Electrical and Mechanical Properties of Conducting Carbon Black Filled Composites Based on Rubber and Rubber Blends

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ABSTRACT: The electrical and mechanical properties of new conductive rubber composites based on ethylene–propylene–diene rubber, acrylonitrile butadiene rubber (NBR), and their 50/50 (weight ratio) blend filled with conductive black were investigated. The threshold concentrations for achieving high conductivity are explained on the basis of the viscosity of the rubber. The electrical conductivity increases with the increase in temperature whereas the activation energy of conduction decreases with an increase in filler loading and NBR concentration in the composites. The electrical hysteresis and electrical set are observed during the heating–cooling cycle, which is mainly due to some kind of irreversible change occurring in the conductive networks during heating. The mechanisms of conduction in these systems are discussed in the light of different theories. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 887–895, 1999

Key words: composite materials; rubber blend; negative coefficient of temperature effect; electrical hysteresis; polymer–filler interaction

INTRODUCTION

The unique versatility of rubber has never before been manifested so acutely as in the development of conducting rubber, a class of materials that is traditionally well known and widely used as insulators. Commodity, as well as specialty, rubbers are insulators because the atoms in the rubber chain are covalently bonded. Metals are conducting due to the presence of metallic bonds in which valence electrons are completely delocalized and form an electron cloud around the metal atoms. In the covalent bonded molecules of saturated carbon compounds there is no scope of delocalization of the valence electrons; consequently, the electron carrier path is not available. One of the important methods to form a carrier path in an insulating rubber matrix is the incorporation of conductive additives like carbon black, carbon fiber, metal, or metal oxide.[1–3] Among the large number of electrically conductive additives, carbon black is widely used because it is easily processed and also produces a reinforcing effect on the rubber raw materials. Recently these conductive composite materials have been very popular due to their low attractive costs, high flexibility, and weather and chemical resistant properties. These are widely used, especially for rubber contact switches, electromagnetic interference (EMI) shielding, floor heating, static electric charge dissipation, and various other electronic and electrical applications.[4–8]

The elastomer blends consisting of incompatible elastomer pairs are very useful in achieving a high degree of conductivity because of their well-defined interface.[9] Accumulation of the black at the interface has the effect of increasing the number of contact points or decreasing the gap width,

Table I   Physical Characteristics of Vulcan XC-72 Black

Nitrogen surface area (m^2/g)	180
DBP[a] absorption number (mL/100 g)	178
Particle diameter (nm)	29
Electron microscopic surface area (m^2/g)	77
Surface area (CTAB[b]) (m^2/g)	86
Pore area (m^2/g)	94

Adapted from Asada.[23]
[a] Dibytyl phthalate.
[b] Cetyl trimethyl ammonium bromide.

and higher loading or poorer dispersion is also obtained. In our earlier communication we prepared conductive composites based on ethylene–propylene–diene monomer rubber (EPDM), acrylonitrile butadiene rubber (NBR), and their blends. The electrical and mechanical properties of these composites were measured in different conditions.[10,11] These composites are also very useful in imparting efficient EMI shielding.[12] The present investigation is concerned with detailed studies on the electrical and mechanical properties of carbon black (vulcan XC-72) filled composites based on NBR, EPDM, and a 50/50 blend of NBR and EPDM. The effect of filler loading on the electrical and mechanical properties has also been studied in different conditions in an attempt to understand the mechanism of conduction in such systems. Some mechanical properties of these blends were also studied to evaluate their potential for use in industrial applications.

EXPERIMENTAL

Materials

The EPDM was supplied by the Japan Synthetic Rubber Co. Ltd. (JSR EP96): Mooney viscosities

(ML_{1+4}) at 100°C = 61 and ML_{1+8} at 120°C = 53; diene monomer ENB (5%); high ethylene content.

The ANBR was supplied by the Japan Synthetic Rubber Co. Ltd.: 32% acrylonitrile content; ML_{1+4} (100°C) = 51.

The carbon black (vulcan XC72) was supplied by Cabot Carbon Black. The physical characteristics of the vulcan XC black are given in Table I.

1,2-Dihydro 2,2,4-trimethyl quinoline (TQ, polymerized) was supplied by ICI (India) Ltd. It acts as an antioxidant.

Dicumyl peroxide (DCP) was used as the curing agent (MP = 80°C) and was supplied by Aldrich.

The formulations used in this work are shown in Table II. Mixing was accomplished on a Brabender plasticorder (model PLE-330), and the mixture was sheeted out on a two roll mixing mill using the same conditions for each mix. The mixes were cured at 170°C in an electrically heated press to optimum cure times that 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).

Testing

The volume resistivity for composites with high resistivity ($\geq 10^6$ ohm cm) was measured using a Hewlett–Packard high resistance meter (model 4329A) coupled with a resistivity cell (model 160084). In the case of composites having low resistivity ($\leq 10^6$ ohm cm), volume resistivities were measured by a four probe technique using the Van der Pauw method as described in the literature.[13] For measuring the volume resistivity at higher temperature (above room temperature) the entire electrode system was placed in an oven where the temperature could be monitored and kept constant. The volume resistivity data re-

Table II   Formulation of Mixes

Ingredients	N E0	N E50	N E100
EPDM	100	50	0
ANBR	0	50	100
TQ	1.5	1.5	1.5
Vulcan-XC	0, 10, 20, . . . , 50, 60	0, 10, 20, . . . , 50, 60	0, 10, 20, . . . , 50, 60
DCP	1.5	1.5	1.5

All the ingredients are in weight per hundred weight of rubber (phr).

ported here were the average of three samples and were reproducible within 5%. The stress–strain properties of different black filled vulcanizates were determined using a Zwick Universal Testing Machine (model-1445) according to ASTM D412, using dumbbell shaped specimens. Three samples were tested, and the variations were within 5%. The hardnesses of the composites were measured using a Durometer, Shore A (ASTM D2240-86). A Mooney viscometer (Negretti Automation Mooney shearing disk viscometer, model MK-111) was used to determine the Mooney viscosity (ML_{1+4}) at 100°C for all the systems per ASTM designation D 1646-1963 and only for the EPDM Mooney viscosity (ML_{1+8}) at 120°C. The hardness and Mooney viscosity values were reproducible within 3–5%.

The volume fraction of the rubber (V_r) in the vulcanizate was determined using the equilibrium swelling method in chloroform according to the following equation[14]:

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}} \quad (1)$$

where T is the weight of the test specimen, F is the weight fraction of the insoluble components in the specimen, D is the deswollen weight of the test specimen, A_0 is the weight of the absorbed solvent (corrected for swelling increment), ρ_r is the density of rubber, and ρ_s is the density of the solvent. The results reported here were the average of three measurements, and the values were reproducible within 2%.

In this study the composites are identified by an alphanumeric 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 loadings of conductive black. For example, NE50.60 represents a 50/50 NBR/EPDM blend containing 60 phr of conductive black.

RESULTS AND DISCUSSION

Effect of Carbon Black Loading on Conductivity

The resistivity of a compound strongly depends upon the carbon black loading. Figure 1 shows the effect of filler loading on the volume resistivity of the conductive carbon black (vulcan XC-72) filled composites based on three insulative rubber systems: NBR, EPDM; and their 50/50 (weight ratio)

Figure 1 Volume resistivity against filler loading for different EPDM–NBR blends: (○) N E0, (△) N E50, and (□) N E100.

blend. It was observed that when the quantity of filler was low, the resistivity of the composites was only slightly different from that of the base polymer. However, beyond a certain critical filler loading a significant drop in resistivity was observed. In this region a relatively small increase in filler loading produced a large increase in conductivity (decrease in resistivity). This region of rapid resistivity decrease is called the percolation region. Further increasing the filler loading beyond the percolation region causes a marginal change in the conductivity of the composites. At a low level of carbon black the electrical properties were dominated by the polymer phase between the aggregates. The distance between the filler particles was very high, and the electrical conductive path was discontinuous. As the carbon black loading was increased the average distance between the aggregates decreased and discrete chain structures formed in the small gaps. If the fillers particles were dispersed to the level of the individual aggregate and the aggregates were uniformly spaced in the compound, then there would be no change in resistivity until the com-

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

posite was so highly loaded that the aggregates would be in contact with one another. Then a small change in loading would give a sharp decrease in resistivity. At that time it forms a continuous conductive chain and shows stable electrical conductivity. The gradual decrease in resistivity with the increase in loading is a result of the random distribution of the aggregates in the compound.[15,16] The conduction in a composite of an insulator filled with conductive particles is explained by percolation theory. The conduction through the bulk of the compound is controlled by conduction over a number of paths of a randomly formed chain of particles. As the number of particles increases the number of continuous chains or conductive paths through the compound increases. The local effect is largest where the first chains have formed. The total resistance for any chain consists of the sum of individual resistances at each point of contact. If the resistance at each point of contact remains constant, the resistivity of the composites at volume loading ϕ follows the form

$$\rho = \rho_0(\phi - \phi_c)^{-t} \qquad (2)$$

where ϕ_c is the volume fraction of filler at the percolation point, ρ_0 is a scale factor, and t is a geometric factor. The value t commonly is 1.6–2. The percolation model usually describes compound performance well into the percolation region.[17] Here it is also interesting to note that the blend N E50 shows a lower resistivity than the pristine rubbers at high concentrations of filler.

This is due to the accumulation of black at the interface of two incompatible rubbers that reduces the gap width by increasing the number of contact points.

Also observe from Figure 1 that the percolation region or critical concentration of conduction is higher in the EPDM that is around 40 phr of vulcan-XC whereas it is lower for NBR and the blend system (around 32 phr). This attainment of a different critical concentration can be explained on the basis of the viscosity of the rubber matrix. The higher the viscosity of the rubber matrix, the higher is the critical concentration. Rubbers having higher Mooney viscosity (ML_{1+4}) experienced higher sheering force during mixing in the Brabender plasticorder. Due to higher sheering force the black agglomerates (structure) that help in the formation of continuous conductive networks degrades; consequently, the formation of conductive networks throughout the matrix is delayed and occurs at a higher concentration. Thus, critical concentration follows same trend as the Mooney viscosity of the rubber matrix that is shown in Figure 2.

Effect of Temperature on Conductivity

The effect of temperature on conductive rubber is quite complex. Figure 3 shows the plots of variation of resistivity with temperature based on the three conductive system of NBR, EPDM, and a blend containing 60 phr black. This figure shows that resistivity decreases with a rise of temperature up to the highest measurement temperature of 120°C. This negative coefficient of temperature effect (NCT) is also observed in the acetylene

Figure 3 The variation of volume resistivity with temperature for (○) N E0.60, (□) N E100.60, and (△) N E50.60.

Figure 4 The variation of volume resistivity with temperature for (○) N E50.40, (△) N E50.50, and (□) N E50.60.

Table III   Change of Hardness in Heating–Cooling Cycles (Shore A)

Sample No.	Heating–Cooling Cycle	
	Before	After
N E0.30	50	61
N E0.40	51	62
N E0.50	56	65
N E0.60	61	69
N E50.0	45	65
N E50.40	50	68
N E50.50	60	70
N E50.60	61	78
N E100.30	50	60
N E100.40	58	62
N E100.50	64	68
N E100.60	61	68

black filled composite systems based on NBR, EPDM, and their blends.[10] The magnitude of change, as well as the rate of change, in resistivity is highest for the pure EPDM based system and least for the NBR based composite system. The rate of change of resistivity with temperature also depends on the amount of filler loading. The rate decreases with the gradual increase of filler loadings against temperature for composites of 50/50 NBR/EPDM blend as shown in Figure 4. This is true for all the composites based on the pure component.

The decrease of resistivity (increase of conductivity) with temperature is attributed mainly to three reasons: the first is thermal emission of electrons through the gap between neighboring black particles when the particles are separated by a distance but not equivalent to physical contact. This leads to an increase in conductivity with rise of temperature. The second reason is that the rearrangement of small carbon black particles takes place during heating, leading to formation of more conductive networks. This enhances the process of conduction. The third is during heating some oxidative crosslinking at the surface takes place,[18] which promotes conductivity. This is due to the incorporation of polar carbonyl groups. This could be due to the free electron pairs in collaboration with the flowing current and polar groups present at the carbon black surface. This system undergoes extensive aging due to the heating and cooling cycle that leads to the increased hardness shown in Table III. The plots of the logarithm of conductivity against the

reciprocal of temperature measured on the absolute scale (K^{-1}) for various composites were found to be fairly linear (Figure 5). The activation energy of conduction for various blends at two different filler loadings (40 and 60 phr) are presented in Table IV. It is clear that the activation energy decreases with increasing NBR concentration. As expected, with the increase in filler loading from 40 to 60 phr the activation energy drops and the process of conduction become easier.

However, due to the higher value of thermal expansion of rubber (220×10^{-6} K^{-1}) compared

Figure 5 The plot of the logarithm of conductivity against the reciprocal of temperature (K^{-1}) for (○) N E50.40, (□) N E0.40, (◇) N E100.40, (*) N E0.60, (◌) N E100.60, and (△) N E50.60.

Table IV   Activation Energy (eV)

Sample No.	Activation Energy
N E0.40	0.98
N E0.60	0.78
N E50.40	0.72
N E50.60	0.22
N E100.40	0.75
N E100.60	0.19

to that of carbon black $(1 \times 10^{-6} \text{ K}^{-1})$, it tends to destroy some continuous conductive paths, leading to an increase of electrical resistivity with an increase of temperature.[19,20] At that time a positive CT effect is observed. But in the present work this effect is marginal and cannot overcome the above three effects. The net result is an NCT effect.

The effect of the heating and cooling cycle on the resistivity of different blends containing 60 phr black are shown in Figure 6. We observed that the change in resistivity against temperature during the heating–cooling cycle does not traverse through the same path. This creates an electrical set (the difference in initial and final

Figure 7   The effect of heating–cooling cycle on conductivity for pure NBR composite containing different amounts of conductive filler: (○) N E100.40, (□) N E100.60, (—) heating, and (. . .) cooling.

Figure 6   The effect of heating–cooling cycle on resistivity of conductive rubber from different blends for (○) N E0.60, (□) N E100.60, and (△) N E50.60.

resistivities before and after the heating–cooling cycle) and the electrical hysteresis (i.e., the difference in the area of resistivity–temperature curve for the heating and cooling process) that are observed for all black filled systems. This electrical set in resistance and electrical hysteresis are dependent on the blend composition. The electrical set is highest for pure EPDM and lowest for pure NBR based composites. These are also dependent on conductive filler concentration. A higher electrical set and higher electrical hysteresis are observed at lower filler loadings (Fig. 7). (However, in this work all the measurements were performed on samples having a loading level beyond the critical concentration of conduction.) Furthermore, the effect of temperature is more pronounced at lower filler loading compared to that at higher filler loading, which is expected because there are 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 loading (around 60 phr) the simultaneous formation and destruction of conductive networks compensates each other, so the temperature effect is marginal. However, at lower filler loading (around 30 phr) the increased contribution of electron emission leads to higher conductivity. Moreover, a higher temperature leads to the formation of some new

Figure 8 Current–voltage plots for various temperatures for N E50.30.

conductive networks that were not previously contributing 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 temperature, because the system becomes more nonohmic in nature as the temperature rises (Fig. 8). Therefore, it can be concluded that at room temperature or slightly above room temperature (up to 60°C) the contribution from the conduction path or tunnel effect theory is more pronounced. Furthermore, at a higher temperature (>60°C) the increased contribution of electron emission is realized and the system becomes more and more nonohmic in nature.

The change of volume resistivity during repeated heating–cooling cycles is shown in Figure 9. The interval of time between each heating–cooling cycle is 12 h. It was observed that the electrical set, as well as electrical hysteresis, is much higher in the first heating–cooling cycle than that in the second cycle. From the second cycle onward the change in resistivity during the heating–cooling cycle becomes marginal. This is mainly due to the irreversible change of carbon black aggregation during heating, and this aggregation becomes stabilized and does not return to the initial state during cooling.

Mechanical Properties

The stress–strain plots of different composites are shown in Figures 10(a–c). On increasing the filler loading, the tensile strength of the composites increases. However, the degree of reinforcement is highest for vulcan-XC filled NBR composites followed by the blend and EPDM based composites. The degree of reinforcement depends on the extent of polymer–filler interaction. The extent of polymer–filler interaction is estimated from the swelling experiment using a plot of V_{r0}/V_{rf} versus the $C/(1 - C)$ plot according to the Kraus equation[21,22]:

$$\frac{V_{r0}}{V_{rf}} = 1 - \frac{mC}{(1 - C)} \tag{3}$$

where V_{rf} is the volume fraction of rubber in the filled vulcanizate, V_{r0} is the volume fraction of rubber in the gum vulcanizate, C is the volume fraction of filler in the vulcanizate, and m is the polymer–filler interaction parameter obtained from the slope of the V_{r0}/V_{rf} versus $C/(1 - C)$ plot. The slope should be positive for a reinforcing filler having good polymer–filler interaction and negative for nonreinforcing filler with very weak polymer–filler interaction. It is observed from Figure 11 that polymer–filler interaction for vulcan-XC filled NBR and the 50/50 blend is high because it shows a higher slope in the plots. The

Figure 9 The variation of resistivity against temperature for repeated heating–cooling cycle of N E50.50: (○) first heating–cooling cycle, (□) second heating–cooling cycle, (—) heating, and (. . .) cooling.

(a)

(b)

(c)

Figure 10 The plots of stress–strain properties of (a) NBR, (b) EPDM, and (c) 50/50 NBR/EPDM blend containing different amounts of filler.

slope is negative at the first stage for EPDM, then it become positive. This indicates that the polymer–filler interaction is lower, especially at a lower concentration of filler. The elongation at break for the carbon black filled composites increases with an increase in filler loading up to 40

phr and then decreases. This reduction is due to stiffening of the matrix by the black particles or filler. Actually, with the increase in filler loading the matrix is progressively reinforced and a higher elongation at break is observed. In fact, with a further increase in filler loading the mo-

Figure 11 Plots according to the Krous equation for pure rubbers and blends: ($\triangle$) N E0, ($\bigcirc$) N E50, and ($\square$) N E100.

lecular mobility decreases due to the formation of physical bonds between the filler particles and polymer chains that stiffen the matrix. This results in a drop in elongation at break with filler loading beyond 40 phr black. However, a higher elongation at break is observed for EPDM based composites followed by the blend and pure NBR based composites. This is mainly because of the EPDM matrix that has greater chain mobility than that of the NBR matrix.

CONCLUSIONS

1. Before percolation, the conductivity of the black–rubber composite mainly depends on the conductivity of the matrix of the 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 to form a conductive network throughout the matrix. Rubber viscosity plays an important role in the formation of the conductive network. As such, the percolation limit depends on the blend composition.
3. An NCT effect in resistivity is observed for these systems. However, the temperature dependence of resistivity becomes mar-

ginal when filler loading is increased well above the percolation limit. The electrical set 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). Activation energy decreases with filler loading.
4. The degree of reinforcement achieved through incorporation of carbon black is the highest for pure NBR followed by the blend and EPDM.

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