Correlation Between Current–Voltage (I–V) Characteristic in the Electric–Thermal Equilibrium State and Resistivity-Temperature Behavior of Electro-Conductive Silicone Rubber

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Received 27 March 2007; accepted 17 September 2007
DOI 10.1002/app.27335

ABSTRACT: In the electric–thermal equilibrium state the current–voltage (I–V) characteristics of conductive silicone rubbers above the percolation threshold are found to be nonlinear. A mathematic model as $I = a_1U \pm (a_2U^2 + C)$ has been built for the nonlinear I–V relations. Constant C and quadratic term a_2U^2 can be considered as deviation from Ohm's law. For the first time, a correlation is found for conductive silicone rubber between the I–V characteristic in the electric–thermal equilibrium state and the resistivity–temperature characteristic. Samples with positive temperature coefficient (PTC) resistivity effect exhibit negative deviation from linearity, with an I–V relation as $I = a_1U - (a_2U^2 + C)$. Samples with negative temperature coefficient (NTC) resistivity effect exhibit positive deviation, with an I–V relation as $I = a_1U + (a_2U^2 + C)$. The higher the loaded voltage, the more pronounced the deviation. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2053–2057, 2008

Key words: conductive; silicone; rubber; I–V characteristics; PTC; NTC

INTRODUCTION

Conductive silicone rubber is the most widely used conductive rubber.[1] It has excellent heat resistance compared with other conductive rubbers. It was reported that silicone rubber can be continuously used for 7500 h at 200°C, and semipermanently at 150°C.[1] The silicone rubber (SR)/carbon blacks (CBs) composites show two types of relationship between temperature and electric resistivity, NTC and low PTC.[2] A thorough study on the PTC effects of SR/CBs composites indicated that both the thermal expansion coefficient of the composite and the interaction between SR and CB correlate with the size of the PTC anomaly.[3] The I–V characteristic is also an important electric property of conductive composite.[4] For most composites, current does not vary linearly with loaded voltage, except at low field.[5-9] Sichel et al.[10] gave an explanation to the nonohmic I–V characteristic of CB-poly(vinyl chloride) at very low temperature. Gefen et al.[11,12] measured I–V characteristic of discontinuous thin gold film near the percolation threshold. They found that current at which nonlinear response takes place, I^{c}_{ex}, scales with the conductance $\sum_0$, as $I^{c}_{ex} \sim \sum_0^x$, $x = 1.47 \pm 0.10$. Two theoretical models, nonlinear-random-resistor-network (NLRRN) and dynamic-random-resistor-network (DRRN), were studied analytically and numerically. The second model was compatible with their experiment. Chakrabarty et al.[13] studied the nonlinear I–V characteristics of carbon-wax samples near the percolation threshold. For low-resistance samples, the I–V curves were smooth and the leading nonlinear term is quadratic. The I–V relation could be written as follows:

$$I = \sum\nolimits_1 V + \sum\nolimits_2 V^2 \qquad (1)$$

$\sum_1$ and $\sum_2$ are fitting parameters. For high-resistance samples, the onset of nonlinearity is marked by

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Contract grant sponsor: Scientific Research Awarding Foundation for Excellent Young Scientist of Shandong Province; contract grant number: 2005BS11015.

Contract grant sponsors: Open Foundation of Key Laboratory of Colloid and Interface Chemistry, Shandong University; PhD Special Research Foundation of China Ministry of Education.

Contract grant sponsor: Ministry of Education, the National Nature Science Foundation of China; contract grant number: 20373034.

Journal of Applied Polymer Science, Vol. 107, 2053–2057 (2008)

TABLE I
Typical Analytical Properties of Carbon Black

Carbon black	Particle size (nm)	Nitrogen surface area (m^2/g)	Dibutyl phthalate absorption (mL/100 g)
VXC-72	30	254	178
BP2000	15	1475	330

the appearance of a small reversible step in the I–V curve that corresponds to a sharp minimum in the resistance R. Neither NLRRN nor DRRN models can fully account the experimental results obtained with the carbon-wax system. Gupta and Sen[14] explained the nonlinear DC response in composite by using a model of random resistor cum tunneling-bond network (RRTN). They simulated the resistor network with appropriate linear and nonlinear bonds and obtained macroscopic nonlinear-response characteristics. They suggested that one may be tempted to fit the nonlinear regime of an I–V curve in general with an nth degree polynomial function. Song and Zheng[15] studied the effect of voltage on the conduction of high-density polyethylene/CBs composite with a CB volume fraction slightly above the percolation threshold at temperatures above T_m, corresponding to the NTC region. The alternating current (AC) I–V characteristic curve was obtained in a relatively wide range of voltage. They found that the nonlinear intrinsic I–V curve could be fairly reproduced by Eq. (1). This result compares well with the result of low-resistance thin gold film reported by Chakrabarty et al.[13] Our previous study has found that the deviation of I–V relation from Ohm's law at high loaded voltages was due to the imbalance between heat generation and loss during measurement process.[16] In other words, the deviation was caused by the changes of rubber temperature. This suggests that there might be a relationship between resistivity–temperature characteristic and I–V characteristic. It would be interesting to know if there is a correlation between them.

The electric current passing through the sample is independent of time at low loading voltage. At high loading voltage, the electric current changes with time. When loading a voltage to the rubber, current is the highest at time zero ($t = 0$) and this sate is called ''starting state.'' Then current decreases and eventually reaches a steady value. This state is called electrical–thermal equilibrium state under which the rates of selfheating and heat-dissipation are equal.[17] It would be valuable to know the correlation between the resistivity–temperature characteristic and the I–V characteristic in the electric–thermal equilibrium state. No report has been found on this correlation.

The present work aims at revealing a correlation between the resistivity–temperature characteristic and the I–V characteristic of conductive SR. The I–V characteristics of conductive SRs with PTC and NTC resistivity effects are studied in the electrical–thermal equilibrium state.

EXPERIMENTAL

Materials

MVQ (M_n, 5.8×10^5; mole content of vinyl groups, 0.15%), Institute of Medical Apparatus and Instrument of Shandong Province, Jinan, China). The 2,5-bis (tert.-butyl peroxy)-2,5-dimethyl hexane (DBPMH), Tianjin Akzo Nobel Peroxides Co., LTD, Tianjin, China. VXC-72 conductive CB and BP2000 super CB, Cabot China, Shanghai. Typical properties of CBs are listed in Table I.

Surface modification of BP2000 super conductive CB

To a solution of 1% hexamathyldisilazne (MM^N) in ethanol was added BP2000 in a 1 : 7 weight ratio of MM^N : BP2000. The resulting mixture was stirred and reacted for 6 h under reflux. The modified BP2000 was obtained on removal of volatile spieces.

Preparation of samples

The formulae of conductive SR are listed in Table II.

Materials were compounded and then vulcanized at 170°C for 20 min under 9.8 MPa.[18,19] The vulcanizate samples, with typical dimensions of $8.0 \times 2.5 \times 0.15$ cm^3, were postcured at 190°C for 3 h. Cu electrodes were embedded in the samples to minimize the contact resistance before preliminary vulcanization. The samples were sit before testing (24 h maturation at room temperature).

Mechanical property measurement

The mechanical properties of vulcanizates were measured on an XLS-A rubber test instrument as described in the literature.[18]

TABLE II
Formula of Conductive Silicone Rubber (weight parts)

Sample no.	1	2	3	4
MVQ	100	100	100	100
BP2000	–	–	10	15
VXC-72	30	40	–	–
DBPMH	1.5	1.5	1.5	1.5

All values are expressed as parts per hundred rubber (phr) by weight.

TABLE III
Mechanical Properties of Samples

Sample no.	Hardness (Shore A)	Tensile strength (MPa)	100% modulus (MPa)	Tearing strength (kN/m)	Elongation at break (%)
1	40	4.35	0.73	24.1	403.3
2	44	4.93	0.92	26.5	416.7
3	37	3.87	0.69	19.8	608.4
4	39	5.62	0.98	22.5	528.0

BP2000 super conductive CBs were treated by a special kind of coupling agent before compounding with MVQ.

Resistivity–temperature characteristic measurement

The electric resistance of samples with typical dimensions of $8.0 \times 2.5 \times 0.15$ cm^3 were determined using four-probe method by Direct Current Electrical Bridge (Model QJ83, by Zhengyang Instrument, Shanghai, China). The current range was from 25 μA to 100 mA, and the electric power consumption within sample was less than 1 W.* The volume resistivity of sample was calculated according to the equation,

$$\rho = RA/t \tag{2}$$

where R is resistance, A is area, and t is thickness of sample.

The temperature dependence of resistivity was measured from 30 to 200°C at a heating rate of 5°C min^{-1}.[2]

I–V characteristics measurement and fitting

I–V characteristics were measured according to voltammetry. Milliammeter or microammeter was used to measure the electric current passing through the samples. All data were fitted to polynomial by a scientific graphing and analysis software Origin 6.1.

RESULTS AND DISCUSSION

Generally the sulfur in CB was thought to be an inhibitor to the crosslinking reaction of peroxide curing silicone composite.[20] In our opinion the active groups of hydroxyl existing on CBs surface play an important role in an insufficient crosslinking of MVQ. This is because that hydroxyl groups act as chain-transfer agent in radical reaction. This phenomenon is obvious in SR/BP2000 composite. To obtain well cured SR, BP2000 super conductive CBs were treated by hexamethyldisilazane before compounding with silicone gum. Some of hydroxyl on the surface of CB was consumed by hexamethyldisilazane and thus the vulcanizates were cured well. The mechanical properties are listed in Table III. MVQ could be strengthened by VXC-72 or BP2000 conductive CB. Tensile strength, hardness, 100% modulus, and tearing strength of vulcanizates increase as CB loading increases. Compared with VXC-72, BP2000 has better strengthening impact due to its smaller particle size (see Table II). High elongation at break of Sample 3 or 4 is due to low CB loading.

Conductive SRs with two different kinds of resistivity–temperature characteristics were used to study the correlation. As shown in Figure 1, which was quoted from Ref. 2, Samples 3 and 4 exhibit NTC resistivity effect. The CB loadings in the two samples are 10 and 15 phr of BP2000 super conductive CBs, respectively. The two CB loadings are slightly above the percolation threshold of SR/BP2000 composite, 5 phr.[2] Sample 2 exhibit PTC resistivity effect, Sample 1 shows PTC resistivity effect at temperatures lower than 156°C and slightly NTC resistivity effect at temperatures higher than 156°C. Samples 1 and 2 were loaded with 30 and 40 phr of VXC-72 conductive CBs, respectively. The two CB loadings are all higher than the percolation threshold of SR/VXC-72 composites, 10 phr.[2] It is not difficult to explain this result if it is assumed that two competing mechanisms occur during heating of the composites: an increase

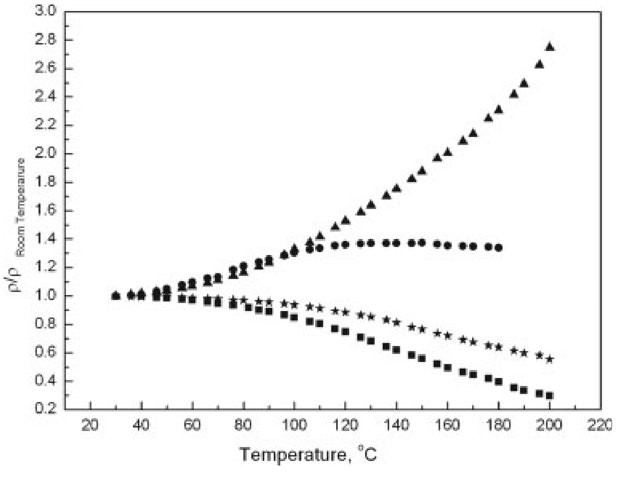

Figure 1 $\rho/\rho_{\text{Room Temperature}}$—temperature curves of samples. (●) Sample 1, (▲) Sample 2, (■) Sample 3, (★) Sample 4.

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*State Stand of People's Republic of China, Conducting and Dissipative Rubbers, Vulcanized or Thermoplastic-Measurement of Resistivity, GB/T2439-2001.

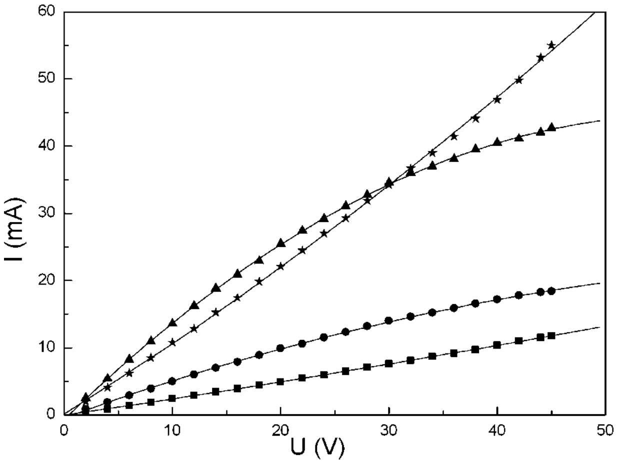

Figure 2 I–V characteristics of samples in the electrical–thermal equilibrium state. Curves are theoretical fits to formulas. (●) Sample 1, (▲) Sample 2, (■) Sample 3, (★) Sample 4.

in resistivity attributed to an increase in the average distance between CB particles during thermal expansion, and a decrease in resistivity attributed to an increase in the activation of the thermal emission of electrons from the CB particles.[21] For Samples 3 and 4 BP2000 concentration is near the percolation region. Under these conditions electron tunneling is the dominant conducting mechanism[22] and thus the influence of the thermal emission of electrons from the CB particles on the resistivity of composites is pronounced while temperature is increasing, therefore NTC effect is observed in Samples 3 and 4. As for Samples 1 and 2 VXC-72 concentration is higher than percolation threshold. Under these conditions, more CB particles contact each other. The influence of the thermal emission of electrons from the CB particles on the resistivity of composites becomes more insignificant and the influence of thermal expansion becomes more significant. Therefore Samples 1 and 2 exhibit PTC resistivity effect generally, except Sample 1 at temperatures higher than 156°C. This is because, besides the existence of the above factors influencing the relation between resistivity and temperature, SR segments or chains have sufficient mobility at higher temperatures and makes the reagglomeration of CBs possible,[15] which results in the NTC effect of Sample1 at high temperatures.

The I–V characteristics of samples in the electric–thermal equilibrium state are shown in Figure 2. Dots in two figures are experimental data, and smooth curves are mathematic fit to equations. (3)–(6). All data are fitted to polynomial very well. Constant and quadratic term of polynomial can be considered as deviation from Ohm's law. As can be seen that the I–V curves are smooth and the leading nonlinear term is quadratic, which is just like the results of low-resistance samples reported by Chakrabarty et al.[13] The tendency of deviation from linearity depends on resistivity–temperature characteristics. For the samples with PTC resistivity effect (Samples 1 and 2), curves bend towards the voltage (*U*) axis, and the I–V relations are fitted to the following equations:

$$I = 0.57189U - (0.0034\mathrm{U}^2 + 0.28122) \qquad (3)$$

$$I = 1.55966U - (0.0134\mathrm{U}^2 + 0.49029) \qquad (4)$$

As mentioned above, the self-heating effect increased temperature of sample in electrical–thermal equilibrium state, resulting in the deviation of I–V characteristic from linearity.[16] The loaded voltage was between 2 and 46 V, at which the sample temperature in electrical–thermal equilibrium state was much lower than 156°C. Namely, compared with the studies on the I–V characteristic of SR/CBs composites in electric–thermal equilibrium state, resistivity–temperature characteristics were studied within a wider temperature range. Thus, the mathematic model built for its nonlinear I–V relations applies to temperatures lower than 156°C, corresponding to the PTC region.

In eqs. (3) and (4), the terms in the brackets are deviation from linearity. It is clear that the two samples show negative deviation from linearity. The higher the loaded voltage, the more pronounced the deviation. For the two samples with NTC resistivity effect (Samples 3 and 4), the curves bend towards the current (I) axis, and the I–V relations are fitted to the following equations:

$$I = 0.23369U + (6.30863E - 4\mathrm{U}^2 + 0.00139) \qquad (5)$$

$$I = 1.00997U + (0.0042\mathrm{U}^2 + 0.09974) \qquad (6)$$

It is obvious that the two samples show positive deviation from linearity. Also, the higher the loaded voltage, the more pronounced the deviation.

The deviation from linearity is attributed to the increase of sample temperature in electric–thermal equilibrium state. At low voltages, the slight self-heating results in slight increase in sample temperature, and leads to slight deviation from linearity. This is also confirmed from the four equations. As a result of the small coefficient, the influence of polynomial's quadratic term on the I–V relation is small at low loaded voltages. The I–V relation is close to linearity with a constant at low loaded voltages. This is different from the I–V relation in starting state, in which the conduction is absolute ohmic at low loaded voltages.[16] The constant can be considered as an amendment from Ohm's law. At high voltages, the selfheating effect leads to increase in sample temperature in the electric–thermal equilibrium state.

NTC resistivity effect means smaller resistivity at higher temperatures while PTC means larger resistivity at higher temperatures. Thus, for samples with NTC resistivity effect electric current at a certain voltage becomes larger in the electric–thermal equilibrium state; for samples with PTC resistivity effect electric current at a certain voltage becomes smaller in the electric–thermal equilibrium state. As a result, samples with NTC resistivity effect show a positive deviation from Ohm's law while samples with PTC resistivity effect show a negative deviation from Ohm's law in the electric–thermal equilibrium state. Thus a correlation is found. PTC resistivity effect leads to negative deviation of I–V characteristic from Ohm's law while NTC resistivity effect leads to positive deviation.

It is interesting that both the constant and the coefficient of quadratic term of Sample 2 are more negative than those of Sample 1. Both the constant and the coefficient of quadratic term of Sample 4 are more positive than those of Sample 3. This is because a high CB loading lowers the resistivity of conductive SR, and causes more serious selfheating effect. As a result, a more pronounced deviation of I–V characteristic from Ohm's law was seen at a certain loaded voltage.

CONCLUSIONS

A correlation for conductive SR between temperature–resistivity characteristic and I–V characteristic in electric–thermal equilibrium state is revealed. Samples with PTC resistivity effect exhibits a negative deviation of I–V characteristic from Ohm's law, with an I–V relation as $I = a_1U - (a_2U^2 + C)$. For sample loading with 30 phr VXC-72 conductive CBs, $a_1 = 0.57189$, $a_2 = 0.0034$, and $C = 0.2812$. For sample loading with 40 phr VXC-72 conductive CBs, $a_1 = 1.55966$, $a_2 = 0.0134$, and $C = 0.49029$. Samples with NTC resistivity effect exhibit a positive deviation, with an I–V relation as $I = a_1U + (a_2U^2 + C)$. For sample loading with 10 phr BP2000 super conductive CBs, $a_1 = 0.23369$, $a_2 = 6.30863\text{E-}4$, and $C = 0.00139$. For sample loading with 15 phr BP2000 super conductive CBs, $a_1 = 1.00997$, $a_2 = 0.00426$, and $C = 0.09974$. The higher the loaded voltage, the more pronounced the deviation. For a given CB type, the higher the CB loading is, the more pronounced the deviation is. An analogous correlation may also exit for other conductive composites.

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