - -), mixed (······)

retard significantly the rate of strain-induced crystallization. Indeed, the broken curve in *Figure 2* was obtained with the same unfilled natural rubber vulcanizate as the full curve but was at −40°C as opposed to 23°C; at the lower temperature, the tearing was steady in nature and the fracture surfaces smooth. Further experiments were carried out on 'trousers' test pieces of natural rubber tested under constant-force conditions. *Figure 12* shows typical results obtained at −50°C for two energy levels. At the higher one, the crack grew quite steadily over a distance of several centimetres before the test piece finally broke. The rate given by the full line in *Figure 12* is about 0.14 cm s^{-1}; this compares with the rate of about 10 m s^{-1} observed by Kadir and Thomas[30] for steady tearing in an unfilled natural rubber vulcanizate at room temperature. The ratio of these rates of crack growth is about 7×10^3. From equation (9), the ratio of the viscoelastic shift factors at the two temperatures is about 4×10^3. Thus the widely differing rates of crack growth, and hence strain rates, at which time-dependent crack growth proceeds unimpeded at the two temperatures are consistent with expected differences in the viscoelastic response.

The test at the lower energy level in *Figure 12* at first showed steady, time-dependent crack growth, but, after the crack had grown about a centimetre, the tip started to deviate from the straight-ahead path and the rate slowed, eventually becoming very low indeed. On removing the load, warming the test piece to room temperature, recooling to −50°C and reapplying the load, the growth rate increased, although not to the original value. This is consistent with the slow development of a crystalline structure at the tip, taking some minutes at −50°C, which melts on warming after removal of the load, allowing faster growth to occur again subsequently at −50°C. The fact that the rate of this growth was initially slower than originally probably reflected the effect of blunting resulting from the transverse deviation of the tip. In further experiments with

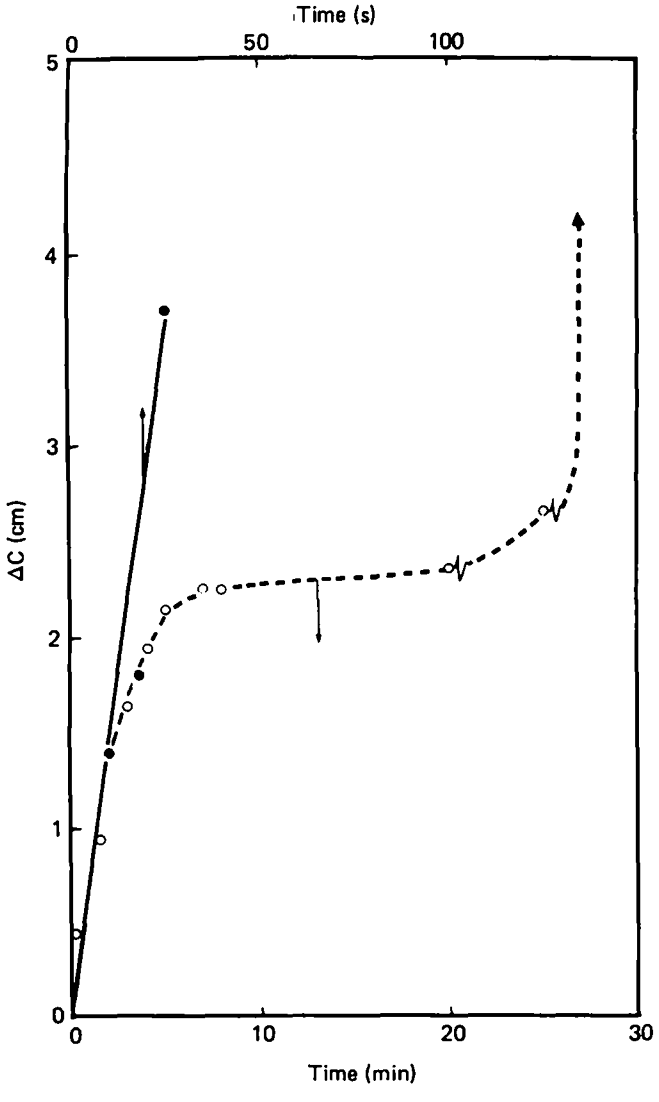

Figure 12 Increase in crack length Δc *versus* time under load for an unfilled natural rubber vulcanizate at −50°C (vulcanizate J, 'trousers' test pieces with no pre-strain). Strain energy release rate: (●) 7 kJ m^{-2} (upper time scale), (○) 5 kJ m^{-2} (lower time scale). The breaks in the latter curve indicate where the load was removed from the test piece, which was then warmed to room temperature, recooled to −50°C and the load then reapplied.

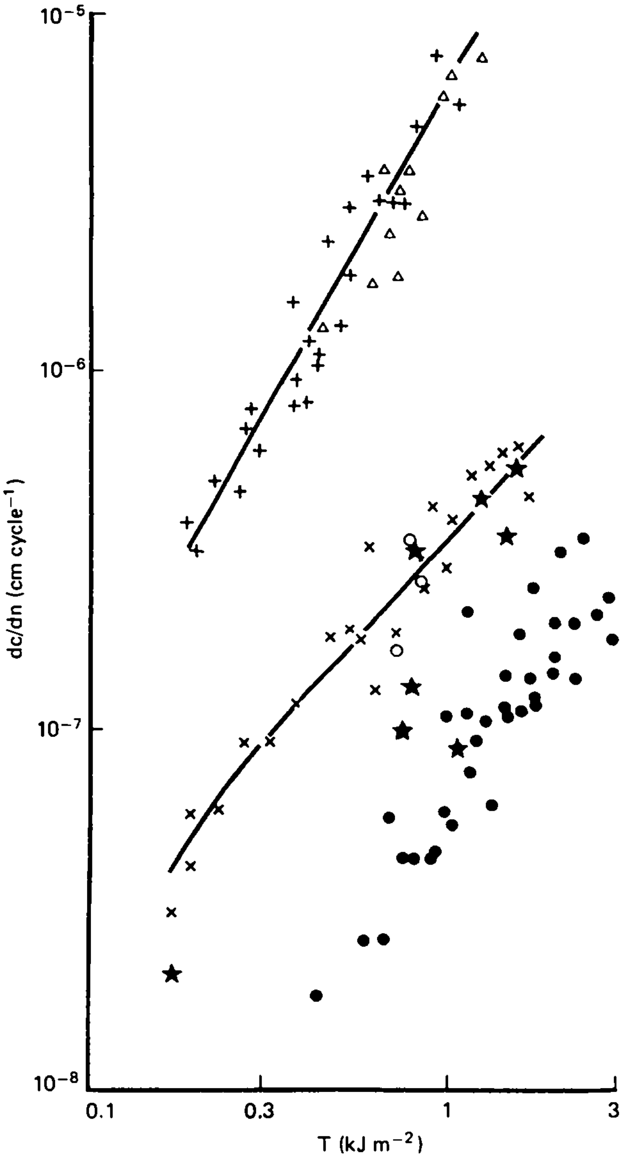

Figure 13 Cyclic crack growth rate d*c*/d*n* *versus* maximum strain energy release rate *T* of the cycle for an unfilled natural rubber vulcanizate (vulcanizate J). Fully 'relaxing' tests (minimum strain zero), initial maximum strain about: 30% (+), 60% (△). 'Non-relaxing' tests, initial strain cycles approximately: 6–30% (×), 11–60% (○); with results where the crack was appreciably branched (cf. *Figure 3c*) indicated by ✱ and ● respectively. (More details of the 'non-relaxing' deformations, including strain energies and effects of set, are given in *Table 4*)

vulcanizates of epoxidized natural rubber at low temperatures, similar time-dependent growth was observed, the required temperatures being higher than for natural rubber in accord with differences in the glass transition temperature.

Cyclic crack growth

The use of a pre-strain in studying crack growth behaviour has potential practical relevance in several respects. Changes in fracture energy and tip sharpness associated with structure development in filled rubbers may occur to a greater extent[31] and at lower deformations[32–34] under repeated strain cycles and may thus influence fatigue performance. Some applications, for example, tyres and other inflated devices, involve biaxial deformations directly. In many springing or mounting applications, a cyclic deformation is imposed on a relatively large dead load such that the material does not return to the unstrained state during the course of a cycle. These non-zero strain cycle or 'non-relaxing' conditions can be very beneficial to the crack growth and fatigue resistance of natural rubber, whether black-filled or unfilled[12,17,18,35], and this is one reason for the pre-eminence of this rubber as a springing material. The enhancement of the fatigue resistance appears to be mainly associated with crystallization, the effect for a non-crystallizing rubber being much less[12,19,36], and has been ascribed solely to hysteresis[35]. *Figure 13* compares cyclic crack growth results for fully 'relaxing' conditions (test pieces returning to the unstrained state during the course of each cycle) with those for non-relaxing conditions, for a natural rubber vulcanizate (vulcanizate J). These experiments were carried out using tensile strip test pieces containing edge cracks (*Figure 1c*), the strain energy release rate *T* being calculated from equation (4) using measured values of the crack length *c*. Measurements of *c* at suitable intervals of cycles *n* enabled the cyclic crack growth rate d*c*/d*t* to be determined.

Considering first the results shown in *Figure 13* for the fully 'relaxing' tests, the amount of crack growth under these conditions is determined mainly by the maximum value of *T* that is attained on each cycle and is relatively little affected by the way in which that maximum is reached (e.g. frequency, waveform)[7,15]. The values of *T* shown in *Figure 13* are therefore the maximum values. Results for two different maximum strains (about 30% or 60%) are shown and it can be seen that they are satisfactorily superimposed in this way. (Not only is this the case for different strains in tension but also cyclic crack growth results for differently shaped test pieces can be superimposed in this way[7,15,16]. Thus the relationship between the rate of growth and *T* is independent of shape, size or type of deformation and can be regarded as a characteristic property of the material.)

The 'non-relaxing' tests for which results are shown in *Figure 13* were carried out with the same maximum strains (about 30% or 60%) as in the 'relaxing' tests but with the minimum strains not zero. The minimum strains were chosen such that the ratio of the minimum to maximum $2KW$ values (and hence T values—equation (4)), which has been proposed previously as a means of assessing such tests[35], was initially about 0.06 (see *Table 4*). The crack growth rates are again plotted against the maximum *T* value attained on each cycle and are clearly much lower than those obtained under 'relaxing' conditions. There are also discrepancies between the results obtained under the two sets of non-relaxing conditions. It appears that these discrepancies are in part associated with differences in the effects of the set that develops (*Table 4*). However, there were noticeable differences in the extent of branching observable (with a low-power microscope) at the crack tip, both between the relaxing and non-relaxing tests and between the two non-relaxing conditions (cf. *Figure 13*). The much greater tendency for branching to occur under the non-relaxing conditions is qualitatively as would be expected if an anisotropic structure was maintained at the crack tip from one cycle to the next. The ability of large 'hammer-head' cracks to develop (*Figure 3c*) suggests, following equation (6), that the strength anisotropy must be at least six-fold in energy terms in such cases. When small tips do start to advance in the 'forward' direction (cf. *Figure 3c*), observation suggests that they are often associated with chemical attack by atmospheric ozone.

Table 4 Non-relaxing crack growth test conditions (these data are representative values from several tests)

First cycle					End of test[a]				
Strain (%)		$2KW$ (MJ m^{-3})			Strain (%)		$2KW$ (MJ m^{-3})		
max.	min.	max.	min.	x^b	max.	min.	max.	min.	x^b
60	11.4	1.02	0.065	0.063	57	9.7	0.97	0.049	0.051
28	5.5	0.325	0.018	0.055	26	3.8	0.275	0.0086	0.031

[a] The total length of the tests varied between 1.9×10^6 and 3.6×10^6 cycles

[b] Ratio of minimum to maximum $2KW$ (and hence T) value (cf. equation (4))

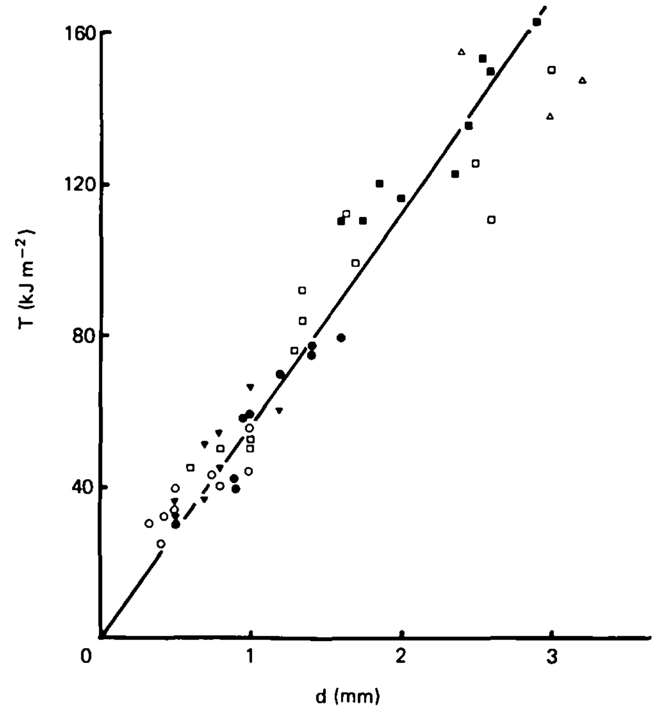

Figure 14 Strain energy release rate T for crack growth from 'knotty' tears of various measured diameters d for 'trousers' test pieces of an HAF black-filled natural rubber vulcanizate (vulcanizate F). The different symbols indicate various rates of grip separation from 0.5 to 1000 mm min^{-1} (at 23°C)

Effect of tip blunting

Even in the absence of anisotropy, the blunting of the crack tip in non-relaxing experiments would be expected to have a marked effect on the rate of growth according to equation (7). The tips formed during cyclic crack growth experiments are often irregular in shape, so that it is difficult to estimate the effective unstrained tip diameter with any precision. However, in constant-rate crack growth measurements when 'knotty' tearing occurs, the tip sometimes follows an arc that is approximately circular in the unstrained state, enabling the diameter to be estimated with more confidence. *Figure 14* shows results for vulcanizate F in which the 'knotty' tear tip diameter was measured directly, variation being obtained partly adventitiously and partly by altering the rate of tearing. The strain energy release rate T required to produce subsequent tearing is plotted against the measured unstrained tip diameter d, and it can be seen that a proportionality holds quite well, in accordance with equation (7). Furthermore the slope of the line gives a value for W_t of the order of the work to break in a standard tensile test, as noted previously for model crack tip diameters of this order[21]. A simple quantitative relation of this form would not be expected to hold for sharper crack tips, as W_t is likely to increase as the tip diameter decreases. However, the results illustrate an effect that is of relevance to many crack growth phenomena in elastomers, since it appears to be rare for a crack tip to attain its limiting molecular sharpness (of the order of the distance between crosslinks for a vulcanized elastomer)[28].

GENERAL DISCUSSION

The phenomena described illustrate the complexity of crack growth processes in vulcanized rubber. In the presence of adequate stress, it appears that time-dependent mechanical crack growth will generally occur unless a mechanism arises to prevent it. One such mechanism involves strain-induced crystallization, which can effectively suppress time-dependent growth under many circumstances and can also greatly restrict cyclic crack growth.

Various explanations have been put forward to account for the effect of crystallization, including either energy dissipation or stress reduction due to the very large mechanical hysteresis induced by crystallization at the high strains necessary to cause fracture. These or other factors may play their part, but from the present observations it appears that a primary factor is probably the formation of an anisotropic structure at the crack tip. Such an idea is by no means new[17–19], but new evidence supporting it has been obtained. Although the anisotropic structure has not been observed directly (direct observation seems likely to be very difficult since only a very small volume of material at the tip is involved), the occurrence of anisotropic crystal formation in the bulk under stress is well documented. Since the stresses near a crack tip can be much higher than those achievable in bulk, it would be surprising if similar crystals were not present near the tip. Quantitative evidence of large anisotropy of strength produced by pre-straining has been obtained, extending earlier observations[23]. If sufficient filler is present in a crystallizing rubber, crack growth in the direction of pre-strain may proceed in a time-dependent manner, presumably because the extent of orientation is such that crystallization is inhibited perpendicular to the direction of growth. Natural rubber, which crystallizes more and has higher tear strength in normal measurements, is weaker than ENR50 in the direction of a large pre-strain. For certain vulcanizates time-dependent growth can occur even after a large pre-strain has been removed. In such a case, the crack growth shows a strong temperature dependence, which correlates with the viscoelastic behaviour, as in unfilled non-crystallizing elastomers. If the rate of crystallization is reduced by carrying out experiments at low temperatures, time-dependent crack growth can occur in crystallizing elastomers in the absence of pre-strain (or filler) when the rate of growth is sufficiently high. The critical rate of growth appears to be associated with the time required for a crystalline structure to develop at the crack tip.

The observations suggest that the suppression of time-dependent cracking in a non-crystallizing rubber containing a fine-particle carbon black filler may arise through a similar mechanism to that above. In this case it appears that an anisotropic structure may develop through time-dependent alignment of the filler particles and agglomerates under stress, again leading to crack deviation and blunting and the arrest of time-dependent growth. A similar effect was not observed with a coarse-particle filler, over the range of rates covered, but even in this case the energy required for crack propagation at a given rate was increased appreciably, presumably reflecting smaller-scale tip blunting and perhaps other effects. Large-scale crack diversion has been observed for chlorosulphonated polyethylene elastomer containing talc as a filler[37]. Independent evidence for structural alignment of filler particles has been obtained from the increase in electrical conductivity with increasing strain, which suggests that strands of carbon black particles may be formed[38], and from pulsed nuclear magnetic resonance and other methods after fatigue cycling[32 34].

With either crystallization or filler orientation under strain, the situation in the elastomer perhaps resembles that in a fibre-reinforced composite, with the elastomer having the ability to produce its own fibrous reinforcement[39]. The 'oriented-structure' mechanism also explains the tendency for cracks to deviate from a 'straight-ahead' fracture path to produce blunt tips or even, in extreme cases, 'knotty' tearing. Indeed, the main benefit from the structure may derive not from greater resistance to crack propagation in the forward direction but from blunting of the tip due to relatively easy transverse propagation, as suggested, in another context, by Cook and Gordon[39].

The mechanism considered appears consistent with various other observations connected with the strength of rubbers. These include the very low tear resistance observed when transverse deviation is prevented[5], or for the initial growth from a very sharp crack tip[28]. The observation of time-dependent failure in experiments on the cutting of a crystallizing rubber by a sharp implement (a razor blade)[40] may reflect the fact that the stress concentration associated with the blade tip is not diverted or diminished. Similarly, the breakdown of a crack growth model for abrasion in the case of crystallizing natural rubber, although the model works well for various non-crystallizing rubbers (including *cis–trans* isomerized natural rubber)[41], may be because the complex nature of the stresses in the abrasion experiments does not allow the normal, oriented crystalline structure to form at the crack tip.

CONCLUSIONS

The observations suggest that time-dependent mechanical crack growth can occur in vulcanized elastomers unless an oriented, anisotropic structure develops at the crack tip. Such a structure may arise through crystallization or filler orientation, and in either case it appears that appreciable time is required for the structure to become fully effective.

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