

# Conductive rubber composites from different blends of ethylene–propylene–diene rubber and nitrile rubber

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Conductive rubber composites were derived from different blends of ethylene–propylene–diene monomer (EPDM) rubber and acrylonitrile butadiene rubber (NBR) containing acetylene black. The electrical and mechanical properties of these composites were measured. The percolation limit for achieving high conductivity of conductive filler depends on the viscosity of the blend. The higher the viscosity, the higher is the percolation limit. The conductivity rises with increasing temperature, and the activation energy of conduction increases with the decrease in the loading of conductive filler and percentage of NBR in the blend. Electrical hysteresis and an electrical resistivity difference during the heating–cooling cycle are observed for these systems, which is mainly due to some kind of irreversible change occurring in the conductive networks during heating. The mechanisms of conduction of these systems were discussed in the light of different theories. It was found that the degree of reinforcement by acetylene black in blends compares with those in the pure components NBR and EPDM. This is due to incompatibility of two elastomers in the blend.

## 1. Introduction

Conductive rubber composites are widely used for different applications such as electrostatic charge dissipation, touch control switches and electromagnetic interference (EMI) shielding, and surface heaters [1, 2]. These materials need the desired electrical properties as well as sound mechanical properties. Various rubbers are being widely used for preparation of such composites, e.g., silicone, nitrile, butyl, natural rubber, ethylene–propylene rubber (EPR) and ethylene–propylene–diene monomer (EPDM) rubber. It has been reported in the literature that rubber blends having differences in polarity are very useful in achieving a high degree of conductivity because of their well-defined interface [3–6]. The distribution of carbon black at the interface of two rubbers gives rise to high conductivity. Accumulation of carbon black at the interface has the effect of increasing the number of contact points or decreasing the gap width as is also accomplished with higher loading or poorer dispersion. A uniform degree of poor dispersion is, however, very difficult to control. The heterogeneous microdispersion explains the higher conductivity of blends compared with the single polymer [6, 7]. The present paper deals with conductive rubber based on blends of EPDM rubber and acrylonitrile butadiene rubber (NBR) in different proportions and filled with different amounts of conductive acetylene black. Electrical properties under different conditions have been

studied in an attempt to understand the mechanism of conduction in such systems. Some mechanical properties of these blends were also studied in order to evaluate their potential for use in industrial applications.

## 2. Experimental procedure

The formulations (in weight per hundred weight of rubber (phr)) used in this work are shown in Table I. Mixing was accomplished on a two roll mixing mill using the same conditions for each mix. The physical characteristics of acetylene black are given in Table II. The mixes were cured at 170 °C in an electrically heated press to optimum cure times which had been previously determined on a Monsanto rheometer (R-100S). In this way sheets of vulcanizates of 2 mm thickness were prepared. These sheets were then conditioned before testing (24 h maturation at room temperature).

### 2.1. Testing

The volume resistivity for composites with a high resistivity was measured using a Hewlett–Packard high resistance meter (model 4329A) coupled with a resistivity cell (model 160084). In the case of composites having a low resistivity, volume resistivities were measured by a four-probe technique, using the

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TABLE I Formulation of mixes

	NE-0 (phr)	NE-25 (phr)	NE-50 (phr)	NE-75 (phr)	NE-100 (phr)
EPDM <sup>a</sup>	100	75	50	25	0
NBR <sup>b</sup>	0	25	50	75	100
TQ <sup>c</sup>	2	2	2	2	2
Acetylene black <sup>d</sup>	0-60	0-60	0-60	0-60	0-60
DCP <sup>e</sup>	1.5	1.5	1.5	1.5	1.5

<sup>a</sup>  $ML_{1+4}$  (100 °C) = 61 and  $ML_{1+8}$  (120 °C) = 53; diene monomer ENB (5%), high ethylene content; JSR EP96 supplied by Japan Synthetic Rubber Co. Ltd., Japan.

<sup>b</sup> (32% acrylonitrile content)  $ML_{1+4}$  (100 °C) = 51; supplied by Japan Synthetic Rubber Co. Ltd, Japan.

<sup>c</sup> 1,2-Dihydro-2,2,4-trimethyl quinoline (polymerized); supplied by ICI (India) Ltd.

<sup>d</sup> Supplied by Shawinigan, P-1250(VSP) Texas E.

<sup>e</sup> Dicumyl peroxide; melting point, 80 °C; supplied by Aldrich Chemical Company, USA.

TABLE II Physical characteristics of acetylene black [8]

Nitrogen surface area ( $m^2 g^{-1}$ )	70
DBP absorption number ( $cm^3$ per 100 g)	250
Particle diameter (nm)	42
Electron microscopic surface area ( $m^2 g^{-1}$ )	77

Van der Pauw method as described in the literature [9]. To measure the volume resistivity at a high temperature the entire electrode system was placed in an oven where the temperature could be monitored and kept constant. The stress-strain properties of different black filled vulcanizates were determined using an Instron universal testing machine (model-1195) according to ASTM standard D412, using dumbbell-shaped specimens. The hardness of the composites were measured using a Shore A durometer (ASTM standard D2240-86). A Mooney viscometer (Negretti Automation Mooney shearing disc viscometer model MK-111) was used to determine the Mooney viscosity  $ML_{(1+4)}$  at 100 °C according to the ASTM standard D-1646-1963 and  $ML_{1+8}$  at 120 °C for EPDM rubber.

In this paper, composites are identified by an alpha-numeric system. The first two letters represent the rubbers used in the blend. The first number after the letters represents the blend composition; the second number indicates the loading of conductive black. For example, NE-50.60 represents a 50-50 NBR-EPDM blend containing 60 phr of conductive black.

### 3. Results and discussion

#### 3.1. Effect of conductive filler loading on conductivity

The incorporation of conductive filler increases the conductivity of insulating rubber matrices. Fig. 1 shows the effect of filler loading (acetylene black) on the volume resistivity of the different NBR-EPDM blends and pure components. At low levels of black loading the conductive particles are insulated by the polymer, i.e., the particles are isolated from each other

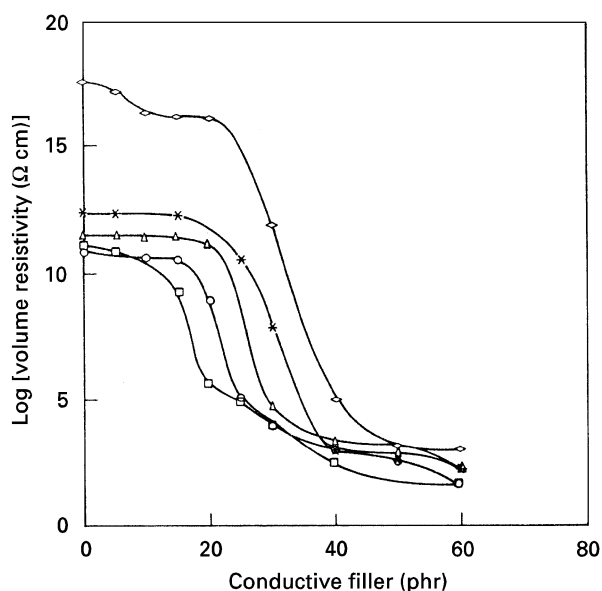


Figure 1 Volume resistivity against filler loading for different EPDM-NBR blends. ( $\diamond$ ), NE-0; (\*), NE-25; ( $\Delta$ ) NE-50; ( $\square$ ), NE-75; ( $\circ$ ), NE-100.

and the composite resistivity is nearly equal to that of pure polymer matrix. The incorporation of conductive filler in the insulating rubber matrix reduces the resistivity of the system. As the filler loading increases, a mutual contact between the carbon black aggregates occurs to an increasing extent and a sharp drop in resistivity is observed at a certain critical concentration defined as percolation limit. In this percolation region a relatively small increase in filler loading produces a large increase in conductivity (large drop in resistivity). This critical concentration is found to be different for different polymers and blends. It is found that the volume resistivities of pure polymers are different from each other. As EPDM is non-polar, it shows a high volume resistivity in the range of  $10^{17} \Omega cm$  whereas NBR (32% acrylonitrile content) which is highly polar shows a volume resistivity in the approximate range of  $10^{10} \Omega cm$ . EPDM-rich blends exhibit higher volume resistivities than NBR-rich blends. It is interesting to note that the volume resistivity of pure components decreases with increase in NBR concentration up to 50 wt%; above this concentration the change is marginal. The attainment of critical concentration also changes with the composition of the blend system. Pure EPDM exhibits the highest critical concentration followed by the blend NE-25 (75% EPDM). However, for blends NE-50, NE-75 and NE-100 the change in critical concentration is relatively less but, at higher filler loadings beyond the critical concentration, all the systems exhibit similar resistivities. The attainment of the percolation limit is also dependent on the viscosity of the polymer. The higher the viscosity of the rubber matrix, the higher is the percolation limit. The structure of black (chain-like aggregation) degrades owing to the high shearing action experienced during mixing. The higher the Mooney viscosity of the base polymer, the higher is the shearing force experienced by the black aggregates and thus the greater is the degree of

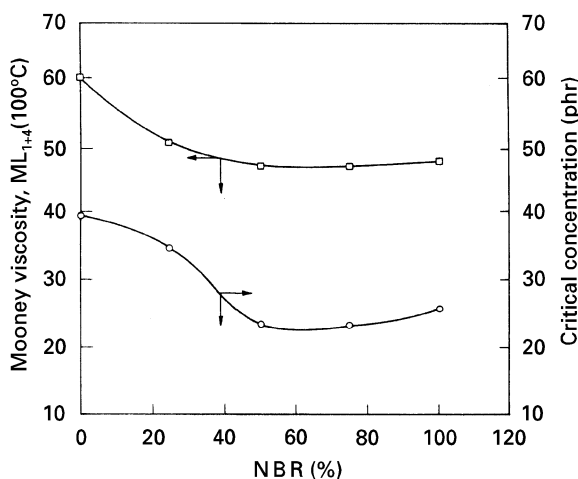


Figure 2 The variation in critical concentration (percolation limit) and Mooney viscosity against blend composition.

structure breakdown of the black. Consequently, the formation of a conductive network throughout the matrix is delayed and occurs at a higher concentration, as observed in the present study. The variation in Mooney viscosity against blend composition has some similarity to the variation in critical concentration against blend composition (Fig. 2). The conductivity of filled polymer composite arises from the conductivity of polymer itself as well as from the conductive filler incorporated in the matrix. At low levels of conductive filler loading, when a continuous conductive network is not formed, the conduction of the system depends mainly on the conductivity of the base polymer but, at higher concentrations at or above the percolation limit (when continuous conductive networks are already formed), the conductivity of the composite mainly depends on the conductivity of filler particles rather than on their ability to form a continuous conductive network through aggregation. Thus, the conductivity of a black filled system depends on structure, particle size, surface area and also the porosity of carbon black [7, 8] at or above percolation limit.

### 3.2. The effect of temperature on conductivity

The effect of temperature on resistivity of conductive rubber is quite complex. Fig. 3 shows the variation in the logarithm of the resistivity with temperature. The resistivity progressively decreases with increase in temperature up to the highest temperature used in this work (i.e., 120 °C). The magnitude of the change in resistivity is the highest for a pure EPDM-based composite. This magnitude is the least for a black filled NBR system. The change in resistivity for any system (either blend or pure polymer) also depends on the conductive filler loading. When the conductive filler loading increases, the change in resistivity against temperature decreases as shown in Fig. 3. This is found to be true for all blends and pure components. The effect of a heating-cooling cycle on the resistivities of different blends is shown in Fig. 4. It is found

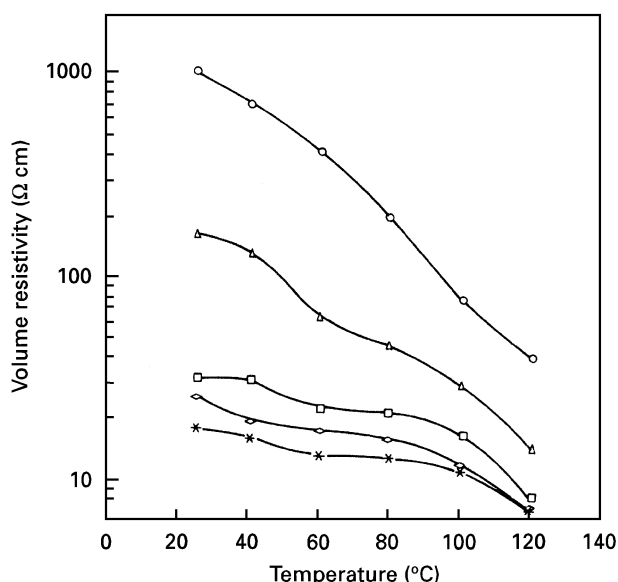


Figure 3 The variation in volume resistivity with temperature. (○), NE-0.60; (Δ) NE-25.60; (□) NE-50.60; (◇), NE-75.60; (\*), NE-100.60.

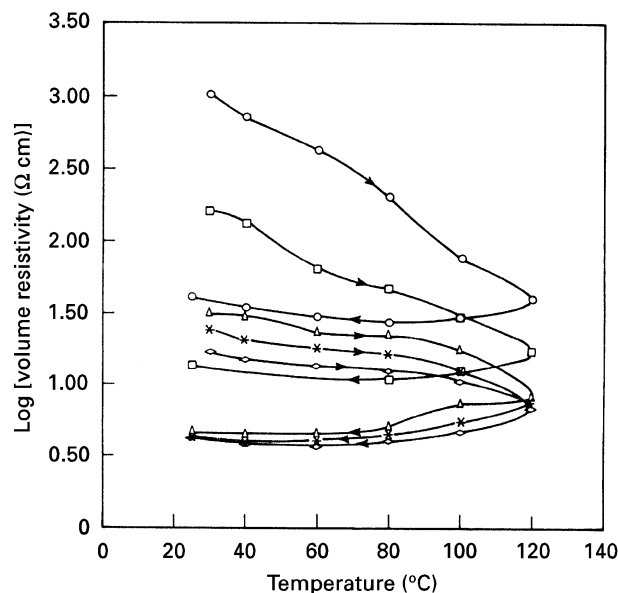


Figure 4 The effect of heating-cooling cycles on the resistivity of conductive rubber from different blends. (○), NE-0.60; (□), NE-25.60; (Δ), NE-50.60; (\*), NE-75.60 (◇), NE-100.60.

that the change in resistivity against temperature during the heating and cooling parts of cycle does not follow the same path. In fact, the change in resistivity during the cooling part of the cycle is marginal. Thus a difference between the initial resistivity,  $R_i$ , and the final resistivity,  $R_f$ , before and after the heating-cooling cycle is observed for all black filled systems. This resistivity difference is dependent on the blend composition as shown in Fig. 5. It is found that it is the highest for pure EPDM and decreases with increase in NBR concentration up to 50 wt%, after which the change in resistivity difference is marginal with blend composition. This resistivity difference is also dependent on the conductive filler concentration; higher

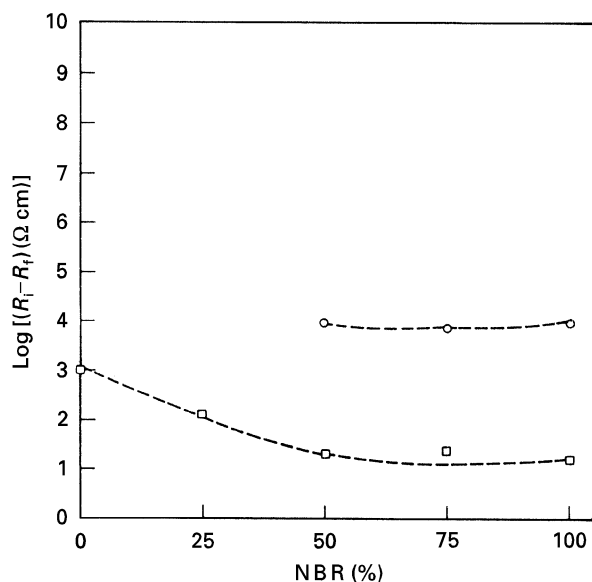


Figure 5 The difference between the initial resistivity,  $R_i$ , and the final resistivity,  $R_f$ , during the heating-cooling cycle for different blend compositions at fixed filler loading. (○), 30 phr black; (□), 60 phr black.

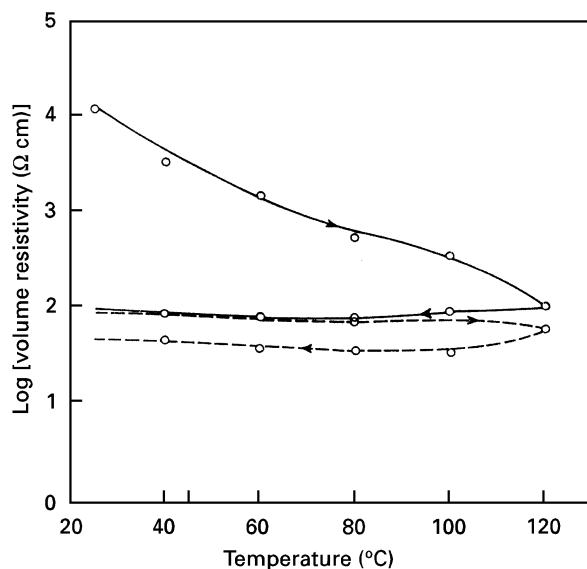


Figure 7 The variation in resistivity against temperature for repeated heating-cooling cycles for pure NBR containing 30 phr black. (—), first heating-cooling cycle; (---), second heating-cooling cycle.

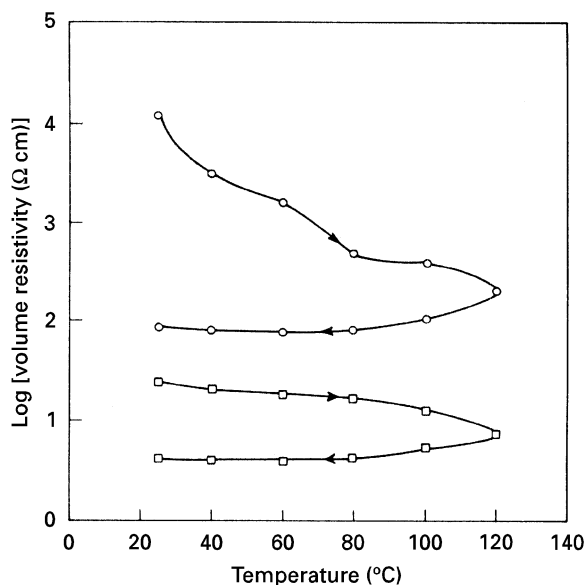


Figure 6 The effect of the heating-cooling cycle on conductivity for pure NBR composite containing different amounts of conductive filler. (○), NE-100.30; (□), NE-100.60.

differences are observed at lower filler loadings (however, in this work all the measurements were performed on samples having loading levels beyond the critical concentration) (Fig. 6). The electrical hysteresis, i.e., the difference between the areas of the resistivity-temperature curve for the heating and the cooling processes, also depends upon the blend composition. A higher hysteresis is observed for pure EPDM black composite and hysteresis decreases with increasing NBR content. The hysteresis also decreases with increasing filler loading. However, the variation in hysteresis for repeated heating-cooling cycles is only marginal (Figs 7 and 8). A large drop in resistivity (i.e., gain in conductivity) is observed for heating part of

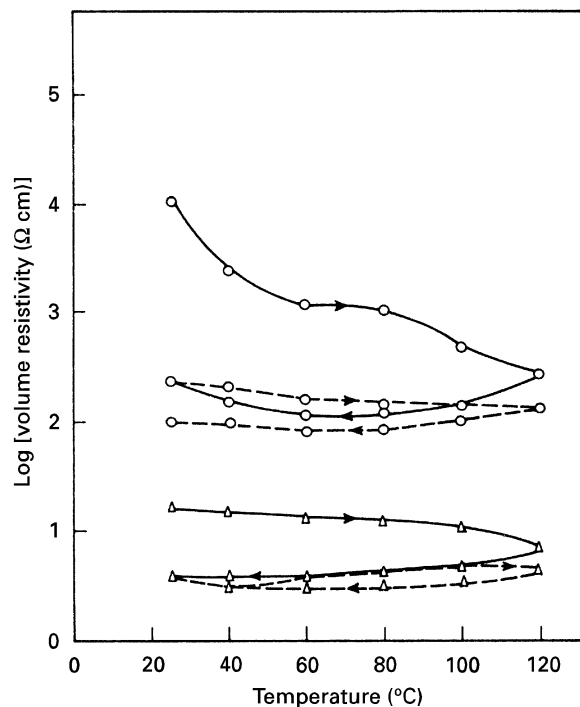


Figure 8 The variation in resistivity against temperature for repeated heating-cooling cycles for blend composition 50-50 EPDM-NBR containing 30 phr (○) and 60 phr black (△). (—) first heating-cooling cycle; (---), second heating-cooling cycle.

the first cycle followed by marginal gain in resistivity during the cooling part of the first cycle. However, the drop as well as the gain in resistivity during the second heating-cooling cycle are again both very small. This was found to be true for all blends and independent of the conductive filler loading. This suggests that during the first heating-cooling cycle the system has attained a somewhat stabilized electrical network, which

remains unaffected during further heating-cooling cycles. This behaviour contradicts the behaviour given in the literature [8, 10]. The positive temperature coefficient of resistivity (PCT effect) was observed in systems where conductivity is mainly due to physical contacts of carbon black particle in the matrix, whus forming a continuous network in an insulating polymer matrix. During heating, the differential expansion of polymer and conductive black causes breakdown of these conductive networks, leading to a decrease in conductivity (or increase in resistivity) with increase in temperature. It is noteworthy that negative temperature coefficients of resistivity (NCT effect) have also been reported in the literature [11, 12]. Because of heating, the electron emission process between two separated carbon black (when the distance of separation is small but not equivalent to physical contact) aggregates increases, leading to an increase in conductivity. Acetylene black filled systems generally exhibit NCT effects [12]. It has been argued that, during heating, there is some rearrangement of carbon black particles (floculation), leading to the formation of further continuous aggregates of black particles which enhances conduction. However, during cooling, these aggregates (which are already formed) are left relatively undisturbed; consequently, during cooling, the change in resistivity with temperature is only marginal. Thus, the differential thermal expansion and contraction process for a polymer compared with that of a filler also has a marginal effect on the conductivity of a filled system.

It has been shown that ageing has a positive effect on conductivity [13], suggesting that the promotive effect of oxidation on conductivity may be due to the creation of clouds of free electrons surrounding carboxylic products formed during ageing. It was found that the present system exhibits extensive ageing during heating, as indicated by the hardness which is increased appreciably as shown in Table III during the heating-cooling cycles.

Both EPDM and NBR vulcanizates exhibit appreciable increase in hardness when subjected to ageing [14]. The plots of the logarithm of conductivity against the reciprocal of temperature measured on the absolute scale (K) for various blends are found to be fairly linear (Fig. 9). The activation energy of conduc-

TABLE III Change in hardness in heating-cooling cycles (Shore A)

Sample	Black loading (phr)	Initial hardness	Hardness after heating-cooling cycle
NE-0	30	48	60
NE-0	60	63	68
NE-25	30	53	65
NE-25	60	65	78
NE-50	30	54	73
NE-50	60	69	93
NE-75	30	56	77
NE-75	60	68	83
NE-100	30	57	78
NE-100	60	68	87

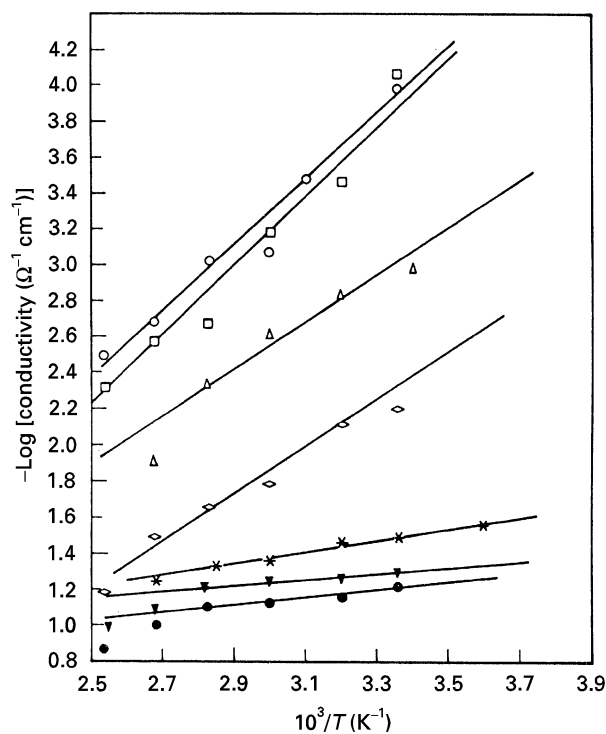


Figure 9 The plot of the logarithm of conductivity against the reciprocal of temperature. (○), NE-50.30; (□), NE-100.30; (△), NE-0.60; (◇), NE-25.60; (●), NE-50.60; (\*), NE-75.60; (▼), NE-100.60.

TABLE IV Activation energy

Black loading (phr)	Activation energy (eV mol <sup>-1</sup> )				
	NE-0	NE-25	NE-50	NE-75	NE-100
30	—	—	0.3675	0.2942	0.2871
60	0.2682	0.2046	0.0463	0.0649	0.0427

tion for various blends at two different filler loadings (30 and 60 phr) are presented in Table IV. It is clear that the activation energy decreases with increase in NBR concentration. As the polymer matrix becomes increasingly more polar and its viscosity decreases, the process of conduction is easier. As expected, with the increase in filler loading from 30 to 60 phr, the activation energy drops. The values of activation energy calculated are in good agreement with similar values reported in the literature [15].

### 3.3. Mechanism of conduction

Three main theories generally account for the underlying mechanism of electrical conduction through composites having a random distribution of conductive fillers [16].

(a) The conductive filler forms a few continuous chains (conductive networks) in the rubber matrix. Through this continuous network, charged species (electrons) move from one end to the other under an applied electrical field. This movement of electrons causes the phenomenon of electrical conduction. This

is the basis of the well-known conduction path theory. Thus, the formation of a conducting network through physical contacts of conductive particles or their aggregates is essential and therefore the formation of a conductive network is more probable above a critical concentration, i.e., percolation limit [17].

(b) In the electron tunnelling theory, the electrical conduction is believed to take place not only by interparticle contact but also by electrons being able to jump (hop) across a gap or tunnel through energy barriers between conducting elements in the polymer matrix. There is a threshold value for these gaps (a few nanometres) which is equivalent to interparticle contact. The basic difference between this theory and conduction path theory lies in the fact that the percolation limit is more probable at lower concentrations of conductive filler than that in conductive path theory [18].

(c) According to electric field radiation theory it is assumed that an emission current is caused to flow by the high electric field being generated between conducting elements separated by a gap of a few nanometres [19]. The basic difference between this theory and the two other theories is that, when the conduction path theory and tunnelling effect theory describe the conduction as ohmic in nature, the electron field radiation theory points to non-ohmic conduction behaviour for the system. Applicability of electric field radiation theory is believed to be valid at concentrations less than the critical limit [20]. However, for the present systems, non-ohmic behaviour is observed at higher temperatures for highly filled composites. So applicability of electric field radiation theory is found to be true for high filler loadings at higher temperatures. Reference is made to this later. However, the actual conduction mechanism seems to be quite complex in nature. The net result may be due to a combined effect of different mechanisms.

In fact, temperature dependence of conduction also explains the validity of different phenomena for various systems. Generally, the PCT effect of resistivity is observed for a system which contains filler concentrations less than or around the percolation limit. The variation in differential thermal expansion of polymer matrix and conductive filler leads to destruction of the conductive network; according to the conduction path and tunnelling effect theory there is a reduction in conductivity, i.e., increase in resistivity with rise in temperature. At higher filler loadings, well beyond the percolation limit the temperature effect is marginal mainly because there is an adequate number of conductive networks already formed in the system; thermal expansion of the polymer is expected to destroy only a few of them. Even at very high filler loadings, as a result of an increase in temperature and molecular mobility of the matrix, there is destruction of some conductive networks as well as the formation of some new networks. This results in only a marginal change in the conductivity with temperature [15]. However, according to electron field radiation theory, the NCT effect in resistivity or (PCT effect in conductivity) is more probable at higher temperatures as the extent of

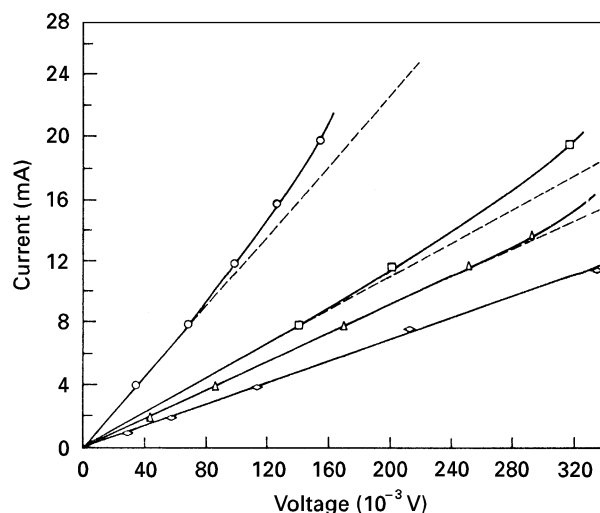


Figure 10 Current–voltage plots for different blends at various temperatures. ( $\diamond$ ), 30 °C; ( $\triangle$ ), 60 °C ( $\square$ ), 100 °C; ( $\circ$ ), 120 °C.

electron radiation process is enhanced owing to thermal activation.

For the present system, at a filler loading equal to or higher than the percolation limit the NCT effect in resistivity (i.e., PCT effect in conductivity) is observed. This indicates an appreciable contribution from the electric field radiation process to the total conduction of the system. Furthermore, the effect of temperature is more pronounced at lower filler loadings than at higher filler loadings, which is expected since there is already a large number of conductive networks active in the electron radiation process. The rise in temperature thermally activates the process further. Moreover, at higher filler loadings (around 60 phr) the simultaneous formation and destruction of conductive networks compensate each other; so the temperature effect is marginal. However, at lower filler loadings (around 30 phr), the increased contribution of electron emission leads to higher conductivity. Moreover, a higher temperature leads to the formation of some new conductive networks which were not contributing previously to the conduction of the system.

This observation is supported by the fact that at a higher temperature the extent of electron radiation is more pronounced than at lower temperatures, because the system becomes more non-ohmic in nature as the temperature rises (Fig. 10). Therefore, it can be concluded that at room temperature or slightly above room temperature (up to 60 °C) the contribution from conduction path or tunnelling effect theory is more pronounced. Furthermore, at higher temperatures (above 60 °C) the increased contribution of electron emission is realized, and the system becomes more and more non-ohmic in nature (Fig. 10).

### 3.4. Mechanical properties

The variations in mechanical properties such as the tensile strength and the elongation at breaking point against filler loading for different blend composition are presented in Figs 11 and 12, respectively. It is found that tensile strength of all blends increases with

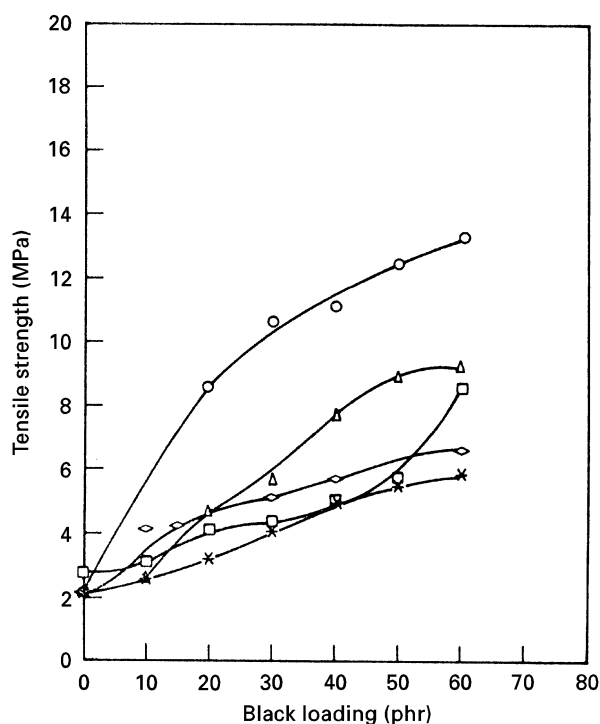


Figure 11 The variation in tensile strength against filler loading for various blends. (○), NE-0; (◇), NE-25; (□), NE-50; (\*), NE-75; (△), NE-100.

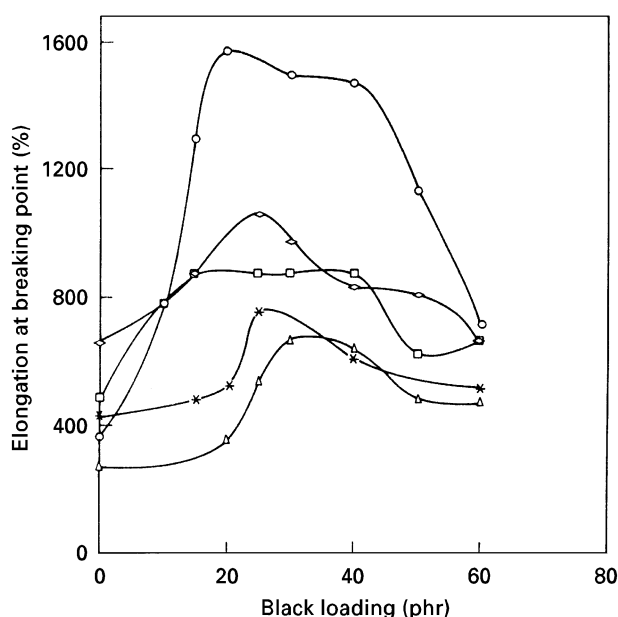


Figure 12 The variation in elongation at breaking point against filler loading for various blends. (○), NE-0; (◇), NE-25; (□), NE-50; (\*), NE-75; (△), NE-100.

filler loading. However, the degree of reinforcement is found to be at its highest for pure EPDM rubber followed by pure NBR. The blends showed relatively lower degree of reinforcement with acetylene black. Both EPDM rubber and NBR are considered as non-self-reinforcing rubbers and acetylene black is regarded as being a semireinforcing filler. Therefore, the degree of reinforcement will depend on the extent of polymer filler interaction and the degree of wetting of filler particles by the polymer matrix. Generally, non-

self-reinforcing rubbers are reinforced through incorporation of reinforcing and semireinforcing fillers. In this work, EPDM rubber and NBR matrices were reinforced with acetylene black. The degree of reinforcement usually increases with filler loading. EPDM rubber and NBR, because of their difference in polarities, are incompatible with each other and, therefore, the degree of reinforcement in each blend is relatively lower than the level of reinforcement that can be achieved in the pure components. The elongation at breaking point shows a maximum against filler loading for all systems. At very low filler loadings when the matrix is not sufficiently reinforced, it cannot sustain load and so failure occurs at lower elongations. However, with increase in filler loading, the matrix is progressively reinforced and a higher elongation at breaking point is observed. In fact, with increase in filler loading, the molecular mobility decreases owing to the formation of physical bonds between filler particles and polymer chains (which is the basis for the mechanism of reinforcement). Consequently, the elongation at breaking point drops with increase in filler loading. However, a higher elongation at breaking point is observed for EPDM and EPDM-rich blends, mainly because the EPDM matrix has greater chain mobility than that of the NBR matrix, since the  $T_g$  of EPDM is  $-80^\circ\text{C}$  whereas for NBR it is  $-40^\circ\text{C}$ . The hardnesses of all blends increase with filler loading. The increase in hardness is less pronounced in EPDM and EPDM-rich blends than in NBR and NBR-rich blends for reasons which were given earlier.

#### 4. Conclusions

1. Before percolation, the conductivity of black-rubber composite mainly depends on the conductivity of the matrix of polymers. The conductivity of the polymer matrix mainly depends on its degree of polarity.
2. Beyond the percolation limit the conductivity mainly depends on the ability of formation of a conductive network throughout the matrix. The polymer viscosity plays an important role in the formation of a conductive network. As such, the percolation limit depends on the blend composition.
3. The NCT effect in resistivity is observed for these systems. However, the temperature dependence of resistivity becomes marginal when the filler loading is increased well above the percolation limit. A resistivity difference is observed during the heating-cooling cycle. The contribution of the electron emission process to the total conductivity especially at elevated temperatures becomes significant. The activation energy of conduction depends on the blend composition, i.e. the polarity of the blend. The activation energy decreases with increasing filler loading.
4. The degree of reinforcement achieved through incorporation of carbon black is the highest for pure EPDM rubber followed by NBR. Blends have lower reinforcing potential than do the pure components. This may be due to the incompatibility of the two constituent polymers in the blend.

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