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Effect of extensional strain on the resistivity of electrically conductive nitrile-rubber composites filled with carbon filler

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The resistivity and mechanical properties of nitrile-rubber based conductive composites filled with short carbon fibres (SCFs) and mixed filler system (SCF + carbon black) are studied as functions of the extensional strain and the strain rate. It has been observed that both strain and strain rate have a strong influence on the resistivity of the composites. The sensitivity of the change in resistivity against the strain and strain rate depends on the concentration as well as the type of conductive filler. SCFs impart higher conductivity to the composite than a blend of SCFs and carbon black at the same level of loading parts per hundred of rubber (p.h.r.). Composites filled with a mixed filler system show high mechanical properties in contrast to those of SCF-filled composites. The change in resistivity with the degree of strain is less pronounced in mixed-filler-filled composites than in only carbon-fibre-filled composites. The mechanical properties of the composites are dependent on the polymer–filler interaction whereas change in resistivity is dependent on the transient arrangement of the conducting components in the polymer matrix. A good correlation exists between mechanical and electrical response to the strain sensitivity.

1. Introduction

A flexible conductive composite can be prepared from a vulcanized elastomer matrix filled with the requisite amount of an appropriate conductive filler. Such composites were developed a long time ago but recently these materials have gained great importance in various electronic applications, such as static-charge dissipaters, sheathing materials in cables, electromagnetic-interference shields, floor heaters, switching devices, sensors etc. [1–4]. A strain-sensitive sensor is a material which exhibits variation in electrical resistivity when applied strain is varied. The resistivity of these conductive rubbers may change with strain, strain rate and time duration under static and dynamic loading [3, 4]. The sensitivity of the electrical response (that is the degree of variation of conductivity or resistivity) to the applied strain depends on various factors; for example, the type of polymer matrix, conductive filler, filler loading, or degree of strain [4].

Several investigations have been carried out in the past to relate the electrical properties of black loaded rubber vulcanizates under static and dynamic stretching [5–9]. The results revealed that the change in conductivity is related to major changes in the carbon–black configuration during the process of elongation. It was postulated that the conductivity change is related to the formation and destruction of transient chains as well as to the alignment of persistent carbon chains. Bulgin [10] proposed that the conductivity of carbon-black-loaded vulcanizates subjected to stress are related to the structural arrangement of carbon particles. Kraus *et al.* [11] found that the conductivity of SBR vulcanizate reinforced with HAF significantly changed, depending on the extent of stretching. Wack *et al.* [12] measured the change in conductance upon stretching of black loaded vulcanizates and concluded that carbon-chain formation takes place in the matrix. Kost *et al.* [13, 14] reported that axial strain and dynamic strain strongly affect the electrical resistivity of carbon-black-filled-silicone-rubber vulcanizates. All these studies suggested that the disruption of carbon networks by destruction and formation of the transient structure is responsible for the reversible changes in resistivity, whereas breaking of the persistent carbon chains is responsible for the irreversible changes.

In earlier communications [15, 16] the authors reported the electrical and mechanical properties of SCF and carbon-black-filled nitrile-rubber composites with the variation of filler concentration and filler blend composition. It has also been reported that the processing parameters [17] and compressive pressure [18] have a pronounced influence on the conductivity of such composites. The present work is an extension of the previous work and describes the behaviour of the electrical resistivity of nitrile-rubber-

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based conductive composites filled with SCF and a mixed filler system (SCF + carbon black) under variable strain in static loading experiments. A good correlation could be established between a mechanical property like the tensile modulus and the electrical resistivity as a function of the degree of strain.

2. Experimental procedure

Materials used in the formulation of the mixes are given in Table I. Analytical properties of the carbon black and SCFs used are shown in Table II. The mixing was carried out on an open two–roll mill under identical conditions of mixing. The optimum cure time was calculated at 150 °C from rheographs obtained from a Monsanto Rheometer (R 100). The vulcanization of composites was accomplished using an electrically heated press operated at 150 °C under a pressure of approximately 4.5 MPa. A Philips 500 model scanning electron microscope (SEM) was used to examine the texture of the composites. SEM micrographs were taken from the fractured surface of a liquid-nitrogen-cooled sample.

The experimental set-up for the resistivity measurement is shown schematically in Fig. 1. Specimens (80 × 3 × 1.7 mm) were uniaxially extended at room temperature using an Instron universal testing machine. A constant crosshead speed was maintained to give a specified strain rate. All the samples were only extended up to 50% elongation to avoid tensile failure of the specimens.

The resistivity was measured by a four-terminal potentiometric method using a constant current of 2.0 mA. The current and voltage electrodes were located 3 mm apart in the clamp and they were insulated from the machine frame (Fig. 1b). Conductive silver paint was applied between the sample surface and electrode to ensure a better electrical contact between them. The specimen's extension was measured from the displacement of the machine head. The voltage was recorded at different times on an $X-Y$ recorder operated in the time mode. The stress and strain at different times was obtained with an Instron universal testing machine. The results of stress, strain and resistivity as functions of time were then analysed.

TABLE I Formulation of the mixes

Ingredients	Mix number				
	CF4	CF5	CF6	XF5	XF4
NBR[a]	100	100	100	100	100
ZnO	5	5	5	5	5
Stearic acid	1	1	1	1	1
DOP[b]	4	5	6	6	6
Conductex 900[c]	–	–	–	10	20
SCF[d]	40	50	60	50	40
Accinox DN[e]	1	1	1	1	1
CBS[f]	1.5	1.5	1.5	1.5	1.5
TMT[g]	0.5	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5	1.5

(All the ingredients are added by weight (i.e. in terms of parts-per-hundred rubber p.h.r.) [a] Acrylonitrile–butadiene rubber, 33% acrylonitrile content. (Synthetics and Chemical Ltd, India); [b] commercial grade dioctylphthalate; [c] conductive carbon black (Columbian Chemicals, Inc., USA); [d] Chopped from continuous carbon fibre (RK 30), R. K. Carbon Fibre Ltd, U.K; [e] Phenyl-β-napthylamine. [f] N-Cyclohexylbenzothiazole-2-Sulphenamide (IEL Limited, India); [g] Tetramethylthiuram disulphide (IEL Limited, India).

TABLE II Analytical properties of: (a) the carbon black, (product name, Conductex 900) and (b) SCF (product name, RK30) used in the composites

(a)		(b)	
ASTM tinting strength (%)	86	Precursor polyacrylonytrile (PAN)	
DBP absorption (ml kg^{-1})	122	Average length (mm)	7.25
Iodine adsorption, (× 10^3 m^{2}kg^{-1})	127	Diameter (μm)	10.1
Toluene discolouration (%)	100	Density (× 10^{-3} kg ml^{-1})	1.78
Residue (× 10^{-3} %), 325 mesh	1.8		
Bulk density (× 10^{-3} kg ml)	0.33		

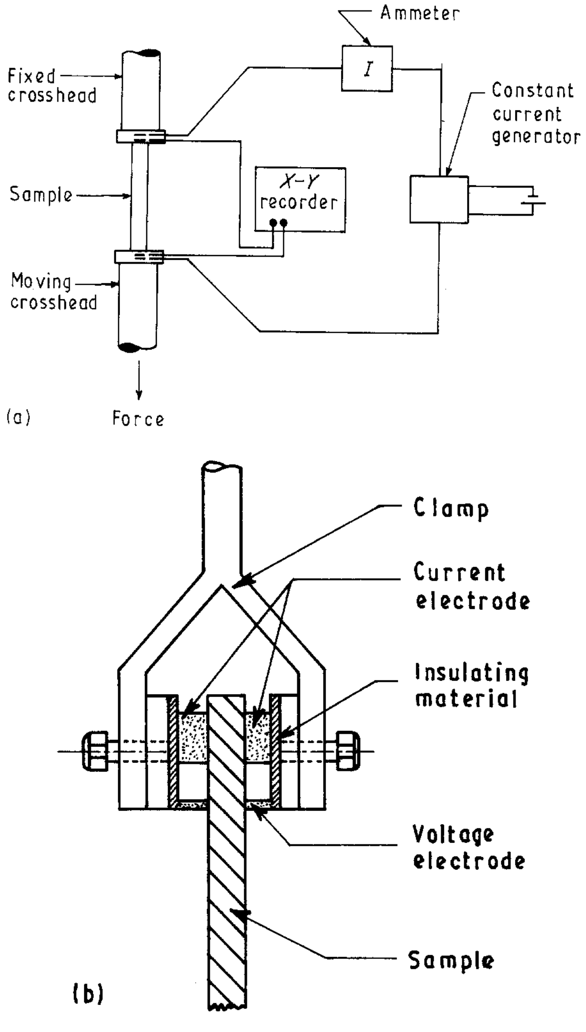

Figure 1 Schematic diagram of: (a) the experimental set-up, and (b) electrodes and sample arrangement inside the clamp.

2.1. Theoretical basis of the measurement technique

The electrical resistivity, ρ, is calculated from $R = \rho L/A$ where R is the resistance of a sample whose length is L and A is the cross-sectional area normal to the electron flow direction. Upon extension, L increases, A decreases and the sample resistance changes simply due to geometrical alteration. The resistivity is expected to remain constant, i.e. independent of the level of strain, unless structural and morphological changes in the dispersed conductive components occur. The composites may exhibit some void formation due to fibre pull-out especially at very high strain. The degree of fibre pull-out increases with strain magnitude. Therefore the experimental strain is kept very low compared to the average ultimate elongation of these samples. Thus the contribution of voids to the volume change during strain can be ignored. Assuming the sample volume remains constant (i.e., $\Delta V = 0$ or $V = V_0$) throughout the experiment – i.e. independent of strain, ε – the resistivity is calculated using data for R, L and A,

$$\rho' = RA/L = RV_0/L^2 \tag{1}$$

where V_0 is the initial volume of the sample.

Since the specimen length, L, is a function of strain, ε, the resistivity–strain relationship can be expressed as

$$\rho' = \frac{RV_0}{L_0^2(1+\varepsilon)^2} \tag{2}$$

where L_0 is the initial length of the unstrained sample. In practice the resistance and strain data were determined for a given sample and then the resistivity, ρ', was calculated from Equation 2.

3. Results and discussion

3.1. SCF in the composite

Severe fibre breakage occurs during mixing with rubber due to the brittle nature of carbon fibre. It was reported earlier that the length of the fibre reduced drastically while the diameter of the fibre remains unchanged [15–17]. Thus the aspect ratio of the fibre in the fibre-filled composites is found to be reduced from 25.2 to 19.8 when the fibre loading is varied from 40 to 60 p.h.r., whereas for filler blend-filled composites it is around 18.8 (Table III). This is due to the difference in shearing force experienced by the fibre during mixing. It is also worth mentioning here that the fibres are randomly distributed in the composites, containing SCFs and carbon fibre + carbon-black blends, as observed from SEM micrographs (Fig. 2a, b). The regions from which fibres have been pulled from the rubber matrix leave voids, which clearly reveals the weak fibre–rubber matrix interaction.

TABLE III Volume fraction of conducting filler and aspect ratio of SCF in the composites, and the resistivity of different conductive composites

	Sample				
	CF4	CF5	CF6	XF5	XF4
Volume fraction of SCF	0.19	0.23	0.26	0.16	0.11
Volume fraction of Conductex 900 black	–	–	–	0.037	0.074
Aspect ratio of SCF	25.2	22.3	19.8	18.8	18.7
Resistivity ($\times 10^{-2}\,\Omega$m)	2.17	0.92	0.29	0.58	1.37

3.2. Mechanical properties

3.2.1. Stress–strain behaviour of different composites

Stress–strain plots of different composites are presented in Fig. 3. A distinct tendency to yield is observed in all stress–strain plots of composites containing carbon fibres as the sole filler. Further, the yielding becomes more pronounced when the fibre concentration is increased from 40 to 60 p.h.r. If a portion of fibrous filler in a 60 p.h.r. filler loaded composite is partially replaced by a particulate filler like conductex 900 black the tendency to yield in stress–strain curves decreases. The yielding of fibre-filled composites defines the irreversible deformation of the matrix beyond the Hookian region, when there is a total failure of the fibre–rubber interface. In our earlier communication [16] it was shown that in SCF–rubber composites there exists a very weak rubber–fibre interaction and this leads to the formation of a relatively weak interface between carbon fibres and the rubber matrix. Whereas a strong polymer–filler interaction exists between particulate carbon black (conductex 900) and the rubber matrix, thus purely black filled composites do not exhibit any tendency to yield. Therefore, in the case of a composite containing a mixed filler (SCF + Conductex 900) this

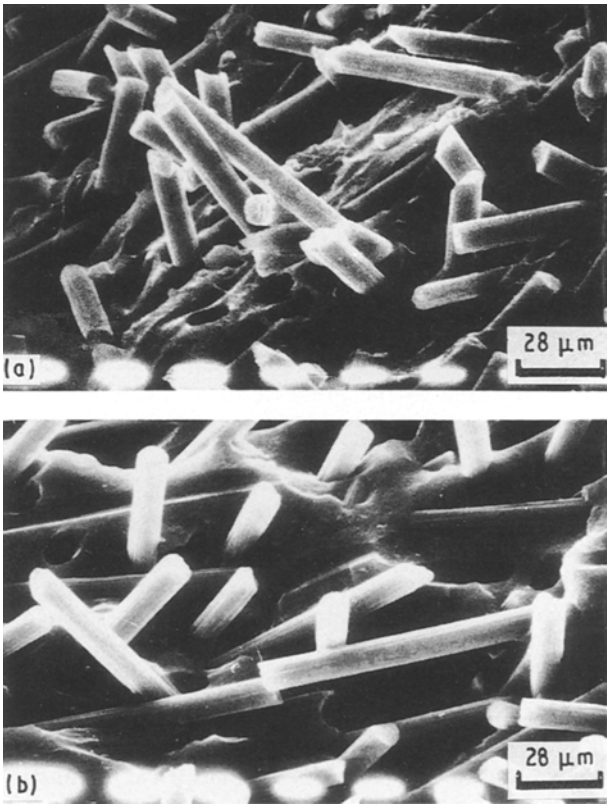

Figure 2 SEM micrograph of composites filled with: (a) 60 p.h.r. SCF, and (b) a 40/20 blend of SCF and carbon black.

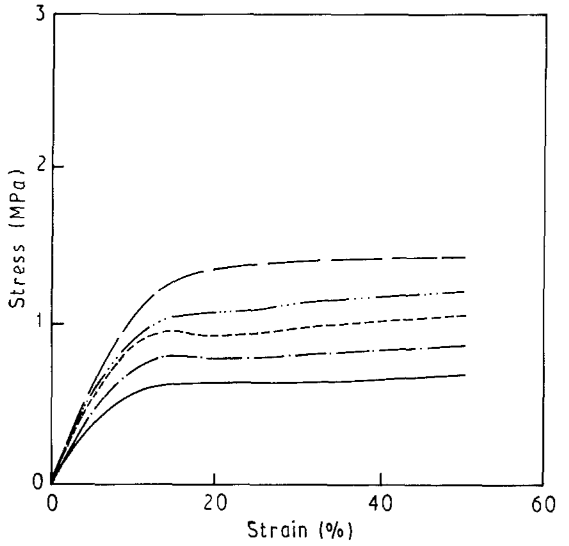

Figure 3 Stress–strain curves of different nitrile-rubber composites: (——) CF4, (–·–) CF5, (–––) CF6, (– · · · –) XF5, and (——) XF4.

tendency to yield reduces with the increase in the proportion of particulate filler.

3.2.2. Effect of strain rate on mechanical properties

Stress–strain plots for different strain rates are presented in the Fig. 4a, b. As the strain rate is increased the yield strength increases. This change becomes more prominent where the rate is increased appreciably i.e., from 0.4 min^{-1} to 10.0 min^{-1}. This behaviour is very much analogous to the failure of a polymer matrix at different strain rates, where breaking strength increases appreciably as the strain rate is increased. For the present system, the yielding in the stress–strain curve may be attributed to the failure of the fibre–rubber interface but not the total failure of the matrix. The weak bonding between fibre–rubber furnishes a low resistance to the extensive change in the arrangement and orientation of the fibre in the matrix prior to yielding. Variation of yield stress with strain rate is also observed for other fibre-filled composites. But the tendency decreases as the portion of fibrous filler is replaced by a particulate filler (Fig. 4b). This indicates that the reinforcement is better in the later case due to the presence of particulate carbon black.

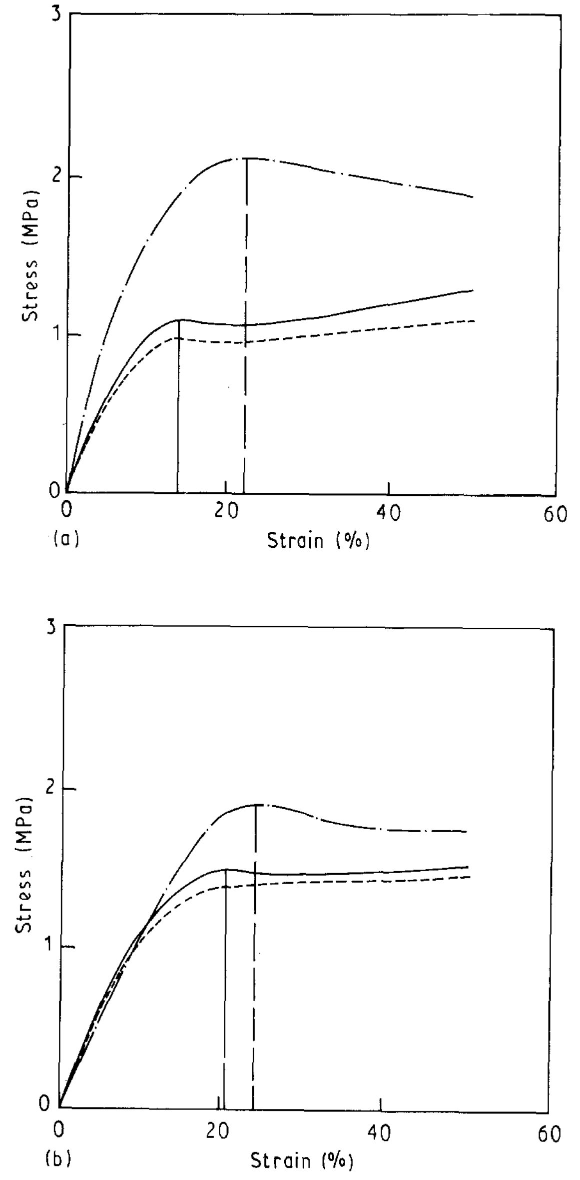

Figure 4 Effect of strain rate on the stress–strain properties of nitrile rubber (NBR) composites filled with: (a) 60 p.h.r. SCF, i.e. CF6 and (b) filler blend i.e. XF4 (SCF/conductex 900 = 40 p.h.r./20 p.h.r.). For strain rates: (– · –) 10 min^{-1}, (——) 0.04 min^{-1}, and (–––) 0.02 min^{-1}.

3.3. Electrical resistivity of the composites

The electrical resistivity of the polymer composites depends on the formation of a continuous conductive network in the insulating polymer matrix. Therefore conducting filler that is capable of forming good continuous paths for electron flow gives rise to high conductivity in the composite. The resistivities of different composites are given in Table III. It has been observed that SCF imparts high electrical conductivity to the composites. This is due to the inherent fibrillar form of the SCF. However the addition of carbon black in the composites improves both the electrical and mechanical properties of the composites. The black particle aggregates (generally called structure) help to form a network structure of conducting components by bridging carbon fibre aggregates, thus facilitating electron flow via these new conductive paths. The presence of carbon black also improves the mechanical properties by reinforcing the polymer matrix.

3.3.1. Effect of strain on resistivity

The variation of electrical resistivity with the applied extensional strain for conductive composites containing different amounts of carbon fibre is presented in Fig. 5. The change in the resistivity is measured in terms of relative resistivity (ρ/ρ_0) where ρ and ρ_0 are the resistivity of the system at a definite strain and in the unstrained state, respectively. It is observed that initially the resistivity of the sample changes

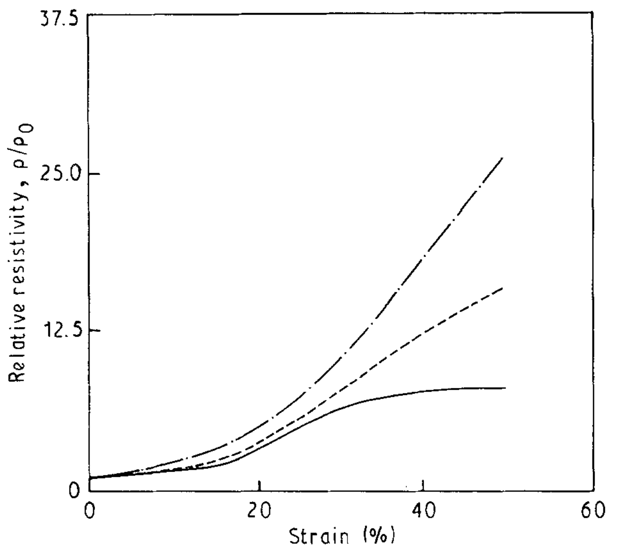

Figure 5 Effect of strain on the relative resistivity (ρ/ρ_0) of different composites filled with SCF: (–·–) CF4, (– – –) CF5, (——) CF6.

marginally with the change in the degree of strain up to a definite strain value; this strain may be referred to as the threshold strain. Beyond the threshold strain, the rate of increase of relative resistivity with strain increases at a much faster rate. It is further noticed that the threshold strain increases with the increase in SCF loading in the matrix, but the rate of increase in resistivity with strain reduces. Alternatively, the system becomes less strain sensitive with the increase in conductive-filler loading. A similar phenomenon was observed during the application of pressure on systems where the pressure sensitivity of conductivity reduces with increases in conductive-filler loading [18].

The present effect can be explained as follows: the conductivity of a composite is due to the formation of a continuous conductive network in the insulating rubber matrix. These conductive networks originate from some specific arrangement of conductive elements in the composite. The high conductivity of SCF-filled composites is due to the fact that an individual SCF may be considered as a long efficient conductive chain of carbon particles; and such long chains can easily bridge together to form a continuous conductive network (Fig. 6). When such polymeric conductive composites are subjected to elongational strain there will be two simultaneous processes operating in the system.

1. The elongation leads to the formation of more conductive chains due to fibre orientation along the stretching direction, which is also the direction of applied electric field. The net result is an increase in the conductivity of the system or a decrease in the relative resistivity.
2. The elongation will also cause the breakage of the existing continuous conducting network due to an increase in the gap between fibres. When the interparticle gap is less than a few tenths, of nanometres, it is practical to assume interparticle contact because electrons can hop across this gap easily.

Below the threshold strain, the rates of both processes are very slow and they can easily counterbalance each other. However, beyond the threshold strain the rate of breakage of conducting networks becomes much more predominant than the fibre orientation, which is responsible for the formation of new networks, and consequently the resistivity increases at a faster rate with respect to strain. As fibre loading increases, the system contains more conducting

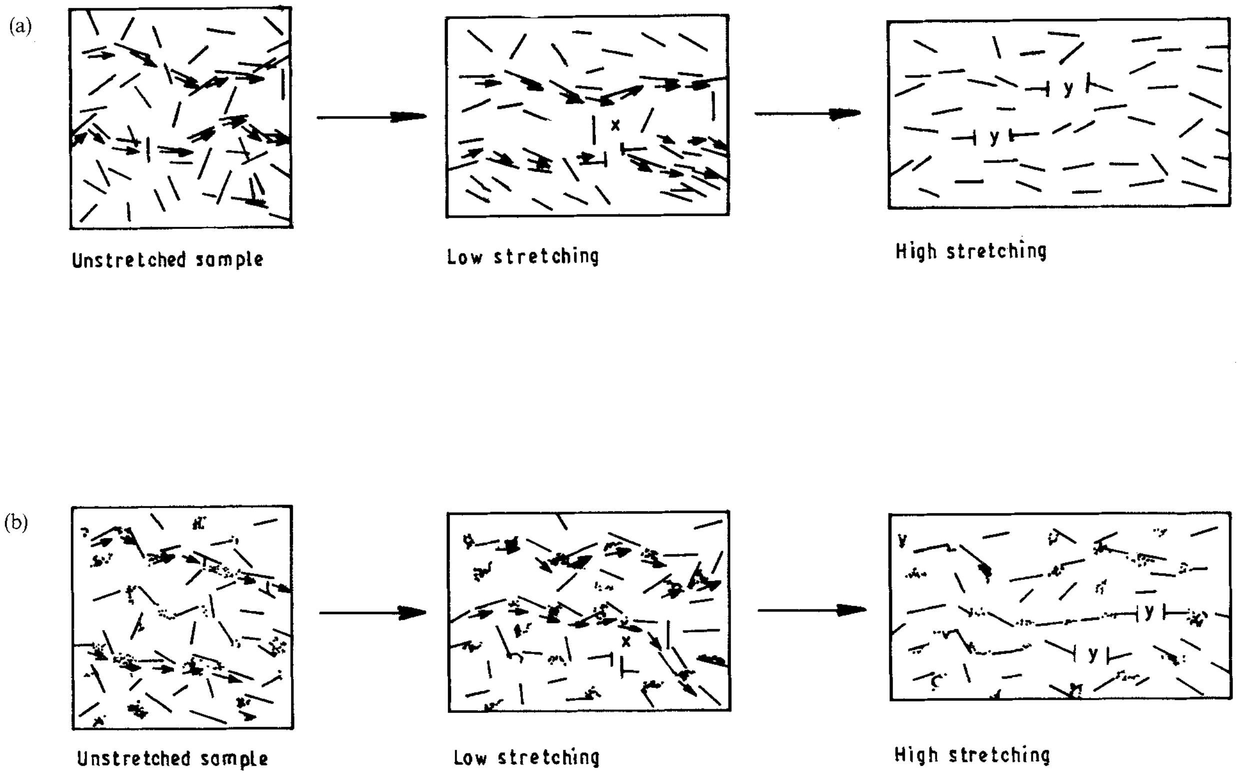

Figure 6 Conceptual model for structural change of the different composites on stretching: (a) fibre-filled composite, and (b) filler-blend-filled composites. (x and y represent gaps between networks at different stages.)

networks and the average interparticle gap among SCF particles decreases. Therefore, the threshold strain increases for higher fibre loading, and the network-breakdown process becomes less efficient. So the rate of increase of resistivity is reduced for higher SCF-loaded composites. The rate of fibre orientation also increases with the degree of strain but the orientation effect may counter-balance scission of conducting networks only at a higher loading of fibre, where the interfibre distance is smaller and the latter process is less efficient. That is why the plateau effect beyond certain elongations is only observed for a 60 p.h.r. fibre loading in the composites.

Fig. 7 presents the variation of relative resistivity for composites containing carbon fibre and mixed filler systems (when fibrous filler is partly replaced by particulate filler, but the total filler loading remains constant at 60 p.h.r.). The particulate filler helps to bridge the fibrous filler, forming a new type of conductive network. Because of its high resistance to bending deformation, SCF exists as short, straight, chains, whereas carbon-black aggregates exist as the fused carbon particles. At low strain the transient arrangement of carbon-particle aggregates in the rubber matrix leads to a reduced breakage of the conducting networks; that is, the change in configuration of carbon-particle aggregates aids the formation of sufficient conducting networks to counter-balance the effect of network breakage with the increase in strain. Thus, for a composite containing a filler blend, the change in resistivity with strain occurs at a much slower rate compared to only carbon-fibre-filled composites and the threshold strain increases with the increased proportion of carbon black. Further, the tendency of an abrupt rise in the relative resistivity beyond the threshold strain also reduces as the system is enriched with carbon-black particles; i.e. where the bridging is by carbon-black aggregates rather than straight SCFs. At a very high degree of strain, the high degree of orientation of both carbon fibres and carbon-black aggregates may nullify the effect of chain breakage and thus a plateau effect is observed; that is, the breakdown process becomes more and more inefficient as the carbon-black concentration is increased.

3.3.2. Effect of strain rate on electrical resistivity

The effect of strain rate on resistivity is shown in Fig. 8. The strain-rate effect is more pronounced for the electrical properties than for the mechanical properties. Mechanical properties, like tensile strength, of a filler-reinforced rubber vulcanizate depend on the formation of reinforcing networks involving rubber matrix and filler particles. These polymer–filler networks are capable of distributing and dissipating the applied stress. Thus, mechanical strength is a bulk property which depends on the polymer matrix, the filler and the polymer–filler interaction. However, the electrical resistivity (or conductivity) of conductive rubber vulcanizates entirely depends on the spatial arrangement of the conductive filler leading to the formation of several continuous conducting networks in the system. With the application of strain, the conductivity, which is due to the transient arrangement of conducting components, shows an appreciable change due to the combined effect of the formation and destruction of conductive networks. In general, the electrical response is more sensitive to small changes in this structure than the mechanical response is. However, a good correlation may be drawn between the effect of strain on the mechanical and electrical properties of fibre-filled composites.

A close examination of both stress–strain curves and the relative-resistivity–strain curves for different filler loading and filler-blend composition reveals a few interesting features common to both phenomena. (Due to a measurement inadequacy, the electrical resistivity at high strain rates (10 min^{-1}) could not be performed.) Prior to the threshold strain, ρ/ρ_0 changes marginally with the applied strain but beyond the threshold strain it increases at a much higher rate.

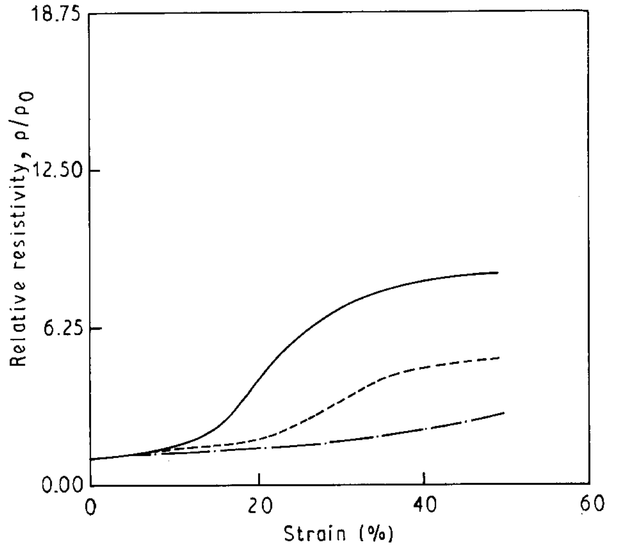

Figure 7 Effect of strain on the relative resistivity, ρ/ρ_0, of different composites filled with filler blend and 60 p.h.r. of SCF: (–·–) XF4, (– – –) XF5, and (——) CF6.

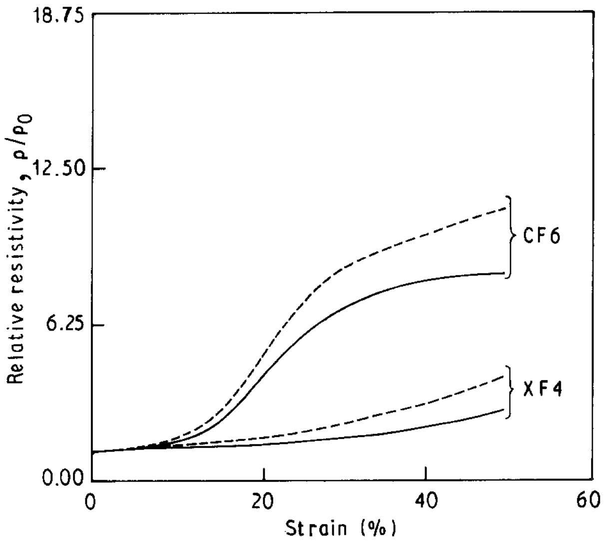

Figure 8 Effect of strain rate on the relative resistivity of different nitrile-rubber composites: (– – –) 0.04 min^{-1}, and (——) 0.02 min^{-1}.

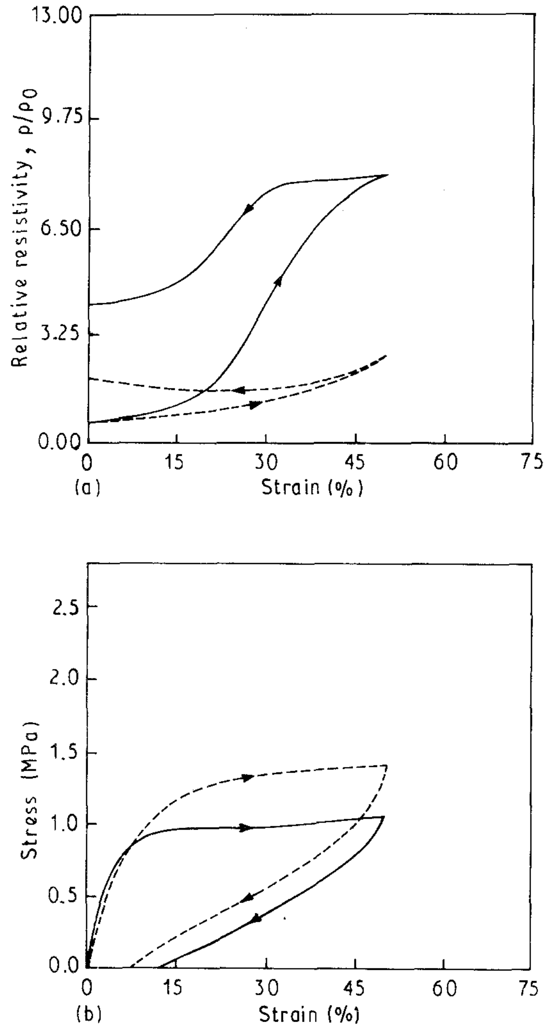

Figure 9 (a) Stress–strain plots for the extension–retraction cycle of various composites and (b) influence of extension–retraction on the relative resistivity of various composites. (——) CF6, and (- - -) XF4.

Likewise, beyond the yield strain, tensile modulus increases faster than prior to yielding. The threshold strain is approximately equal to the yield strain. Yielding represents an extensive failure of the rubber–fibre interface which is nothing but the breakdown of conductive networks formed in the system. Thus the phenomenon which is responsible for failure of the rubber–fibre interface is greatly responsible for the increase in the resistivity due to breakdown of conductive networks. With the increase of particulate filler in the composites, the tendency of yielding reduces and the rate-of-change in resistivity with strain diminishes.

3.4. Irreversibility effects

The composites containing fibres exhibit a strong irreversible effect in the stress–strain plots. It has been reported in our earlier communication [15] that high hysteresis is observed as the concentration of fibre is increased in the composites. The materials which exhibit yielding in the stress–strain plots are also expected to show a high degree of tensile set. The materials studied here have shown high tensile set as observed from Fig. 9a. However, the presence of carbon black in the composites reduces the set property which in turn reflects a better interaction between black and rubber matrix.

The composites also display appreciable irreversibility in the variation of relative resistivity with applied strain during the loading–unloading cycle. The hysteresis loop for relative resistivity versus applied strain is very high for composites containing carbon fibre compared to systems where a portion of the fibre is replaced by carbon black (Fig. 9b). The set is observed in terms of a change in the relative resistivity (i.e. change in relative resistivity at zero strain before loading and after loading). The reduction in the resistivity of the composites is due to the permanent breakdown of some conducting networks existing in the system.

4. Conclusion

Static strain has an appreciable effect on the tensile modulus and electrical resistivity of nitrite-rubber-based conductive composites. Both electrical and mechanical responses depend on strain and strain rate. However, the sensitivity of these responses strongly depends on conductive-filler concentration and filler-blend composition. Electrical response decreases with an increase in fibre concentration in the matrix and also with increased proportions of particulate carbon black in the filler-blend composition. Yielding in stress–strain curves decreases with an increase in the proportion of particulate filler (carbon black). A good correlation exists between electrical and mechanical properties as functions of strain and strain rate.

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