DC Current Voltage Characteristics of Silicone Rubber Filled with Conductive Carbon Black

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Abstract: Direct current (DC) current-voltage (*I-V*) characteristics of silicone rubber filled with conductive carbon black (CB) were studied at room temperature in the voltage range of 1–46 V. The current-voltage relationship can be expressed as $I = AV^B$, where A and B are constants that show capability and property of electrical conduction, respectively. The *I-V* curve can be divided into ohmic and nonohmic regions. In nonohmic region, $B < 1$, and the resistance increases with the rise of voltage. Higher CB loading leads to lower transforming voltage from ohmic to nonohmic region and much deviation from Ohm's law. The reason for this deviation is the unbalance between the heat generated and the heat loss of conductive silicone rubber during the measurement. When the heat effect is eliminated completely, the electrical conduction is ohmic. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 587–592, 2004

Key words: silicones; rubber; carbon black; conducting polymers; current-voltage characteristics

INTRODUCTION

Current-voltage (*I-V*) characteristics are very important electrical properties of carbon black (CB)–polymer composites.[1] For most CB–polymer composites, the current does not vary linearly with applied voltage except at low field.[2–6] *I-V* characteristics of butyl rubber (IIR) filled with two different types of CB show that the conduction is ohmic ($I \propto V$) at low field, while at intermediate field, $I \propto V^2$. At high field, the behavior of I with V is different for the samples filled with different types of CB, indicating that different conduction mechanisms exist in the different types of composites.[2] Su et al.[3] studied the DC *I-V* characteristics of polyethylene filled with five different CB loadings, which corresponds to different transforming voltages from ohmic to nonohmic region. In nonohmic region, the resistance decreases with the rise of voltage. Low CB loading or high temperature results in much deviation from Ohm's law. *I-V* characteristics of low-density polyethylene/chlorinated polyethylene/CB three-phase conductive composite[5] are well consistent with the results of Su et al.,[3] and higher chlorinated polyethylene content in composite weakens the deviation from Ohm's law. However, the electrical conduction of composite depends on a large number of parameters, such as properties of CB and polymer matrix, and the interaction between CB and polymer matrix.[7–10] Therefore, DC *I-V* characteristics of conductive composites are very complicated. Sichel et al.[11] provided the reason for nonohmic *I-V* characteristics of CB–poly(vinyl chloride) at very low temperatures. The manner of explaining the nonohmic *I-V* characteristics of CB–polymer composites, especially at room temperature, has not been reached.

Compared with the polymer materials mentioned above, silicone rubber has a lot of special physical properties, such as high coefficients of thermal expansion and thermal conduction.[12] No report has been found concerning the *I-V* characteristics of silicone rubber filled with conductive CB.

In this article, DC *I-V* characteristics of silicone rubber filled with five different conductive CB loadings were studied at room temperature in the voltage range of 1–46 V. The constants A and B were calculated.

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EXPERIMENTAL

Materials

Methylvinylsilicone gum (M_n, 5.8×10^5; mole content of vinyl group, 0.15%), VXC-72 conductive CB, $4^{\#}$ SiO_2 (specific surface area, 176 m^2/g), and 2,5-bis(*tert*-butyl

TABLE I
The Formulae of Samples of Conductive Silicone Rubber

Sample no.	Silicone gum (wt parts)	CB (wt parts)	Silica (wt parts)	DBPMH (wt parts)
1	100	20	40	1.5
2	100	25	35	1.5
3	100	30	30	1.5
4	100	35	25	1.5
5	100	40	20	1.5
6	100	15	45	1.5

peroxy)-2,5-dimethyl hexane (DBPMH) were supplied by the Institute of Medical Apparatus and Instrument of Shandong Province (Jinan, China), Cabot China Ltd. (Shanghai, China), and Chenguang Institute of Chemical Industry (Chengdu, China), respectively.

Preparation of samples

The formulae of conductive silicone rubber are listed in Table I.

Materials were compounded and then vulcanized at 170°C for 20 min under 9.8 MPa.[13,14] The vulcanizate samples, with typical dimensions of 8.0 × 2.5 × 0.15 cm^3, were postcured at 190°C for 3 h. The Cu electrodes were embedded in the samples to minimize the contact resistance before preliminary vulcanization. The samples were left standing before testing (24 h maturation at room temperature).

Physical measurements

The resistance of samples was measured by Direct Current Electrical Resistance Meter Model QJ83 manufactured by Zhengyang Instrument Ltd. (Shanghai, China). The measuring current range is from 25 μ A to 100 mA, and the electrical power consumption in sample is less than 1 W.[15] *I-V* characteristics were measured according to voltammetry. Milliammeter or microammeter was used to measure the electrical current flowing through the samples.

RESULTS AND DISCUSSION

Time dependence of current at constant voltage

The time dependence of electrical current flowing through sample 3 at constant voltage was shown in Figure 1.

As seen, the electrical current is free from time (t) when the measuring voltages are 10 and 15 V, respectively. In the cases of 30 and 40 V, the electrical current changes with time. At the instant of loading a certain voltage (t = 0), the current reaches the maximum value, which is named I_0. Then, the current flowing through the sample decreases consequently until it reaches a steady value of I_e. I_e is affected by the factor of heat transmitting, whereas I_0 is not; therefore, I_0 reflects the inherent properties of testing materials better than I_e. The current mentioned below is I_0.

I-V characteristics at room temperature

The relationship between I and V for CB–polymer composites can be expressed as.[16]

$$I = AV^B \quad (1)$$

where A and B are constants representing capability and property of electrical conduction, respectively. In ohmic region, $B = 1$, and A is electrical conductance, which is usually expressed as A_0. In the nonohmic region, $B \neq 1$, and A has relevance to electrical conductance, which is usually expressed as A_N, and then A_N^{-1} is equal to nonohmic resistance when the applied voltage is 1 V. Making a logarithmic operation in eq. (1), it becomes

$$\log I = \log A + B \log V \quad (2)$$

It can be found from eq. (2) that, in both ohmic and nonohmic regions, there is a linear relationship between $\log I$ and $\log V$. The slope is $B \cdot A_0^{-1}$ or A_N^{-1} can be determined by the intercept.

Because CB–polymer composites with different CB loadings obey different conduction mechanisms, the relationship between the volume resistivity and the content of VXC-72 conductive CB was studied first, as illustrated in Figure 2. For conductive silicone rubbers with CB loadings below the percolation threshold, the current density flowing through them is extremely

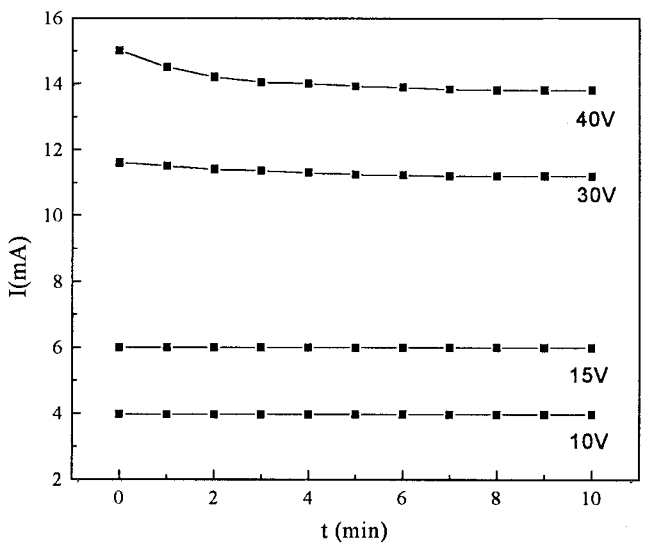

Figure 1 Time dependence of current at constant voltage.

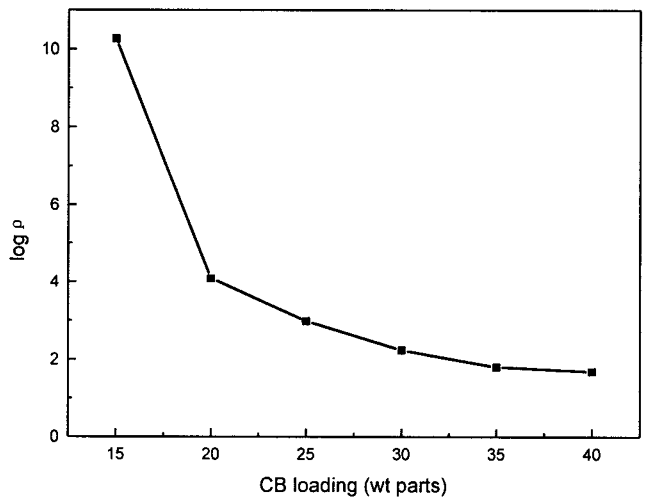

Figure 2 Resistivity of conductive silicone rubber with conductive CB loading.

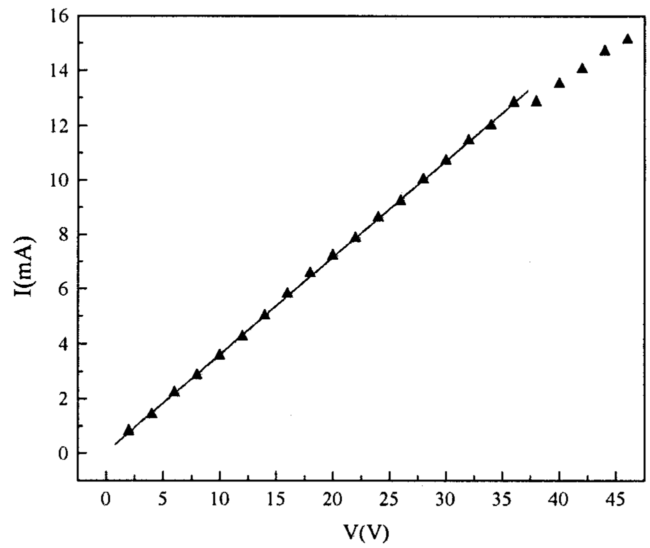

Figure 4 *I-V* characteristics of conductive silicone rubber with 30 wt parts of CB.

low, and the composites have little value in practice. Thus, we only studied the *I-V* characteristics of the conductive silicone rubbers with CB loadings above the percolation threshold; under this circumstance, resistivity no longer changes rapidly as CB loading increases. This is because a conducting path is formed then.

Figure 3 shows the *I-V* characteristics of samples 1 and 2 at room temperature, respectively. For the two samples, in the whole measuring voltage range, the constant *B* is 1, which means ohmic conduction.

When the CB loading increases further, the cases are different. Figures 4, 5, and 6 show the *I-V* characteristics of samples 3, 4, and 5, respectively. It can be found that, at low voltages, the conduction is ohmic. As the voltages increase, there are apparent deviations from Ohm's law. The current values are below the straight line that stands for the extrapolated ohmic behavior. Additionally, the transforming voltages V_s from ohmic to nonohmic region decrease as the CB loading increases.

To determine the constants A_N^{-1} and *B*, log*I* is plotted against log*V* in the nonohmic region, which are illustrated in Figure 7. The calculated results are listed in Table II.

From Table II, it can be found that A_N^{-1} is smaller than the corresponding value of R_0, and *B* is smaller than 1 and decreases with the increase of CB loading, which are quite different from other kinds of CB–polymer composites.[2,3,5] For CB–butyl rubber[2] or CB–polyethylene composites,[3,5] *B* is bigger than 1 in the

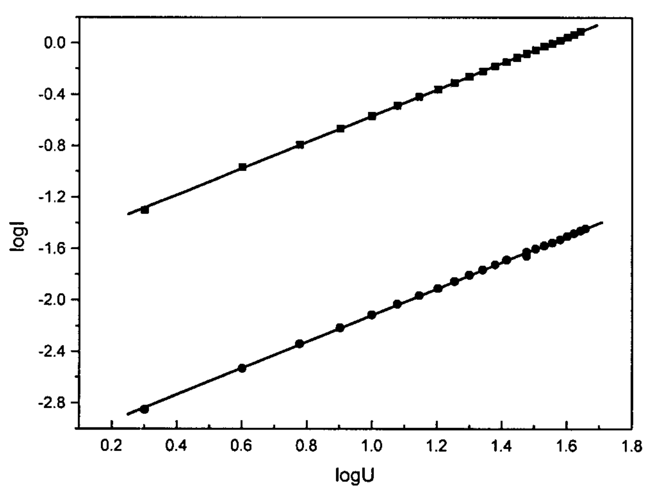

Figure 3 *I-V* characteristics of conductive silicone rubber with 20 wt parts (●) and 25 wt parts (■) of CB.

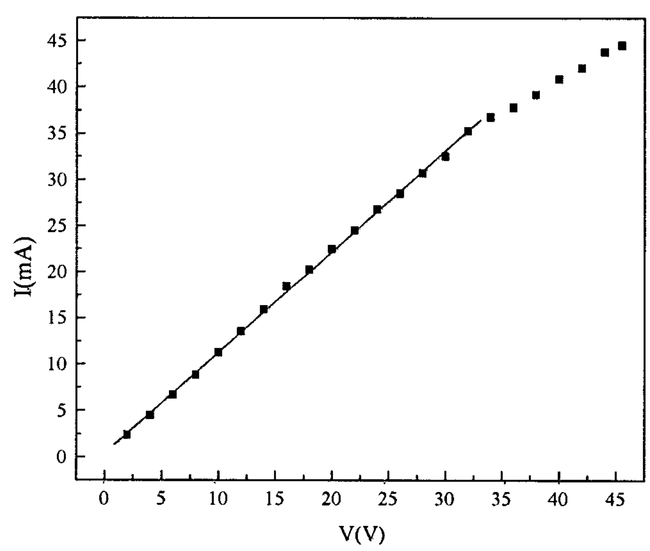

Figure 5 *I-V* characteristics of conductive silicone rubber with 35 wt parts of CB.

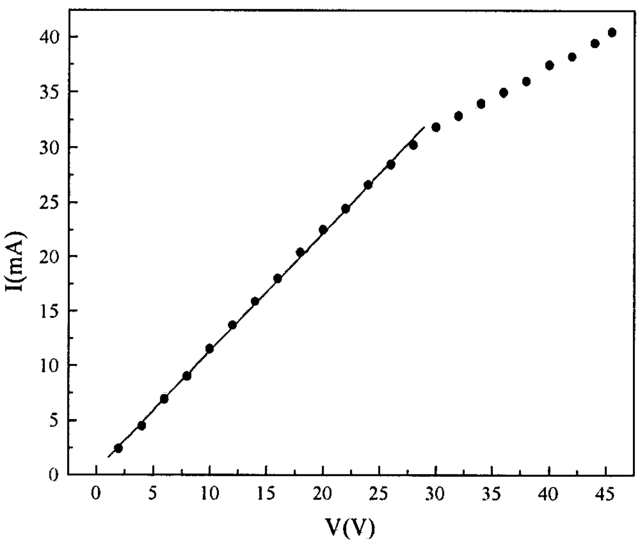

Figure 6 *I-V* characteristics of conductive silicone rubber with 40 wt parts of CB.

nonohmic region and tends towards 1 with the increase of CB loading.

A straightforward explanation is to ascribe the observed experimental facts to self-heating of the sample. Regarding samples 1 and 2, high resistivity leads to small current flowing through them, which results in unapparent self-heating in the whole measuring voltage range, and therefore, the conduction is ohmic. As the CB loading increases, the resistivity of conductive silicone rubber decreases; thus, current flowing through samples 3, 4, and 5 becomes bigger and bigger and the effect of self-heating becomes more and more serious with the rise of applied voltage. As mentioned above, the thermal expansion coefficient of silicone rubber is 2.0–2.5 times as big as other organic

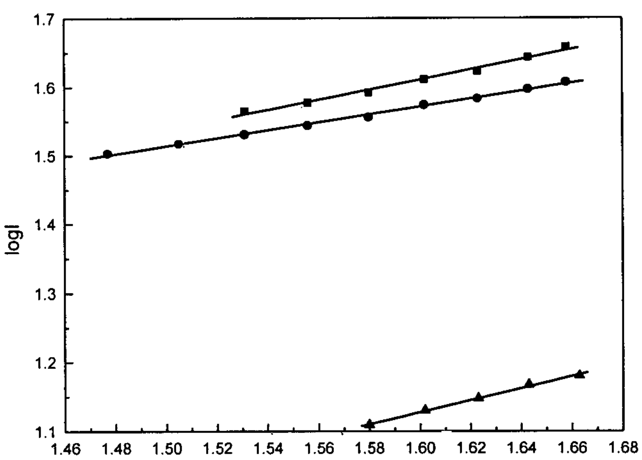

Figure 7 *I-V* characteristics of conductive silicone rubber with 30 (▲), 35 (■), and 40 (●) wt parts of CB in nonohmic region.

TABLE II
Constants of I-V Characteristics in Nonohmic Region

Sample no.	CB (wt parts)	R_0 (ohm)	A_N^{-1} (ohm)	B	V_s (V)
3	30	2.594E3	1.8E3	0.865	38
4	35	761.2	302.7	0.681	34
5	40	725.2	223.8	0.576	30

rubber; meanwhile, the thermal conduction coefficient of silicone rubber is also very high;[12] so, serious self-heating results in increasing temperature of the sample and apparent thermal expansion thereby, which makes the formed conducting path of CB aggregates in composites destroyed. Then, the dominant conduction mechanism tunnels through the gap of CB aggregates, assisted by thermal fluctuations.[17,18] Sheng et al.[19] showed that a special type of tunneling activated by thermal fluctuations of the electrical potential is suitable to CB–polymer composites. It is expressed as

$$\sigma = \sigma_0 \exp\left(-T_1/(T + T_0)\right) \tag{3}$$

where

$$T_1 = u\varepsilon_0{}^2/k \tag{4}$$

and

$$T_0 = 2u\varepsilon_0{}^2/\pi\chi\omega k \tag{5}$$

where σ is the conductivity of the junction formed by small regions of CB aggregates (of area A) on either side of the gap of polymer; σ_0 is treated as a constant; $u = \omega A/8\pi$, where ω is the gap width; $\chi = (2m\mathrm{V}_0/\mathrm{h}^2)^{1/2}$, where m is the rest mass of an electron, h is Plank's constant divided by 2π, and V_0 is the potential barrier; and $\varepsilon_0 = 4V_0/e\omega$, where e is the charge of an electron. Thus, T_1 may be regarded as the energy required for an electron to cross the polymer gap between CB aggregates.

Equation (3) shows that the tunneling conductivity is the function of temperature (T) and gap width (ω). It can be seen from eq. (3) that the influences of self-heating on tunneling conductivity are twofold: (1) the tunneling conductivity increases as temperature increases; (2) thermal expansion leads to an increase of gap width, resulting in a decrease in conductivity. The thermal expansion coefficient of silicone rubber is 2.0–2.5 times as big as other organic rubber.[12] At high field, as for conductive silicone rubber samples with high CB loadings (samples 3, 4, and 5 in this paper), the influence (2) may prevail over the influence (1). Therefore, the conduction of samples 3, 4, and 5 becomes nonohmic at certain high voltage and in

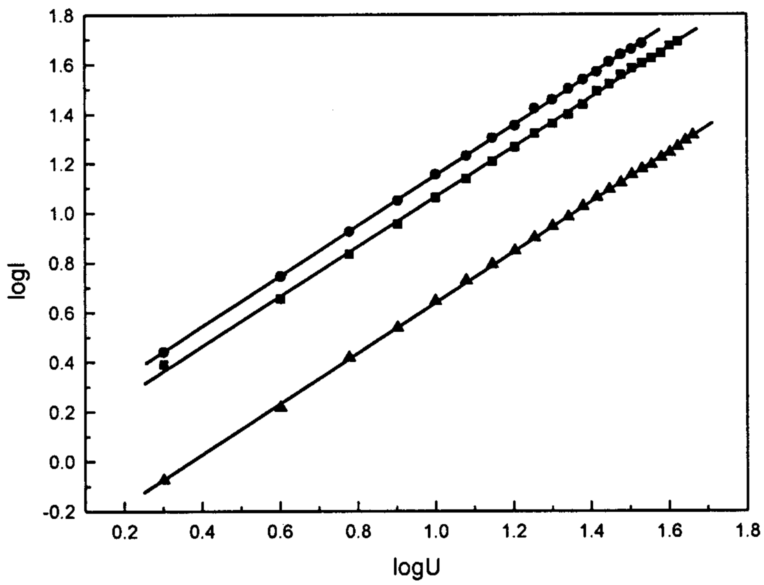

Figure 8 *I-V* characteristics of conductive silicone rubber with 30 (▲), 35 (■), and 40 (●) wt parts of CB after getting rid of heat effect completely.

nonohmic region the resistance increases with the rise of voltage, which leads to $B < 1$. Because the effect of self-heating, which is considered to be the reason for thermal expansion, becomes more serious as the CB loading increases, the value of B strays from 1 much as the CB loading increases. This is also why the *I-V* curve of sample 5 is below that of sample 4 in Figure 7, though the resistance of sample 5 is smaller than that of sample 4 at room temperature.

In summary, it can be concluded that the unbalance between the heat generated and the heat lost is the main reason for nonohmic conduction of conductive silicone rubber. The very big thermal expansion coefficient of silicone rubber and the big thermal conduction coefficient of silicone rubber as well lead to the difference in *I-V* characteristics between CB–silicone rubber composites and other CB–polymer composites.

Now that the heat unbalance is considered to be the main reason for nonohmic conduction, what will the case become if the heat effect is eliminated completely? To get rid of the heat effect completely, the following three methods were adopted: (1) the current flowing through the sample was measured instantly as the circuit was set up; (2) the circuit was cut off instantly as the current was read; (3) the next datum was taken after a time long enough to make sure the heat generated was completely balanced by the heat loss. On this condition, the *I-V* characteristics of samples 3, 4, and 5 were shown in Figure 8.

It can be found from Figure 8 that in the measuring voltage range of 1–46 V, the conduction of samples 3, 4, and 5 obeys the same mechanism and the slope of the three lines are all equal to 1, which means ohmic conduction. This can demonstrate that (1) our consideration of nonohmic conduction is reasonable; (2) the resistance change at high voltage is reversible.

CONCLUSION

For silicone rubber filled with VXC-72 conductive CB, when the CB loadings are above percolation threshold, the *I-V* characteristics obey Ohm's law at low voltages and deviate from Ohm's law at high voltages. The deviation becomes more serious as the CB loading increases. The reason for this deviation is the unbalance between the heat generated and the heat lost during the measurement. The differences in *I-V* characteristics between CB–silicone rubber composites and other kinds of CB–polymer composites are due to the special physical properties of silicone rubber, especially the very big thermal expansion coefficient. When the heat effect in the measuring course is eliminated completely, the conduction is ohmic.

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