

Carbon fibre filled conductive composites based on nitrile rubber (NBR), ethylene propylene diene rubber (EPDM) and their blend

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The conductivity of nitrile rubber (NBR), ethylene-propylene-diene rubber (EPDM) and 50/50 NBR/EPDM blend has been measured against the loading of conductive carbon fibre to check the percolation limit for each system. The volume resistivity of all fibre-rubber composites increases with the increase in temperature, and the rate of increase in resistivity against temperature depends on the loading of carbon fibre and the nature of the base polymer. The change in volume resistivity during the heating and cooling cycle does not follow the same route, leading to the phenomena of electrical hysteresis and electrical set. The current-voltage relation is linear at room temperature, but becomes nonlinear at higher temperature. Some mechanical properties of these composites are also measured. The applicability of different theoretical models to predict the modulus and conductivity of these systems has been tested. Deviations between theoretical and experimental values are also discussed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: volume resistivity; mechanical properties; theoretical modelling)

INTRODUCTION

Flexible conductive rubbers have been a subject of interest for a long time. Recently interest has been growing in these electrically conductive polymer composites due to their applications in newer areas such as electronic equipment, pressure sensitive switches, important strategic materials such as EMI shielding, floor heating elements, apart from the conventional application of semiconducting materials for dissipation of static electricity¹⁻³. It is well known that insulating rubber can be made conductive through incorporation of a conductive filler⁴⁻⁷. Common conductive fillers include electrically conductive carbon black, carbon and graphite fibre, metal-coated inorganic oxide particles and metal powders⁸⁻¹¹. Among different types of conductive additives, carbon black is the most widely used material for rubber matrices. It not only provides a high degree of conductivity but also imparts good reinforcement to the rubber matrix. However, for many applications high conductivity is the main requirement and the mechanical properties of such a system may be a secondary consideration. Short carbon fibre may be a better choice as conductive filler than conductive carbon black, as it can provide higher conductivity at lower loading¹². Various rubbers are used for preparation of such composites, for example silicone rubber, nitrile rubber (NBR), butyl rubber, natural rubber and EPDM rubber¹³. Blends of rubbers having different polarity are also very useful for achieving a high degree of conductivity, particularly because of their well defined interface¹⁴.

The present paper deals with the electrical and mechanical properties of conductive rubber composites based on EPDM, NBR and 50/50 (wt ratio) blends of EPDM/NBR containing different loadings of short carbon fibre (SCF). The effect of temperature on the electrical resistivity of

these systems has been studied in detail with a view to understanding the mechanism of conductivity. Some mechanical properties are also measured to check the suitability of these composites in practical application. The applicability of different theoretical models to predict the modulus and conductivity of these systems has also been tested.

EXPERIMENTAL

Materials

Ethylene-propylene-diene rubber (EPDM), Grade JSR EP96 (ENB content, 5–7%), ML₁₊₄ at 100°C = 61 and ML₁₊₈ at 120°C = 53 supplied by JSR Co Ltd, Japan.

Acrylonitrile butadiene rubber (NBR) (ACN content 32%), ML₁₊₄ at 100°C = 51 supplied by JSR Co Ltd, Japan.

Carbon fibre, grade RK-30 from RK Carbon Fibre, Stockport, UK. The physical characteristics of the fibre used in the experiment are listed in *Table 1*.

1,2-dihydro-2,2,4-trimethyl quinoline (TQ) obtained from ICI (India) Ltd, India.

Dicumyl peroxide (DCP) obtained from Aldrich Chemical Company Inc, USA.

Mixing and vulcanization

The compound formulations are given in *Table 2*. The short carbon fibre (SCF) of initial length ~6 mm was mixed with the rubber in a Brabender plasticorder (PLE 330) under identical conditions of time, temperature, rotor speed and sequence of mixing of all compounding ingredients. The mixes were sheeted out in a laboratory-size two-roll mixing mill. The optimum cure times at 170°C for these compounds were determined from a Monsanto rheometer R-100S, and all the mixes were cured at 170°C in an electrically heated press under identical pressure (5 MPa). These cure sheets were then conditioned before testing (24 h maturation at room temperature).

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Measurement of volume resistivity

The volume resistivity for all composites with resistivity $\geq 10^8$ ohm cm was measured using a Hewlett-Packard high resistance meter (Model 4329A) coupled with a resistivity cell (Model 160084). For composites with resistivity $\leq 10^6$ ohm cm, the volume resistivity was measured by the four-probe technique using the Van der Pauw method as described in literature¹⁵ over the temperature range 25–120°C. The method is based on application of current and measurement of voltage. The instrument used for current application was a programmable DC voltage/current generator (Advantest TR 6142), and for voltage measurement a digital precision voltmeter (Schlumberger, UK, 7071) was used.

Physical testing of samples

Physical properties such as tensile strength, modulus (%) and elongation at break were measured using a Zwick universal testing machine (Model 1445) as per ASTM Standard D 412–87, Method A. The hardness of the composites were measured using a Shore A durometer (ASTM D 2240–86). A Mooney viscometer (Negretti Automation Mooney sheering disc viscometer, Model MK-111) was employed to measure the Mooney viscosity (ML₁₊₄) at 100°C in accordance with D 1646–1963.

Evaluation of final size of fibre in the rubber matrix

A portion of mixed compounds just before vulcanization was solubilized in chloroform (CHCl₃) to separate the fibre from the rubber matrix. The collected fibres were then washed thoroughly with fresh CHCl₃ to ensure complete removal of rubber from the fibre surface. The washed fibres

were then placed on a glass slide and examined under a Leitz Laborlux (Model 11 POL) optical microscope (Ernst Leitz GmbH, Wetzlar, Germany) to estimate the final fibre length and aspect ratio (i.e. L/D , where L and D are the length and diameter of SCF respectively). The SEM observations of the brittle fractured surface of SCF loaded composites were made using a Hitachi scanning electron microscope (Model S-415A). The samples were subjected to brittle fracture in liquid nitrogen and the fractured surfaces were sputter coated with gold within 24 h of testing.

In this paper, all composites are identified by an alphanumeric system. The first two block letters represent the rubber used in the blend. The first number after these letters represents the blend composition. The second number indicates the loadings of conducting SCF and the letter F indicates a fibre filled composite. For example, NE50.40F represents a 50/50 NBR/EPDM blend containing 40 phr of conductive SCF.

RESULTS AND DISCUSSION

Effect of mixing of carbon fibre

The carbon fibre is brittle in nature, like glass fibre, and because of its low bending strength it undergoes extensive breakdown during mixing and processing, shortening into different lengths. The distributions of fibre lengths after mixing of 40 phr loaded compositions are shown in Figure 1. There is no change in the fibre diameter during mixing. However, it is difficult to control the fibre length, so the aspect ratio (L/D) drops during processing. Table 3 shows

Table 1 Physical properties of short carbon fibre used in the composites

| | |
|-------------------------------|-----------------------------|
| Product name | RK-30 |
| Precursor | Polyacrylonitrile (PAN) |
| Average length (mm) | 6.0 |
| Diameter (mm) | 0.0101 |
| Density (g ml ⁻¹) | 1.78 |
| Electrical resistivity | 1.5×10^{-3} ohm cm |
| Typical carbon content | 95% (mass) |
| Young's modulus | 2.3×10^5 MPa |

Table 2 Formulations of the base rubber compounds^a

| Ingredients ^b | NE0 | NE50 | NE100 |
|--------------------------|-----|------|-------|
| EPDM | 100 | 50 | 0 |
| NBR | 0 | 50 | 100 |
| TQ | 1.5 | 1.5 | 1.5 |
| SCF | — | — | — |
| DCP | 1.5 | 1.5 | 1.5 |

^aIn all the base rubber compounds, short carbon fibre concentration is varied between 0, 5, 10, 15, 20, 25, 30 and 40 phr

^bAll the ingredients are in phr (weight per hundred weight of rubber)

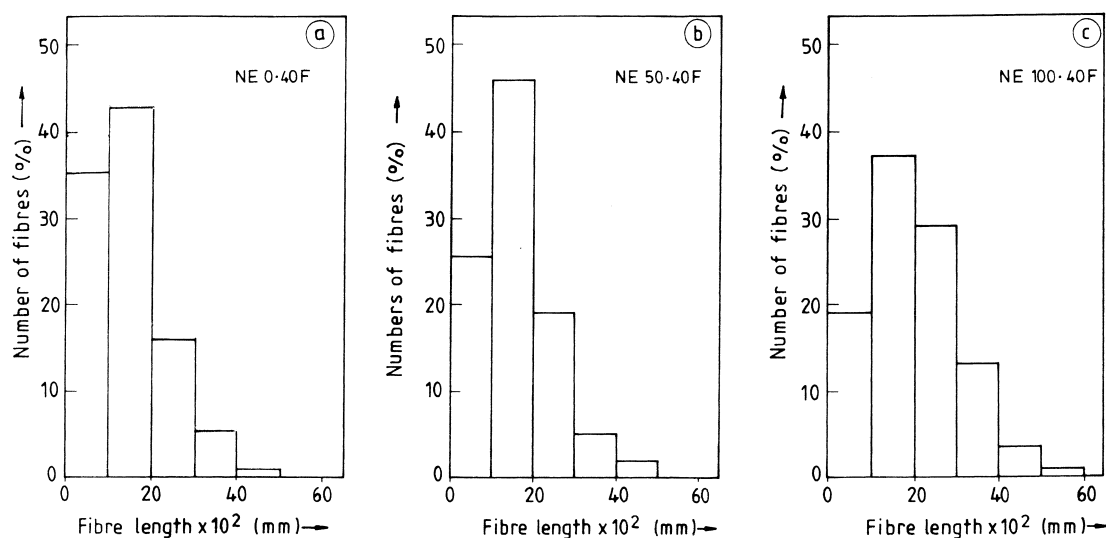


Figure 1 Distribution of fibre length after mixing of three composite systems based on (a) EPDM, (b) NBR, (c) 50/50 blend of EPDM/NBR, respectively containing 40 phr SCF

the extent of fibre breakage and the aspect ratio for different blend systems containing different concentrations of fibre.

The mixing conditions were kept identical for each compound, to avoid any influence of mixing on the fibre breakage and consequently on the electrical properties of the composites. The retention of fibre integrity is expressed as the ratio $(L_0 - L_t)/L_0$ in %, where L_0 and L_t are fibre length before and after processing, respectively (Figure 2). It has been observed that on increasing SCF concentration the extent of fibre breakage increases. The increase in SCF concentration increases the viscosity of the mix; consequently brittle fibres will experience a higher degree of shearing force during mixing and this leads to extensive fibre breakage¹⁶.

Effect of fibre concentration on electrical properties of different blends

The volume resistivity of pure polymers, namely EPDM and NBR, differs from one to another. EPDM being nonpolar, its intrinsic volume resistivity is very high, in the order of 10^{18} ohm cm, whereas NBR is polar and has a volume resistivity in the order of 10^{10} ohm cm. The volume resistivity of the 50/50 blend of EPDM/NBR is in the order of 10^{12} ohm cm. Figure 3 shows the variation of volume resistivity against SCF loading for three different polymeric systems, namely pure EPDM, a 50/50 blend of EPDM/NBR and pure NBR. Initially the resistivity decreases slowly with the increase in fibre concentration. But at certain critical concentration, a sharp change in the electrical resistivity is observed; that is, resistivity decreases appreciably from the insulating range to the conductive range. However, beyond this critical concentration the change in resistivity against fibre loading becomes marginal. This critical concentration of conductive filler which converts the insulating polymer matrix to a conductive one is popularly known as the percolation limit. The same observation is found to be true for all three rubber systems. The critical concentration (percolation limit) is found to be almost independent of composition of the base polymer. The percolation limit of SCF for pure EPDM, pure NBR and their 50/50 blend is found to be around 14 phr. In fact, at this concentration of SCF, a continuous conductive network is formed in the insulating rubber matrix due to the physical contact of filler particles (SCF). Below this critical concentration of SCF, no

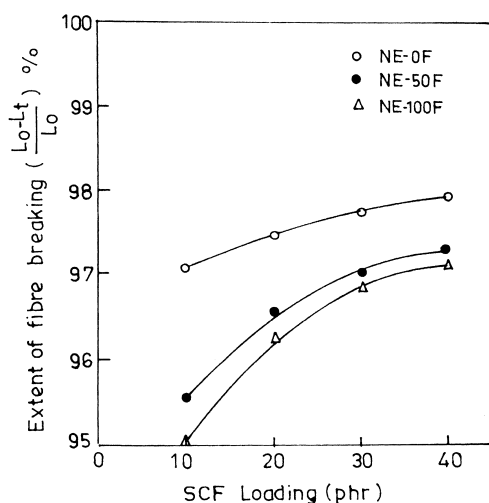


Figure 2 Effect of SCF loading on the extent of fibre breakage $(L_0 - L_t)/L_0$ (%) for the different composites

continuous conductive network is formed and the conduction of the system depends mainly on the conductivity of the base polymer. But at concentrations equal to or higher than the percolation limit continuous conductive networks are formed and the conductivity of the composite mainly depends on the conductivity of the continuous conductive network of SCF formed through aggregation. But, above the critical concentration, the change in volume resistivity again becomes marginal against SCF loading. This effect may be considered as very similar to the effect of increasing the diameter of a conducting wire on its conductivity.

It is interesting to note that the critical concentration of SCF to achieve a conductive network is much lower than that of a particulate filler such as conductive carbon black. In our earlier experiment with acetylene black it was observed that the critical concentration of the black was around 30–40 phr, which is much higher than that of SCF. However, the critical concentration of conductive filler depends on the base polymer matrix, mainly on its viscosity¹⁷. If the polymer matrix has higher viscosity the percolation limit for conductive filler to form a continuous conductive network is also higher, compared to a polymer with lower viscosity. In fact the short carbon fibre may be considered as a very long chain of carbon black particles which aids in the easy formation of a conductive network throughout the insulating matrix, and this accounts for the lower loading of SCF, compared to carbon black, to attain the percolation limit.

Effect of temperature on conductivity

The effect of temperature on the resistivity of a conductive composite is rather complex. Various factors

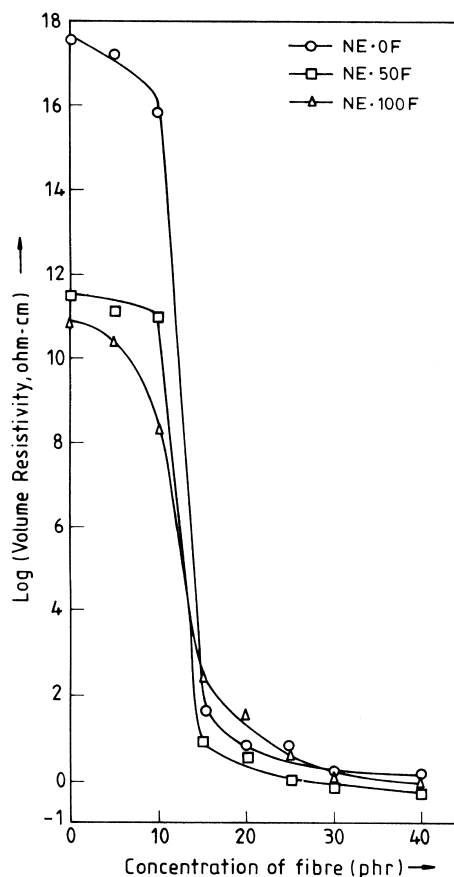


Figure 3 Effect of SCF loading on the volume resistivity of the composites

influence the variation of resistivity against temperature. Figure 4a–c show the variation of log resistivity against temperature for EPDM, NBR and 50/50 NBR/EPDM blends filled with different concentrations of SCF. It is observed that the resistivity progressively increases with the increase in temperature up to the highest measured temperature of 120°C used in these experiments; i.e., a positive temperature coefficient of resistivity (PCT effect) is observed. It is found that the slope of resistivity against temperature (i.e. the slope of $R = f(t)$ curves) increases with an increase in EPDM in the blend for a fixed concentration of SCF, and decreases with increase in SCF loading for each blend. In

fact the $R = f(1/T)$ plots have two slopes, one at the lower temperature range 25–60°C (298–333 K) and the other at the higher temperature range 80–120°C (353–393 K) (Figure 5a–b). Both lower and higher temperature slopes for $R = f(t)$ curves are the highest for composites based on pure EPDM, followed by 50/50 EPDM/NBR blends and pure NBR based composites having equal loadings of SCF (Figure 5c).

The mechanism of $R = f(t)$ curves can be explained in terms of the hopping or tunnelling mechanism of charged particles (i.e. electrons) present in the system. According to this mechanism it is believed that, with increasing

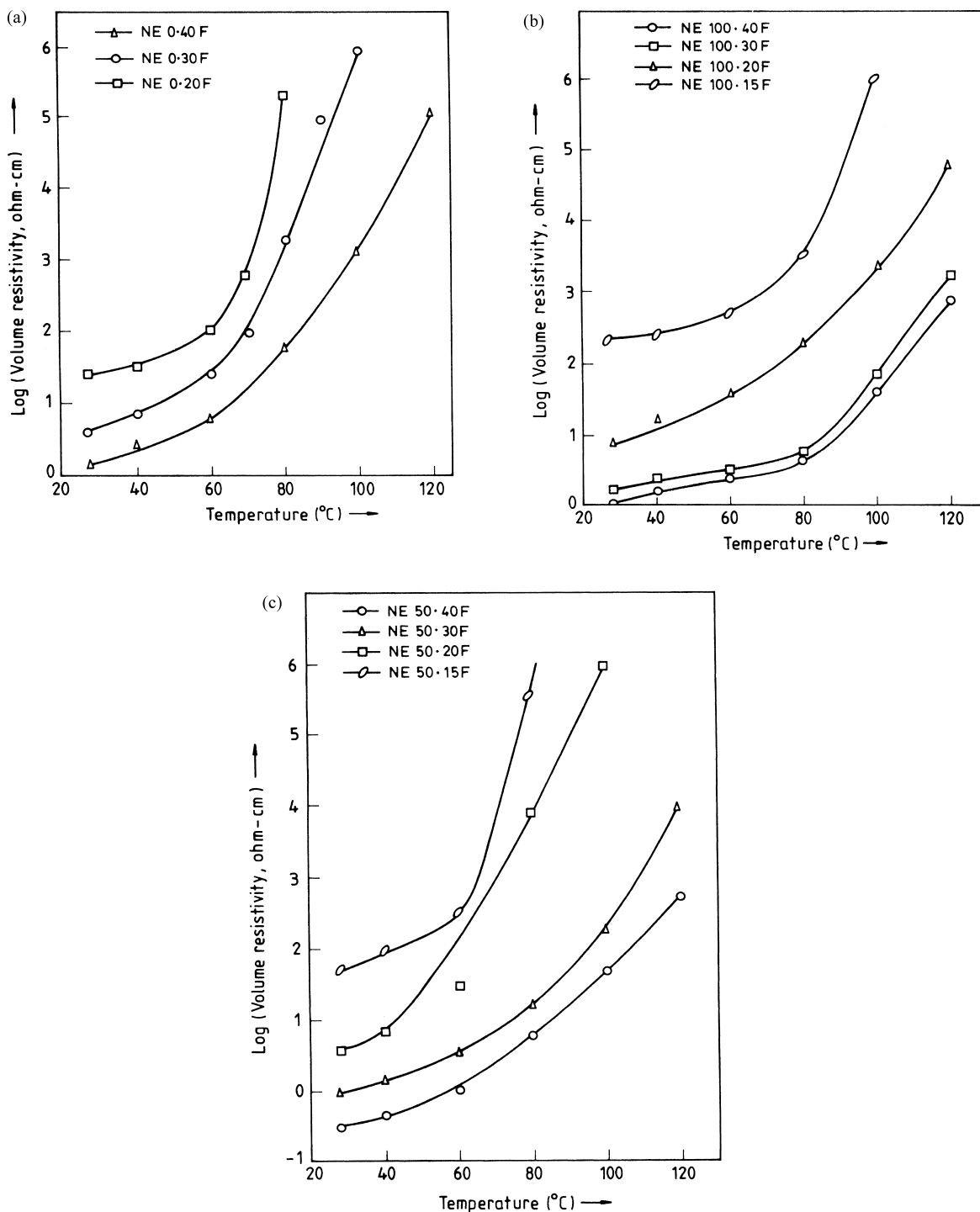


Figure 4 Influence of temperature on the volume resistivity of the composites based on (a) EPDM, (b) NBR, (c) 50/50 blend of EPDM/NBR, for different concentrations of SCF

temperature, the interfibre average distance increases due to the uneven thermal expansion of rubber and carbon fibre. The thermal expansion coefficient of rubber is positive ($190\text{--}220 \times 10^{-6}$) whereas it is negative (-1.45×10^{-6}) for carbon fibre^{18,19}. The ease of tunnelling or hopping of charge carriers (electrons) deteriorates because of the increased gap between the fibres. Accordingly, in such a condition the probability of tunnelling becomes less and less due to scattering of carriers in the rubber layers between the fibres. This is reflected in a significant increase in resistivity with temperature. But, with gradual increase of fibre loading, the above effect progressively decreases due to the presence of a larger number of interfibre contacts which ensure a much higher probability of tunnelling through the

numerous closely knitted interfibre positions. This was indicated by a gradual fall of steepness in $R = f(t)$ plots with increase in fibre concentration.

The temperature dependence of conductivity for SCF filled composites is different from that of composites filled with carbon black. In acetylene black filled systems the NCT effect of resistivity is observed¹⁷; i.e., the resistivity of these composites decreases with increase in temperature. In SCF filled systems the difference in thermal expansion between base polymer and carbon fibre is the main reason for the PCT effect in resistivity. In particulate composites (conductive black filled systems), apart from differential thermal expansion of filler aggregate and polymer matrix, a few other phenomena are operative in the system; for

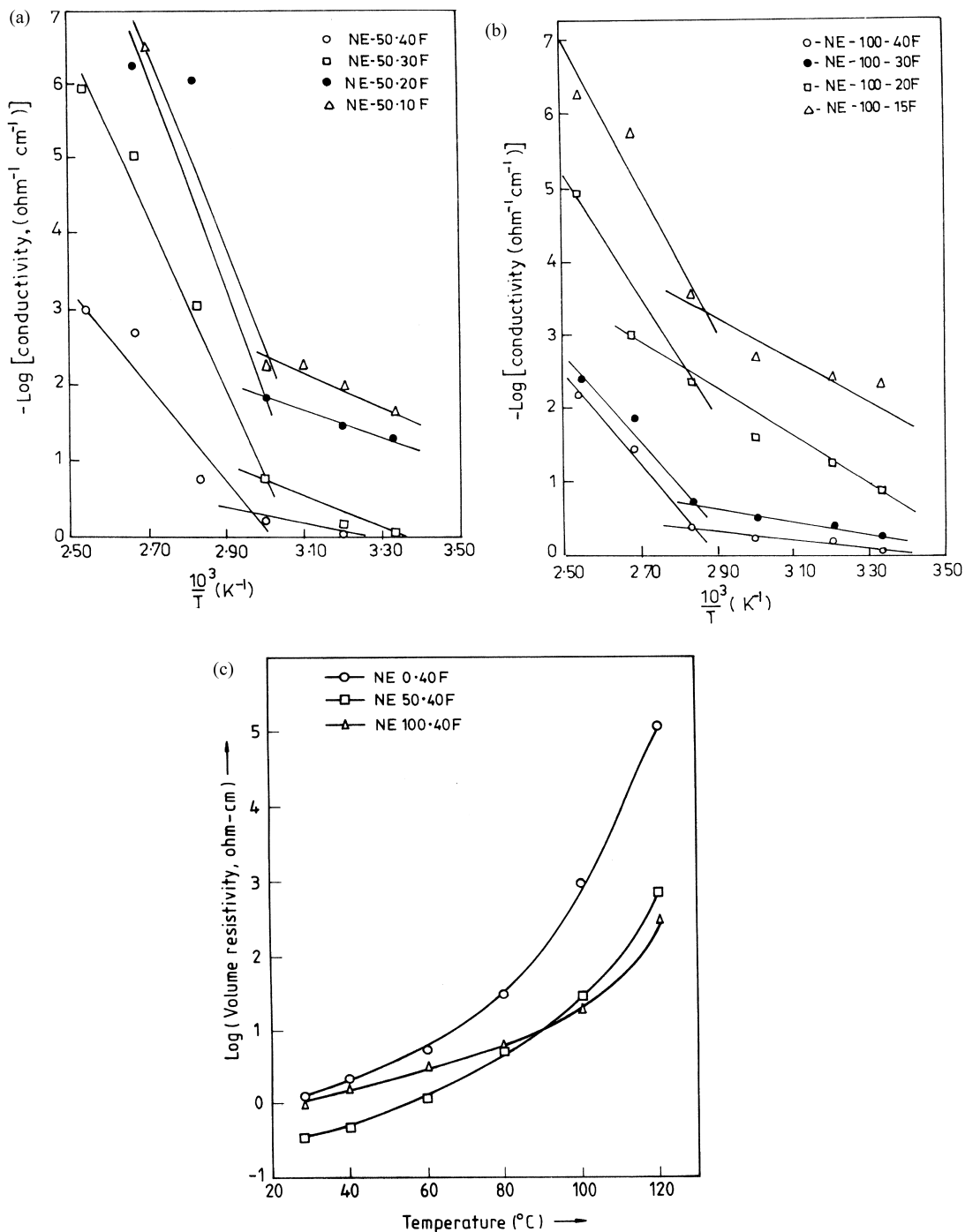


Figure 5 Plots of the logarithm of conductivity versus the reciprocal of temperature ($1/T$) on (a) 50/50 NBR/EPDM blend, (b) NBR containing different concentrations of fibre; (c) increase of volume resistivity with temperature for different composite systems containing the same filler loading (40 phr)

Table 3 Breakage of SCF after processing (before mixing the length (L) of SCF is 6 mm and the diameter (D) is 0.0101 mm)

| SCF (phr) | NE0 | | NE50 | | NE100 | |
|-----------|-----------------------------------|--------------------|--------------------|--------------------|-----------------------------------|------------------|
| | Fibre length (after mixing) L(mm) | Aspect ratio (L/D) | Fibre length L(mm) | Aspect ratio (L/D) | Fibre length (after mixing) L(mm) | Aspect ratio L/D |
| 10 | 0.1775 | 17.50 | 0.2691 | 26.60 | 0.3051 | 30.20 |
| 20 | 0.1548 | 15.32 | 0.2073 | 20.52 | 0.2170 | 22.60 |
| 30 | 0.1379 | 13.65 | 0.1807 | 17.89 | 0.1892 | 18.73 |
| 40 | 0.1271 | 12.60 | 0.1620 | 16.06 | 0.1758 | 17.62 |

Table 4 Calculated E_h value (ev/mol)

| Sample No. | Lower temp. range | Upper temp. range |
|------------|-------------------|-------------------|
| NE100.40F | 0.125 | 1.17 |
| NE100.30F | 0.172 | 1.28 |
| NE100.20F | 0.193 | 1.68 |
| NE100.15F | 0.613 | 1.98 |
| NE50.40F | 0.186 | 2.05 |
| NE50.30F | 0.396 | 2.27 |
| NE50.20F | 0.450 | 3.06 |
| NE50.15F | 0.475 | 2.85 |
| NE0.40F | 0.728 | 2.05 |
| NE0.30F | 0.551 | 2.07 |
| NE0.20F | 0.434 | 1.82 |

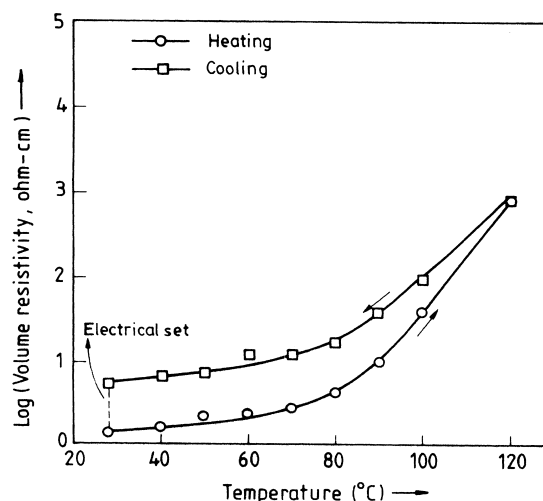
example, the flocculation of particulate filler, leading to formation of further conductive networks during heating, high temperature electron emission between two ends of black aggregates which are separated by a smaller gap, and aerial oxidation leading to the formation of polar groups. All these phenomena increase the conductivity with increase in temperature and more than compensate the NCT effect due to differential thermal expansion of conductive network and polymer matrix.

Another important factor which influences the resistivity is the viscosity of the rubber. Rubber having a higher viscosity exerts much higher shearing force (torque) on brittle carbon fibres during processing, as discussed earlier. The higher the shearing force, the more is the degree of fibre breakage and the more is the gap between fibres and therefore the interfibre contact resistance. On increasing the temperature this interfibre contact resistance increases further and consequently the probability of hopping or tunnelling of electrons between gaps decreases. As a result the volume resistivity increases with the increase in the viscosity of the polymer matrix for the same amount of fibre loading. Here the viscosity of EPDM is higher ($ML_{1+4}@100^\circ\text{C} = 61$) than that of NBR ($ML_{1+4}@100^\circ\text{C} = 51$). So the $R = f(t)$ curves gradually become steeper with the EPDM-rich systems for the same fibre loading.

The temperature dependence of volume resistivity can be interpreted on the basis of the following equation:

$$R = R_0 T \exp(E_h/kT)$$

where R is the volume resistivity, E_h represents the activation energy for hopping, k is the Boltzmann constant, R_0 represents the pre-exponential factor and T is the temperature on the absolute scale (K). The plot of log resistivity against $1/T$ (K^{-1}) is linear with a break at a certain temperature; that is, it has two linear portions (Figure 5a–b). So two activation energies for the hopping process may be calculated from the two slopes. The apparent values of E_h for different loadings of fibre in various compositions have been calculated for two different ranges of temperature, and two sets of E_h thus calculated are given in Table 4. On increasing the fibre concentration in the composite the

**Figure 6** Variation of volume resistivity versus temperature during heating-cooling cycle for NE100.40F

value of activation energy decreases. It has also been found that at the higher temperature region the activation energy value is comparatively higher than that at the lower temperature region. The heating-cooling curves in the $R = f(t)$ plots do not follow the same path; consequently a hysteresis cycle for resistivity-temperature plots has been generated (Figure 6). The initial and final resistivities at the starting temperature (25°C) after the heating-cooling cycle are found to be different and thus an electrical set is observed for each system after the heating-cooling cycle. However, this electrical set gradually increases on decreasing fibre loading, as observed in Figure 7. On further increasing the EPDM content in the system, the electrical set also increases.

The change of volume resistivity during repeated heating-cooling cycles is shown in Figure 8. It has been observed that the electrical set is much higher in the first heating-cooling cycle than that in the second cycle, and it progressively decreases and becomes invariant from the third cycle onwards. This change in resistivity during the heating-cooling cycle reveals that the change of volume resistivity against temperature is irreversible in nature, which may be due to some irreversible change that occurs in conducting networks, present in the system during heating and not completely reversed during cooling (Figure 8).

Current-voltage characteristics

The current-voltage ($I-V$) characteristics of different fibre filled composites have been investigated at different temperatures (Figure 9). Such studies can provide useful information on the conduction mechanism. The $I-V$ curve of the EPDM composite containing 20 phr of SCF loading shows a linear relationship at 25°C , indicating the ohmic behaviour of the system. But at higher temperatures (above

60°C) a departure from linearity in the $I-V$ curves is observed. This observation can be explained as follows. At room temperature ($\leq 25^\circ\text{C}$), interfibre contacts leading to the formation of continuous conductive networks are ensured in the composite. But at higher temperatures there is a drop in electric field strength between the interfibre particles with increasing the gap distance due to the unequal thermal expansion of fibre and rubber, leading to non-ohmic behaviour of the current-voltage characteristics. The $I-V$ curves at different temperatures for these composites are found to be almost alike.

Mechanical properties

Stress-strain plots of the different composites of the EPDM, 50/50 blend of NBR/EPDM and NBR are presented

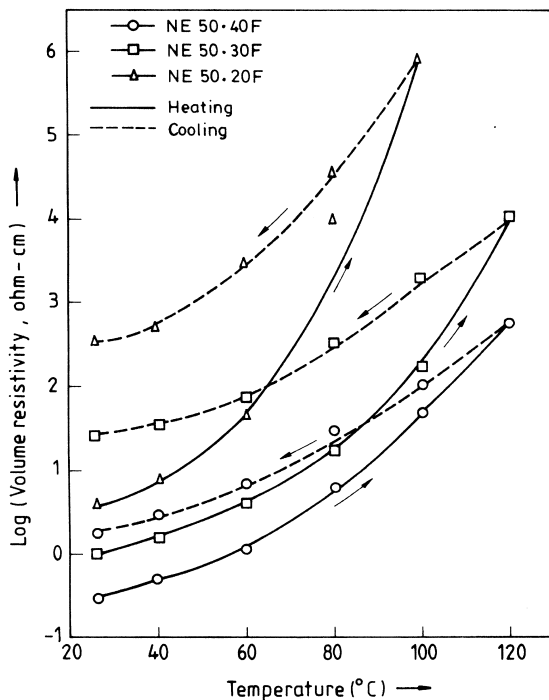


Figure 7 Semilog plots of volume resistivity versus temperature during heating-cooling cycle for composites of 50/50 EPDM/NBR blend

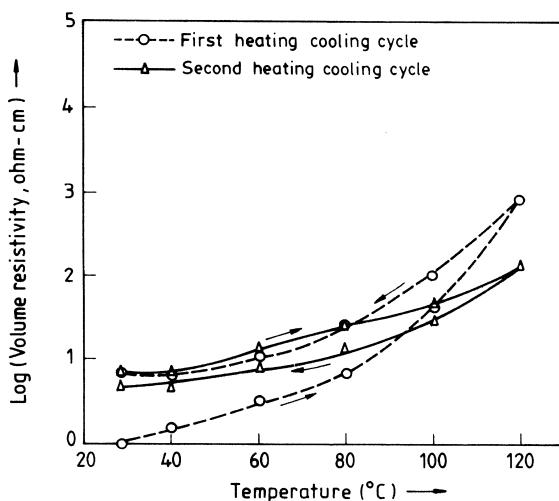


Figure 8 Change in volume resistivity versus temperature for repeated heating-cooling cycle of NE100.40F

in Figure 10(a-c) respectively. It is observed that all SCF filled composites show some yielding tendency, like plastic materials. The tensile strengths of all the composites are very low and the degree of reinforcement increases only marginally with the increase in fibre loading. The modulus at 50% elongation increases somewhat as the proportion of fibre is increased in the system.

By contrast, in carbon black-rubber systems high reinforcement is generally observed because of the very small particle size (very high surface area) of the black particles; moreover, physico-mechanical bonding between carbon black and rubber occurs, due to some active groups (such as $-\text{CO}$, $-\text{COOH}$, $-\text{CHO}$, $-\text{OH}$, $=\text{CHOH}$) being present on the surface of the black²⁰. However, these active groups are absent on the surface of carbon fibres, mainly because carbon fibres are produced through several steps. There are some steps where the fibre precursor is subjected to a very high temperature, leading to destruction of these active groups which are responsible for the high degree of reinforcement observed in the case of reinforcing carbon black. Further, in contrast to the carbon black particle size, the final particle size of carbon fibre is very high. The strength of rubber-fibre composites depends on the strength of the rubber matrix, rubber-fibre interaction, the degree of wetting of fibre particles by the rubber macromolecular chain. Both EPDM and NBR are non-self-reinforcing rubber (gum vulcanisates exhibit poor strength); moreover, short carbon fibre is a non-reinforcing filler, so the strength of the composite is also poor¹².

The extent of polymer-filler interaction can be estimated from a swelling experiment according to the Kraus method^{21,22}. The experiment revealed the existence of poor polymer-fibre interaction. Only some weak physical interaction (mechanical bonding) may be there. That is why the tensile strength increases marginally with increase in fibre loading. Carbon fibre is brittle in nature, so fibre-containing composites exhibit ductile behaviour. On application of stress these composites undergo irreversible deformation due to loosening of weakly bonded fibres from the matrix. The weak bonding of carbon fibre with rubber matrices can be observed from SEM photomicrographs of fractured surfaces of these composites. It is found that some fibres get detached from the rubber matrix easily, leaving behind the holes from which they became detached during fracture. The smooth fibre surface does not even form a

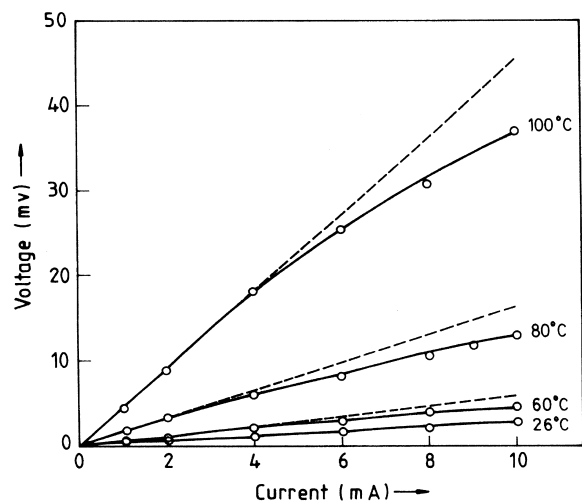


Figure 9 Current-voltage plots at various temperatures for NE100.20F

strong mechanical lock with rubber. It is also clear from these photographs that there is no trace of rubber left on the debonded fibre surface (Figure 11a-c).

The higher elongation is observed for composites based on EPDM, followed by 50/50 EPDM/NBR blend and pure NBR. This is mainly because the EPDM matrix is more flexible than the NBR matrix. The T_g of EPDM is -80°C whereas for NBR it is only -40°C . The hardness of all blends increases with increase in fibre loading.

Applicability of different models to explain mechanical and electrical properties

It is obvious that the properties of a composite must in some way represent an average of the properties of its individual constituents. However the precise nature of 'average' is a sensitive function of microstructural geometry as well as the interfaces existing among the constituents. Three idealized geometries may be: (a) arrangement of the short fibres along the direction of the applied stress/strain; (b) arrangement of SCF along the direction perpendicular to the applied stress/strain; (c) randomly activated and more or less uniformly distributed fibres in the rubber matrix — that is, the system is more or less isotropic in nature (Figure 12).

The first two cases represent two extremes in anisotropy of fibre filled composites. In the first case the composite has the maximum contribution for short fibres and in the second

case the composite strength has the minimum contribution for SCF. If the matrix is intimately bonded to the reinforcing fibres, the strain experienced by both matrix and fibre must be the same. Under such a condition the total load carried by

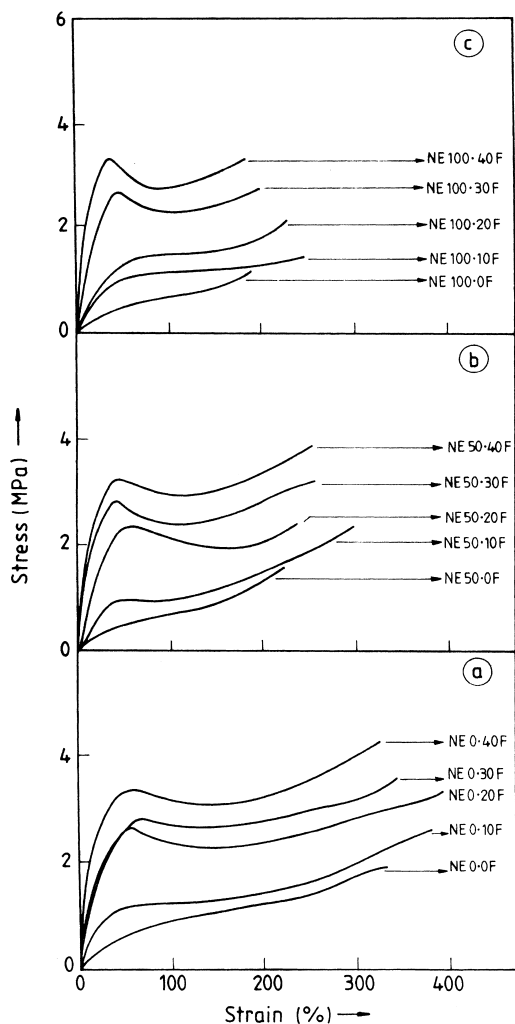


Figure 10 Stress-strain plots of (a) EPDM, (b) NBR, (c) 50/50 EPDM/NBR blend, at different concentrations of fibre

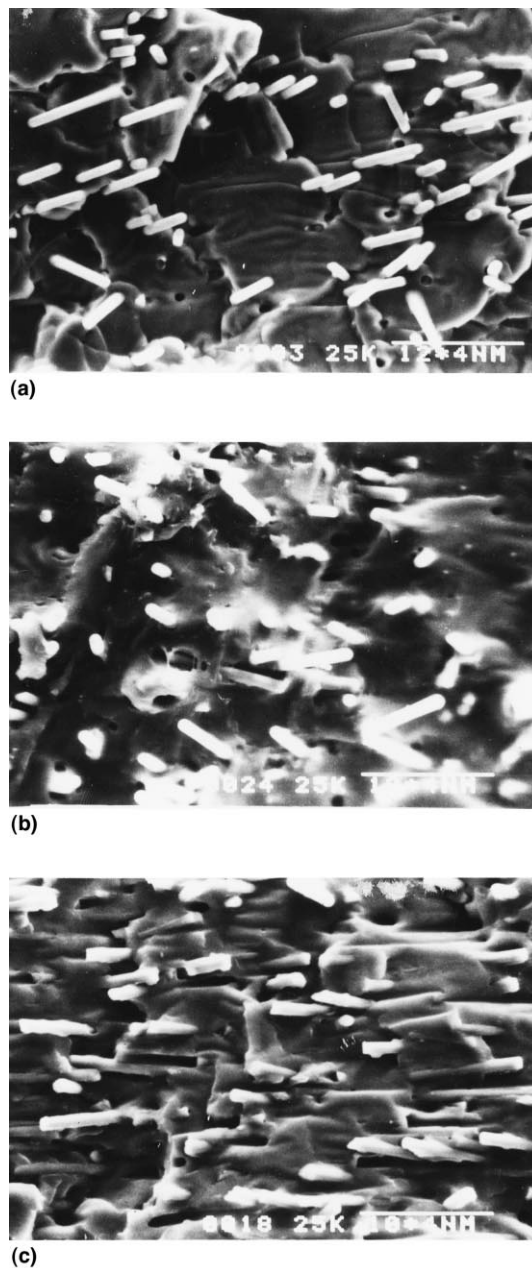


Figure 11 SEM photomicrographs of brittle fractured surface at 300x magnification for (a) NE0.40F, (b) NE50.40F, (c) NE100.40F

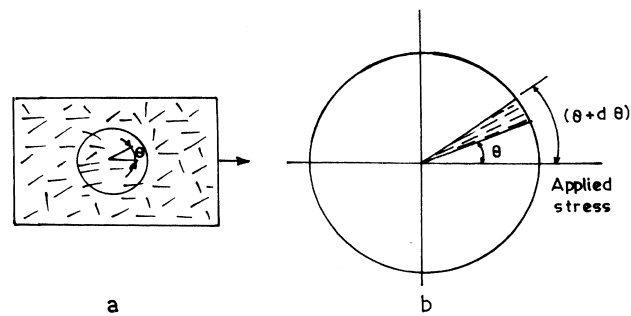


Figure 12 Schematic representation of (a) randomly dispersed fibre in rubber matrix, (b) fibre orientation with respect to applied stress

the composite P_c is the sum of the loads carried by the fibre P_f and the rubber matrix P_r :

$$P_c = P_f + P_r$$

The modulus of elasticity for the composite can be derived as

$$E_c = V_f E_f + V_r E_r \quad (1)$$

where E_c , E_f and E_r represent the modulus of elasticity of the composite, fibre and rubber respectively and V_f and V_r represent the volume fraction of fibre and rubber respectively.

$$V_f + V_r = 1$$

For loading perpendicular to the fibre isostress the equation can be derived as

$$1/E_c = V_m/E_m + V_f/E_f$$

which can be regarded as

$$E_c = \frac{E_m E_f}{V_m E_f + V_f E_m} \quad (2)$$

For loading of uniformity dispersed fibres in the composite, the equation can be derived as

$$E_c^n = V_f E_f^n + V_r E_r^n \quad (3)$$

where n may be a fraction or a whole number.

In a composite containing randomly distributed short fibres, the alignment of fibre out of the direction of stress must effectively reduce its contribution towards loadbearing capacity. Consider a straight segment of fibre inclined at an angle to the applied stress direction. Comparing the strength contribution of this segment with that of the same amount of fibre arranged uniformly and parallel to the applied stress direction, its contribution is reduced by a factor of $\cos^2\theta$. For a random array of fibres the probability of orientation in the range θ to $\theta + d\theta$ is proportional to $\sin\theta^3$. Taking into

account all the orientation gives a mean reduction factor g , where

$$g = \frac{\int_0^{\pi/2} \cos^2\theta \sin\theta d\theta}{\pi/2} = \frac{2}{3\pi} \quad (4)$$

So, for randomly oriented short fibres in a composite, the composite strength can be written as

$$E_c = V_r E_r + g V_f E_f \quad (5)$$

but $V_f + V_r = 1$.

Figure 13 shows semilog plots of the Young's modulus against volume fraction of fibre loading, calculated using equations for isostress and isostrain as well as random and probable distribution conditions for fibres in the matrix along with moduli obtained experimentally. This wide deviation between different theoretical and experimental plots is found to be true for composites based on EPDM, NBR and 50/50 NBR/EPDM blend. However plots for only one system, that is 50/50 NBR/EPDM blend based composites, have been shown.

The moduli calculated according to isostress (equation (1)) and random distribution (equation (3)) mainly depend on the modulus of carbon fibre, whereas the isostress condition (equation (2)) mainly depends on the modulus of the matrix, as is apparent from this equation. However, the experimental results show much lower values than those calculated according to equations (1) and (5), but somewhat higher than the values calculated according to equation (2). This reflects the fact that some degree of reinforcement is achieved in the elastomer matrix but this reinforcement is much lower than what is expected according to isostress or random distribution of SCF in the matrix.

However, while deriving these equations one important consideration has been taken for granted, that is, the interface between the matrix and the discontinuous phase must be strong enough to transmit the stress or strain due to mechanical load from one phase to other. Without this strength the disperse phase can fail to communicate with the matrix. If the interface is not strong enough the reinforcing fibres easily slip out of the matrix, as has been seen in these systems. Poor bonding of the SCF with rubber is the main reason for low strength and modulus of the composites. The

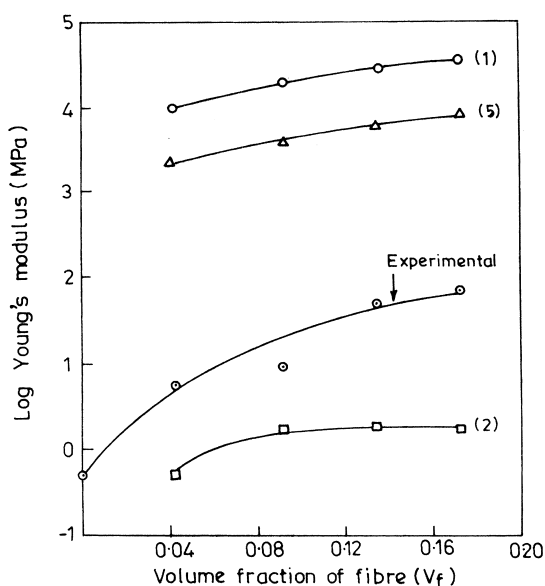


Figure 13 Comparison between experimental and different theoretical values (according to equations (1), (2) and (5)) of Young's modulus versus volume fraction of fibre (V_f) in the matrix

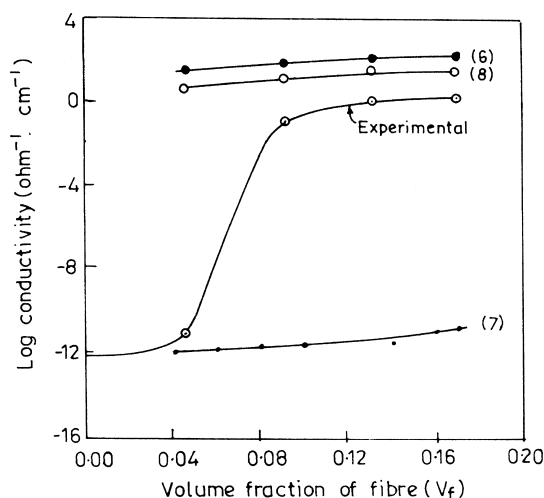


Figure 14 Comparison between experimental and different theoretical values (according to equations (6)–(8)) of electrical conductivity versus volume fraction of fibre (V_f) in the matrix

very weak interface is the cause of failure of such composites, as discussed earlier.

Electrical properties

Similar modelling may be applied to predict other properties of composites such as: (1) diffusivity; (2) Poisson's ratio; (3) thermal conductivity; (4) electrical conductivity²⁴. An effort has been made to test the applicability of these equations to predict the conductivity of these composites, and a similar comparison has been made to check the deviation between experimental and theoretically calculated values of conductivity using the equations given earlier.

When an electric field is parallel to the conductive network formed due to aggregation of SCF in the matrix, then the composite conductivity σ_c is equal to

$$\sigma_c = V_f \sigma_f + V_r \sigma_r \quad (6)$$

where σ_f and σ_r represent the conductivity of fibre and matrix rubber respectively. According to this equation, the conductivity of the composite is mainly governed by the particles present in the system.

When the applied electric field is perpendicular to the conductive network formed due to aggregation of SCF in the matrix,

$$\sigma_c = \frac{\sigma_m \sigma_f}{V_m \sigma_f + V_f \sigma_m} \quad (7)$$

According to this equation, the conductivity of the composite is mainly due to the conductivity of the matrix.

For randomly distributed fibre in the matrix, a conductive network is also formed in a random fashion. So, when the electric field is applied, on average the network may be aligned randomly with respect to the electric field:

$$\sigma_c = V_r \sigma_r + g V_f \sigma_f \quad (8)$$

However, even under this condition the conductivity derived from this theoretical equation is mainly governed by the conductivity of the SCF particles.

It is observed that the plot of logarithm of conductivity versus volume fraction of SCF obtained from experimental results is closer to the theoretical curve based on equation (7) at lower fibre loading (Figure 14). However, the experimental curve is closer to the theoretical curves derived from equations (6) and (8), i.e. where SCF are arranged parallel to the electric field. However, an abrupt change of conductivity against SCF loading is observed only in the experimental curve, which signifies that at or beyond a certain critical concentration a continuous conductive network is formed through aggregation of SCF particles in the insulating rubber matrix. The conductivity of the composite is therefore closer to that of the insulating matrix and the experimental curve is closer to the curve based on equation (7). However, at and beyond the critical concentration the conductivity of the system is mainly governed by the conductivity of the conductive filler present in the matrix. The experimental curves become closer to those derived for equations (6) and (7). However, none of these curves take into account the percolation limit, mainly because all these theoretical curves are based on the assumption of formation of a conductive network at all concentrations of conductive filler, or that the probability of formation of a conductive network is possible at all concentrations of SCF in the matrix. But in an actual situation the formation of a conductive network is possible at or beyond the percolation limit, below which it is zero.

There is a further reason for the difference between experimental and theoretical values. In the theory, it was assumed that all fibres are electrically active along their length and are connected by interfibre contacts between the electrodes, and there are no dead ends or internal resistance between the fibres. From a practical viewpoint, a fraction of the fibre does not contribute to the electrical performance because of contact resistance or dead ends.

CONCLUSIONS

- (1) Due to the brittle nature of carbon fibre, extensive breakage of fibre occurs during mixing and processing with rubber; the extent of breakage increases with increase in matrix viscosity and fibre loading.
- (2) SCF filled rubber composite provides a high level of conductivity and the percolation limit can be reached at relatively much lower loading than with conductive carbon black. SCF may be considered as a long chain of carbon black particles, and this aids in the formation of a continuous conductive network through aggregation of SCF in the matrix.
- (3) The increase in volume resistivity with temperature (PCT effect) is mainly due to breakdown of the conductive network which in turn is due to the difference in thermal expansion of rubber and SCF. However, at a high loading of SCF when a large number of networks are present in the matrix and the gap between the SCF particles is quite small, the PCT effect becomes marginal.
- (4) Electrical set and electrical hysteresis are observed in the resistivity versus temperature plot during a heating-cooling cycle. This is due to some irreversible change occurring in the system.
- (5) Nonlinearity of the current-voltage relationship at elevated temperatures is mainly due to a drop in field strength between fibre particles resulting from the increased gap.
- (6) The degree of reinforcement achieved through incorporation of SCF is marginal due to poor fibre-rubber interaction as well as the large particle size of SCF.

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