Preparation of Positive-Temperature Coefficient Heaters Using Platinum-Catalyzed Silicone Rubber

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ABSTRACT: Various output heaters were extruded with acetylene black–filled platinum-catalyzed silicone rubber. The resistivity–temperature behavior of extruded heaters exhibited a positive-temperature coefficient (PTC) effect without any negative-temperature coefficient (NTC) effect. Resistivity and thermal reproducibility of the extruded heaters were investigated during heating and cooling cycles at an applied voltage of 220 V. These heaters initially showed poor reproducibility of resistivity during the repeated cycles and this effect increased significantly as the acetylene black content decreased. PTC effect and electrical reproducibility were improved significantly during the thermal ageing process. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1611–1617, 2004

Key words: silicones; elastomers; extrusion; positive-temperature coefficient (PTC); resistivity

INTRODUCTION

The resistivity–temperature behavior of polymeric composites filled with conductive carbon black (CB) exhibits a positive-temperature coefficient (PTC) effect.[1,2] However, these PTC materials show poor reproducibility of resistivity after a long time of use or when subjected to thermal cycles attributed to the change in dispersion of CB particles in the composites.[3] The PTC effect strongly depends on the specific type of conductive filler and characteristics of the polymer matrix including chemical structure, degree of crystallinity, processing conditions, and thermal history to which they were exposed. Bending or other deformations can cause serious problems in conductive plastics and elastomers used for resistors, strain-measuring devices,[4] or heating elements.[5]

Abdel-Bary et al.[6] reported that milling conditions have a marked effect on temperature dependency of the electrical conductivity of poly(styrene-*random*-butadiene rubber)/CB composites. In this system, the resistivity of the prepared samples increases with remilling and thermal-oxidative ageing. Many experimental results showed that the electrical reproducibility of the materials during heating and cooling cycles can be improved by doping different sized CBs or by crosslinking.[7,8]

The widely used high-output PTC heaters use polyvinylidenefluoride (PVDF) for the heating element and an ethylene tetrafluoroethylene copolymer (ETFE) for insulation. These materials are both mechanically strong, but they lack flexibility. Silicone rubber is one of a versatile family of semiorganic synthetics known as silicones. Silicone elastomers can be used up to 300°C. The elastomers remain flexible and are serviceable over a wide range of temperatures.

In this study, various output heaters were extruded with acetylene black–filled platinum-catalyzed silicone rubber. Resistivity and thermal reproducibility of the extruded heaters were investigated during heating and cooling cycles. The effect of thermal ageing on the electrical resistivity was also studied.

EXPERIMENTAL

Materials

Conductive silicone rubber (acetylene black 32 wt %, ECR 360U; Dow Corning, Korea) and dilution silicone rubber (K-730; Tail Chemical Co., Korea) were used as received. ECR360U and K-740 were a 1 : 1 mix of platinum-catalyzed (platinum-curing) silicone rubber. Platinum-catalyzed silicone was supplied with two components containing catalyst, fillers, and polydimethyl siloxane polymer. These components were blended in preparation for the vulcanization process. Other chemicals were used as received without further purification.

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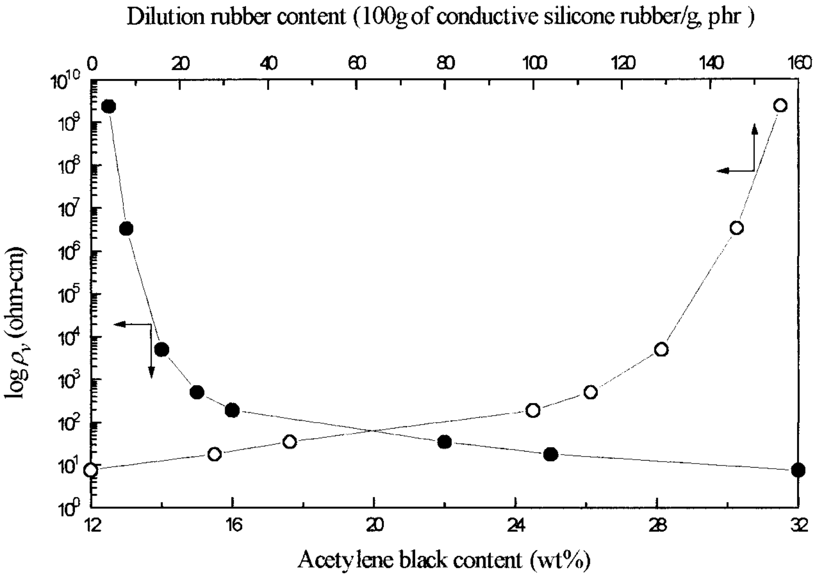


Figure 1 Volume resistivity (ρ_v) versus the acetylene black and dilution silicone rubber content.

Instrumentation

The thermal stability of samples was determined by thermogravimetry (TG, Perkin–Elmer TGS-2; Perkin Elmer Cetus Instruments, Norwalk, CT) scanning from 20 to 1000°C at a heating rate of 20°C/min.

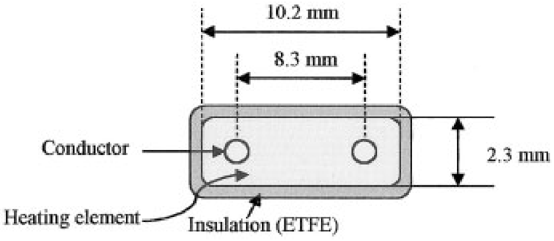
Tensile properties of conductive films were determined with a universal test machine (UTM, Model DECMC00; Dawha Test Machine, Korea) at a crosshead speed of 100 mm/min according to ASTM D 638 at 20 ± 2°C.

Measurement of volume resistivity

The conductive silicone rubber (7.62 Ω cm) and dilute silicone rubber (2.29×10^{13} Ω cm) were compounded with a two-roll mill at room temperature for 20 min. Conductive films were made by a mini roll-mixer at a fixed thickness and cured in a convection oven at 200°C for 1 h. Volume resistivity of the specimens was measured by a Wheatstone bridge (2755, Portable Wheatstone Bridge, Yokogawa, Japan) according to ASTM D 257 at 20 ± 1°C.

Extrusion of PTC heater

All the heating elements were extruded under a speed of 100 rpm using a single-screw extruder equipped with a 2.5-mm-diameter die and a 1 : 10 compression-ratio screw. Extruded samples were precured by passing through the heating box at 500°C. The out-jacket of heaters was extruded under a speed of 150 rpm using a single-screw extruder equipped with a 2.5-mm-diameter die and a 1 : 5 compression-ratio screw.



Conductor resistivity measurement of extruded heaters

Conductor resistivity (ρ_c) is defined as the resistivity between the conductors of an extruded heater per meter (Ω/m of heater). ρ_c was measured by a digital multimeter (HC-260TR; Hungchang Co., Korea). Each electrical probe of the multimeter was connected to the heater's conductor using an ETFE insulated cable and resistivity measurements were conducted at 20 ± 1°C. The measurements of the conductor resistivity–temperature behavior were conducted with a convection oven from 20 to 250°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

The volume resistivity (ρ_v) of prepared conductive films was calculated by use of the following equation:

$$\rho_v = \frac{AR_v}{L_e} \tag{1}$$

where A, R_v, and L_e, represent the area of the effective electrode (cm^2), measured resistance (ohms), and dis-

TABLE I
Volume Resistivity (ρ_v) and Tensile Properties of Silicone Rubber/Acetylene Black Composites

Sample code	Blend ratio[a] (Phr. 100 g/g)	CB content (wt %)	ρ_v (ohm cm)	Tensile properties: Tensile strength (kg f mm^{-2})	Max. load (kg f)	Elongation at break (%)
Conductive Silicone Rubber	pure	32.0	7.62	0.66 ± 0.02	3.0 ± 0.3	258 ± 10
CSR01	100/28	25.0	17.8	0.56 ± 0.02	2.5 ± 0.3	295 ± 12
CSR02	100/45	22.0	34.0	0.55 ± 0.03	2.5 ± 0.4	313 ± 20
CSR03	100/100	16.0	189.0	0.54 ± 0.03	2.4 ± 0.4	320 ± 28
CSR04	100/220	10.0	1.32×10^{10}	0.53 ± 0.04	2.4 ± 0.5	340 ± 37
Dilution Silicone Rubber	pure	0.0	2.29×10^{13}	0.49 ± 0.03	2.2 ± 0.4	404 ± 22

[a] 100 g of conductive silicone rubber/g of dilution silicone rubber.

tance between electrodes (cm), respectively. The value of ρ_v is extremely important in the design of heating elements.

Figure 1 shows the logarithmic ρ_v versus the acetylene black and dilution silicone rubber content. The ρ_v increased with increasing dilution silicone rubber loading levels. Elongation at break increased as well with dilution rubber content (Table I). A significant increase of ρ_v was observed when acetylene black content was less than 15.0 wt %.

The electrical resistivity change depends on the polymer matrix and formation of conducting pathways through the filler phase. Conductive CB consists of very fine particles fused together to form aggregates. Both the number of CB particles per aggregate and the shape of the aggregate affect the conduction level of the polymer/aggregate composite system.[9] It seems that conductive aggregates may be rapidly decreased as the dilution rubber loading level increase up to above 120 phr.

Silicone elastomers are cured either by peroxide curing or by platinum curing. The peroxide-cured system requires an additional postcuring step to remove byproducts generated by decomposition of the peroxide. In contrast, platinum curing provides a very low level of extractables. However, byproducts of platinum catalyst increase the resistivity.

Table II demonstrates conductor resistivity (ρ_c) of the extruded heater before and after the postcuring at 250°C for 1 h. Adhesion of silicone rubber and conductor were improved significantly after the postcuring process (Fig. 2). Decrease of ρ_c of the extruded heaters after the postcuring is ascribed to a decrease of the catalyst byproducts and to a decrease of surface resistivity (ρ_s) between the conductor and CB particles in the composites.

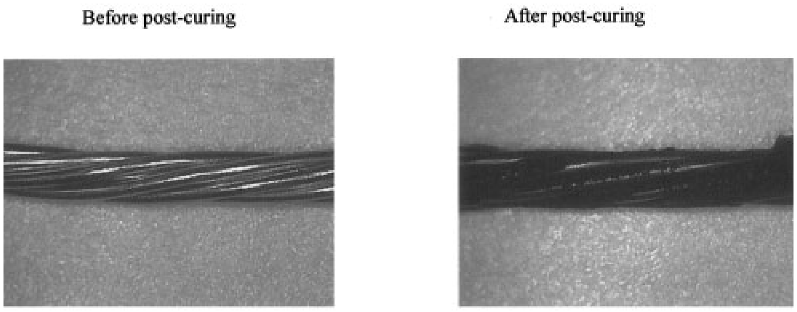
Figure 3 represents ρ_c and maximum heater-output temperature of the extruded heater as a function of the acetylene black content. The heater-output characteristics were measured at the heater surface temperature with applied AC voltage of 220 V. The heater can be used in the range from 40 to 150°C. ρ_c was determined according to the heater-output level.

Figure 4 indicates the conductor resistivity–temperature behavior of the extruded heaters. The PTC effect was significant when the acetylene black content was

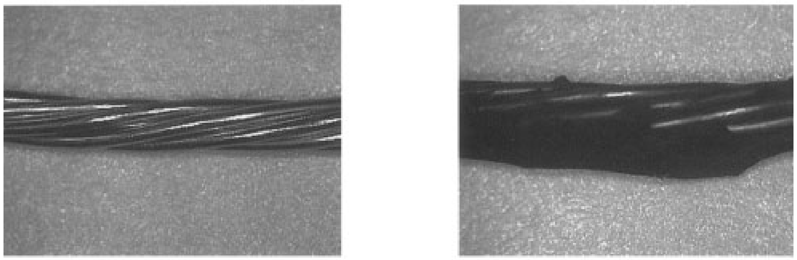
TABLE II
Heater-Output Properties of the Extruded Heater

Sample code	Acctylene black content	ρ_c (Ω/m, 20°C): Extruded	Postcured[a]	Thermally aged[b]	Output (watt/m, AC 220 V, 20°C)	Max. heater-output temperature (°C, AC 220 V)
Heater01	25.0	4	3	4	36[c]	76[c]
Heater02	22.0	10	8	10	14[c]	15[c]
Heater03	16.0	84	79	116	417	168
Heater04	14.5	218	168	240	202	106
Heater05	14.0	816	620	960	50	85
Heater06	13.5	2,330	1,630	2,500	20	50
Heater07	13.0	27,000	13,000	30,000	2	0

[a] Postcured at 250°C for 1 h.
[b] Thermally aged at 250°C for 7 days.
[c] At an applied voltage of DC 12 V.



(a) Heater03



(b) Heater04

Figure 2 Optical photographs of the conductor surface before and after postcuring.

less than 15.0 wt %. In sharp contrast, the PTC effect was almost undetectable at the acetylene black content of 25.0 wt %. This PTC variation is attributed to a breakdown of conductive pathways resulting from thermal volume expansion because the thermal expansion coefficient of the polymer matrix is different from that of the conductive filler.[10] Thus at a lower CB concentration, an increase of temperature easily breaks down contact and overlapping of CB.

Polyethylene filled with carbon black is a prototypical composite that displays resistance switching. These materials exhibit either a PTC or a NTC effect. The lack of electrical reproducibility and the NTC effect of the PE/CB composite discourage its use in application as PTC materials.[11–14]

In contrast, the platinum curing silicone rubber/acetylene black system did not show any NTC effect. Silicone rubber is very flexible because its backbone is

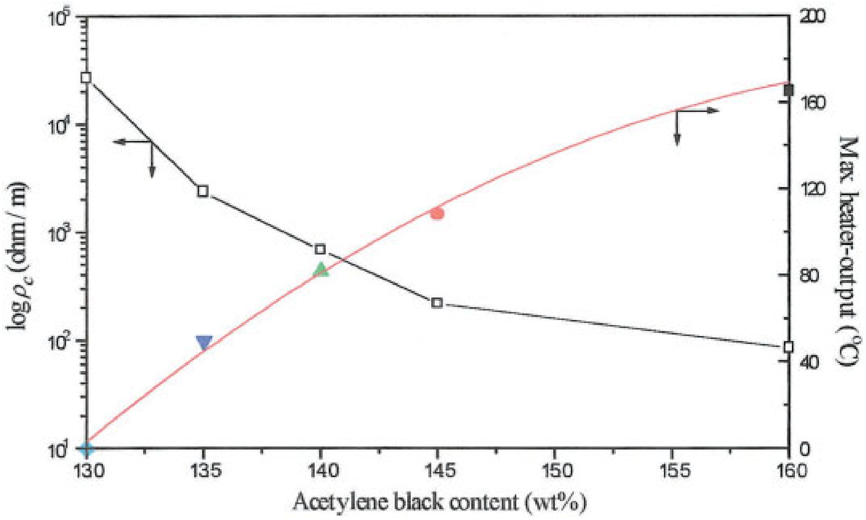


Figure 3 Conductor resistivity (ρ_c) and maximum heater-output temperature of the extruded heaters as a function of the acetylene black content.

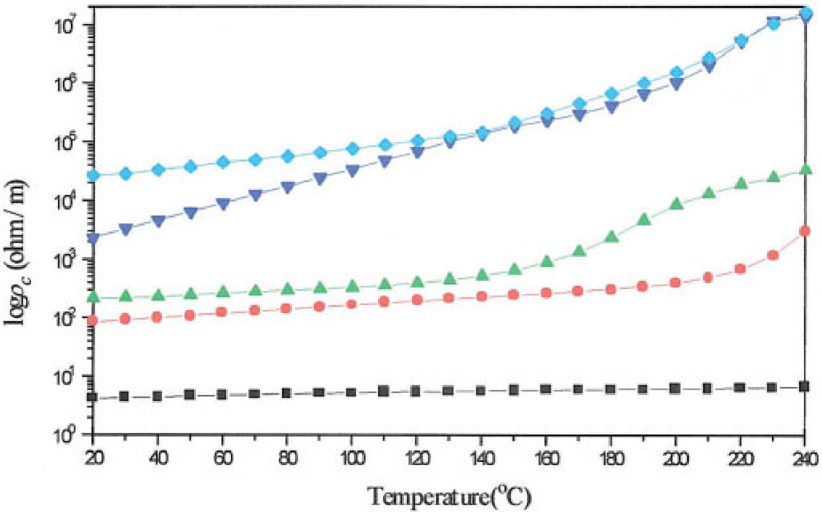


Figure 4 Conductor resistivity (ρ_c) of the extruded heaters as a function of temperature: ■, Heater01; ●, Heater03; ▲, Heater04; ▼, Heater06; ◆, Heater07.

not a chain of carbon atoms but an arrangement of silicone and oxygen atoms. High mobility of CB and the flexible polymer matrix are believed to cause the high PTC intensity.[11]

High-output heaters are designed for high-temperature process control in hazardous fields as well as in general ones. The heater should endure high temperature without serious deterioration. TGA analysis in Figure 5 reveals that the silicone rubber/CB composites were thermally stable up to 300°C.

Under long-term voltage applications, the heat-output reproducibility is one of the most important requirements for heating elements. Figure 6 demonstrates the stability of Heater04 subjected to heating and cooling cycles with a periodic change in voltage of AC 220 V. The switch was turned off after 10 min of voltage applications. After the heater cooled to room temperature, the voltage was applied again. As shown in Figure 6, a significant decrease of heater output was observed for Heater04 as the number of the cycles increased. It can be seen that after five runs resistivity and PTC intensity approached an asymptotic value and they became almost constant thereafter. Resistivity increased at an early stage of the cycling test because of gradual randomization of the aligned anisotropic conductive particles. Such effects were dependent on CB concentration. As the CB concentration decreased to the threshold percolation concentration, where transition from conductor to insulator occurred for the elastomer/CB system,[3] the increase of resistivity became more pronounced.

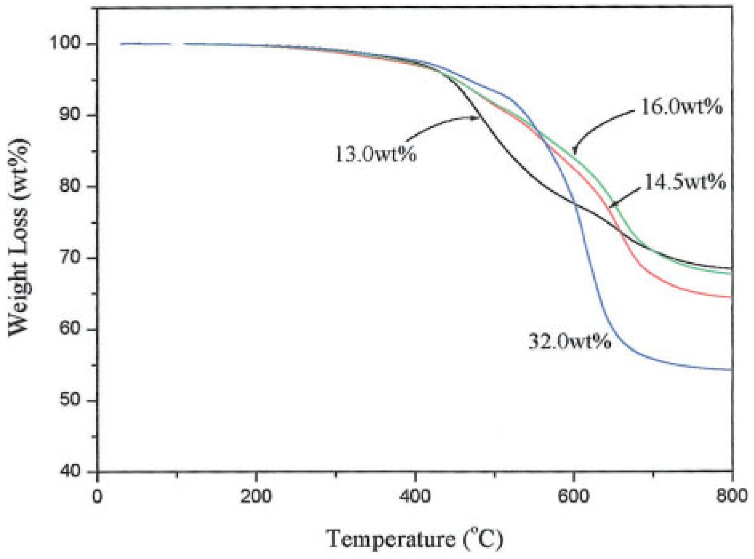
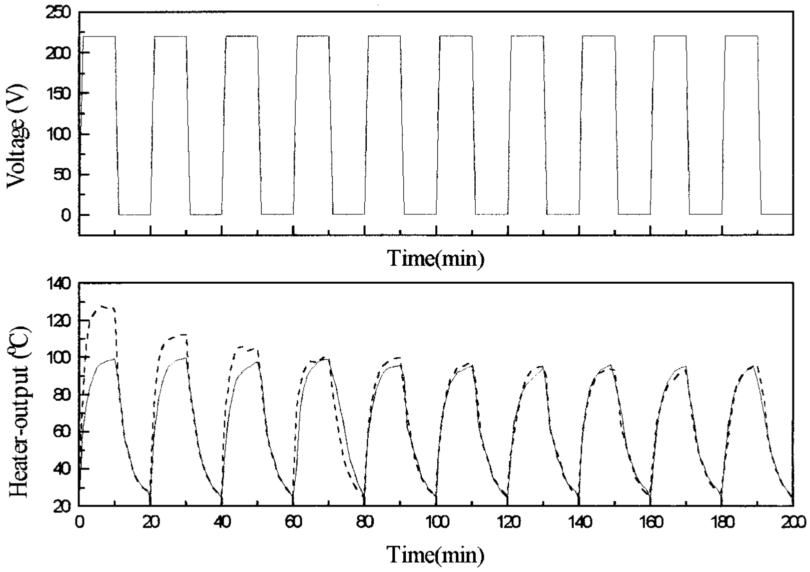
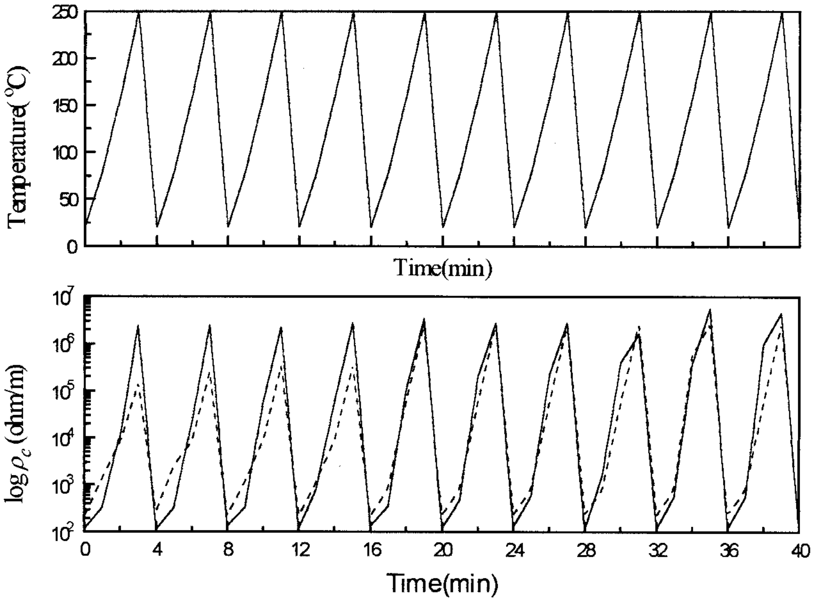


Figure 5 TGA curves of silicone rubber/acetylene black composites.



(a) Heater-output change due to periodic-change in voltage AC 220V



(b) Resistivity–temperature behavior of extruded heater

Figure 6 Cycling experiments of Heater04 containing 14.5 wt % acetylene black: - - -, before thermal ageing; —, after thermal ageing at 250°C for 7 days.

Figure 6 illustrates experimental results of the heating and cooling cycle for Heater04 before and after thermal ageing at 250°C for 7 days. After thermal ageing, no significant change was observed between the first and the 10th individual run, indicating that thermal ageing increased the heater-output reproducibility. Resistivity–temperature behavior of Heater04 was examined according to cycles composed of heating from 20 to 250°C and then cooling to 20°C. The PTC intensity of the heaters increased after the thermal ageing process. The electrical hysteresis and electrical set come mainly from an irreversible change in the conductive networks during the heating and cooling cycles. The resistivity increase of the heaters after the thermal cycles is attributed to variation of the dispersed state of CB particles in the composites.

Figure 7 shows the relative resistivity change of Heater04 as a function of the heating and cooling cycles. Here the relative resistivity is defined as the ratio of the ρ_c value to the corresponding value at 20°C. Resistivity increased at an early stage of the cycling test because of gradual randomization of the

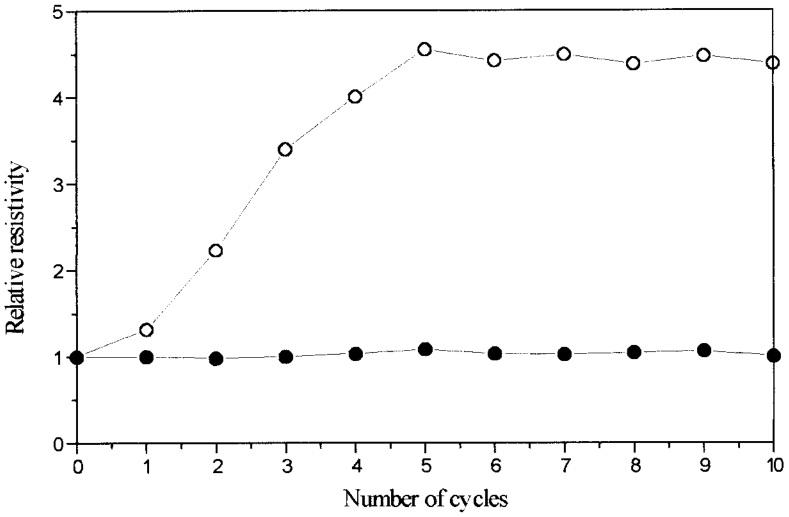


Figure 7 Relative resistivity of Heater04 before and after thermal ageing at 250°C for 7 days: ○, before thermal ageing; ●, after thermal ageing.

conductive aggregates and then approached a maximum value attributed to rebuilding of the carbon network previously destroyed during the heating step.

The thermal ageing of the heaters results in a tightening in the silicone rubber matrix, which increases the contact point between conductive particles and the metal electrode. As a result the conductive pathway may be more stabilized. The thermal ageing process also enhanced the randomization of the aligned conductive aggregates and thereby considerably improved the electrical reproducibility of the silicone elastomer/CB systems.

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