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Crack growth resistance of fluoroelastomer vulcanizates filled with particulate and fibre filler

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Crack growth characteristics of fluoroelastomer vulcanizates filled with carbon black (size: 30 nm) and short Kevlar fibre (6 mm length) under static and dynamic conditions have been evaluated. The fibre reinforced vulcanizate shows higher J_c values (80 kJ m^{-2}) than both the carbon black filled sample (44 kJ m^{-2}) and the control (15 kJ m^{-2}). However, under dynamic fatigue conditions, the black filled sample is stronger.

1. Introduction

In recent years, there have been an increasing number of fluoroelastomer parts used in defence applications and engine and fuel systems. These elastomers exhibit far superior chemical resistance and thermal stability over their hydrocarbon analogue due to shielding of the polymer backbone by the fluorine atom. Though the chemical resistance of these elastomers has been widely reported, the fracture behaviour has not received much attention. It is understandable that inspite of its chemical inertness, failure does take place under a variety of conditions. The present investigation is aimed at understanding the failure behaviour of fluorocarbon elastomers filled with particulate and fibre filler under tensile static and dynamic conditions.

Failure of hydrocarbon rubber is a widely studied subject. Gent [1] has made several excellent reviews on strength and failure of elastomers. Rivlin, Thomas, Lake and Lindley [2–4] in their series of publications indicated the importance of tearing energy in understanding the failure mechanism of elastomers. We have followed the same approach from our laboratory [5]. An alternative approach for characterizing the fracture properties of elastomers is the application of the J integral concept introduced by Rice [6]. Begley and Landes [7] applied this concept as a failure criteria to metals exhibiting large scale plasticity. Lee and Donovan evaluated the fracture properties of rubber vulcanizates by J integral methods [8]. Fundamentally, both the J integral and tearing energy, G_c, methods assume that a critical amount of energy is required to advance a crack by unit area, and hence are the same, provided the right experimental approach and data analysis have been adopted. Therefore

$$G_c = J_c = -\frac{1}{a}\left(\frac{dW}{dc}\right) \quad (1)$$

where dW is the energy released when the crack is increased by dc, and a is the thickness of the specimen. The reason for this equality ($G_c = J_c$) is that at the critical tearing energy, the stress distribution around the crack tip does not change when the crack length is increased, and moves simply with the crack tip. For example, the J integral is defined as

$$J = \int_\Gamma (W(x, y)dy - T_r(du/dx)\,ds) \quad (2)$$

where W is the strain energy density of any element on any integration path, Γ, surrounding the crack tip; T_r is the traction vector of the element; u is the displacement vector, and s is the arc length. If the integration path is taken along the blunted notch, then the traction vector is everywhere zero and

$$J = \int W dy \quad (3)$$

which is similar to the relationship derived by Thomas [2, 3].

The tearing energy for a specimen with an edge crack of length c is given by

$$G_c = 2kcW \quad (4)$$

where k is a function of the extension ratio. Cut growth rate under fatigue is empirically written as

$$dc/dN = k(G_c)^n \quad (5)$$

or after substituting the values of G_c and integrating the failure life, N is given by

$$N = \frac{B}{(2kW)^n c_o^{n-1}} \quad (6)$$

where B and n are constants, and c_o is the initial flaw size.

2. Experimental procedure

2.1. Materials

Fluoroelastomer (Viton A, a 70:30 copolymer of vinylidene fluoride and hexa fluoropropylene) has a fluo-

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rine content of 66% and a specific gravity of 1.82. The formulations are given in Table I. The rubber was crosslinked with hexamethylene diamine carbamate (DIAK 1). Carbon black (N330) and Kevlar short fibre (length 6 mm, L/D 500) after treatment were used as fillers. [A 100 gm of virgin Kevlar fibre was dipped in a 5% solution by wt. of bis (3-triethoxysilyl propyl) tetrasulphide (Si-69 wt %) and Desmodur in dichloromethylene in a beaker for 6 h. The fibres were taken out and spread in an air oven for 1 h at 70 °C.]

2.2. Processing

Mixing was carried out on a conventional two-roll mixing mill (330 × 152 mm) at a friction ratio of 1:1.1 at room temperature. The order of addition of ingredients was the same as the order shown in Table I. The vulcanization was carried out at 160 °C for 30 min under a pressure of 5 MPa in an hydraulic press, followed by post-curing in an air oven at 120 °C for 8 h and then at 200 °C for 16 h.

2.3. Physical properties

Tensile strength, modulus and elongation at break, were measured according to ASTM D 412–80, using dumb bell specimen at room temperature at 500 mm min^{-1} in MTS-880. Tear strength was measured using angled test pieces as per ASTM D 624–75 at room temperature at 500 mm min^{-1}. Heat ageing was carried out for 72 h at 150 °C in a circulating oven using dumb bell specimens following ASTM D 573–80. The tensile strength of aged and unaged samples was measured to calculate retention of properties.

2.4. Crack growth study under tension mode

Crack growth studies were carried out on single edge notch specimens having the dimensions 150 × 25 × 6 mm (filled samples) and 150 × 25 × 3 mm (gum samples). Initial notch lengths were 2, 4, 6, 8 and 10 mm for filled samples and 1, 2, 3 and 4 mm for gum samples. The crack growth resistance under tension mode was measured using the universal testing machine MTS-880. The specimens of composition B were also subjected to oil ageing and air ageing at 200 °C for 72 h. The single edge notches of 2, 4, 6 and 10 mm were then introduced into the aged specimen and their crack growth resistance was measured using the same procedure.

2.5. Crack growth study under dynamic mode

Crack growth resistance under dynamic conditions was measured using Dynamat Rubber Stretching Apparatus by giving a notch of 2 mm at the edge of the rectangular specimens (150 × 25 × 3 mm) at a stretching rate of 30 c.p.m. at room temperature at different strain levels: 20, 35, 40, 45 and 50%.

TABLE I Formulation of the mixes

Mix no.	A	B	C
Viton A	100.0	100.0	100.0
MgO	15.0	15.0	15.0
Stearic acid	2.0	2.0	2.0
N330	–	20.0	–
Kevlar	–	–	10.0
DIAK	1.5	1.5	1.5

3. Results and discussion

Load–displacement curves for various samples (A–C) with a range of notch lengths have been drawn. A representative curve is shown in Fig. 1. As expected, at a particular displacement, lower values of load are recorded for larger initial crack length. The displacement at which the crack starts propagating is noted for all the samples, and its magnitude is deducted from the original displacement. Such plots are shown in

TABLE II Technical and rheological properties of different fluoroelastomer vulcanizates

Properties	A	B	C
Hardness (Shore A)	70	75	85
Tensile strength (MPa)	5	15.2	18.1[a] 12.7[b]
Elongation at break (%)	150	300	50[a] 75[b]
Tear strength (N mm^{-1})	11	36	59[a]
Compression set per cent (20% (strain at 150 °C)	24	42	30
DeMattia flex			
To initiate (cycles)	37	19 223	260
Total failure (cycles)	37	157 142	613
Volume swell (%) (in oil, OM-270 at 150 °C, for 72 h)	No volume swelling observed		
Change of tensile strength (after air ageing at 150 °C, for 72 h)	No change of tensile strength observed		
V_r	0.42	0.49	0.51
Optimum cure time (min)	20.2	22.5	24.2

[a] Roll direction.
[b] Transverse direction.

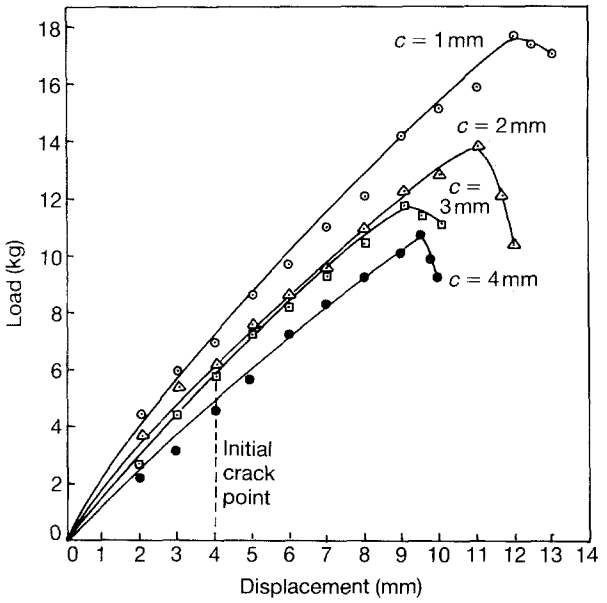

Figure 1 Load versus displacement curve for compound A.

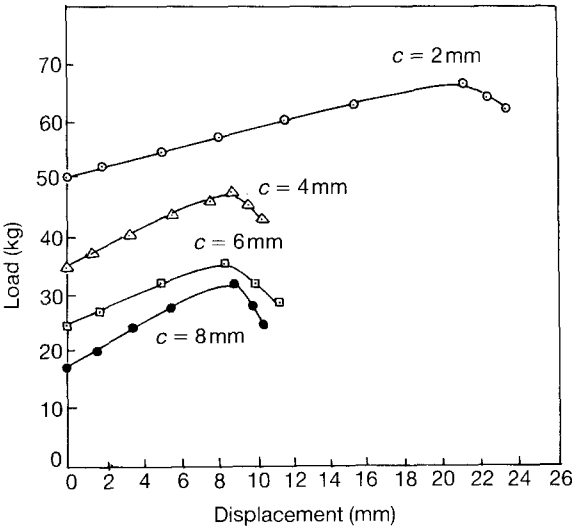

Figure 2 Load versus displacement curve for compound B.

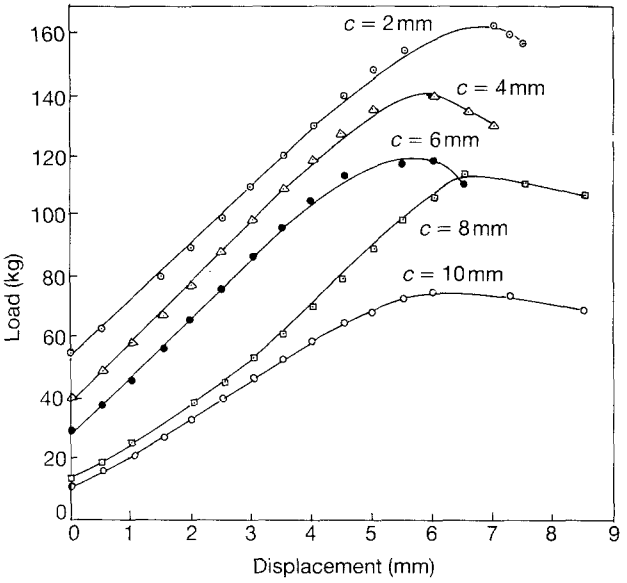

Figure 3 Load versus displacement curve for compound C.

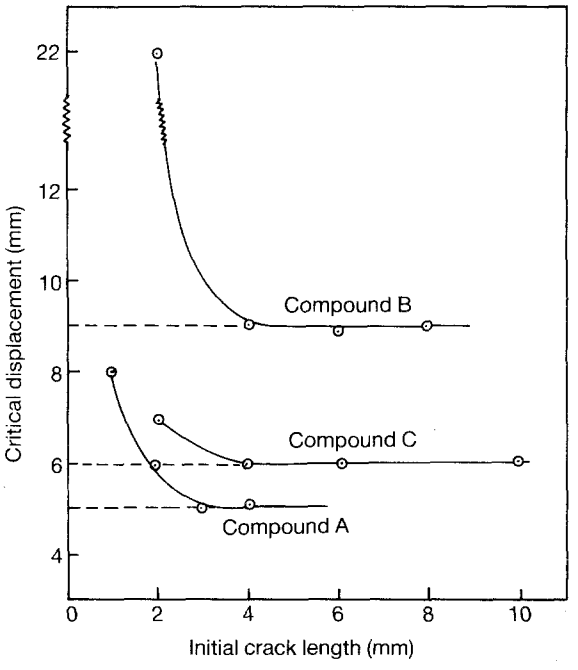

Figure 4 Plot of critical displacement versus initial crack length.

Figs 2 and 3 for carbon black filled sample, B, and fibre filled sample, C, having an initial crack length of 2, 4, 6, 8 and 10 mm. At lower values of notch length, the load required for a particular displacement is higher. Also, the fibre filled sample, C, displayed higher load than the carbon black filled sample at all displacements (Figs 2 and 3). The final displacement for the fibre filled matrix is, however, lower because of the higher stiffness and modulus of C. The figures also indicate that there is an optimum value of displacement at which the load decreases with displacement. This is referred to as the "critical displacement". These values are plotted against the initial crack length for various samples (Fig. 4). The critical displacement decreases with crack length in the initial stage, and then remains constant after 3–4 mm crack length depending on the nature of the compound. The strain energy is also obtained from the area under the load–displacement curves for several displacements of each vulcanizate. These are then plotted against initial crack length. Fig. 5 shows a representative plot for compound C. For a given displacement, the energy absorbed by a specimen decreases as the crack length increases, as expected, because of lower energy dissipation. The J integral values are obtained from the slope of these energy curves. A plot of J values against displacement is shown in Fig. 6. The higher the displacement, the larger the J value. The value of J corresponding to the critical displacement, shown by a dotted arrow in Fig. 6, is denoted as J_c. These are given in Table III, which also includes the values for compound B aged in oil and air for 72 h at 200 °C. At similar values of crosslink density proportional to volume fraction of rubber, V_r (Table I), the J_c value is almost double for the fibre-filled system compared to that for the carbon black filled one. With ageing, these values are drastically reduced, especially when the ageing conditions are very severe, i.e. in oil. The critical displacement is, however, maximum for com-

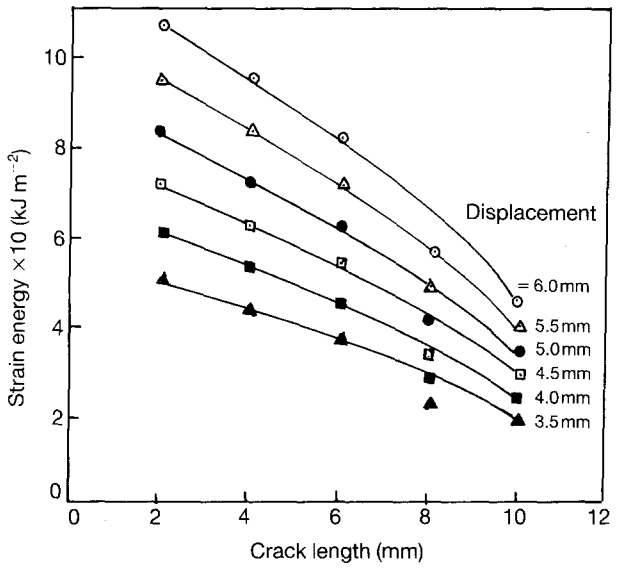

Figure 5 Plot of strain energy versus crack length for compound C.

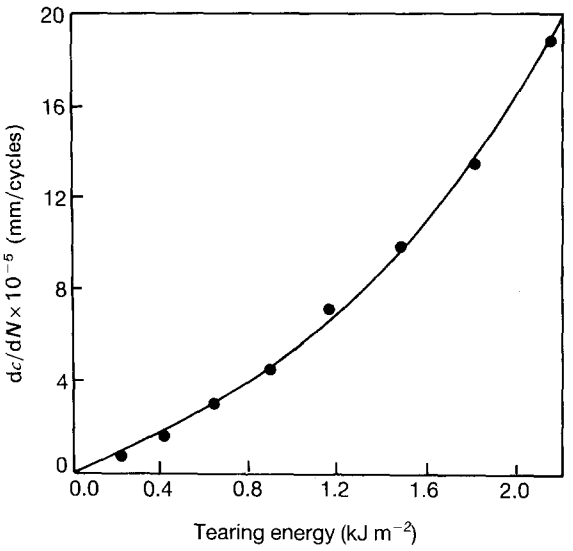

Figure 7 Crack growth rate versus tearing energy for compound B.

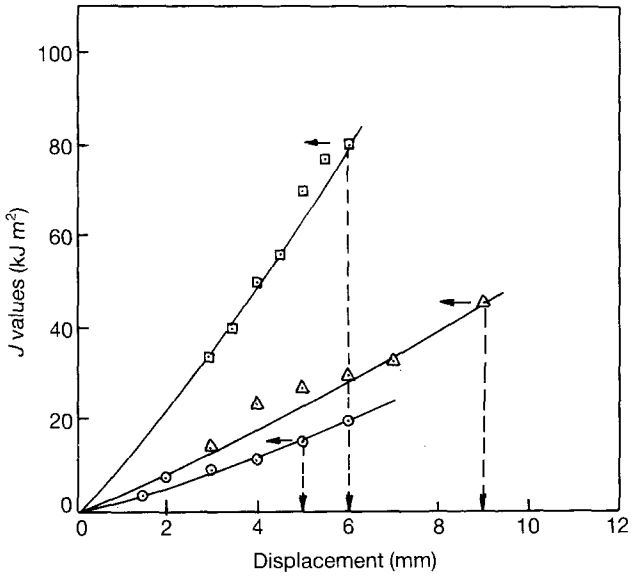

Figure 6 Plot of J values versus displacement for: (⊡) compound C, (△) compound B, and (⊙) compound A.

TABLE III Variation of J_c value and critical displacement for different fluoroelastomer vulcanizates

Composition no.	Critical displacement (mm)	J_c(kJ m^{-2})
A	5	15
B	9	44
B (aged in oil)	6	8
B (aged in air)	6	10
C	6	80

position B. These values are probably a combined function of stiffness and strength of the matrix.

3.1. Crack growth resistance under dynamic conditions

The crack growth rate, dc/dN measured at different strain levels is shown in Fig. 7. Increased strain causes faster growth because of the higher input energy (Equation 6). Contrary to the results reported in the preceding section, crack propagation in short fibre reinforced fluoroelastomer composites was too fast to measure at the strain rates studied. Hence, a detailed investigation was carried out on vulcanizate B. Tearing energy was measured and calculated from Equation 4. The dc/dN data are plotted against G_c values on a logarithmic scale. The slope of the line is 1.6. Earlier, values of two for gum natural rubber (NR) and four for gum styrene-butadiene rubber were reported. Neogi *et al.* [9] also obtained n = 1.3–2.7 for a series of carbon black filled NR at different temperatures. These studies clearly indicate that the fibre reinforced vulcanizate shows poor crack growth resistance under dynamic conditions, though at lower strain rates under tensile mode, this shows a higher value of J_c. The shorter fatigue life of compound C could also be understood from Equation 6.

4. Conclusions

Crack growth resistance of fluoroelastomer vulcanizates filled with carbon black and short Kevlar fibre under static and dynamic conditions was determined.

1. The fibre reinforced fluoroelastomer showed higher values of J_c than the carbon black filled sample at lower strain rates under a tensile mode.
2. Ageing reduced the value of J_c considerably.
3. Crack propagation under dynamic fatigue was faster in fibre filled vulcanizate. A value of 1.6 for the exponent was determined for the plot of cut growth against the tearing energy of carbon black filled vulcanizate B.

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