

Pressure-sensitive electrically conductive nitrile rubber composites filled with particulate carbon black and short carbon fibre

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The electrical conductivity of pressure-sensitive nitrile rubber composites, containing different loadings of particulate carbon black filler and short carbon fibre, have been studied. The conductivity of composites increases with increasing of filler concentration as well as with increased applied pressure up to a certain limit. The composites containing particulate fillers register low conductivity as compared to composites containing short carbon fibres, due to easy formation of an interconnecting network in the latter case. The effect of the orientation of short carbon fibre with respect to an applied electric field has also been studied. The pressure dependence of composites with transversely oriented carbon fibres with respect to electric fields is higher than that of composites with longitudinally oriented carbon fibres. The results are interpreted on the basis of the formation of interconnecting continuous conducting networks.

1. Introduction

Incorporation of the appropriate type and amount of conductive filler can convert an insulating rubber matrix into a conductive one [1-3]. In general, two types of filler materials are used for this purpose: conductive carbon and metal. These fillers may be in the form of particulate, flake or fibre. Electrically conductive elastomer composites which exhibit variable conductivity in response to varying pressure are known as pressure-sensitive conductive rubber [4-6]. These materials are widely used for various electronic applications such as touch control switches for televisions, cameras, watches, variable volume control elements for electronic organs, and as strain sensors for various applications such as robot hands, artificial limbs etc.

Here we present the results of our studies on the development of pressure-sensitive conductive rubber based on nitrile rubber-carbon filler systems. Both particulate carbon black and short carbon fibres have been used as conducting fillers.

2. Experimental procedures

Formulations of the mixes are given in Table I. Mixing was carried out on an open two-roll mill under identical conditions of time, temperature and sequence for all compounds. Optimum cure times for these compounds varied from 7.5 to 8 min at 150°C as observed with a Monsanto Rheometer R-100. The compounds were cured for a fixed time of 8 min at 150°C and at a pressure of 0.34 MPa. Mouldings were cooled rapidly in water at the end of the curing cycles, and then conditioned for 24 h before testing.

The physical properties of the samples were measured by a Zwick Universal Testing machine (model 1440) and are summarized in Table III. Tensile testing was carried out using ASTM C-type dumb-bell specimens according to ASTM D412-51T. Tear strength was determined according to the ASTM D624-81 test method using 90° angle test pieces.

Electrical properties were measured with the resistivity measurement equipment, which consisted of a regulated voltage supplier, a typical cell where pressure on the sample can be varied and a multimeter which measured current accurately to the level of 10⁻⁴ A (accuracy ± 0.5%).

For the measurement of fibre breakage and fibre length distribution in the final mix, the fibres were collected after dissolving the unvulcanized final compound in chloroform: the rubber is dissolved in the solvent leaving the fibre intact. The fibres were washed three times with chloroform for complete removal of rubber from the fibre surfaces. The washed fibres were then collected on the watch-glass plate and were examined both under optical and scanning electron microscopes (SEM) to estimate the average fibre length and length distribution.

The volume fraction of rubber (V_r) in the vulcanizates was determined by an equilibrium swelling method in acetone at 37°C using the following equation [7]

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_o\rho_s^{-1}} \quad (1)$$

where T is the weight of the test specimen, F the weight fraction of the insoluble components in the sample, D the unswollen weight of the test specimen, A_o the

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TABLE I Formulations of the mixes

Ingredients	Mix numbers			
	CB30	CB60	CF30	CF60
NBR*	100	100	100	100
ZnO	5	5	5	5
Stearic acid	2	2	2	2
DOP†	6	6	6	6
Carbon black, HAF	30	60	–	–
Carbon fibre	–	–	30	60
Accinox DN‡	1	1	1	1
CBS§	1.5	1.5	1.5	1.5
TMTD¶	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5

*Acrylonitrile-butadiene rubber, 33% acrylonitrile content.

† Dioctylphthalate.

‡ Phenyl- β -naphthylamine.

§ Cyclohexyl benzothiazyl sulphonamide.

¶ Tetramethyl thiouram disulphide.

weight of absorbed solvent, corrected for swelling increment, ρ_r the density of rubber and ρ_s the density of the solvent.

The SEM observations of fractured surfaces of different short-fibre loaded composites were made using a Cam Scan Series 2DV scanning electron microscope. These were made in order to correlate the morphology with electrical conductivity. The samples were subjected to brittle fracture in liquid nitrogen and the fractured surfaces were sputter coated with gold within 24 h of testing. The direction of fracture and surface for the SEM scan are shown in Fig. 1.

3. Results and discussion

3.1. Fibre breakage and fibre distribution

The fibre length and distribution of fibres in the rubber matrix are important factors in controlling both mechanical and electrical properties of conductive composites [8–11]. The fibre to be mixed with the rubber matrix should have a certain length: it should not be too long or it may act against proper dispersion due to fibre–fibre entanglements; very short fibres may adversely affect the electrical properties leading to the formation of discontinuation among the continuous conduction paths responsible for high conductivity.

As reported by several workers [12–15], we also observed that control of the final length of fibre in a rubber matrix is very difficult because extensive fibre breakage occurs during processing. The severity of breakage depends mainly on the type of fibre, initial aspect ratio (the ratio of length to diameter), and the magnitude of stress and strain experienced by the fibre during processing. Carbon fibre, being brittle like glass fibre, possesses a low bending strength. Thus severe breakage occurs compared to ductile cellulosic fibres, the latter having more flexibility and resistance

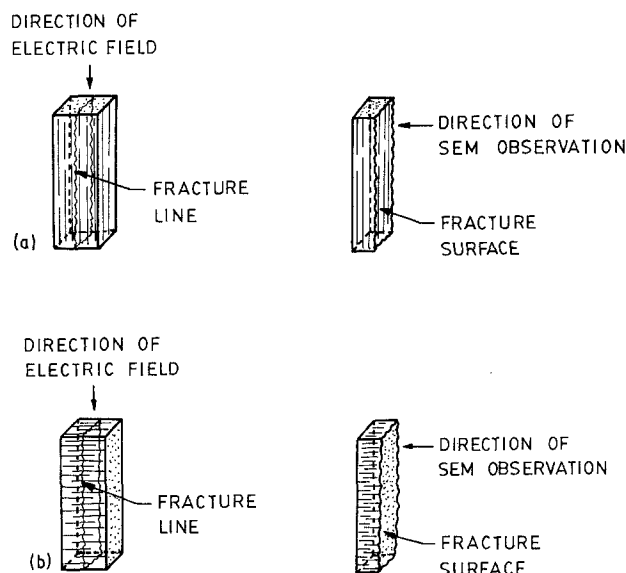


Figure 1 Direction of fracture and the surface of SEM observations. (a) Longitudinal and (b) transverse orientation with respect to applied electric field.

to bending failure. For each type of fibre, depending on its resistance to bending, there exists a certain aspect ratio below which no further breakage can occur. During mixing of carbon fibre with nitrile rubber in an open mixing mill, severe fibre breakage was observed (Fig. 2). It was also found that the severity of breakage increases with increased mixing time. To avoid the effect of different mixing variables on fibre breakage, and in turn its effect on electrical properties, the mixing was performed under identical conditions of time, temperatures, nip gap, friction ratio and mill-roll speed.

The extent of breakage was found also to depend on fibre loading. The higher the concentration of fibre, the more extensive is the reduction in fibre length and aspect ratio (Fig. 2). Thus in a 30 p.h.r.* fibre-loaded sample, fibre length decreases from 7.31 to 0.277 mm and the aspect ratio drops from 725 to 28, and in 60 p.h.r.-loaded samples, the final average fibre length decreases from 7.31 to 0.199 mm and the aspect ratio from 725 to 20, as presented in Table II. It was also noted that during mixing we observed only a reduction of average length, but there was no change in the diameter of the fibre. The distribution of fibre length in 30 and 60 p.h.r. fibre-loaded compounds is shown in Fig. 3. It is evident that fibre breakage is more severe in 60 p.h.r. than in 30 p.h.r. loaded compounds.

3.2. Variation of physical properties

The variation of physical properties with respect to filler loading is presented in Table III. Nitrile rubber, being a non-strain-crystallizing rubber, has poor gum

TABLE II Breakage of fibres after processing

Mix No.	Loading of carbon fibre (p.h.r.)	Fibre length before processing (mm)	Fibre diameter before and after processing (mm)	l/d before processing	Fibre length after processing (mm)	Aspect ratio (l/d) after processing
CF30	30	7.31	0.0101	725	0.277	28
CF60	60	7.31	0.0101	725	0.199	20

*Parts per hundred rubber

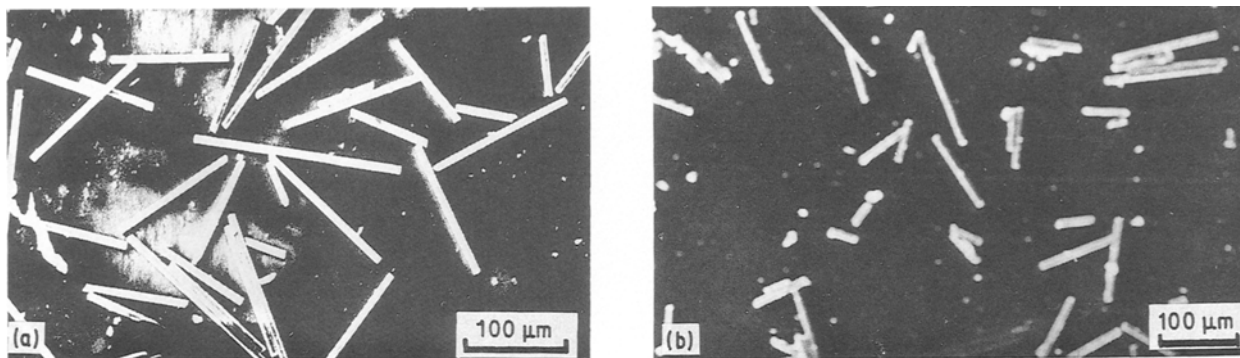


Figure 2 SEM photomicrographs of broken fibres, (a) of mix CF30; (b) of mix CF60.

vulcanizate strength of the order of 1 MPa. The presence of particulate reinforcing fillers like carbon black (HAF) increases the strength properties of the matrix significantly (Fig. 4a). For example, incorporation of 30 p.h.r. HAF black increases the tensile strength to a level of 10 MPa. Elongation at break, modulus at 200% elongation and tear strength follow the same trend. However, a fibrous filler like short carbon fibre (RK30) does not reinforce the matrix significantly. There is only a marginal increase in strength and the variation of strength with the increase in fibre loading is marginal. There is a slight deterioration of strength as filler loading is increased from 30 to 60 p.h.r. Stress-strain curves of different carbon-fibre-filled rubber vulcanizates reveal ductile fracture and poor strength properties (Figure 4b). Both modulus and elongation at break for fibre-filled systems are inferior to the results for particulate filled systems. This reflects poor polymer-filler interaction in the case of fibre-rubber systems.

The extent of polymer-filler interactions is estimated from a swelling experiment using a plot of V_{ro}/V_{rf} against $C/1 - C$ according to Kraus's equation [16, 17]

$$\frac{V_{ro}}{V_{rf}} = 1 - \frac{mC}{1 - C} \quad (2)$$

where V_{ro} is the volume fraction of rubber for gum vulcanizates and V_{rf} the volume fraction of rubber for filled vulcanizates (calculated according to Equation 1), C is the concentration of filler expressed in the volume fraction, and m is the polymer-filler interaction parameter obtained from the slope of the plot of V_{ro}/V_{rf} against $C/1 - C$. For reinforcing fillers with a high polymer-filler interaction, m should be positive, and non-reinforcing filler with a weak polymer-filler interaction shows negative values of m . Plots of V_{ro}/V_{rf} against $C/1 - C$ (Fig. 5) for particulate-filler-filled and short-carbon-fibre-filled rubber vulcanizates

TABLE III Physical properties of rubber vulcanizates

Mix No.	CB30	CB60	CF30	CF60
Modulus at 200% elongation (MPa)	5.08	13.08	1.33	1.12
Tensile strength (MPa)	10.01	15.37	1.62	1.54
Elongation at break (%)	318	391	270	227
Tear strength (N mm ⁻¹)	36.44	41.58	6.20	3.49

reveals a strong polymer-filler interaction in the case of HAF black, compared to that of short carbon fibre. This is further substantiated by SEM micrographs of the fractured surface of the carbon-fibre-filled rubber matrix. SEM micrographs (Fig. 6) show the regions from which fibres have been pulled out from the rubber matrix leaving behind voids.

3.3. Effect of pressure on conductivity

3.3.1. Particulate carbon black-rubber composites

Resistivity of black-rubber composites for different filler loadings are presented in Fig. 7. The resistivity of all the composites decreases sharply as the applied pressure is increased up to a limit of 0.4 kg cm⁻², and further increase in applied pressure has a marginal effect on the decrease of resistivity. This variation of

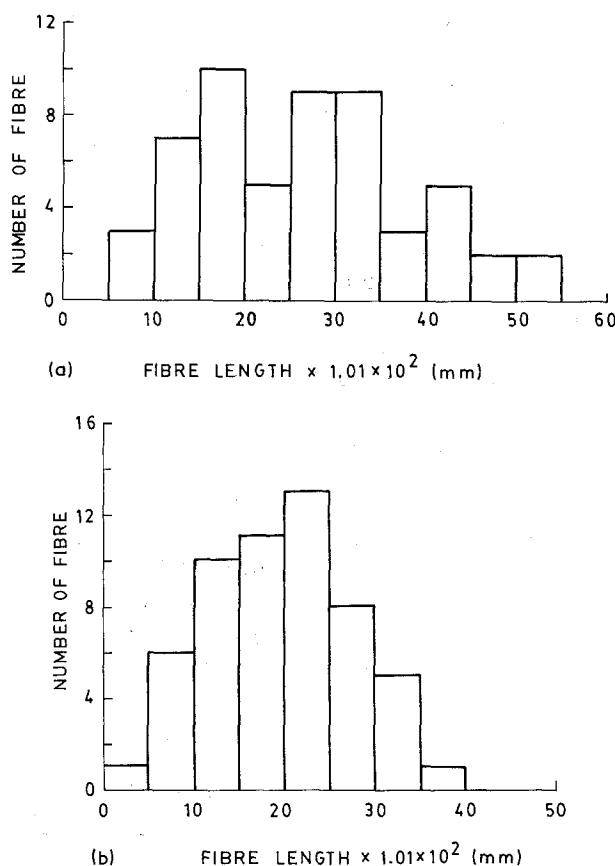


Figure 3 Distribution of fibre length after mixing in different mixes, (a) mix CF30; (b) mix CF60.

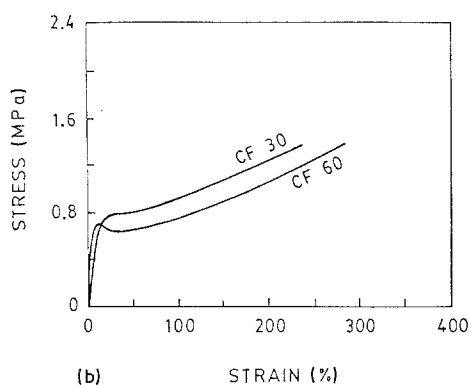
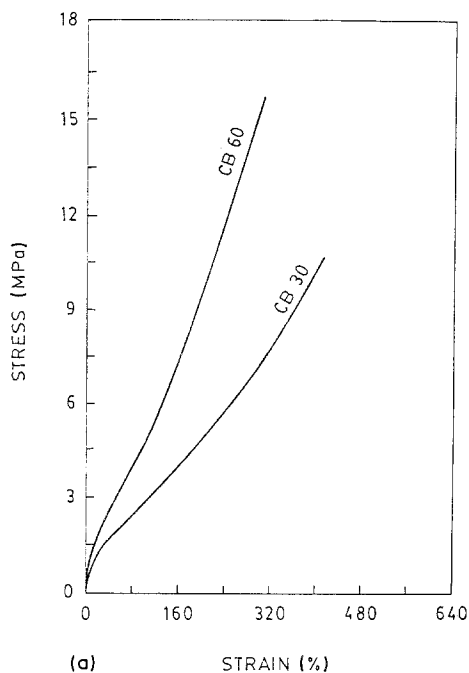


Figure 4 Stress-strain curves of vulcanizates containing (a) carbon black (mix CB30 and CB60); (b) carbon fibre (mix CF30 and CF60).

conductivity with applied pressure follows a similar pattern at different black loadings. Thus there exists a critical pressure below which there is an appreciable change of conductivity with applied pressure, and the system can efficiently act as a pressure-sensitive conductive rubber. But when the applied pressure is increased above this critical value, the change of conductivity with increased pressure is marginal (that is, the system fails to behave like an efficient transducer). This critical pressure range, over which the system behaves like pressure-sensitive conductive rubber, is found to be more or less the same for the different compositions studied. But the range of conductivity variation shifts as the filler loading is varied. For example, for a 30 p.h.r. black-filled system, resistivity changes from 14.02×10^6 to $1.02 \times 10^6 \Omega \text{cm}$ when pressure is increased to 0.6 kg cm^{-2} , and for a 60 p.h.r. black-filled system the drop is from 5.8×10^3 to $1.3 \times 10^3 \Omega \text{cm}$ over the same range of pressure variation.

3.3.2. Short carbon fibre-rubber composite

The incorporation of carbon fibre into a nitrile rubber matrix makes it more conductive as compared to a particulate carbon black-filled system for the same loading. Due to the fibrous nature of the filler, both

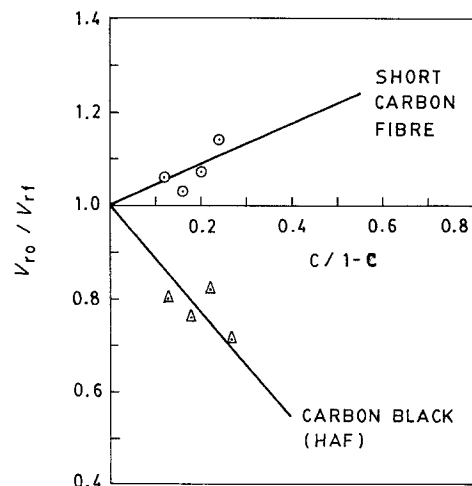


Figure 5 Plots according to Kraus's equation [16, 17]. (Δ) HAF-filled vulcanizate; (\odot) short-carbon-fibre-filled vulcanizates.

conductivity and pressure dependence of conductivity are affected by different factors like fibre loading, distribution of fibre in the rubber matrix and orientation of fibre in the matrix with respect to the applied electric field.

As the fibre loading increases, the conductivity also increases. As observed in the case of particulate black-filled systems, both initial resistivity (resistivity in the absence of applied pressure) and changes in resistivity with increased applied pressure are affected by fibrous filler loading.

For a transversely oriented fibre matrix (that is, when the fibre axis is perpendicular to the applied electric field), the conductivity varies from 16 to about $9.6 \Omega \text{cm}$ for 30 p.h.r. fibre loading when the applied pressure during measurement is varied from 0.06 to 1 kg cm^{-2} . Similarly, for a 60 p.h.r. fibre filled sample, this drop in resistivity is from 8.8 to $5.8 \Omega \text{cm}$ for the same range of pressure variation when the measurement voltage is fixed at 30 V (Fig. 8a). A sharp fall in resistivity is observed when the pressure is roughly varied between 0.06 and 0.7 kg cm^{-2} , and this range of pressure sensitivity is roughly the same for all compositions used in the present study. But in each case, response to pressure sensitivity decreases on further increase of pressure beyond 0.7 kg cm^{-2} .

3.4. Effect of fibre orientation on electrical properties

The orientation of fibres has a significant effect on the conductivity of the filled matrix. Fibre orientation in different composites can be followed from SEM fractographs (Figs 6a-d). When fibres are longitudinally oriented with respect to the applied electric field, there is an appreciable increase in conductivity, that is, for 30 p.h.r. longitudinally oriented fibre-loaded composites, the resistivity is $2.8 \Omega \text{cm}$ and for 60 p.h.r. fibre-loaded composites the resistivity is $0.7 \Omega \text{cm}$ at 0.5 kg cm^{-2} pressure. It is further observed that the extent of pressure sensitivity is less in composites having longitudinally oriented fibres. Here the decrease in resistivity is observed when the pressure is increased from 0.16 to 0.5 kg cm^{-2} , and on a further increase of

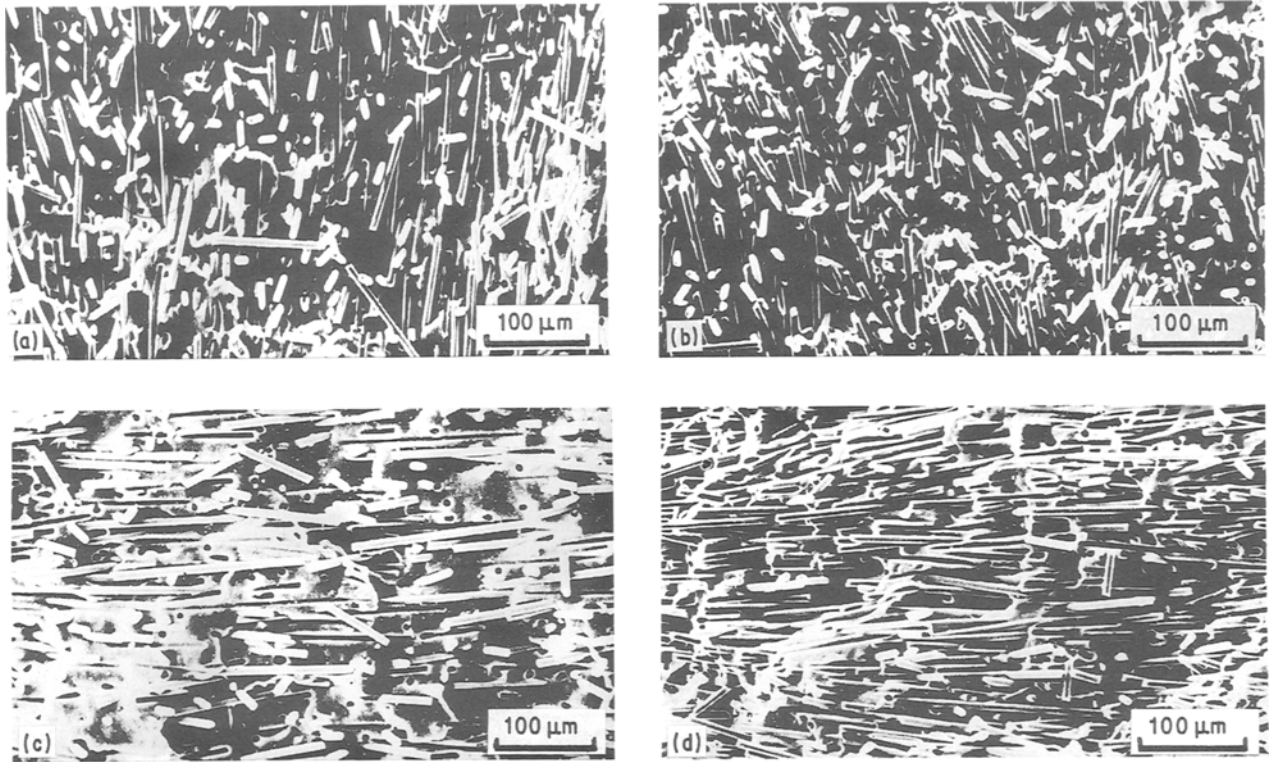


Figure 6 Fibre orientation with respect to applied electric field in the vulcanizates containing carbon fibre. Transverse orientation of fibres in (a) mix CF30; (b) mix CF60. Longitudinal orientation of fibres in (c) mix CF30; (d) mix CF60.

pressure, conductivity remains almost unaffected (Fig. 8b). Thus for composites having longitudinally oriented fibres in a nitrile rubber matrix we obtain conductive composites at relatively lower filler loading (that is, for 30 p.h.r. fibre loading resistivity is $2.8 \Omega \text{ cm}$ at 0.5 kg cm^{-2} pressure).

This phenomenon can be explained in the light of the formation of a continuous conduction path responsible for high conductivity. The formation of this continuous conducting path occurs not only by direct contact between the electrically conductive particles dispersed in the rubber matrix, but also when interparticle distances are just a few nanometres when electrons can easily jump across the gap (tunnelling effect) [18]. Thus there exists a threshold value (the minimum value) for this interparticle gap which is electrically equivalent to the occurrence of interparticle contact. When fibres are oriented mainly

along the transverse direction, to achieve a sufficient number of continuous interconnecting networks along the field direction, both high pressure and high filler loadings are required. Since there are fewer fibres along the electric field direction, the average gap between these fibres is higher. When fibre loading is increased, more and more fibres are oriented along the longitudinal axis (that is, along the field direction) and conductivity progressively increases. But when pressure is increased, formation of a continuous conduction path is further facilitated because the applied pressure decreases the interparticle gap in the discontinuous region. Thus there is a drop in resistivity with the increase of pressure. But beyond a certain pressure level, there is no further increase of conductivity because the threshold distance between two continuous chains required for conduction is already achieved. Accordingly, a further increase in pressure does not

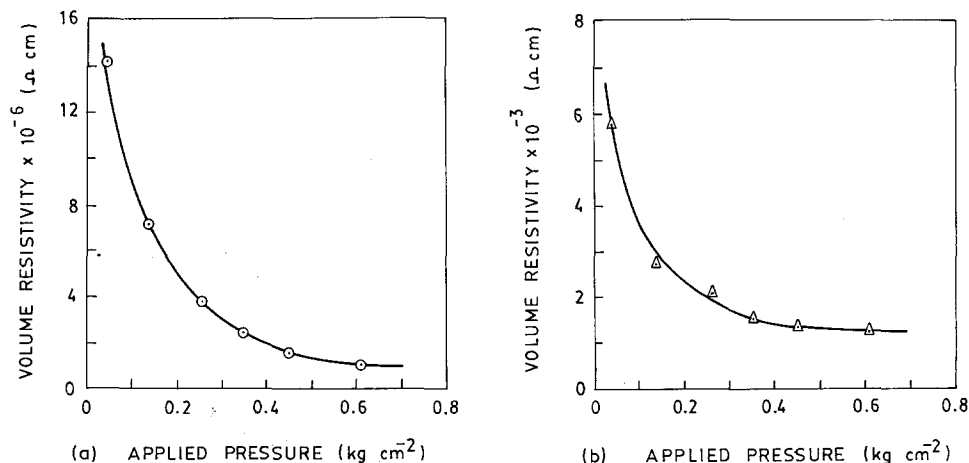


Figure 7 Dependence of volume resistivity on pressure for vulcanizates containing carbon black at 30 V, (a) mix CB30; (b) mix CB60.

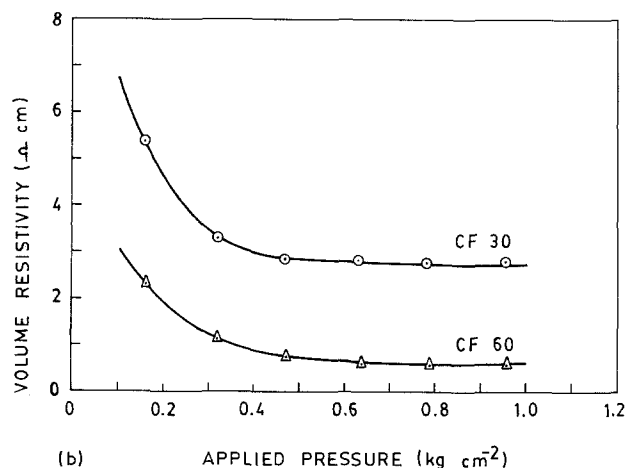
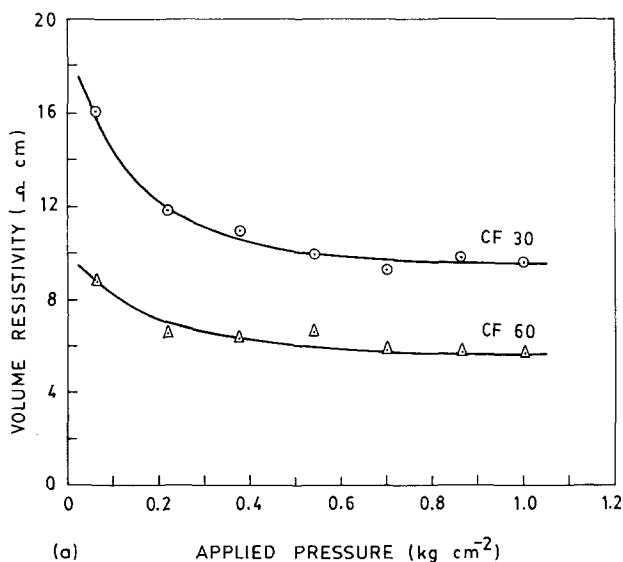


Figure 8 Dependence of volume resistivity (Ωcm) on pressure for vulcanizates containing carbon fibre. (a) Voltage (30 V) applied in transverse direction of fibre orientation; (b) voltage (30 V) applied in longitudinal direction of fibre orientation.

increase the conductivity much. A similar type of pressure sensitivity is observed at varying fibre loading because the increased fibre loading increases the number of continuous paths along the field direction.

When fibres are oriented along the field direction, the maximum number of fibres have already taken part in the formation of a long conducting path and the average gap between these conducting paths is smaller. The conductivity is higher and less pressure sensitivity is expected: that is what is observed in the experiment. Longitudinally oriented fibre-filled composites exhibit high conductivity as compared to transversely oriented composites at the same fibre loading. For longitudinally oriented samples, pressure sensitivity is observed up to 0.5 kg cm^{-2} , whereas for transversely oriented fibre-loaded composites conductivity changes progressively up to 0.8 kg cm^{-2} and then levels off (Figs 8a and b).

4. Conclusions

Carbon fibre filled composites have higher conductivity compared to particulate carbon filled composites at the same loading. Both conductivity and pressure sensitivity of conductivity are affected by fibre loading and its orientation with respect to the electric field. When fibres are oriented along the longitudinal direction with respect to the electric field, higher conductivity is observed but pressure sensitivity is decreased. Composites with transversely

oriented fibres show better pressure sensitivity and relatively lower conductivity compared to longitudinally oriented composites.

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