The Effect of Heating–Cooling Cycles on PTCC and NTCC Made of FEF/NBR Composites

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ABSTRACT: Electrically conductive acrylonitrile butadiene rubber compounds filled with different concentrations of fast extrusion furnace black were experimentally investigated. The percolation concentration of the investigated composites was found to be 65 phr. Samples below percolation concentration are PTCC and above percolation concentration are NTCC. Sample N70 that belongs to the percolation concentration exhibits NTCC and PTCC. The effect of heating–cooling cycles shows that samples with high concentration have small hysteresis compared with low concentrations. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2837–2842, 2007

Key words: FEF; cyclic heating; NBR

INTRODUCTION

There is a great economic interest in negative and positive temperature coefficient of conductivity (NTCC and PTCC) materials because of their technological applications as heater, temperature or current sensors, electromagnetic radiation shielding, and others.[1–3] Whenever such polymer composites are used as thermistor devices for electrical heater, they are subjected to repeated thermal cycles, and it becomes necessary to understand how electrical conductivity changes with loading filler and repeated thermal cycles. In this paper, an experimental study of the electric properties of fast extrusion furnace (FEF) carbon black loaded Nitrile butadiene rubber (NBR) composites is presented. The influence of the volume fraction of carbon black and of the temperature on the DC conductivity is analyzed. The effect of heating–cooling cycles on the electrical properties of FEF/NBR composites is also investigated.

EXPERIMENTAL

Acrylonitrile butadiene rubber (NBR) (density 0.98 g/cm^3 and acrylonitrile content 26%) was used as polymer matrix. FEF carbon black (38 nm particle size diameter; dibutyl phthalate absorption number 121 cm^3/100 g; 45 m^2/g surface area) was used as reinforcing filler. Other compounding ingredients were used and compounded according to the recipe listed in Table I.

For the compounding a home made two-roll mixing mill (length 0.3 m, radius 0.15 m, speed of slow roll 18 rev/min, and gear ratio 1.4) was used. The compounded rubbers were compression molded into cylinders of 1×10^{-4} m^2 area and 0.01 m in height. The vulcanization was conducted under a heating press (KARL KOLB, Germany) at a pressure of $P = 0.40$ MPa. The optimum conditions of temperature and time were $T = 150^{\circ}$C and $t = 30$ min. The vulcanized samples were shelf aged for 48 h before test. Brass electrodes were attached to the parallel faces of the samples during vulcanization. In electrical measurements a digital electrometer (616 Keithly, USA) was used. A regulated noninductive furnace cell connected to a temperature controller (Digi-Sense, IL 60,010, USA) was used to vary sample temperature from 30 to 180°C with constant rate of 2°C/min.

RESULTS AND DISCUSSION

Effect of carbon black concentration on electrical properties

Figure 1 shows the variation of the resistivity against carbon black volume fractions. Initially the resistivity decreases slowly with the increase of carbon black volume fraction. But at certain critical volume fraction, 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 the carbon loading becomes marginal. This

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TABLE I
Composition of the Investigated NBR Samples

	Ingredients (phr)[a]							
Sample	NBR	Stearic acid	Zinc oxide	FEF	DOP[b]	MBTS[c]	PBN[d]	Sulfur
N10	100	2	5	10	10	2	1	2.5
N20	100	2	5	20	10	2	1	2.5
N30	100	2	5	30	10	2	1	2.5
N40	100	2	5	40	10	2	1	2.5
N50	100	2	5	50	10	2	1	2.5
N60	100	2	5	60	10	2	1	2.5
N70	100	2	5	70	10	2	1	2.5
N80	100	2	5	80	10	2	1	2.5
N90	100	2	5	90	10	2	1	2.5
N100	100	2	5	100	10	2	1	2.5

[a] Part per hundred parts of rubber by weight.
[b] Dioctyle phthalate.
[c] MBTS is dibenzthiazyl disulphide.
[d] PBN is phenyl-β-naphthyl-amine, a possible carcinogenic compound.

critical concentration of conductive filler that converts the insulating polymer matrix to a conductive one is popularly known as the percolation concentration.

The model that is most often used to quantify the changes in the transition and conductive regions is the so-called statistical percolation model.[4] Proposed by Kirkpatrick[5] and Zallen,[6] this model predicts the electrical resistivity of an insulator–conductor binary mixture by assuming random positions of the filler particles. The result is a power-law variation of the resistivity ρ, above the percolation threshold:

$$\rho \propto \left(\frac{\phi - \phi_c}{1 - \phi_c}\right)^{-1} \quad (1)$$

where ϕ is the volume fraction of filler, ϕ_c the percolation threshold, and t is a universal exponent that is close to 2 for a 3D dispersion.[7] The two-parameter fit is represented in Figure 1 by the solid line and gives $V_c = 0.65$ and $t = 2.03$. The value of the exponent t is consistent with the model prediction.

Effect of temperature on electrical conductivity

Figure 2 shows the variation of electrical conductivity with temperature for NBR loaded different concentrations of FEF carbon black. Several features are observed; first, all samples below the percolation concentration (from N10 to N60) exhibits PTCC (i.e., positive temperature coefficient of conductivity), which means that the conductivity increases against temperature. Second, the samples above percolation concentration (N80, N90, and N100) exhibits NTCC (i.e., negative temperature coefficient of temperature), which means that the conductivity decreases against temperature. Third, sample N70, which belongs to the region of percolation concentration, exhibits NTCC up to temperature 393 K and after this temperature it exhibits PTCC.

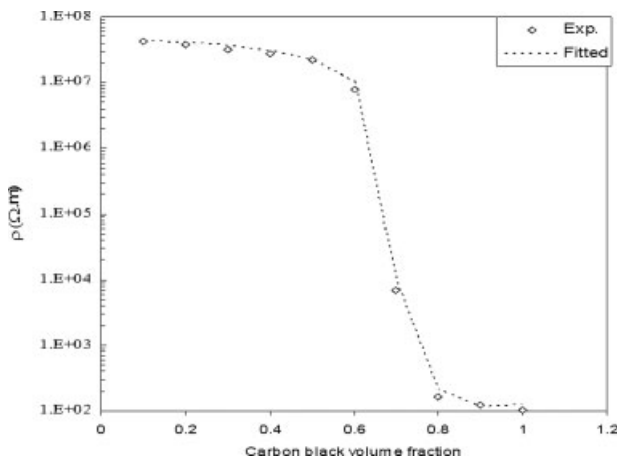

Figure 1 The relation between resistivity and carbon black volume fraction.

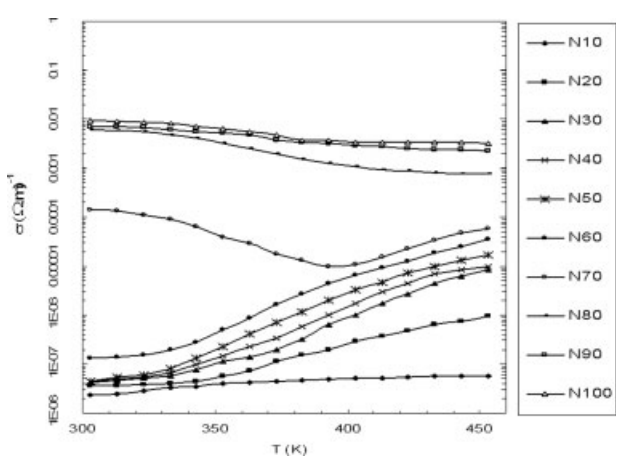

Figure 2 The relation between conductivity and temperature for NBR composites.

TABLE II
Values of NTCC and PTCC Calculated from Temperature–Conductivity Curve for NBR Composites

Sample	NTCC (10^{-3} °C^{-1})	PTCC (10^{-3} °C^{-1})
N10	–	0.01
N20	–	0.16
N30	–	1.30
N40	–	1.49
N50	–	1.77
N60	–	2.44
N70	8.21	3.01
N80	5.80	–
N90	4.49	–
N100	4.45	–

The NTCC and PTCC can be estimated according to the equation:

$$(\text{NTCC, PTCC}) = \pm\left(\frac{1}{\sigma}\right)\left(\frac{d\sigma}{dT}\right) \quad (2)$$

NTCC and PTCC values for all samples are recorded in Table II.

To compare the NTCC and PTCC intensity quantitatively, the NTCC intensity (I_{NTCC}) and the PTCC intensity (I_{PTCC}) is defined as[8]

$$I_{NTCC} = \log\left(\frac{\sigma}{\sigma_{RT}}\right) \quad (3)$$

where σ and σ_{RT} are the conductivities at higher and at room temperature, respectively. The NTCC and PTCC intensities were calculated and summarized in Table III.

It is found that PTCC increase with increasing carbon black concentrations, while NTCC decrease with increasing carbon black concentrations. This indicates that FEF carbon black increases the ordering and texturing of the rubber matrix. This means that NBR/FEF composites can be used as NTCC and PTCC thermistors. To explain these behaviors, one considers each behavior alone as follow.

TABLE III
The Calculated Values of I_{NTCC} and I_{PTCC} for NBR Composites

Sample	I_{NTCC}	I_{PTCC}
N10	–	0.39
N20	–	1.42
N30	–	2.28
N40	–	2.30
N50	–	2.42
N60	–	2.56
N70	1.15	2.77
N80	0.89	–
N90	0.50	–
N100	0.47	–

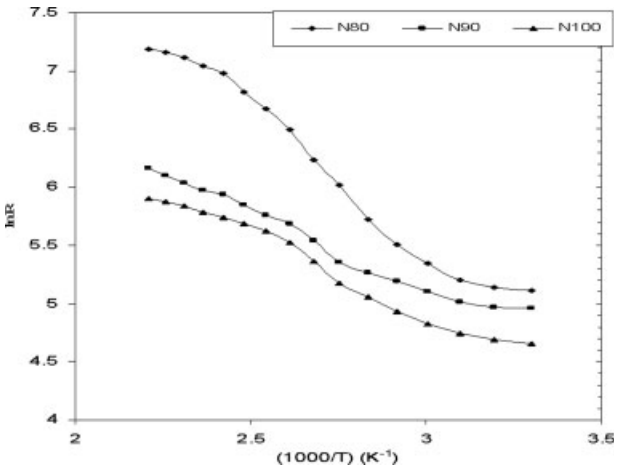

Figure 3 The relation between ln resistivity and temperature.

Figure 3 depicts the relation between (ln R) and ($1000/T$) for samples N80, N90, and N100. It is found that the slope of resistivity against temperature decreases by increasing the carbon black concentrations. In fact the resistivity- temperature plot has two slopes, one at the low temperature range 303–343 K for sample N80, 303–363 K for sample N90, and 303–373 K for sample N100, and the other slope at high temperature range 343–453 K for sample N80, 363–453 K for sample N90, and 373–453 K for sample N100. The mechanism of the increase of resistivity against temperature can be explained in terms of the hopping or tunneling mechanism of electrons present inside the matrix. According to this mechanism it is believed that, with increasing temperature, the average distance between carbon black particles increases because of the thermal expansion of host rubber. Therefore, the ease of tunneling or hopping of electrons decreases because of the increase of gap distance between carbon black particles. When carbon black concentrations increase, the aforementioned effect decreases due to the presence of a large number of carbon interparticle contacts that ensure a much higher probability of tunneling.

The temperature dependence of resistivity can be interpreted on the basis of the following equation[9]:

$$R = R_0 T \exp\left(\frac{E_h}{kT}\right) \quad (4)$$

where R is the electrical volume resistivity, E_h represents the activation energy for hopping, k is Boltzmann constant, R_0 represents the pre-exponential factor, and T is the absolute temperature (K). The activation energy values E_h for samples N80, N90, and N100 have been calculated for the two different ranges of temperature and presented in Table IV.

It is found that by increasing the carbon black concentration, the value of activation energy decreases.

TABLE IV
The Calculated Values of Hopping Activation Energy for NTCC Samples

Sample	E_h (eV)	
	Low temperature region	High temperature region
N80	1.02	2.14
N90	0.70	1.31
N100	0.62	1.25

It has also been found that the activation energy at the high temperature region is greater than that at low temperature region.

Figure 4 represents the relation between (log σ) and (1000/T) for samples N10 to N60. It is found that the slope of conductivity against temperature increases by increasing the carbon black concentrations. In fact the conductivity–temperature plot has two slopes, one at the low temperature range 303–343 K depending on the sample type, and the other slope at high temperature range 343–453 K. At low temperature range (303–343 K), there is a small change in conductivity against temperature due to the competition between two different mechanisms the thermal expansion of host rubber and tunneling or hopping mechanism. After temperature 303 K, a thermal activation takes place that causes a progressive increase in conductivity against temperature.

The temperature dependence of conductivity can be interpreted on the basis of Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (5)$$

where σ is the electrical conductivity, E_a represents the apparent activation energy, k is Boltzmann constant, and T is the absolute temperature (K). The activation energy values E_a for samples (N10 to N60) have been calculated for the two different ranges of temperature and presented in Table V.

TABLE V
The Calculated Values of Activation Energy for PTCC Samples

Sample	E_a (eV)	
	Low temperature region	High temperature region
N10	2.59	7.48
N20	1.94	6.85
N30	1.86	5.99
N40	1.43	4.69
N50	1.31	4.60
N60	0.51	2.76

It is found that by increasing the carbon black concentration, the value of activation energy decreases. It has also been found that the activation energy at the high temperature region is greater than that at low temperature region.

Figure 5 illustrates the temperature dependence of the electric conductivity of sample N70. It was found that at relatively low temperatures, the conductivity is slightly dependent on temperature. This may be attributed to the direct contact of conductive aggregates, which resist breakage as the rubber is thermally expanded. At moderate temperatures, the conductivity decreases with temperature. This may be due to the polymer particles expand with an increasing temperature, and the dimensions of the continuous conductive paths decrease, resulting in a decrease in conductivity of the composite. In particular, the thin conductive aggregate channels may even break up as the polymer expands. This decrease in the number of the conductive paths decreases the conductivity significantly. The rise in temperature produces a significant volume expansion, which increases the interparticle distance of conductive particles and reduces the

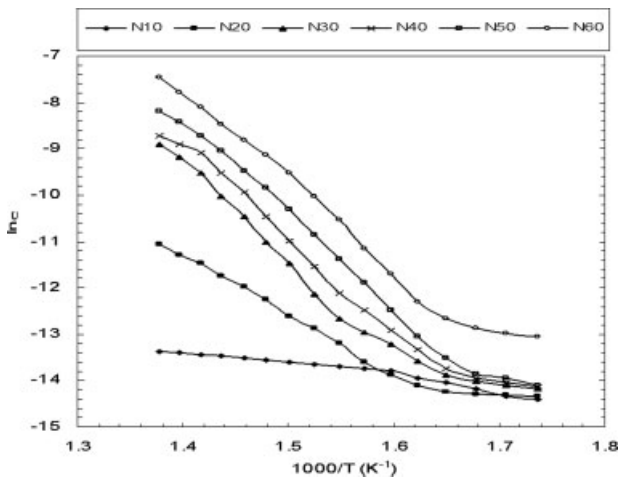

Figure 4 The relation between ln conductivity and temperature.

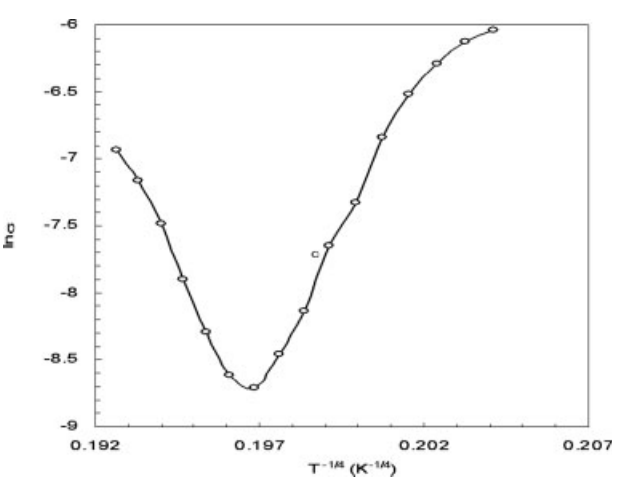

Figure 5 The relation between ln conductivity and temperature for sample N70.

TABLE VI
The Calculated Values of Interparticle Distance between Conductive Aggregates of Sample N70 at Different Temperatures up to T_c

T (K)	R (nm)
303	59
323	64
343	73
363	82
393	91

number of conductive paths, resulting in lower conductivity of the composites. At high temperatures, the conductivity of NTTC behavior changes abruptly to PTCC at a specific temperature, namely the critical temperature ($T_c = 393$ K). Two possible explanations may be evoked for this change. First, the conductive particles at T_c have a tendency to agglomerate or at T_c the viscosity of the composites is very high, and the diffusion of conductive particles increases and they align to form new conducting networks, resulting in an abrupt increase in conductivity. Second, at T_c the interparticle distance between conductive aggregates becomes large that simultaneously the intrinsic conduction due to the carriers of the FEF carbon black begins to appear (i.e., thermal activation conduction becomes the predominant mechanism). In confirmation of this assumption, the interparticle distance between conductive aggregates, at different temperatures, are determined by using Mott equation.[10]

$$\sigma = \sigma_0 \exp\left(-\left(\frac{T_0}{T}\right)^{1/4}\right) \tag{6}$$

The constants T_0 and σ_0 are given by

$$T_0 = \frac{\lambda\alpha^3}{k_B N(E_f)} \tag{7}$$

$$\sigma_0 = e^2 R^2(T)\gamma_0 N(E_f) \tag{8}$$

where hopping distance $R(T)$ is expressed by

$$R(T) = \left[\frac{9}{8\pi\alpha k_B T N(E_f)}\right]^{1/4} \tag{9}$$

where e is the electron charge, $N(E_f)$ is the state density at the Fermi level, k_B is the Boltzmann constant, α is the inverse rate of fall-off of the wave function (α^{-1} is the radius of the localized wave function), λ is a dimensionless constant having a value -18.1, and ν_0 is the jump rate prefactor.

Table VI represents the variation of interparticle distance between conductive aggregates against temperature. It is clear that the interparticle distance increases with an increase in temperature up to T_c.

Effect of heating–cooling cycles on electrical conductivity

To examine the effect of cyclic heating–cooling on stability and reproducibility of NBR composites, the conductivity versus temperature for all samples was measured during the heating and cooling cycle as shown in Figure 6. It was found that these samples do not follow the same path; consequently, a hysteresis cycle has been generated. It has also been found that the effect of temperature is more prominent for composites where black loading is somewhat less (say 70 phr) compared to a highly filled system (above 70 phr). This is mainly because, in a highly filled system, conducting elements are greater in number and the average distance between conducting elements is much less. Consequently, the process of flocculation, or electron emission, becomes less effective in the sense that, with the occurrence of these phenomena, a few more conducting networks will be effectively added to the large number of conducting elements already present in the system. So the increase in conductivity will be marginal. But in case of composites containing lower filler loading, the gap between conducting networks is higher and the number of conducting network is relatively lower. The contribution of these phenomena will be more significant in the sense that the effective number of conducting elements formed by these phenomena will be greater, and their contribution towards the total conduction will be significantly higher. As a result the effect of cooling is relatively less prominent. Therefore, the hysteresis for samples above N70 is less than that of samples below it.

CONCLUSIONS

Electrically conductive NBR compounds filled with different concentrations of FEF black were experimentally investigated. The percolation concentration of the

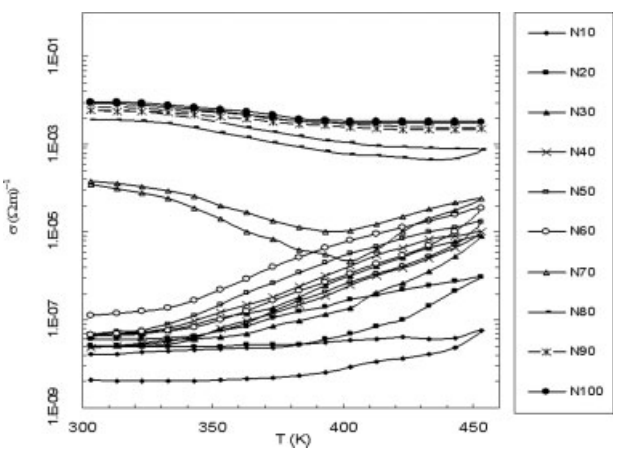

Figure 6 The heating–cooling cycle for all samples.

investigated composites was found to be 65 phr. Samples below percolation concentration are PTCC and above percolation concentration are NTCC. Sample N70 that belongs to the percolation concentration exhibits NTCC and PTCC. The effect of heating–cooling cycles shows that samples with high concentration have small hysteresis compared with low concentrations.

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