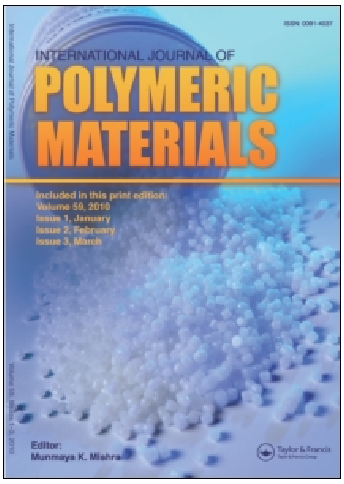

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DC ELECTRICAL PROPERTIES OF GRAPHYTIZED CARBON–BLACK FILLED RUBBERS

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The dc electrical behavior of graphytized carbon-blacks filled rubbers was investigated in the temperature range 25°C to 125°C. The volume fraction of the fillers varied from 30% to 60%. The observed conductivity increases with increasing filler contents. At a temperature higher than 25°C for 60% filler concentration the behavior is ohmic, where at lower concentration two well defined regions were observed to indicate two types of conduction mechanism. The activation energy for conduction process increases from 0.3 eV for 60% to attain about 0.98 eV for 30% fillers concentration. At 60% fillers concentration, fillers form a conductive network which is ohmic in nature.

Keywords: rubbers, graphytized carbon-blacks, activation energy, dc conductivity

1. INTRODUCTION

The electrical conductivity of polymers and composites has been studied extensively due to its wide applications in industry and technology. The interest in composite materials is due to their durability, thermal stability, favorable electrical and mechanical properties, and ability to withstand adverse environmental conditions [1,2]. The applications of such composites include wire and cable sheathing, shielding against electromagnetic interference and antistatic materials [3]. The electrical properties of such materials can be improved by changing the content and type of fillers [4–7].

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A number of mechanisms for electrical conduction in polymers and composites has been proposed, such as electronic [8], ionic [9], and protonic [10]. However, other mechanisms were adopted by many authors to explain the electrical conductivity in polymer films such as tunnelling, Richardson-Schottky, Poole-Frenkel emission [11], and space charge limited conduction [12].

Graphite/polymer composites present an attractive alternative to metal conductors in certain applications: In general, rubber is seldom used in a pure state as it is usually loaded with carbon blacks. Carbon-blacks exhibit fairly high conductivity, while loaded rubber is usually an insulator. The electrical conductivity in graphite/polymer composites can only be attained when a connected network of graphite fibers is present. Goul et al. [13] obtained a value of the specific resistivity for conductive rubber of the order of 10-100 Ω-cm.

The present paper is concerned with studying the dc electrical properties of graphytized carbon-black filled rubbers with different volume fractions of graphytized carbon blacks, namely 30%, 45%, and 60% in the temperature range 25°C to 125°C.

2. EXPERIMENTAL

2.1 Materials

Carbon–black filled rubbers were commercially manufactured in the form of 2–mm–thickness sheets by Degussa A. G. (Germany). Disc samples of 1 cm diameter were cut from these sheets using Cork borer. The samples were first cleaned with Spec-Pure Carbon Tetrachloride and then dried in an oven at 40°C. A Leybold commercial evaporator was used to evaporate silver electrodes.

2.2 Measurements

The dc electrical measurements were performed according to the four points probe method using a Keithly 236 source-measure unit (SMU). The temperature and voltage dependence leakage current were studied for graphytized carbon–black filled rubbers with various graphytized concentrations. Temperatures up to 125°C and voltage up to 50 volts were used. All measurements were done using computer-controlled data acquisition systems.

3. RESULTS AND DISCUSSION

Figure 1 shows the plot of dc conductivity as a function of temperature for three concentrations of graphytized carbon–black fillers. The

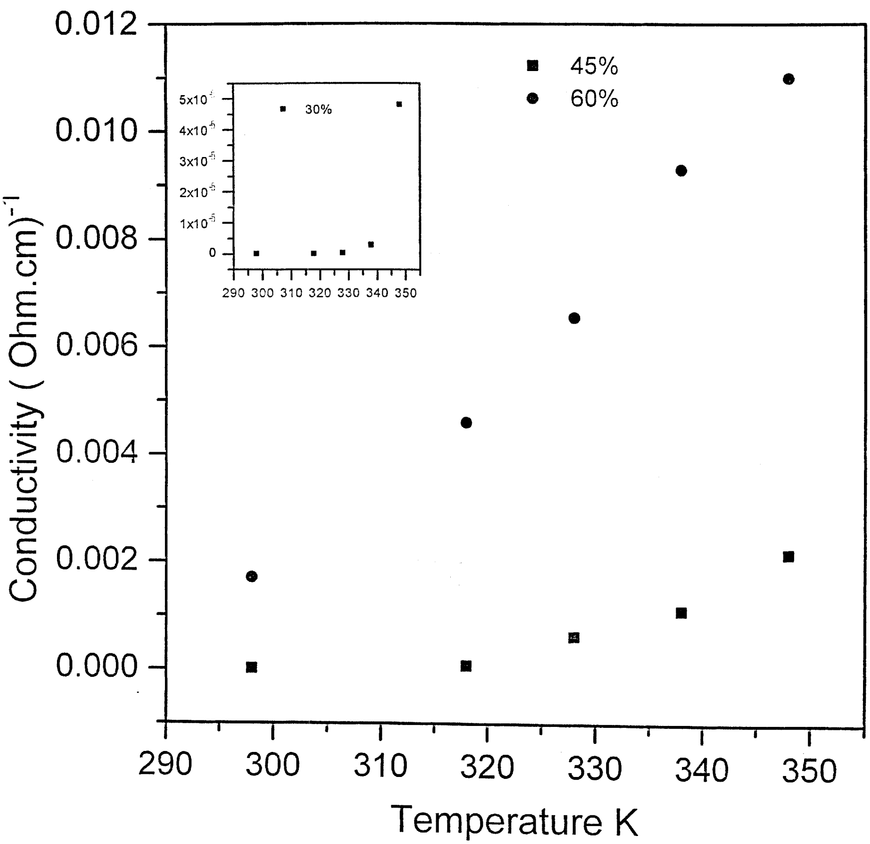


FIGURE 1 dc conductivity $(\Omega.cm)^{-1}$ vs. temperature for graphytized carbon–black filled rubbers.

conductivity increases with increasing temperature and concentration. The conductivity at room temperature (25°C) for 60% fillers concentration is in the order of 0.0127 $(\Omega.cm)^{-1}$ and increases to reach 0.05 $(\Omega.cm)^{-1}$ at 125°C. These values are much higher than those found for the other concentrations. For 45% fillers concentration, the conductivity at room temperature 1.59×10^{-6} $(\Omega.cm)^{-1}$ increases to 5.3×10^{-3} $(\Omega.cm)^{-1}$ and for 30% fillers concentration the conductivity of 5.5×10^{-9} at 25°C increases to 6.4×10^{-7} $(\Omega.cm)^{-1}$. The significant difference in electrical conductivity in the three filler concentrations may be due to the way that graphite is dispersed in the host material. Graphite particles are mainly present as agglomerates in rubber. As the concentration increases, the number of the agglomerates increases, too. The low conductivity values for fillers

TABLE 1 Activation energy for Graphytized Carbon−Black Filled Rubbers

Graphite percentage	Activation energy (eV)
30%	0.98
45%	0.86
60%	0.3

concentration, which is less than 45%, may be due to the fact that the agglomerates have no contact with each other and are distributed homogeneously through the host material and thus cannot cause the electron transfer. Therefore, the conduction mechanism in this case cannot be considered as electronic in nature. By increasing the fillers content, the agglomerates grow and become sensitive to the shearing forces produced by the host material, and so begin to break and gradually increase the number of fine particles. Above 45% fillers content, the particles start to form clusters of various sizes. The clusters of the individualized particles touch each other, forming a continuous network of electrically conductive particles where the electrons can transfer through the material.

Voet et al. [14] suggested a theory for low concentration fillers based on non-ohmic conduction in the system. It is believed that some kind of electron emission process controls the conductivity, probably tunnelling of electrons from one particle to the next when the gap between them is less than few nanometers. At high concentration, Scarisbrick [15] proposed a theory based on the formation of a conductive network and assumes that the inter-particle contacts are ohmic in nature. Where the conductivity of the composite can be obtained from the following relation

$$\delta_c/\delta_f = V_f^2(\exp V_f^{-2/3})C^2 \quad (1)$$

TABLE 2 Calculated and measured conductivity $(\sigma)\,(\Omega.\mathrm{cm})^{-1}$ for Graphytized Carbon−Black Filled Rubbers

Fillers Concentration %	Calculated σ Scarisbrick [15]	Calculated σ Blythe [16]	Measured σ
30	.0090	0.0063	5.5×10^{-9}
45	0.011	0.0095	1.6×10^{-6}
60	0.014	0.0128	.0127

where δ_c and δ_f are the conductivity of the composite and conducing fillers respectively, V_f is the volume fraction of the fillers and C^2 is the geometrical factor. Blythe [16] proposed a theory for randomly oriented fibers in contact with each other, the conductivity of the composite is given by the relation

$$\delta_c = (2/3\pi)\delta_f V_f \tag{2}$$

It is very difficult to determine the exact conductivity of the graphytized carbon blacks. As reported in the literature, the conductivity of graphytized rubbers varies from 1 to 10^{-2} $(\mathrm{Ohm.cm})^{-1}$ and C^2 varies from 1 to 10^{-3}. Assuming $C^2 = 1$ and $\delta_f = 0.1$ $(\mathrm{ohm.cm})^{-1}$, a comparison of the conductivity obtained from equations (1) and 2 is given

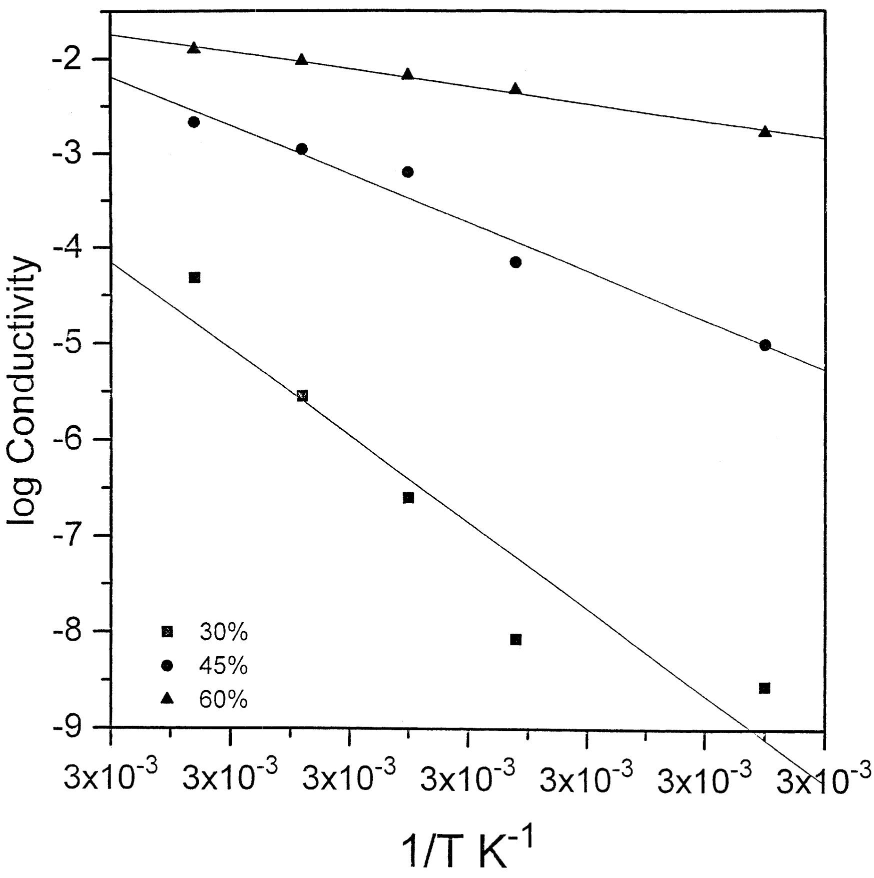


FIGURE 2 log dc conductivity vs. 1/temperature for graphytized carbon–black filled rubbers.

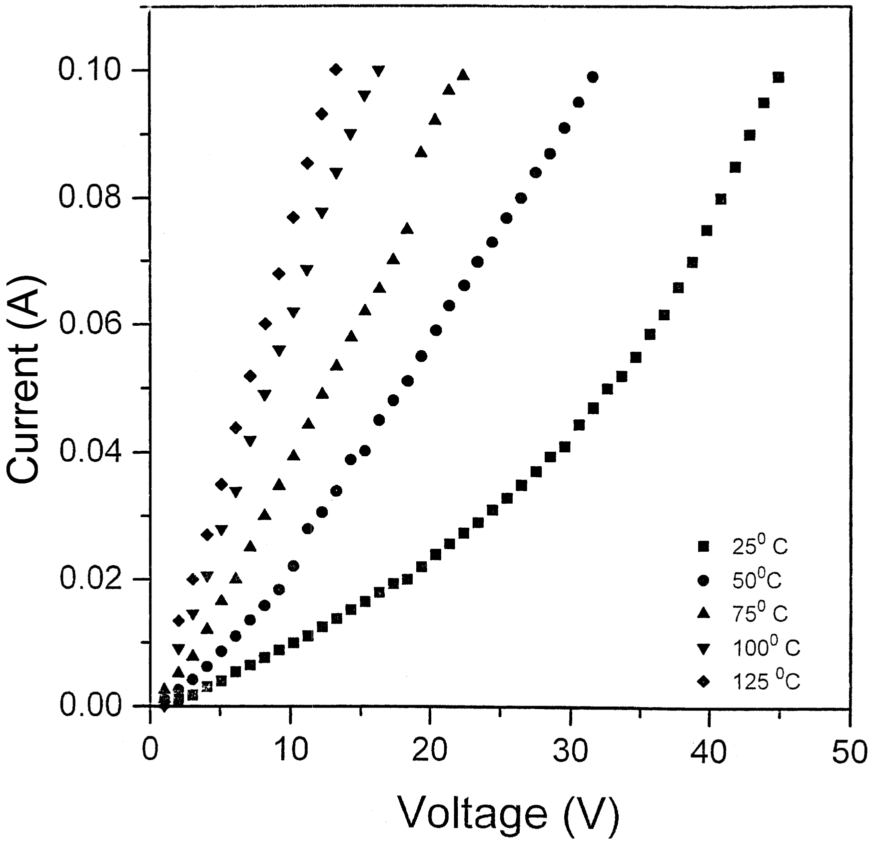
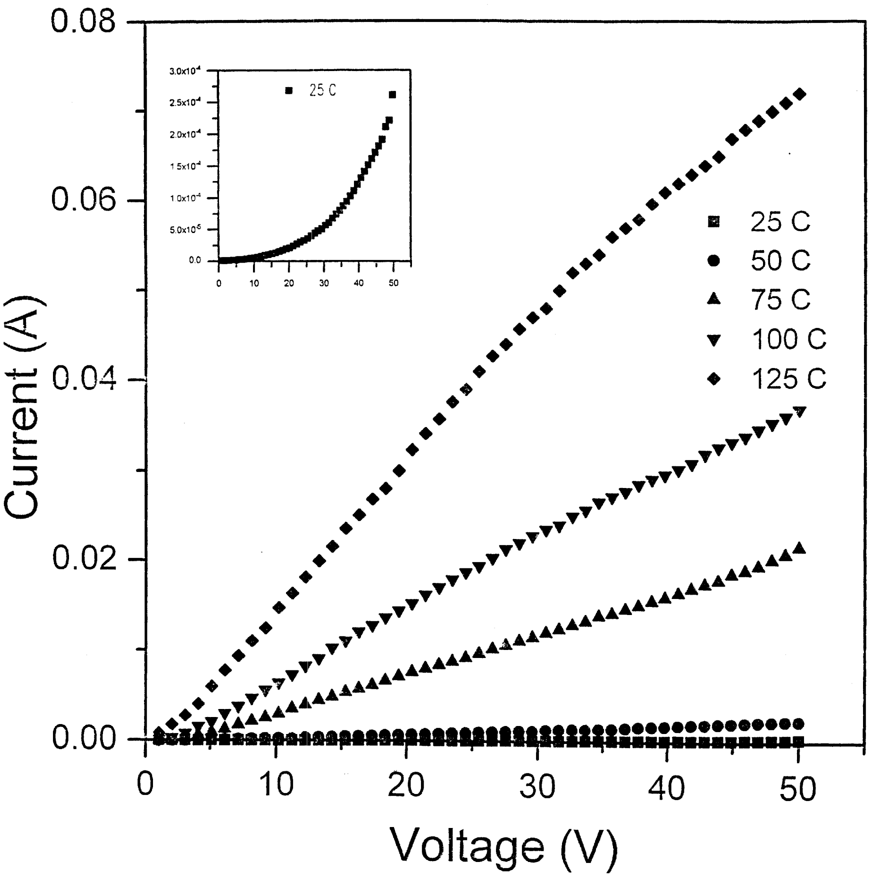


FIGURE 3 I-V for graphytized carbon–black filled rubbers. (a) 60%, (b) 45%, (c) 30%. (*Continued*).

in Table 2. There is close agreement between the theoretical and experimental values only for 60% fillers concentration according to Blythe theory, assuming a random orientation of conductive network fillers in the host material, which indicates that the conductivity in this concentration is ohmic in nature. A significant difference between the experimental and theoretical values of conductivity was observed for fillers concentration 30% and 45%. This may indicate that the electronic movement responsible for conduction can also occur by tunnelling or an electron emission effect and ionic transport, which is non-ohmic in nature. The increase in conductivity with increasing temperature indicates that conduction in these samples is a thermally



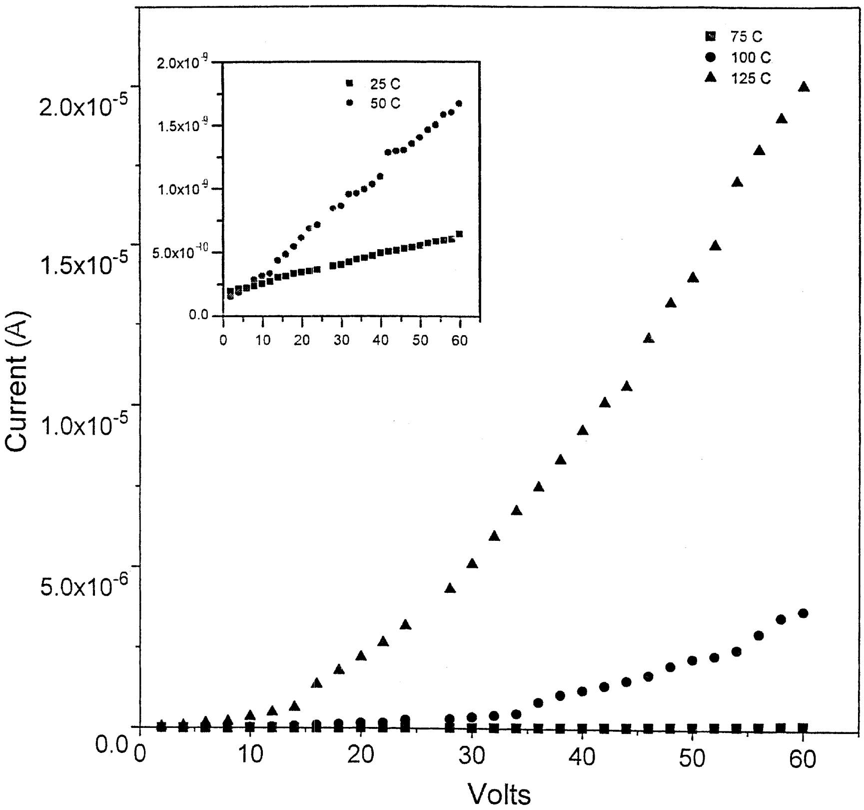
(b)

FIGURE 3 (*Continued*).

activated process. Figure 2 shows a plot of rubber/graphite conductivity vs. the reciprocal of the measured temperature. The date fit a straight line over the investigated temperature range (25°C to 125°C) quite well, especially for 60% volume fraction, which indicates that the conductivity dependence on temperature is of the form

$$\sigma = \sigma_0 \exp . - \mathrm{E_a/kT} \tag{3}$$

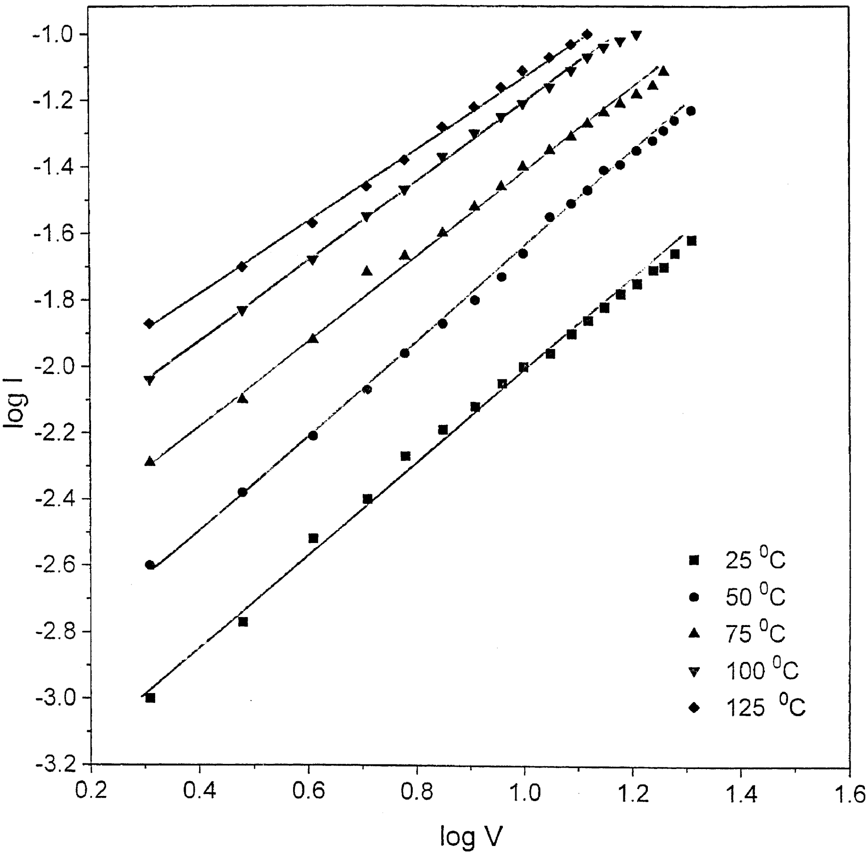
where σ is the sample conductivity, $\mathrm{E_a}$ is the activation energy of the conduction process, k is the Boltzman constant and T is the temperature in Kelvin. From the slope of the straight lines fit, as shown in Fig. 2, we extracted the activation energy of the conduction process,



(c)

FIGURE 3 (*Continued*).

which increases from 0.3 eV for 60% graphytized carbon blacks to a value of 0.98 eV for the fillers volume fraction of 30% as given in Table 1. This indicates that more than one conduction mechanism may be considered according to the filler concentrations in the host material. In general the distinction between electronic and ionic conduction is difficult. However, it is suggested that while ionic conduction is characterized by low mobilities and high activation energies, electronic conduction is associated with relatively high mobilities and lower activation energies. Jonscher [17] suggested that values less than 0.8 eV would normally be considered as the electronic conduction mechanism, while values excess of 0.8 eV would normally be attributed to ionic transport. Therefore, the dominant conduction



(a)

FIGURE 4 log I vs. log V for graphytized carbon–black filled rubbers. (a) 60%, (b) 45%, (c) 30%. (*Continued*).

mechanism in sample containing 60% of the filler is electronic conduction while in the lower concentration the dominant conduction mechanism is due to ionic transport.

It should be noted that the conductivity values in Fig. 3 were obtained from the I-V curves in the region where I-V is a straight line (showed ohmic behavior). A careful analysis of the I-V curves revealed that there are two well defined distinct regions for 30% and 45%, which apparently indicates two different leakage current mechanisms: The first region occurs at voltages roughly below 30 Volts and the second region occurs at higher voltages. However, in the low voltage

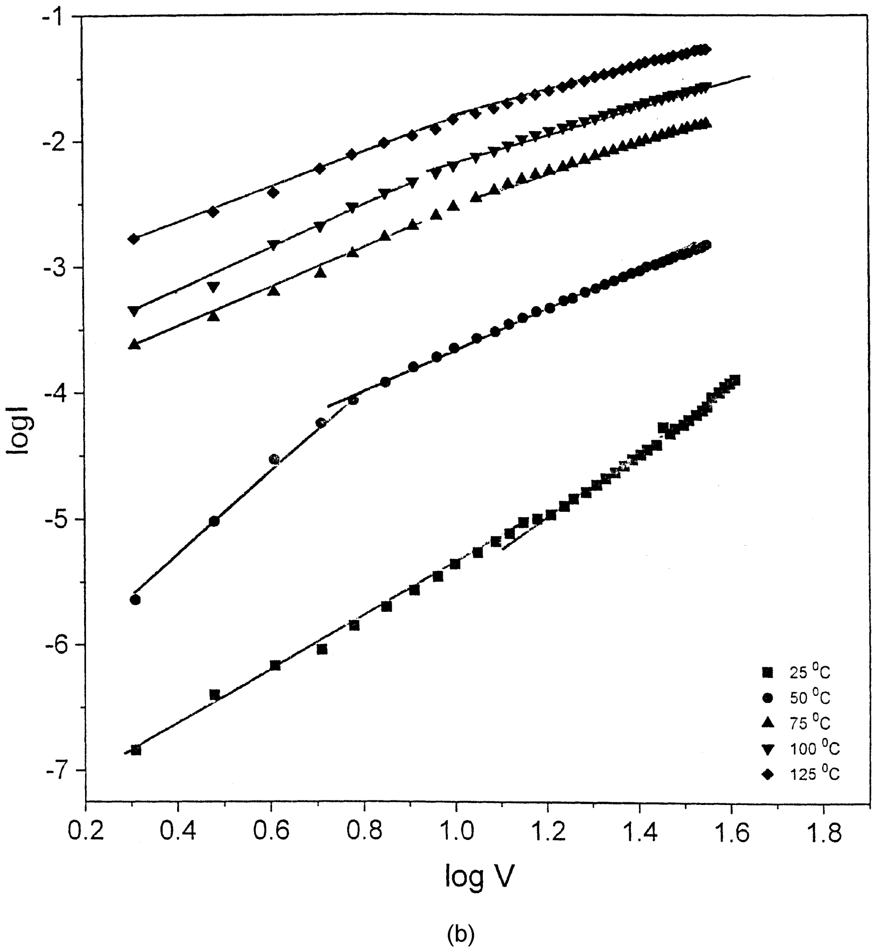
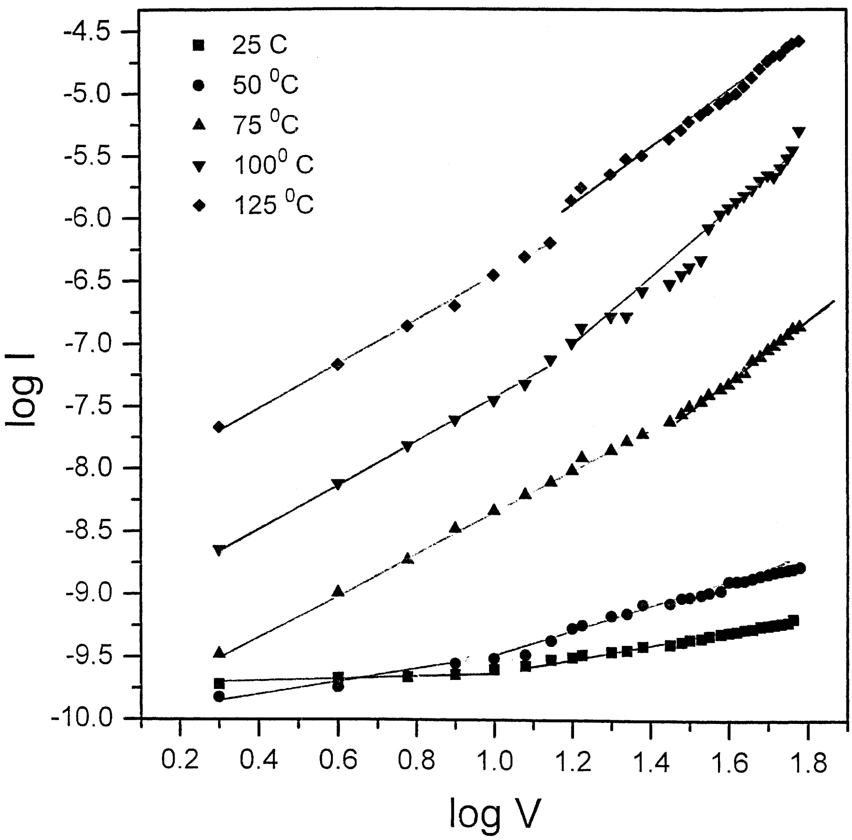


FIGURE 4 (*Continued*).

region, ohmic behavior IR = V is clearly obeyed. In the case of ohmic behavior, the slope of the I-V curve on the log-log plot should equal unity. Figure 4 shows plots of log I vs. log V for the three samples. The slope of the I-V curves for 60% concentration and on the log-log plots ranged from 1 to 1.3, which indicates that ohmic conduction is dominating. For other concentrations, the curves deviated from ohmic behavior. Generally, the current dependence on voltage was of the form $I \propto V^n$, where n was in the range of 2 to 3 depending on the sample composition.



(c)

FIGURE 4 (*Continued*).

For filler concentration of 30% and 45%, the fillers were distributed homogeneously in the volume of the insulating host. Therefore, it can be suggested that the conduction process in this region is non-ohmic, which is mainly due to electronic emission effect. At high concentration, the filler particles begin to form clusters exceeding the percolation threshold of graphite, [18,19] in contact with each other, which makes the electrical process ohmic in nature.

4. CONCLUSIONS

The dc electrical conductivity of carbon–black filled rubbers attains a maximum value when the conductive particles form a continuous network. The conduction mechanism is ohmic in nature. The activation energy in this case is of the order of 0.3 eV. At lower concentration the activation energy reaches a value of 0.98 eV, indicating that the conduction mechanism is non-ohmic in nature. The conduction in low fillers concentration is due to contribution of more than one mechanism. Blythe [16] theory can be employed only for a random distribution of conductive particles that form a continuous network.

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