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Effect of short fibres on critical cut length in tensile failure of rubber vulcanizates

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Variation of critical cut length l_c in tensile failure of rubber vulcanizates has been studied with respect to the following variables: addition of short silk fibre, fibre concentration and orientation, ageing, reinforcing carbon black filler and elevated temperature. Strain crystallizing rubbers, e.g. natural (NR) and polychloroprene (CR), show higher l_c values than non-strain crystallizing nitrile rubber (NBR). The addition of short fibres was found to cause an increase in l_c in all cases. The increase is more prominent in the case of NBR than for NR and CR. The l_c values for unfilled NBR vulcanizates are low and a marginal increase is noted on the addition of carbon black. Addition of short fibres leads to a significant improvement in the l_c values, which show a gradual increase with increase in fibre concentration in the composites. l_c exists only in the composites wherein the fibres are oriented along the direction of application of tensile stress rather than across it, and the decrease in tensile strength is marginal at the initial stages but a sharp fall is observed with increasing size of cut lengths. On ageing, l_c values for composites increase while those for unfilled vulcanizates decrease. Critical cut length values for the fibre reinforced composites at a higher temperature (e.g. 100° C) remained unchanged, but dropped in the case of unfilled vulcanizates.

1. Introduction

The failure of elastomeric materials in tension is generally thought to initiate from the naturally occurring flaws acting as stress raisers. Inherent flaws result from factors such as imperfect cutting of the sample edges, moulding imperfections, dirt particles, and inhomogeneities in the process of preparation of the elastomeric composites. The effect of these flaws, having an effective size of the order of 30 μm, on the tensile failure and fatigue life of natural rubber (NR) vulcanizates has been studied by Thomas [1]. The application of cut and crack growth phenomena in the fatigue failure of rubber vulcanizates has been studied by many researchers [2–6]. Rivlin and Thomas [7] and Greensmith [8] have applied the tearing energy criterion and the change in stored energy to the problem of the tearing of a rubber strip containing a small cut on one edge and held in simple extension. The effects of crosslink density on the critical flaw size have been studied by Hamed [9]. The effects of the size and shape of the precut and its location on the tensile failure of ethylene propylene diene, EPDM, rubber vulcanizates have also been studied [10]. Reports on the studies of loss of tensile strength at higher temperature and the variation of critical cut length with increase of temperature in different rubber vulcanizates and in glass-fibre–epoxy and glass-fibre–unsaturated polyester composites have been published [11–16]. However, no study has so far been made on critical cut length phenomena in short fibre reinforced rubber composites. Lately, short-fibre–rubber composites have attracted the attention of technologists due to easy processing and anisotropy in physical properties [17–19].

The difference between the concepts of critical

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TABLE I Formulations of the mixes

Ingredient	Content of mix (parts by weight)								
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*
NBR	100	–	–	100	–	–	100	100	100
NR†	–	100	–	–	100	–	–	–	–
CR‡	–	–	100	–	–	100	–	–	–
ZnO	5	5	5	5	5	5	5	5	5
Stearic acid	2.0	2.0	0.5	2.0	2.0	0.5	2.0	2.0	2.0
PBNA[1]	–	–	2	–	–	2	–	–	–
MgO	–	–	4	–	–	4	–	–	–
Silica (Vulcasil–S)	10.0	5.0	10.0	10.0	5.0	10.0	2.5	5.0	–
Carbon black (FEF–N550)	–	–	–	–	–	–	–	–	40
Processing oil	–	–	–	–	–	–	–	–	4
Resorcinol	5.00	2.50	–	5.00	2.50	–	1.25	2.50	–
Cohedur RK	–	–	10	–	–	10	–	–	–
Silk fibre§	–	–	–	20	20	20	5	10	–
Cohedur A	–	–	3.2	–	–	3.2	–	–	–
Hexamethylenetetramine	3.2	1.6	–	3.2	1.6	–	0.8	1.6	–
Sulphur	2.0	2.0	0.5	2.0	2.0	0.5	2.0	2.0	2.0
CBS[2]	0.8	0.8	–	0.8	0.8	–	0.8	0.8	0.8
TMTM[3]	–	–	1	–	–	1	–	–	–
DOTG[4]	–	–	0.5	–	–	0.5	–	–	–
Optimum cure time (min)	10.50	9.00	34.00	10.50	7.50	31.50	12.00	11.25	11.50

*Nitrile rubber, Perbunan N 3307 (NS Grade), supplied by Bayer Ltd, West Germany.
†Crumb natural rubber, ISNR Grade 5, supplied by the Rubber Research Institute of India, Kottayam.
‡Neoprene, WM–1 grade, supplied by Bengal Waterproof Ltd, Panihati, Calcutta.
§Waste silk fibre (mulberry type), obtained in filatures from Silk Khadi Mondol, Bishnupur, West Bengal, India.
[1]PBNA = Phenyl-β-naphthylamine
[2]CBS = N-cyclohexyl 2-benzothiazole sulphenamide
[3]TMTM = Tetramethyl thiuram monosulphide
[4]DOTG = Di-*ortho*-tolyl guanidine

cut length in the present work and the work done by Thomas and co-workers [1, 3, 13] is that Thomas's work is concerned with the razor cuts artificially inserted normal to the test piece edge with the aid of a jig, and the critical size was correlated with the sharp fall in tensile strength due to lack of overall crystallization in rubber vulcanizates. But in the present investigations the cuts were applied through the exact centre and directed perpendicularly towards the applied tensile force, and the initiation of failure at the tip of the applied cut closely resembles the tearing phenomenon applicable to the Die C type of tear test specimen in ASTM procedure D 624–54. However, the difference between the two processes is that the tear test specimen contains an unnotched 90° angled cut, unlike the small chisel cuts applied at the centre of the tensile test specimens used in the present studies.

In the present paper we have reported the results of our studies on the variation of critical cut length in short silk fibre reinforced rubber composites. Addition of reinforcing carbon black and the effect of elevated temperature have also been undertaken.

2. Experimental procedure

Formulations of the mixes are given in Table I. Silk fibre was first separated from undesirable foreign matter and chopped to 6 mm length. Mixing was done on a conventional laboratory two-roll open mill (150 mm × 330 mm) at 30 to 40° C according to ASTM procedure D 15–70. Nip gap, mill roll speed ratio and time of mixing were kept the same for all the mixes. The rubber compounds were vulcanized at 150° C to their respective optimum cure times, obtained by using a Monsanto rheometer (R–100), and at 4.5 N mm^{-2} pressure in a hydraulic press having electrically heated platens. Details of the mixing, sequence of addition of the ingredients, preparation of the vulcanizates and the extent of fibre breakage by shearing forces during mixing have been reported elsewhere [17–20].

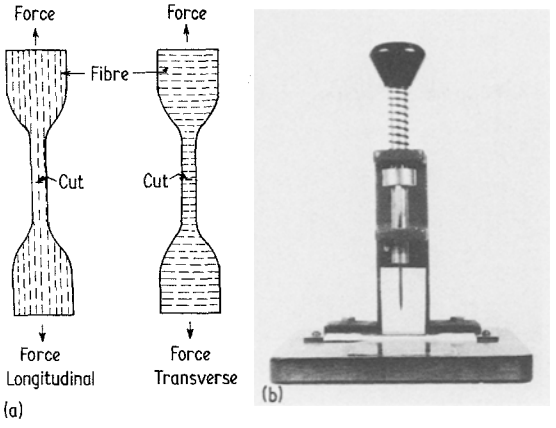

Figure 1 (a) Shape of tensile test specimens with longitudinal and transverse fibre orientation, direction of the applied force, and geometry of the applied precut; (b) Shape of the jig attached with a chisel of an arbitrary cut length, and position of a test specimen held rigidly by a die over the baseplate of the construction.

Dumb-bell test pieces were stamped from the moulded sheets along the grain direction and great care was taken to ensure cutter sharpness. In some cases, namely for fibre-filled nitrile rubber (NBR) composites, dumb-bells were punched out both along (longitudinally oriented fibres) and across (transversely oriented fibres) the grain direction. A special jig was constructed to rigidly hold the specimens while the prescribed chisel cuts were applied through the exact centre and directed perpendicularly towards the applied tensile stress. The diameters of all the chisels of different cut lengths were maintained to be the same. Shape of the tensile test specimens with longitudinally and transversely oriented fibres, direction of applied force and the geometry of a precut applied over the samples are shown in Fig. 1a. Fig. 1b shows the shape of the jig attached with a chisel of an arbitrary cut length and the position of a test specimen held rigidly by a die over the baseplate of the construction.

Tensile strength of the vulcanizates were measured on a Zwick tensile testing machine at room temperature (30° C) according to ASTM method D 412–51T. A model 3110 temperature cabinet with a temperature controller attachment accurate to ± 0.5° C fitted to an Instron Universal testing machine (Model 1195) was used for the measurement of tensile strength at higher temperature (100° C). Samples were tested after 15 min of storage at the elevated temperature in order to attain thermal equilibrium. The rate of separation of the grips in all cases was adjusted to 500 mm min^{-1}. On an average, five samples were tested for each cut length value and the consistency in the tensile strength values in each case were reproducible within $\pm 5\%$.

The tensile test specimens were aged for 48 h at 100° C in a Blue MFC 712 air oven and stored in the dark for 16 h for maturation before testing.

3. Results and discussion

3.1. Type of elastomer

Fig. 2 shows plots of tensile strength values of different elastomers against the size of the applied cut lengths. It is evident from Fig. 2 that the critical cut length values in the case of strain crystallizing rubber, e.g. NR (l_c = 1.5 to 1.7 mm) and polychloroprene CR, (l_c = 1.3 to 1.5 mm) are higher than that of the non-crystallizing NBR (l_c = 0.3 to 0.5 mm). Specimens undergo failure by two processes [14]: below the critical cut length, failure initiates from the edge of the specimen and proceeds towards the centre, and beyond l_c the failure occurs mainly due to tearing originating from the tip of the applied cut. Therefore, the fall in tensile strength with increase in cut length below the critical level is less; this is, however, followed by an abrupt fall at the critical point. Further decrease in tensile strength results after the critical cut length is exceeded. In the case of NR and CR, stretching induces crystallization at the tear tip which causes hindrance for the advancing tear.

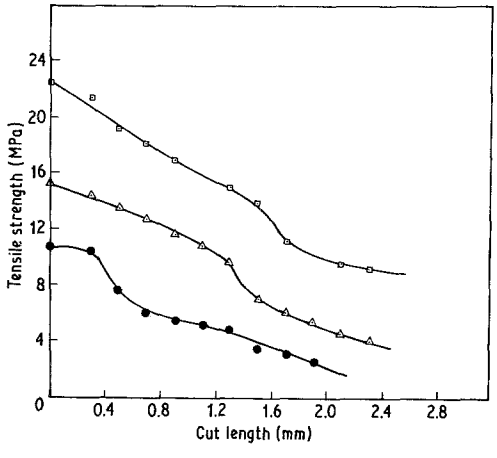

Figure 2 Plots of tensile strength values against the size of the applied cut length: ● Mix *A* (NBR), □ Mix *B* (NR), △ Mix *C* (CR).

Higher critical cut length is, therefore, observed in NR and CR compared to that of NBR. Again, the higher extent of strain crystallization in the case of NR gives rise to a higher critical cut length value for this rubber than for CR.

3.2. Effect of fibre addition

The reduction of tensile strength on the addition of short fibres in the mixes has been explained by Dzyura [21]. He expressed the strength of fibre–rubber composites by the additivity rule, provided that adhesion and orientation coefficient are introduced and the true influence of the matrix is considered. The tensile strength σ_c of the fibre reinforced rubber composites is expressed as

$$\sigma_c = \sigma_f V_f (1 - L_i/2L) K + \sigma_m V_m \quad (1)$$

where σ_c = composite strength, σ_f = strength of the fibre, V_f = volume fraction of fibre, σ_m = strength of the matrix at its maximum attainable deformation, L = average length of the fibre, K = coefficient of fibre orientation, L_i = ineffective length of the fibre. L_i is calculated on the condition that the force required for breaking the fibre is equal to the maximum shear force on the fibre–rubber boundary, so that

$$L_i = \frac{\sigma_f d}{2\tau} \quad (2)$$

where d = diameter of the fibre and τ = minimum shear stress on the boundary. The influence of the matrix on the value of σ_c was reported [21] to be dependent not on the matrix strength σ'_m but on its stretching resistance at the maximum composite deformation σ_m. For composites with a higher σ'_m/σ_m ratio (as in the case of NR) the fall in the tensile strength due to the addition of short fibres is greater compared to the matrices with a lower σ'_m/σ_m ratio (as in the case of CR and NBR).

The explanation suggested above supports our experimental observation of a sharp fall in tensile strength of the fibre-filled composite of Mix *E* compared to its control unfilled vulcanizate of Mix *B*. However, lower values of the σ'_m/σ_m ratio in the case of NBR and CR account for a marginal drop in tensile strength for the fibre-filled composites of Mixes *D* and *F* compared to their control unfilled vulcanizates of Mixes *A* and *C* respectively.

A significant improvement in critical cut length values is observed on the addition of fibres in the mixes. Fig. 3 shows plots of the size of applied cut lengths against tensile strength values of fibre–rubber composites of Mixes *D* (NBR), *E* (NR) and *F* (CR) with longitudinal fibre orientation. Below the critical point the fall in tensile strength with increasing cut length is negligible, beyond which the drop becomes faster. This is true for the three types of elastomer studied. The critical cut length values for different composites follow the order: NR(l_c = 2.5 to 2.7 mm) > CR(l_c = 2.3 to 2.5 mm) > NBR(l_c = 1.7 to 1.9 mm). The presence of the longitudinally oriented fibres physically obstructs the advancing tear by deviating the tear path and the fibres undergo breakage during the course of propagation of the fracture path; further resistance to tearing is thereby experienced. Critical cut length values for the fibre-filled composites (Mixes *D*, *E* and *F*) are, therefore, higher than the corresponding unfilled control vulcanizates (Mixes *A*, *B* and *C*).

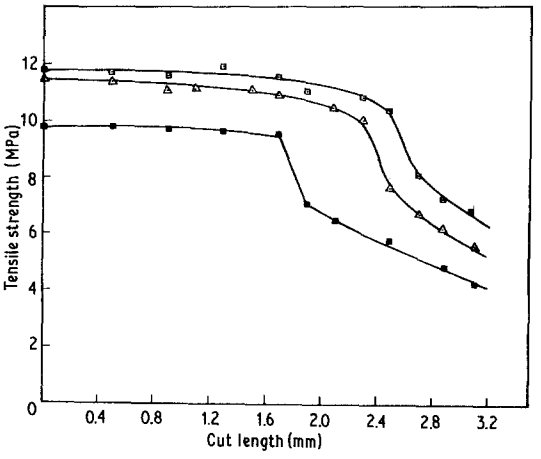

Figure 3 Plots of tensile strength values of fibre–rubber composites with longitudinal fibre orientation against the size of the applied cut length: ■ Mix *D* (NBR), □ Mix *E* (NR), △ Mix *F* (CR).

3.3. Effect of fibre concentration

Fig. 4 shows plots of the size of applied cut lengths against tensile strength values with increasing fibre concentration in NBR composites (Mixes *A*, *G*, *H* and *D*) with longitudinally oriented fibres. The extent of physical obstruction caused by the fibres, as discussed in Section 3.2, is proportional to the fibre concentration in the composites. A gradual increase

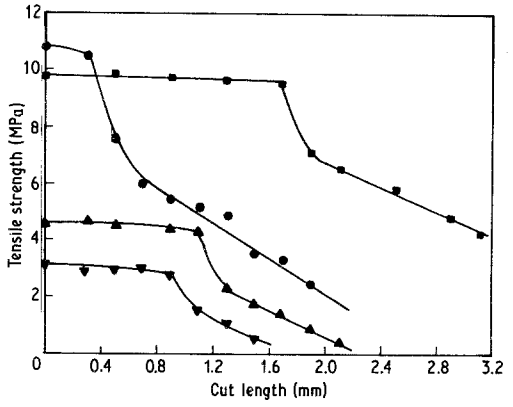

Figure 4 Plots of tensile strength values of Mixes *A*, *G*, *H* and *D* against the size of the applied cut lengths; fibre oriented longitudinally in Mixes *G*, *H* and *D*. ● Mix *A* (0 phr), ▼ Mix *G* (5 phr), ▲ Mix *H* (10 phr), ■ Mix *D* (20 phr).

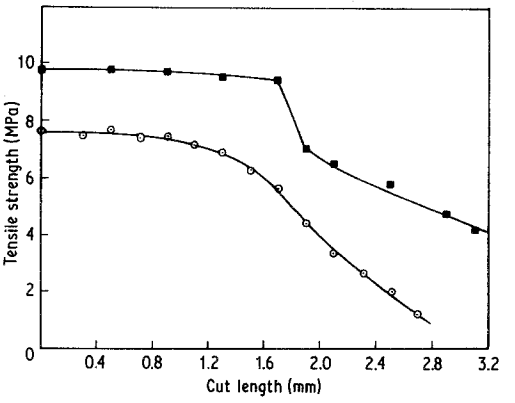

Figure 6 Plots of tensile strength values of Mix *D* with longitudinal (■) and transverse (○) fibre orientations against the size of the applied cut lengths.

in critical cut length values is, therefore, observed with increase in fibre loading (Fig. 5). Critical cut length values of different NBR vulcanizates follow the order: control unfilled vulcanizate (l_c = 0.3 to 0.5 mm) < 5 phr fibre-filled vulcanizate (l_c = 0.9 to 1.1 mm) < 10 phr fibre-filled vulcanizate (l_c 1.1 to 1.3 mm) < 20 phr fibre-filled vulcanizate (l_c = 1.7 to 1.9 mm), where phr is parts per hundred rubber.

3.4. Effect of fibre orientation

Remarkable changes in the critical cut length phenomena are observed on variation of fibre orientation. Fig. 6 shows plots of tensile strength values against the size of the applied cut lengths for the Mix *D* with both longitudinal and transverse orientations of fibres in the dumb-bell specimens (Fig. 1a). While the specimens with longitudinal fibre orientation show a critical cut length value of 1.7 to 1.9 mm, the specimens with transversely oriented fibres show a marginal fall in tensile strength at the initial stages of increasing cut lengths up to 0.9 mm, beyond which a sharp fall in tensile strength is observed. In the transverse fibre orientation the crack progresses parallel to the direction of fibre orientation, and resistance offered by the fibres to the propagating tear is less. Here the matrix with properly bonded fibres constitutes one system, and the strength required to rupture the sample is governed by the breaking energy of the system [17]. The increase in breaking energy for the fibre-filled composite of Mix *D* with transverse fibre orientation, compared to that for the control vulcanizate of Mix *A*, counteracts the initial decrease of tensile strength up to the cut length of 0.9 mm beyond which the rate of decrease is faster.

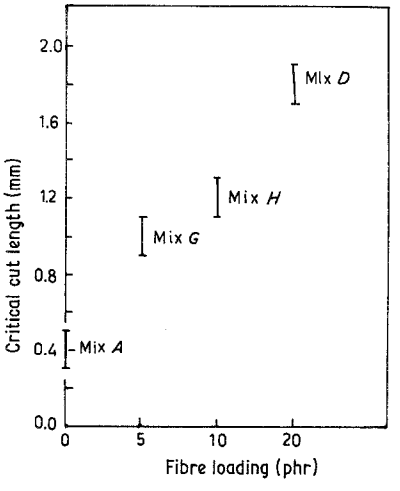

Figure 5 Plots of critical cut length values against fibre concentration of Mixes *A*, *G*, *H* and *D*; fibres oriented longitudinally in Mixes *G*, *H* and *D*.

3.5. Effect of ageing

It has been observed earlier [17] that ageing improves the adhesion level between the fibres and the rubber matrix and thereby enhances the tensile strength of the composites. Similar enhancement was not observed in the case of unfilled vulcanizates due to cleavage of cross-links in presence of resorcinol and hexamethylenetetramine during the post-curing process. This is also reflected in the critical cut length values for the aged vulcanizates of Mixes *A* and

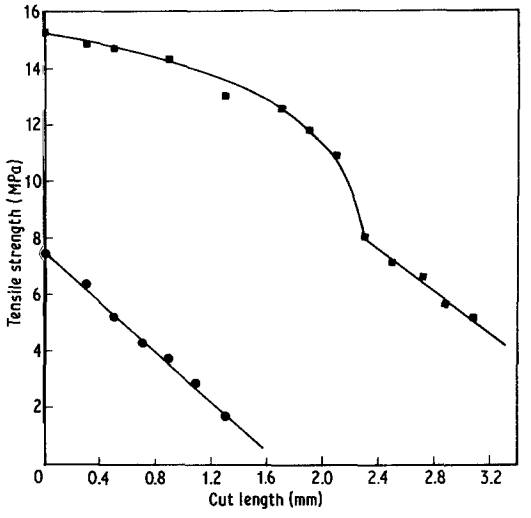

Figure 7 Plots of tensile strength values of the aged vulcanizates of Mixes *A* and *D* against the size of the applied cut lengths; fibres oriented longitudinally in Mix *D*. ● Mix *A* (unfilled), ■ Mix *D* (20 phr fibre).

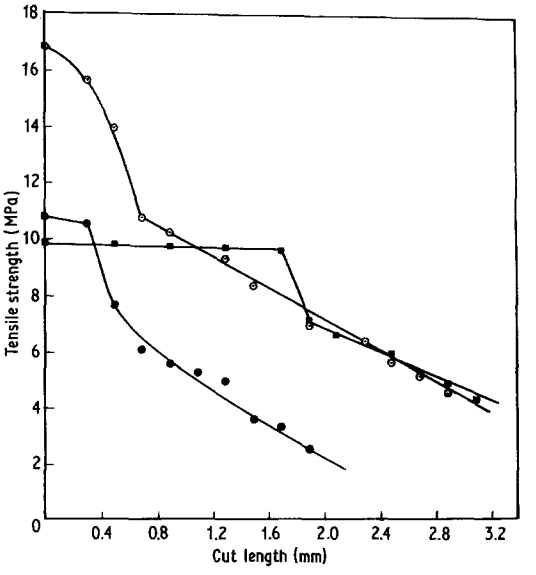

Figure 8 Plots of tensile strength values of Mixes *A*, *D* and *I* against the size of the applied cut lengths; fibres oriented longitudinally in Mix *D*. ● Mix *A* (unfilled), ■ Mix *D* (20 phr fibre), ○ Mix *I* (carbon black).

D, as shown in Fig. 7. An increase in the adhesion level between the fibres and the matrix due to ageing further enhances the resistance to tearing of the test specimens. Consequently, the aged vulcanizate of Mix D with longitudinal fibre orientation shows an increase in critical cut length values from 1.7 to 1.9 mm up to 2.1 to 2.3 mm. However, cleavage of crosslinks due to post-curing during ageing reduces the overall tearing energy of the system, and the aged vulcanizate of Mix *A* shows a sharp fall in tensile strength and no critical cut length value was obtained, while the unaged vulcanizate showed an l_c value of 0.3 to 0.5 mm.

3.6. Effect of addition of carbon black

Fig. 8 shows plots of tensile strength values against the size of applied cut length for Mixes *A*, *D* (longitudinal fibre orientation) and *I*. Addition of reinforcing carbon black involves an additional mechanism through which dissipation of strain energy at the tear tip occurs [22–24]. Reinforcing carbon black serves to arrest the growing crack by deviating the fracture front. A marginal increase in critical cut length, therefore, occurs for Mix *I* (l_c = 0.5 to 0.7 mm) as compared to that of Mix *A* (l_c = 0.3 to 0.5 mm). However, the efficiency of carbon black agglomerates in deviating the fracture front is less than that of short fibres. The increase of critical cut length due to addition of short fibres in Mix *D* (l_c = 1.7 to 1.9 mm) is therefore much higher than that achieved by the addition of carbon black in Mix *I* (l_c = 0.5 to 0.7 mm).

3.7. Effect of temperature

Fig. 9 shows plots of tensile strength values at 100° C against the size of applied cut length for Mixes *A* and *D* (longitudinal fibre orientation). At higher temperature the matrix becomes soft and offers comparatively less resistance to the

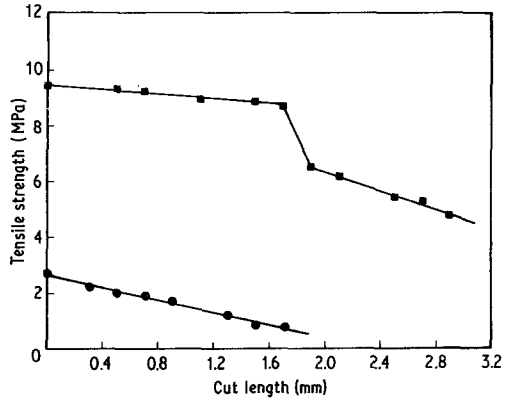

Figure 9 Plots of tensile strength values at 100° C of Mixes *A* and *D* against the size of the applied cut lengths; fibres oriented longitudinally in Mix *D*. ● Mix *A* (unfilled), ■ Mix *D* (20 phr fibre).

propagating tear. A sharp fall in tensile properties without any critical cut length value is, therefore, observed in the case of Mix *A* at 100° C. But in the case of Mix *D*, the resistance offered by the fibres remains unchanged since the fibres do not undergo any change due to increase in temperature up to 100° C. The critical cut length value, therefore, remains unchanged (l_c = 1.7 to 1.9 mm), although the absolute values of tensile strength decrease marginally due to the increase in temperature.

3.8. Effect of fibre length on critical cut length

In the present investigations, for all types of rubbers the initial fibre length before mixing was maintained at 6 mm. Due to shear forces during mixing in the open mixing mill the fibres undergo breakage and are also oriented along the grain direction. The extent of fibre breakage and the fall in the mean aspect ratio (average length to diameter ratio) of the fibres from its original value (before mixing) was determined by dissolution of the mixes in benzene in the case of NR, and in chloroform in the case of NBR and CR, followed by extraction of the fibres and examination of length and diameter of the extracted fibres by a polarizing microscope under reflected light (Leitz Model HM–Pol). A batch size of 200 fibres was taken in each case; the distribution of fibre lengths has been reported earlier [17–19]. The average length *L* of the fibres after mixing for different fibre–rubber compositions is given in Table II.

From Table II it is observed that the average fibre length in all cases is much lower than the corresponding critical cut length value obtained for different fibre–rubber composites. Thus the role of the fibres, when oriented longitudinally in the composites, in improving the critical cut length is to deflect the propagating fracture front. Besides deflecting the fracture path, the fibres also undergo breakage and consequently more energy is expended in the process of deviation of fracture path as well as due to breakage of fibres on its way. Higher critical cut length values in longitudinal fibre orientation are, therefore, observed for Mixes *D*, *E* and *F* compared to the unfilled Mixes *A*, *B* and *C*. However, when the fibres are oriented transversely in the composites both deviation of fracture path and fibre breakage do not occur as the fibres are aligned in the direction of fracture propagation. In this case a matrix with properly bonded fibres simply increases the breaking energy of the system. This counteracts the initial deterioration of tensile strength up to a certain cut length value, beyond which the fall becomes similar to the control unfilled mixes.

The nature of fibre breakage in tension and the distribution of broken fibres after mixing have already been reported elsewhere [18].

TABLE II Breakage characteristics of silk fibres in different rubbers

Type of rubber	Average fibre length before mixing (mm)	Average fibre length after mixing (mm)
NBR	6	0.9
NR	6	1.3
CR	6	1.0

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