Temperature Effects of Electrical Resistivity of Conductive Silicone Rubber Filled with Carbon Blacks

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ABSTRACT: The temperature effects of electrical resistivity of conductive silicone rubber filled with widely varying concentrations of carbon blacks (CBs: GPF 660 carbon black, HAF N-330 carbon black, VXC-72 conductive carbon black, and BP2000 superconductive carbon black) were studied from 30 to 200°C. Both low positive temperature coefficient (L-PTC) and negative temperature coefficient (NTC) phenomena were observed, whose intensity and temperature range depend on the type and the concentration of CBs. A stronger temperature dependency of resistivity was observed when the CB concentration was in the percolation region. Unlike crystalline polymers/CBs composites, the high positive temperature coefficient (H-PTC) phenomenon was not observed in CB-filled silicone rubber when the CB concentration was near the percolation threshold. Generally, pronounced the NTC phenomenon appears in composites with small particles of CBs at concentrations near the percolation threshold, whereas a pronounced PTC phenomenon appears in composites with large CB particles of at concentrations exceeding the percolation region. If both PTC and NTC phenomena were in the same sample of conductive silicone rubber, the PTC phenomenon always appeared at relatively low temperatures and NTC at relatively high temperatures. The results were discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3889–3895, 2003

Key words: silicones; rubber; carbon black; resistivity; temperature effect

INTRODUCTION

There are three types of relation between temperature and electrical resistivity of conductive composites: negative temperature coefficient (NTC), low positive temperature coefficient (L-PTC), and high positive temperature coefficient (H-PTC).[1] The resistivity increase upon increasing temperature is described by a positive temperature coefficient (PTC), whereas the resistivity decrease is described by a negative temperature coefficient (NTC). PTC materials can be used as self-limiting and switching materials, and thus have attracted considerable attention.[2–4] Crystalline polymers are usually used as matrices of PTC materials,[5–8] in which there is an abrupt resistivity increase at the melting point of the polymer matrix. The shorter the melting region, the more precipitous the PTC effect. After crystalline melting is complete, the resistivity decreases quite rapidly, which means an obvious NTC effect.

There is no general theory to explain these phenomena, but there are many contributions elucidating specific aspects.[9–12] According to Kohler,[9] the conductive fillers are initially spread through the polymer matrix in a network of conductive chains, and when the material is heated, the conductive particles are separated further, increasing the resistivity. Sudden expansion of the matrix at the crystalline melting point is assumed to be the cause of the PTC effect. Aneli's experimental evidence[10] is consistent with Kohler's viewpoint. However, Meyer found that the thermal expansion coefficients of the matrices had no effect on the PTC anomaly of conductive composites with crystalline polymer matrices.[11] He suggested the only way to predict the intensity of the PTC effect of a crystalline polymer filled with CBs was through the knowledge of glass-transition temperature (T_g) of the polymer. Nevertheless, the theories mentioned above cannot explain the NTC effect that all composite PTC materials display above the crystalline melting point.

Conductive silicone rubber is now the most widely used conductive rubber because of its good properties.[13] Its excellent heat resistance is the most outstanding property compared with other kinds of conductive rubber. It is reported that silicone rubber can be used continuously for 7500 h at 200°C and semipermanently at 150°C.[14] Therefore the temperature characteristics of conductive silicone rubber are of importance and obviously deserve to be studied when considering its possible applications.

According to Voet,[1] if the CB concentration is in the percolation region, where major resistivity changes

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TABLE I
Typical Analytical Properties of Carbon Black

Property	Carbon black			
	BP 2000	VXC-72	HAF N-330	GPF 660
Particle size (nm)	15	30	27	70
Nitrogen surface area (m^2/g)	1475	254	82	39
Dibutyl phthalate absorption (mL/100 g)	330	178	102	70

result from minor changes in interparticle distances, a pronounced PTC effect could be produced. The cases of CB-filled low-density polyethylene and ethylene–vinyl acetate copolymer[5] supported Voet's hypothesis. The author attributed the cause of the PTC effect to the thermal expansion of the polymer matrix, which separates the just-formed conducting path when the CB concentration is near the percolation threshold. However, few studies on temperature characteristics of CB-filled silicone rubber have been reported. Princy et al.[15] studied the temperature dependency of resistivity of silicone rubber filled with varying concentrations of acetylene and both lamp and ISAF blacks, respectively. Both L-PTC and NTC phenomena were observed from 25 to 150°C. However, for a certain type of CB only two concentrations of filled silicone rubber were studied and the concentrations were all significantly above the percolation threshold; that is, the CB concentrations were limited to a narrow range. What about the cases of CB-filled silicone rubbers when the CB concentration is in the percolation region? Does a pronounced PTC effect exist? No report was found. To find the influences of both the types and the concentrations of CBs on the temperature characteristics of conductive silicone rubber, it is necessary to make a systematic study. In this investigation silicone rubber filled with four different types of CBs, varying widely in both properties and concentrations, were studied.

EXPERIMENTAL

Materials

Methylvinylsilicone gum ($M_n = 5.8 \times 10^5$; content of vinyl groups, 0.15 mol %) was supplied by Institute of Medical Apparatus and Instrument of Shandong Province (Jinan, China). 2,5-Bis(*tert*-butyl peroxy)-2,5-dimethyl hexane (DBPMH) was supplied by Tianjin Akzo Nobel Peroxides Co., Ltd. (Tianjin, China). GPF 660 and HAF N-330 blacks were supplied by Qinzhou Chemical Industry Ltd. (Qingzhou, China). VXC-72 conductive black and BP2000 superconductive black were supplied by Cabot China Ltd. (Shanghai, China).

Typical analytical properties of carbon blacks are listed in Table I.

Preparation of conductive silicone rubber

The formulae of conductive silicone rubbers are listed in Table II. Among them, when the CB concentrations are high, the amounts of DBPMH used in samples filled with BP2000 superconductive CBs and VXC-72 conductive CBs were increased to obtain samples with good vulcanization characteristics. Referring to the literature,[16,17] materials were compounded and then vulcanized at 170°C for 20 min under 9.8 MPa. The vulcanizate samples were postcured at 190°C for 3 h.

Testing

The resistance of samples (typical dimensions: $8.0 \times 2.5 \times 0.15$ cm^3) was determined using a four-probe method by direct current electrical bridge (Model QJ83) manufactured by Zhengyang Instrument Ltd. (Shanghai, China). The current range was from 25 μA to 100 mA, and the electrical power consumption within the samples was less than 1 W.[18] The volume resistivity (ρ) of samples was calculated according to the following equation:

$$\rho = RA/t \tag{1}$$

where R is resistance, A is the area, and t is the thickness of sample. The temperature dependency of resistivity was measured from 30 to 200°C at a heating rate of 5°C min^{-1}. The cooling rate was 4°C min^{-1} to 60°C and then was 2°C min^{-1} to 40°C.

RESULTS AND DISCUSSION

Figure 1 shows the variation in resistivity of conductive silicone rubber with concentrations of various CBs

TABLE II
Formula of Conductive Silicone Rubber[a]

Silicone rubber	100	100	100	100	100	100	100	100	100
BP2000 black	5–15	15	20	25–30	—	—	—	—	—
VXC-72 black	—	—	—	—	5–30	40	50	—	—
HAF N-330 black	—	—	—	—	—	—	—	10–50	—
GPF 660 black	—	—	—	—	—	—	—	—	20–60
DBPMH[b]	2	2.5	3	3.5	1.5	2	2.5	1.5	1.5

[a] All values are expressed as parts per hundred rubber (phr) by weight.
[b] DBPMH, 2,5-bis(*tert*-butyl peroxy)-2,5-dimethyl hexane.

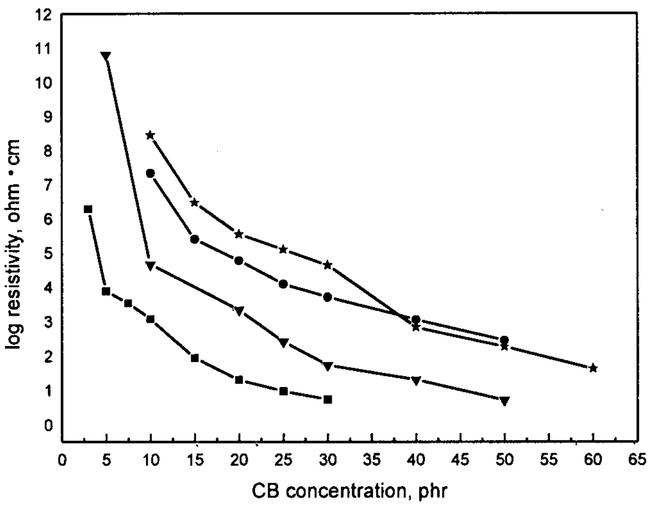

Figure 1 Log(resistivity) versus CB concentration: (■) BP2000 superconductive CB; (▲) VXC-72 conductive CB; (●) HAF N-330 CB; (★) GPF 660 CB.

at room temperature. It may be seen that for every type of CB a rather narrow range of concentrations exists in which a small change in concentration causes a major change in resistivity. This critical range is usually called the percolation region.[19] It can also be seen from Figure 1 that silicone rubbers filled with the same concentration of different CBs show marked differences in resistivity. Among the four types of CBs, BP2000 superconductive blacks conferred to the composites the best conductivity and VXC-72 conductive blacks next. This is attributed to the high inherent conductivity of the two types of CBs. At the same concentrations of CBs, HAF N-330 blacks imparted better conductivity than GPF blacks below the concentration of 30 phr, whereas just the opposite is the case above 30 phr. Anyway, the differences are very small.

Even as PTC intensity is defined as the ratio of the peak resistivity in the resistivity–temperature curve to room resistivity,[11] in this study NTC intensity is defined as the ratio of room resistivity to the valley resistivity in the resistivity–temperature curve as well. Figure 2 shows the $\rho/\rho_{\text{Room Temperature}}$ versus temperature curves of conductive silicone rubber filled with varying concentrations of BP2000 superconductive blacks upon heating and cooling. On heating the samples filled with 5, 10, and 15 phr of BP2000 blacks, which are in the percolation region,[19] all exhibited NTC phenomena. The NTC intensity was 3.8 (calculated from the original data of Fig. 2) when the CB concentration was 5 phr and decreased to 1.8 when the CB concentration was increased to 15 phr; that is, the NTC intensity decreased with increasing concentrations of BP2000 blacks. When the concentrations were above 20 phr, which exceeded the percolation region and gradually neared the saturation concentration,[20] both NTC and L-PTC phenomena were observed. The latter appeared at relatively low temperatures and the former appeared at relatively high temperatures. Corresponding to the BP2000 black concentrations of 20, 25, and 30 phr, the transition temperatures from PTC to NTC phenomenon were 126, 150, and 190°C, respectively. The transition temperature from PTC to NTC was determined accurately from the original data of Figure 2, although this transition can also be seen from the $\rho/\rho_{\text{Room Temperature}}$ versus temperature curves.

The differences in transition temperatures suggest as the BP2000 concentration increases from 20 to 25 phr, and then to 30 phr, the PTC region in the curves of $\rho/\rho_{\text{Room Temperature}}$ versus temperature grows larger, which means the PTC effect becomes obvious with increases of BP2000 concentration.

As for conductive silicone rubber filled with varying concentrations of VXC-72 conductive blacks, it can be seen from Figure 3 that on heating when the CB concentration is 10 phr, which is near the percolation threshold,[19] a pronounced NTC phenomenon, whose intensity is 5.8, can be observed. While the CB concentration is increased, both L-PTC and NTC phenomena are observed. For example, the transition temperatures are 100 and 156°C for conductive silicone rubber filled with 20 and 30 phr of CBs, respectively. Meanwhile, the NTC intensity is weakened as the CB concentration increases. The NTC phenomenon disappears and the PTC intensity increases to the maximum, whose intensity is 2.8, when the CB concentration is increased to 40 phr. Thereafter the PTC intensity decreases as the CB concentration increases further.

Figure 4 shows the results for conductive silicone rubber filled with HAF N-330 blacks. On heating NTC

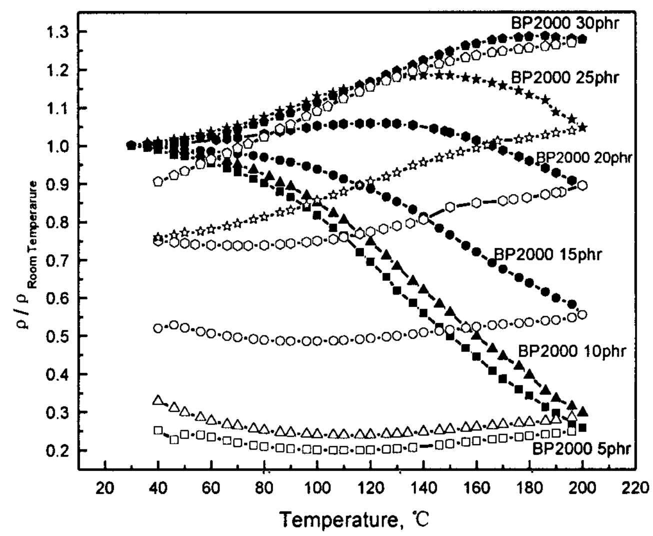

Figure 2 $\rho/\rho_{\text{Room Temperature}}$ versus temperature curves of conductive silicone rubber filled with BP2000 superconductive CB. Filled symbols: heating cycle; open symbols: cooling cycle.

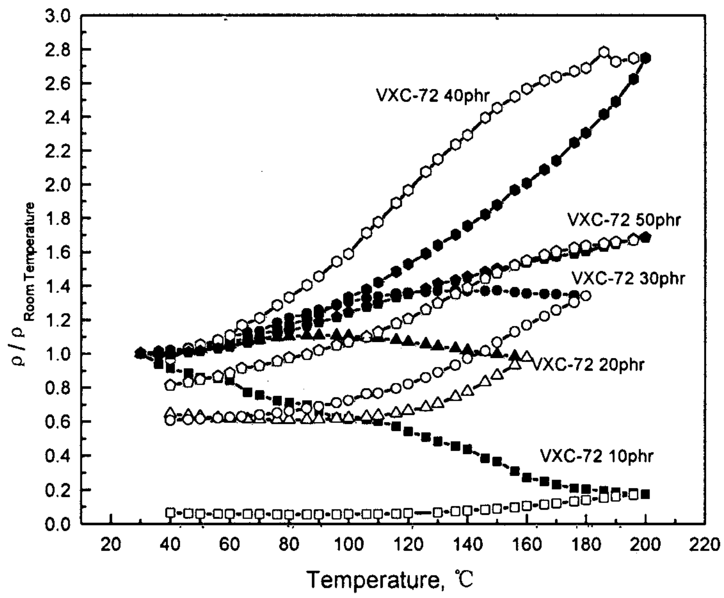

Figure 3 $\rho/\rho_{\text{Room Temperature}}$ versus temperature curves of conductive silicone rubber filled with VXC-72 conductive CB. Filled symbols: heating cycle; open symbols: cooling cycle.

phenomena are observed for all the samples with widely varying concentrations of CBs. The sample filled with 20 phr of HAF N-330 blacks exhibits only the NTC phenomenon. As the CB concentration increases, the L-PTC phenomenon appears. Its intensity and temperature range do not change obviously with increasing CB concentrations. A complete PTC phenomenon was not observed even when the CB concentration was near saturation concentration.

Conductive silicone rubber filled with GPF 660 blacks exhibited more a pronounced PTC phenomenon than that of the other kinds of conductive silicone rubbers mentioned above, which can be seen from Figure 5. When the concentration of GPF 660 blacks is 30 phr, on heating both L-PTC and NTC phenomena exist. The PTC intensity is 8.6 and reaches the maximum when the concentration of GPF 660 blacks is 40 phr, and then decreases to 5.5 and then 4.1 when the CB concentration increases to 50 and then 60 phr, respectively. These cases are like those of conductive silicone rubber filled with VCX-72 blacks.

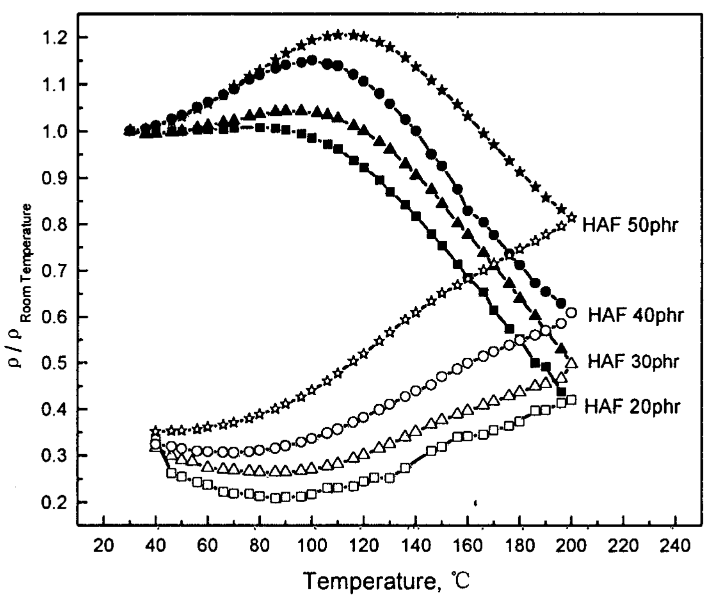

Figure 4 $\rho/\rho_{\text{Room Temperature}}$ versus temperature curves of conductive silicone rubber filled with HAF N-330 CB. Filled symbols: heating cycle; open symbols: cooling cycle.

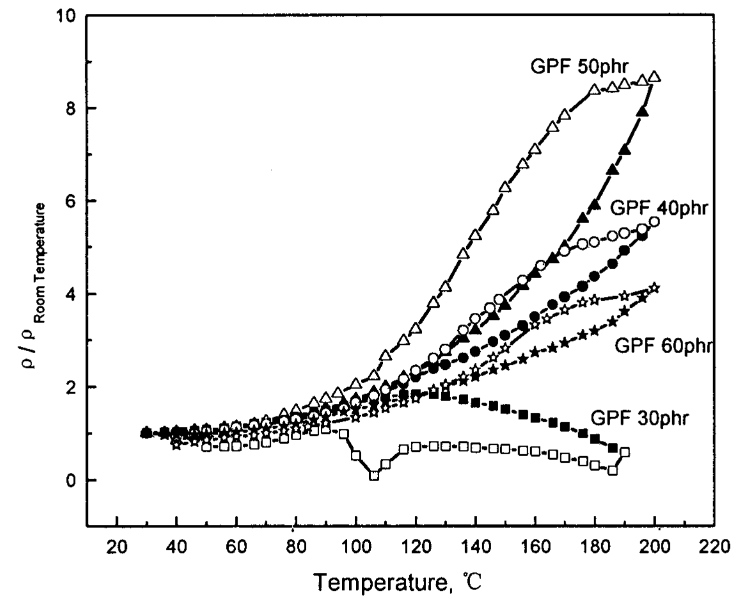

Figure 5 $\rho/\rho_{\text{Room Temperature}}$ versus temperature curve of conductive silicone rubber filled with GPF 660 CB. Filled symbols: heating cycle; open symbols: cooling cycle.

On cooling, in the majority of cases, the resistivity of the four kinds of conductive silicone rubber decreased with decreasing temperatures. Sometimes the resistivity of samples with low concentrations of CBs first decreased and then increased slightly with decreasing temperatures. There is a hysteresis loop in the resistivity–temperature curve during the heating/cooling cycle. We think there are two major reasons for the creation of the hysteresis loop. First, although the contraction of silicone rubber takes place on cooling, it is still impossible for the expanded silicone rubber to recover immediately its original volume, thus resulting in the differences in resistivity at the same temperatures. Second, reagglomeration of CB particles on cooling leads to a new distribution[21,22] of the CB network structure. This will also lead to differences in resistivity at the same temperatures. The factors mentioned above will decrease the average gap width between the cluster or aggregates of CB, thus resulting in decreased resistivity. Because the hysteresis also depends on the heating/cooling rate, it is difficult to compare the values of resistivity on cooling with those on heating when the heating and cooling rates are different. The experimental results showed the resistivity generally decreases as temperature decreases on the process of cooling; when the heating and cooling cycle finishes, the values of resistivity are smaller than the original ones.

H-PTC effects have been found in crystalline polymers/CB composites.[3–6] The melting of the crystalline phase results in a marked increase in resistivity. Silicone rubber is a noncrystalline polymer and there is no sudden expansion upon increasing temperature; thus the H-PTC effect is seldom found in silicone rubber/CB composites.[23]

A stronger temperature dependency of resistivity is observed in CB-filled silicone rubber when the CB concentration is in the percolation region. However, contrary to Voet's expectation,[1] the NTC effect other than the H-PTC effect exists. This suggests that besides the thermal expansion of the matrix there is another factor that influences the relation of resistivity to temperature. It is not difficult to explain this result if it is assumed that two competing processes occur during heating of the materials investigated: an increase 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.[10] A conducting path is formed when the CB concentration is in the percolation region. At that time electron tunneling is the dominant conducting mechanism[24] and thus the influence of the thermal emission of electrons from the CB particles on the resistivity of composites is pronounced in the process of increasing temperature, and thus the NTC effect is observed. As the CB concentration is increased, there are increasingly more CB particles to contact each other. Under these conditions, the influence of the thermal emission of electrons from the CB particles[10] on the resistivity of composites becomes steadily more insignificant. Therefore the NTC intensity decreases with increasing CB concentrations, whereas the PTC intensity increases. For GPF 660 and VXC-72 blacks, which can promote a pronounced PTC phenomenon in conductive silicone rubber, the PTC intensity reaches the maximum when the CB concentration increases to a certain value and then decreases with further increase of CB concentration. This is because, as a continuous thoroughly conducting network of CBs is created,[15] the resistivity of composites is less influenced by both of the competing process mentioned above and is thus less sensitive to temperature.

It is interesting to note that if both PTC and NTC phenomena exist in the same sample, the PTC phenomenon always appears at relatively low temperatures and NTC at relatively high temperatures. It is accepted that the agglomeration of CB particles or aggregates results in a decrease in resistivity.[6] At higher temperatures, besides the existence of two factors influencing the relation of resistivity to temperature mentioned above, silicone rubber segments or chains have sufficient mobility to make the movement of CB particles possible, which results in a new CB distribution of better conductivity.

It can thus be concluded for a given type of CB that concentration is the determining factor influencing temperature characteristics of resistivity of conductive silicone rubber. At a given CB concentration, the differences of temperature characteristics of resistivity in the four kinds of conductive silicone rubber are attributed to the differences in CB properties. For example, GPF 660 black, with the largest particle size, smallest surface area, and lowest structure of the four types of CBs, imparts silicone rubber with the most pronounced PTC effect, whereas BP2000 black, with the smallest particle size, biggest surface area, and highest structure, imparts silicone rubber with the most pronounced NTC effect. Among the CB properties mentioned above, particle size is most important to the temperature characteristics of resistivity of CB-filled silicone rubber. As mentioned above, the increase in the activation of the thermal emission of electrons from the CB particles leads to the NTC effect. It is known that the active centers of CB, free electrons, exist on the surface of CB particles.[25] Generally, the smaller the particle size, the greater the surface area.[25] When the quantity of CB is fixed, there are more active centers to exist for the type of CB with small particle size. This is why CBs with small particle size give silicone rubber a pronounced NTC effect; the case is just the opposite, however, for CBs of large particle size. With fewer active centers existing on the surface of CBs of large particle size, the temperature effect of resistivity of conductive silicone rubber filled with large particle size CB will be less influenced by the activation of the thermal emission of electrons from the CB particles, and thus will be more influenced by the thermal expansion. Because there is a big difference in the thermal expansion coefficient of CB (1.6×10^{-5}/K) and silicone rubber (120×10^{-5}/K),[26] thermal expansion leads to increases in resistivity of conductive silicone rubber filled with large particle size CB, and thus more pronounced PTC effect results.

It is worth mentioning that VXC-72 black is an exception, which has a larger particle size and a greater surface area than those of HAF N-330 black. This is because there are a large number of pits on the surface of VXC-72 black, resulting in extra surface area. Considering this it is not difficult to explain that HAF N-330 black imparts to silicone rubber a more pronounced NTC effect than does VXC-72 black.

CONCLUSIONS

Unlike crystalline polymers/CBs composites, no H-PTC phenomenon is found in silicone rubber/CB composites over a narrow temperature interval of 10–20°C when the CB concentration is in the percolation region. Both L-PTC and NTC phenomena are observed in silicone rubber filled with the four types of CBs from 30 to 200°C. Concentration and properties of CBs, especially the particle size, are of importance to the temperature characteristics of resistivity of CB-filled silicone rubber. Proper high concentration and large particle size of CBs lead to the PTC effect, whereas small particle size and low concentration of CBs lead to the NTC effect. If both PTC and NTC phenomena are observed in the same sample, the PTC phenomenon always appears at relatively low temperatures and the NTC phenomenon appears at relatively high temperatures.

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