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Short Fibre and Particulate-reinforced Rubber Composites

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ABSTRACT

Particulate fillers (carbon black and silica) and short fibre (aromatic polyamide, Kevlar®) have been utilised to produce rubber composites based on acrylonitrile-co-butadiene rubber (NBR). Mechanical properties of these composites have been determined and compared with unfilled rubber vulcanisate. The effect of surface treatment on the improvement of strength, in case of Kevlar, has also been considered. The influence of elevated temperature on tear strength, an important failure criterion, has been evaluated. Scanning electron microscopy has been used as a tool to correlate the topographical features associated with changes in the tear strength of the composites.

Keywords: Rubber composites, Kevlar, SEM, tear strength, composites, particulate fillers, short fibres, nitrile rubber, reinforcing fillers, acrylonitrile-co-butadiene rubber (NBR), scanning electron microscopy, aromatic polyamide

1. INTRODUCTION

Nitrile rubber (NBR), because of its high oil and fuel resistance, finds widespread use as seals, gaskets, diaphragm, etc. in a variety of applications, including defence equipment. However, the rubber as such without the incorporation of any reinforcing filler offers poor mechanical strength. Significant improvement in strength can be achieved through addition of either particulate (carbon black or silica) or short fibre as filler into NBR. Short fibres, in contrast to particulate fillers, are known to produce mechanical anisotropy as the fibres are oriented inside the matrix in a particular direction. Setua[1-7], *et al.*, have reported, in quite a few papers, on the reinforcement characteristics of such fillers in NBR or similar matrices.

In engineering applications, crack growth and failure of composite materials depend on the growth of microcracks present inherently during fabrication or generated under repeated stress cycles on prolonged use. Generally, tear is a very important criterion of failure. Higher tear resistance shows better toughness and superior ballistic properties. Rivlin and Thomas[8] have shown that the tear resistance of viscoelastic materials can be expressed by a characteristic energy which is related to the elastic energy stored in the highly strained zone and at the tip of the growing tear. The tear energy (T) follows the relationship:

$$T = d \,.\, E_b \qquad (1)$$

where E_b is the strain energy per unit volume required to break the specimen, and d is the effective diameter of the small zone of tear. The tear energy depends on various factors like methods of testing, (eg, tear, impact or flexing), nature of the base polymer, temperature, sample geometry, etc. If a minimum tear energy is required for any crack to grow and that is more than the strain energy, then the life

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of the composite will be infinite. Various factors, particularly the temperature, play a crucial role in damage and degradation of the composite, leading to premature failure. The incorporation of antioxidants has been widely practiced, but of limited success. The effect of elevated temperatures on the tear resistance of elastomers has been studied by Setua[9]. Reinforcement and thermal analysis of particulate and short fibres-filled elastomeric matrices have also been reported[10,11].

Contributions from Medalia[12], Gent[13] and Bartenev and Zuyev [14] suggest two-stage mechanism of tearing of rubber composites–the deformation of the specimen, followed by the growth of the sectioned region. Since little is known about the damaged zone, where deformation and fracture take place, the use of scanning electron microscopy (SEM) is ideal as it provides an insight into the problem. Setua[4,7,15,16], *et al.* have made successful attempts in the correlation of physico-mechanical properties of elastomers and composites with the topography of the fractured surfaces recorded under SEM.

In the present paper, the effect of various fillers on the mechanical properties of NBR and the influence of elevated temperatures on tear strength have been studied. Kevlar, a material of strategic importance, finds widespread applications as reinforcement for polymer composites for ballistic resistance and high temperature resistance for aerospace and defence. Major properties of Kevlar which make it superior to other synthetic polyamides (aliphatic eg, nylon 66/nylon 6, or aromatic eg, Nomex) are: (i) high strength modulus/unit weight, (ii) low elongation, (iii) flame resistance, (iv) non-melting nature, and (v) wide temperature range. There are two reasons to undertake this study. First, the tear strength of short fibre-filled composites is higher than those of the particulate ones, and secondly, the Kevlar has better temperature resistance than nylon.

2. EXPERIMENTAL WORK

Kevlar-29 fibres were first chopped to 6 mm (length) and then treated with isocyanate coupling agent (2 % desmodur–R in dichloromethane) for 2 h and dried at 70 °C for 4 h to remove the solvent completely. Formulations of the mixes are given in Table 1. Mixing was done on a conventional laboratory open mill (150 mm x 330 mm) at 30–40°C according to ASTM designation D15-70. Nip gap, mill roll speed ratio, time of mixing, and the sequence of addition of the ingredients were kept the same for all the mixes. Mixes were vulcanised at 150 °C and 4.5 MPa in a hydraulic press for 15 min.

Table 1. Formulations of mixes

Ingredient (phr*)	Mix Nos A	B	C	D	E
NBR**	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Sulphur	1.5	1.5	1.5	1.5	1.5
PBNA***	3.5	3.5	3.5	3.5	3.5
MBTS•	1.5	1.5	1.5	1.5	1.5
TMT••	0.5	0.5	0.5	0.5	0.5
Kevlar+	---	15 (untreated)	15 (treated)	---	---
Carbon black++	---	---	---	40	---
Silica#	---	---	---	---	30

* phr stands for parts per hundred (weight, in g) parts of rubber

** NBR (acrylonitrile content: 38 mol per cent, specific gravity: 0.99 supplied by the Synthetics and Chemicals Ltd., India).

*** PBNA (phenyl β-napthyl amine)

• MBTS (mercapto benzothiazole sulphenamide)

•• TMT (tetramethyl thiuram monosulphide), supplied by the Alkali and Chemical Corporation of India Ltd., Rishra, Kolkata.

\+ Kevlar-29 obtained from E.I. Du Pont de Nemours. Inc., DE, USA.

++ High Abrasion furnace (HAF, ASTM No. N 330) carbon black obtained from the Philips Carbon Black Ltd., Durgapur.

\# Precipitated grade of silica (vulcasil-S), supplied by the Bata India Ltd., Kolkata. All other chemicals are of pure analytical grade.

Tensile testing was done as per ASTM designation D 412-51 T, using dumb-bell specimens. The test also helps to measure elongation at break values.

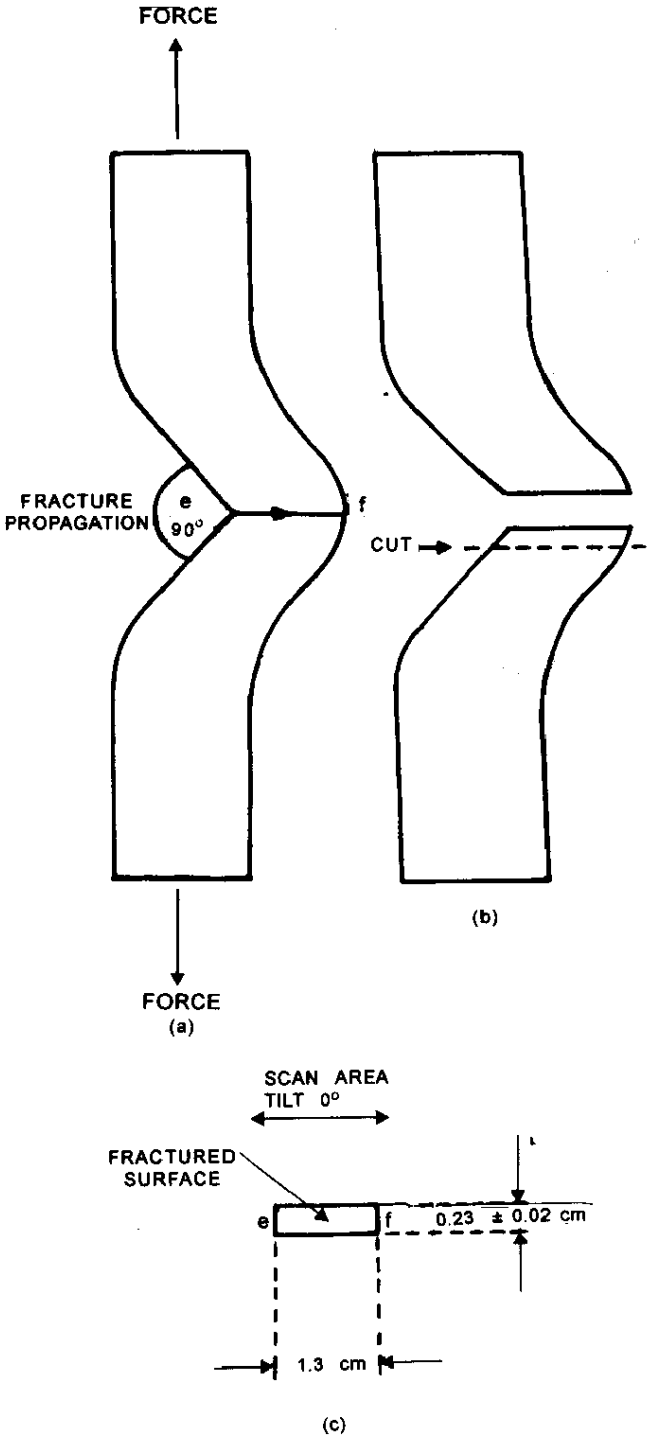

Figure 1. (a) Original test specimen (thickness 0.23 ± 0.02 cm) indicates e, the point at which tear starts; f, the point at which tear ends, (b) failed specimen, and (c) scan area of the fractured surface.

The tear strength was measured with an un-notched 90° test specimen [die C, shown in Fig. 1(a)] according to ASTM designation D 624-54. Both the tensile and the tear tests were carried out in a Zwick tensile testing machine at 25 ° ± 2 °C. Samples were stretched at 500 mm min^{-1}. Fracture propagates perpendicular to the direction of the applied force as shown in Fig. 1(a). Figure 1(b) shows the shape of two failed pieces after complete fracture has occurred. The fractured surfaces were then carefully cut out from the failed test pieces without touching the surface. These specimens were stored in a dessicator to avoid contamination by dust particles and then sputter-coated with gold within 24 h of testing.

2.1 Scanning Electron Microscopy

The SEM photomicrographs were taken by an ISI:60 model SEM within 72 h of tesing. From the preliminary experiments, it has been found that the fracture mode does not change even after 72 h of storage of the specimen (without gold coating) after the test. The scanning area is shown in Fig. 1(c). Photomicrographs were taken along the direction (e → f) as shown in Fig. 1(a), which is the same as the direction of fracture propagation. The tilt was adjusted to zero degree in all the cases.

2.2 Measurement of Tear Strength at Elevated Temperatures

A standard width temperature cabinet of FPZ 10 tensile tester with pneumatic clamps and 0.5871 MPa air pressure was used. Elevated temperatures were obtained by powerful air circulation to apply very high heating rate. This resulted in uniform temperature distribution throughout the interior cabinet and test specimen. Based on the thermal response of the test specimen, standard 10 min waiting period was given.

2.3 Fibre Orientation

Preferential orientation of the fibres takes place along the direction of milling in the mixing mill and this direction is called the grain direction. Care was taken to maintain the grain direction fixed

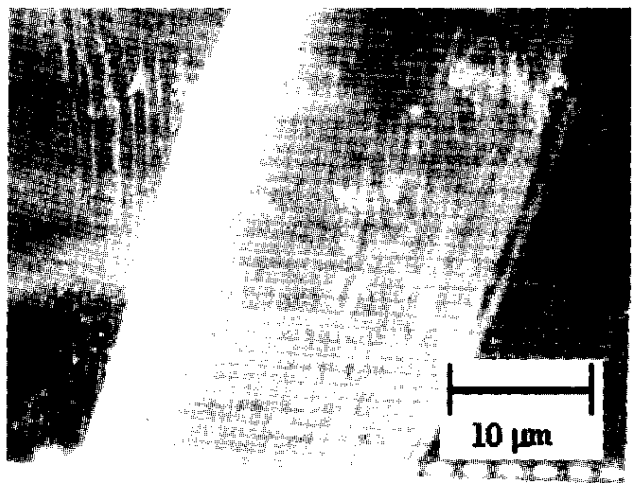

Figure 2. Rough Kevlar surface and protrusion of one fibril from its end, X 2000.

while moulding of the test slabs. Tests like tensile, elongation at break, tear and compression set (as per ASTM designation D 395–61A at 400 lb constant load and 25 % strain) were carried out, both along (longitudinally oriented fibres) and across (transversely oriented fibres) the grain direction. Hardness was measured (as per ASTM designation D 676–52T) with tensile sheet specimen and orientation of the fibres, in this case, was normal to the direction of the application of the load.

3. RESULTS & DISCUSSIONS

In the process of failure of composite materials, polarity of the fibre surface plays a vital role. Also important are the surface energy difference between the fibre and the rubber, as well as surface roughness of the fibre which imparts better physical interlocking between the fibre and the matrix resin. Figure 2 shows the surface of Kevlar which has a rough surface and a protrusion of one fibril at the edge. Kevlar is polar, as is the nitrile rubber, and as such is expected to generate adequate fibre-matrix adhesion. To further improve the adhesion level, fibres were treated with 2 per cent desmodur–R. The composite properties with untreated and treated fibres have been compared in Table 2 (composite numbers B and C). The surface treatment has been found to improve the mechanical properties. Table 2 also gives the mechanical properties of other composites eg, unfilled (A) and filled [treated Kevlar (C), carbon black (D) and silica (E)]. Superior tear strength, lower tensile strength and elongation at break values, higher hardness and compression set of the fibre-filled composite (C) compared to either silica (E) or carbon black (D) systems were obtained. These indicate that the shape and size of a filler control the final physical properties of the composites.

Table 2. Mechanical properties of composites

Property		Composite Nos.				
		A	B	C	D	E
Hardness (shore A)		51	80	86	66	66
Tensile strength (MPa)	L$^{\$}$	1.2232	6.5562	11.2728	10.0985	12.5155
	T$^{\$}$		3.9435	5.1373		
Elongation at break (%)	L	300	45	25	225	250
	T		100	65		
Compression set at 70 °C for 24 h (%)	L	20.5	34.6	27.5	16.7	7.9
	T		39.1	32.4		
Tear strength (N/cm)	L	0.8665	6.0754	8.2263	2.0795	2.1203
	T		3.9144	4.9745		

L$^{\$}$: Longitudinal fibre orientation,

T$^{\$}$: Transverse fibre orientation.

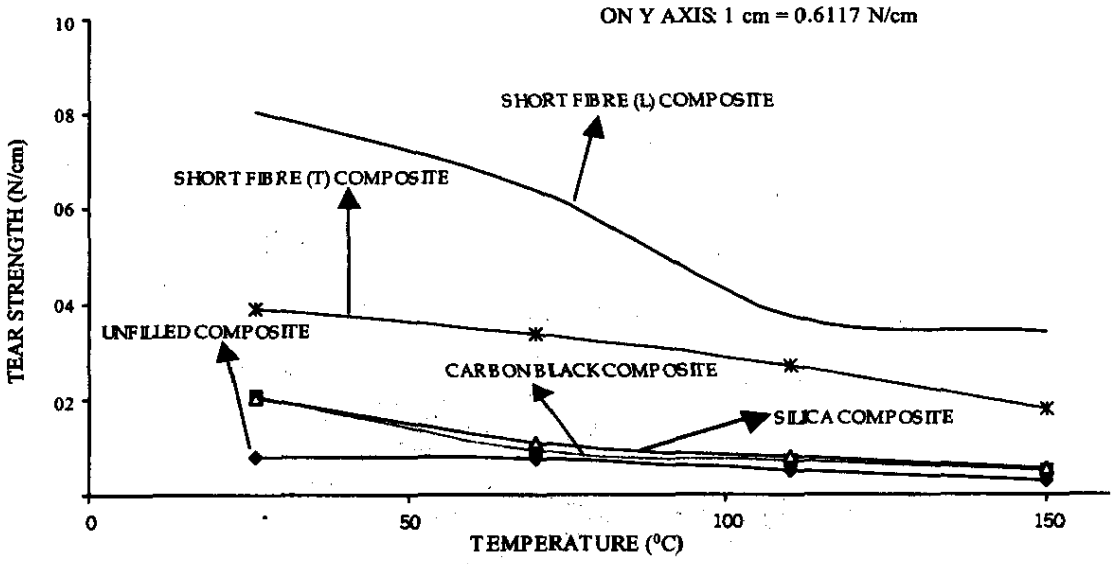

Figure 3. Plots of tear strength *vs* temperature. L and T are the longitudinal and transverse orientations of the fibre, respectively

The temperature dependence of the tear strength of fibre-filled and particulate-filled composites is given in Fig. 3. It is seen that the rate of fall of tear strength is higher in the fibre-filled composites than particulate-filled composites. Besides, the fall wrt temperature in case of longitudinally oriented fibres is more than the transversely oriented fibres. While transversely oriented, the fibres play no role in the growth of the tear path and the failure in the matrix at elevated temperatures depend on the matrix softening. But in the longitudinal orientation, the adhesion between the fibre and the matrix is important. The absolute value of tear strength for composite with longitudinally oriented fibre, is therefore, higher than the transversely oriented one. At elevated temperatures, fibre-matrix debonding occurs and causes enhancement in the rate of fall of tear strength. However, the tear strength of fibre-filled composite in both the directions of fibre orientations are always higher compared to either silica or carbon black-filled composites. A line drawing showing various features observed in the SEM photomicrographs eg, tear lines, branching, rounded tear lines, etc., is given in Fig. 4.

Figure 5 is the SEM photomicrograph of the tear-fractured surface at room temperature, 25 ± 2 °C, of the unfilled rubber (mix A). Presence of many steady tear lines in different planes with occasional branching have been observed. A tear surface of the same vulcanisate fractured at 150 °C, shows abrupt changes (Fig. 6). Steady tear lines have vanished. Slip lines, characteristics of a catastrophic failure, appeared as well as the formation of vacuoles with nodular cavitation. All these signify very poor tear strength of the amorphous nitrile rubber at an elevated temperature.

The SEM photomicrograph (Fig. 7) of the surface of silica-filled composite (mix E), fractured at room temperature (25 ± 2 °C), shows the presence of many tear paths and extensive tear branching. Extensive tear branching leads to better energy absorption due to deformation and extension of length of fracture paths. Silica-filled composite, therefore, shows better tear strength than unfilled composite (Table 2). Tearing at elevated temperature (150 °C) causes remarkable changes in the fracture surface topography (Fig. 8). Brittle failure in different planes and thick tear paths without any branching are observed. These lead to a sharp fall in the tear strength at elevated temperature.

The SEM photomicrograph of carbon black-filled composite (mix D), fractured at room temperature (25 ± 2 °C), is shown in Fig. 9. The topography has no steady but many short and rounded tear lines. Carbon black agglomerates are also seen in the figure (indicated with arrows).

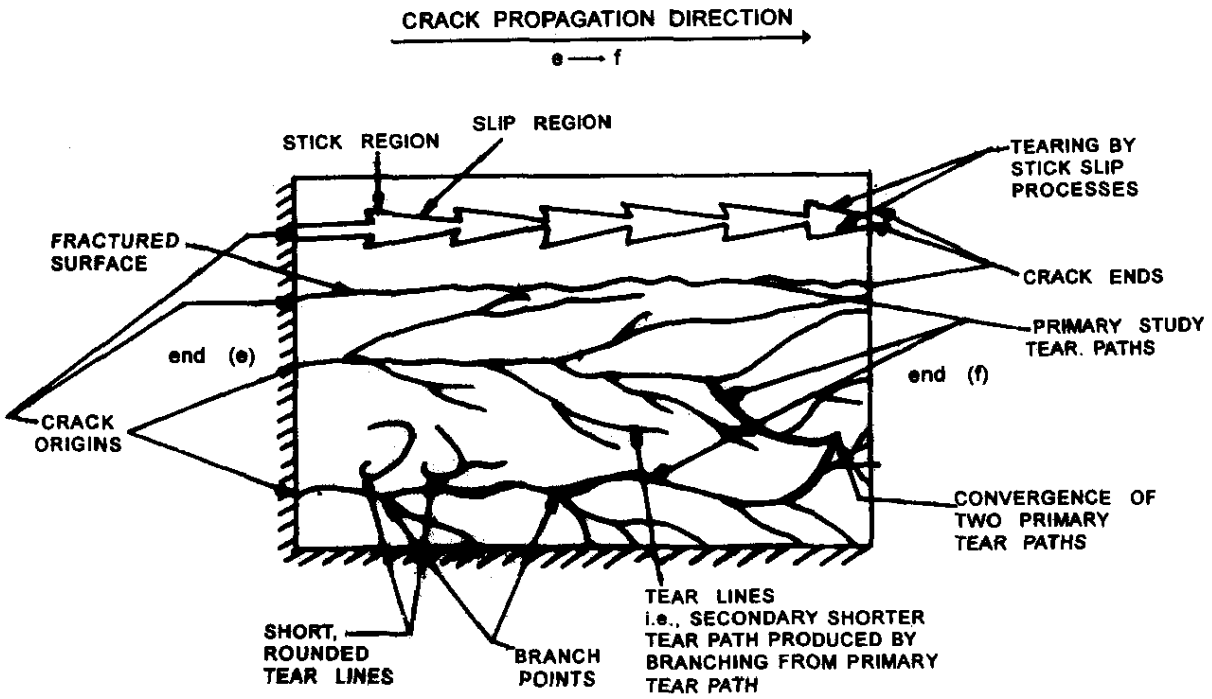

Figure 4. Line drawing showing various features observed in SEM photomicrographs

Addition of reinforcing carbon black induces additional mechanism by which strain energy is dissipated. Mechanical energy dissipation through increased hysteresis resulting from the inclusion of particles in a viscoelastic medium has been studied by Rodak and Tai[17]. Any loss of segmental mobility in the polymer matrix resulting from interaction with the filler, further increases the hysteresis. Motion of filler particles, chain slippage or breakage and dewetting at high strains also accentuate the hysteretic behaviour. In addition to causing increased energy dissipation, dispersed particles finally serve to deflect or arrest the growing cracks, thereby further delaying failure and enhancing tear energy. Tear strength of the carbon-filled composite sharply falls at 150 °C as evident in the failure pattern

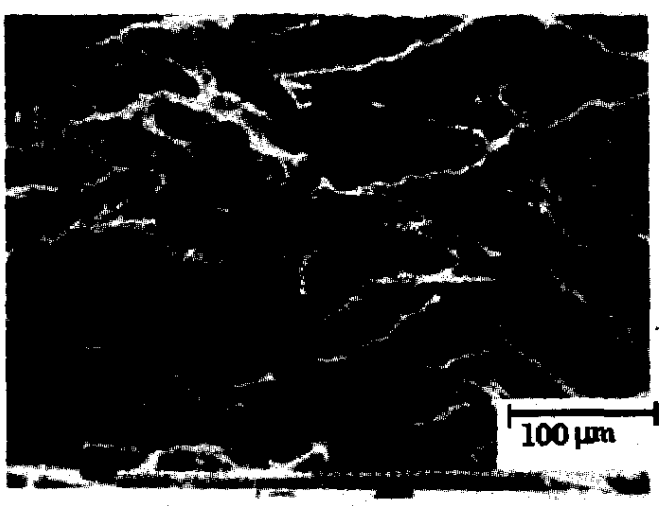

Figure 5. Tear-fractured surface of the unfilled rubber composite (mix A) at room temperature, X100.

Figure 6. Tear-fractured surface of the unfilled composite (mix A) at 150 °C, X100.

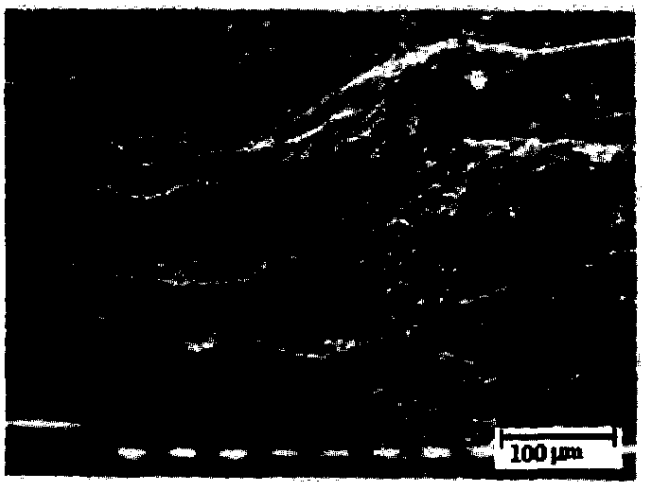

Figure 7. Tear-fractured surface of silica-filled composite (mix E) at room temperature, X200.

Figure 8. Tear-fractured surface of silica-filled composite (mix E) at 150 °C, X200.

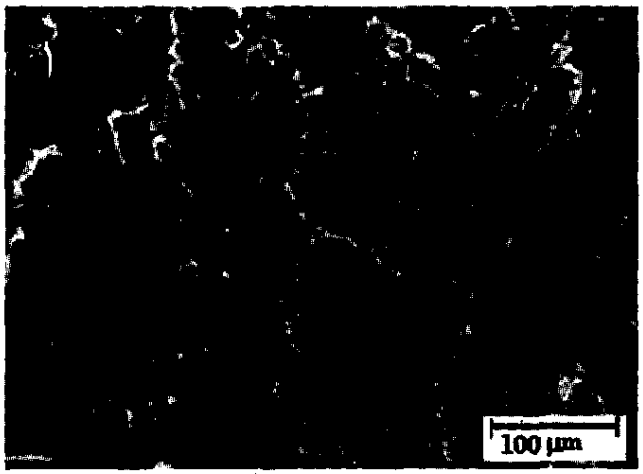

Figure 9. Tear-fractured surface of carbon black composite (mix D) at room temperature, X50.

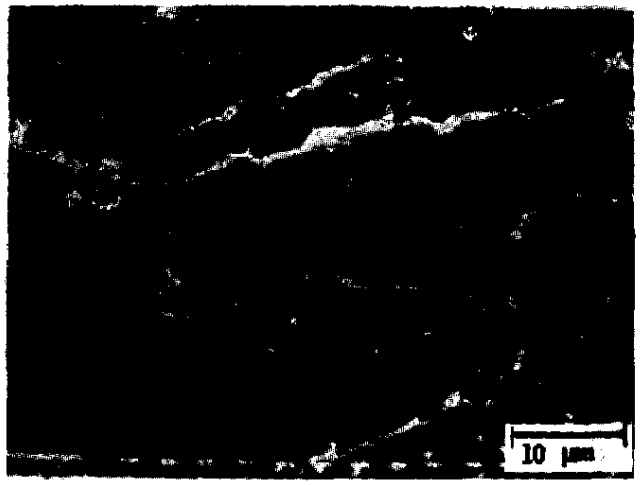

Figure 10. Tear-fractured surface of carbon black composite (mix D) at 150 °C, X400.

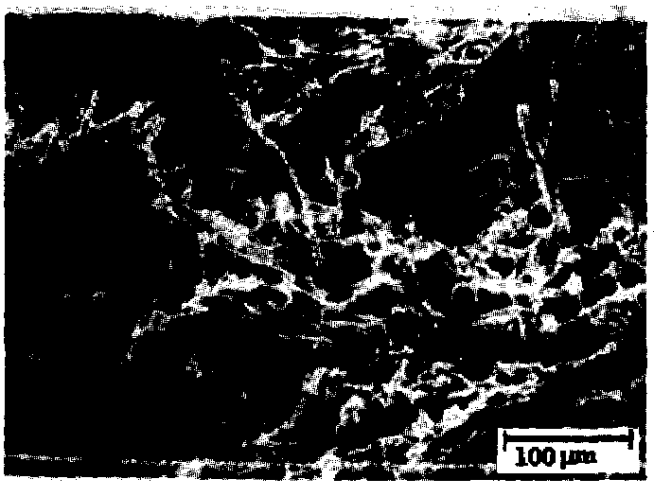

Figure 11. Tear-fractured surface of the Kevlar composite (mix C) with fibre oriented in the longitudinal direction and fractured at room temperature, X200.

(Fig. 10). The figure marks the presence of matrix hardening with formation of channel cracks across the main fracture fronts. Micropitting and grooves are also evident.

The SEM photomicrograph of the composite with Kevlar oriented in the longitudinal direction and fractured at room temperature is shown in Fig. 11. As described earlier, the fibres offer physical hindrance to the propagation of the tear paths. The photograph, therefore, shows matrix deformation and inhibition of the propagating fracture path by the bonded fibres. There are few voids but

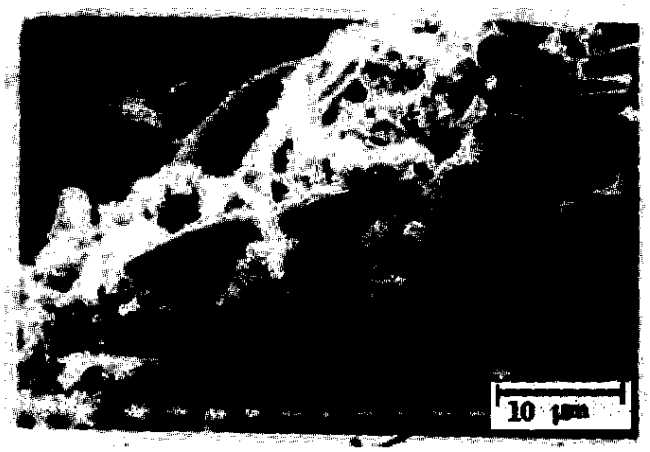

Figure 12. Very good fibre-matrix adhesion shown at higher magnification, X400.

these are due to shear deformation and not because of de-bonding of the fibres. Very good adhesion of the fibres with the matrix is also evident in another photomicrograph at slightly higher magnification (Fig. 12). Figure 13 shows the breakage pattern of a single Kevlar fibre of a tear-failed composite specimen. The broken fibre surface shows rough texture with long tail of material around fracture locus. The SEM photomicrograph of the fractured surface at 150 °C is shown in Fig. 14. Formation of groves across the fibre-matrix interface due to decreasing fibre-matrix adhesion is clearly observed. The lowering of the tear strength is due to matrix softening and fibre-matrix de-bonding.

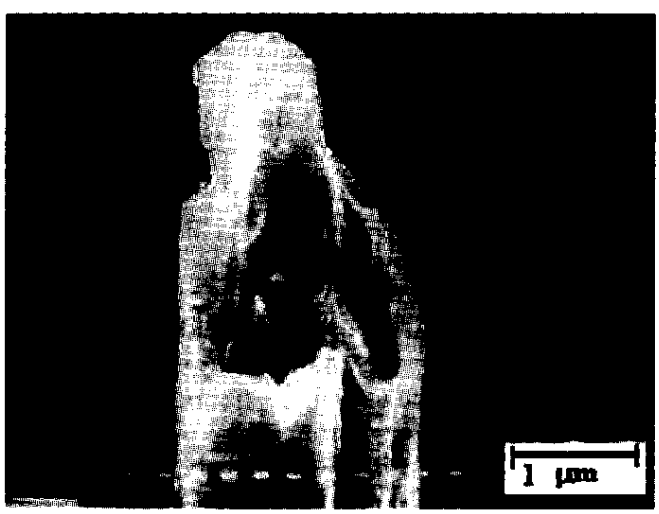

Figure 13. Breakage pattern of Kevlar, X3500

Figure 14. Tear-fractured surface of the Kevlar composite (mix C) at 150 °C, X200.

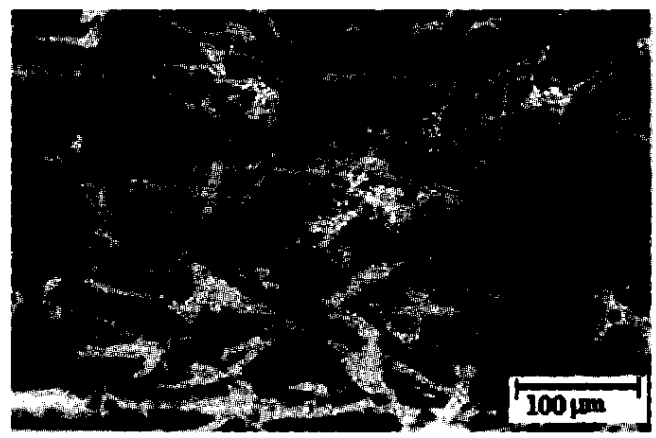

Figure 15. Tear-fractured surface of the Kevlar composite (mix C) with fibre oriented in the transverse direction at room temperature, X200.

The SEM photomicrograph of the fractured surface at room temperature of the composite with transversely oriented fibres is shown in Fig. 15. It is clearly seen that the fibres in this direction offer very little resistance to crack propagation from one end to the other of the fracture zone. This leads to lowering of the tear strength of the composite. The photograph also shows the absence of fibre breakage, de-bonding and orientation of fibre along the grain direction. Elevated temperature (150 °C) causes matrix softening similar to that observed for the composite with longitudinal fibre orientation. The photomicrograph (Fig. 16) shows extensive groove formation as well as matrix flow in the direction of tear. These signify loss of tear strength at elevated temperature.

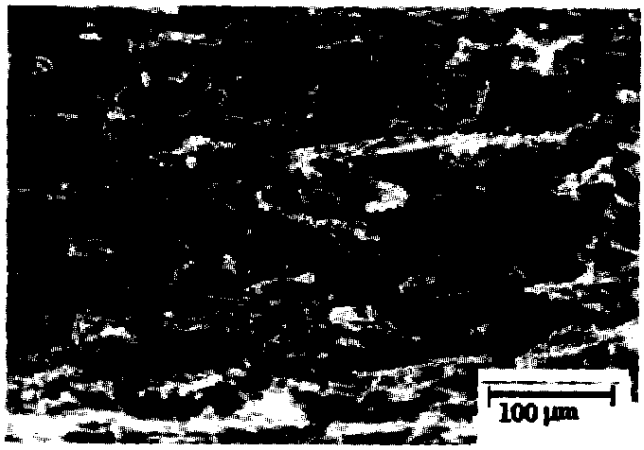

Figure 16. Tear-fractured surface of Kevlar composite (mix C) with transversely oriented fibres at 150 °C, X100.

4. CONCLUSIONS

The following conclusions have been drawn:

- Substantial improvement in the mechanical properties can be envisaged through addition of fillers (either short fibre or particulate) into nitrile rubber. However, the addition of short fibre has been found to be more effective.
- With increasing temperature, a continuous fall in the tear strength for unfilled, carbon black and silica-filled composites are observed which can be attributed to enhance matrix softening as well as reducing hindrance offered by the filler agglomerates (eg, silica or carbon black) to the propagating tear fronts.
- Increasing temperature also causes substantial deterioration of the fibre-matrix adhesion which has a pronounced effect on the tear strength of the composites. The fibre-filled composites always show better tear properties than unfilled or particulate-filled composites.
- The SEM has been demonstrated to be an effective tool in the correlation of the strength properties with the features observed on the fractured surface.

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