Resistivity and Thermal Reproducibility of Carbon Black and Metallic Powder Filled Silicone Rubber Heaters

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Received 12 January 2004; accepted 10 May 2004
DOI 10.1002/app.21340

ABSTRACT: Flexible heaters were prepared by extruding platinum-catalyzed silicone rubber composites with conductive carbon black (CB) and metallic fillers. The conductor resistivity of the extruded heaters decreased in order of conductive titanium dioxide (TiO_2) $>$ aluminum powder $\approx$ zinc powder $>$ copper powder. Thermoelectric switching phenomena were investigated for the silicone rubber/CB/metallic powder systems. The positive temperature coefficient effect was dependent mainly on the CB content rather than on the content of the metallic powders. Resistivity and thermal reproducibility of the extruded heaters were also investigated by periodically applying AC voltage of 110 V. The heaters containing copper and TiO_2 powders exhibited excellent electrical reproducibility. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1122–1128, 2005

Key words: electrical resistance; rubber; filler; composites

INTRODUCTION

Conductive elastomers usually employ vulcanized rubber as a matrix for dispersion of conductive fillers including metal powders, such as Al, Au, Ag, and Cu. Stainless steel, carbon, and graphite powders are also frequently employed as conductive fillers.[1–4] The fillers improves not only electrical conductivity but also electrical environmental resistance and mechanical properties. These elastomers exhibit good flexibility and processability and they are widely used as contact point materials for electrostatic charge dissipation, surface heaters, EMI shielding, and rubber contact switches.[5,6]

However, these materials frequently lack in reproducibility of resistivity when they are used for a long period of time or when they are subject to thermal cycles.[7] Bending or other deformations of the conductive plastics or elastomers can sometimes cause failure as resistors, strain measuring devices,[8] or heating elements.[9]

Narkis and Vaxman[10] reported that high-density polyethylene /carbon black (CB)/carbon fiber composites containing very low concentration of carbon fibers exhibited significant switching behavior. Chaki and colleagues[11] reported that silicone rubber (SR) composites containing acetylene black and short carbon fiber showed a high level of conductivity and the percolation region for conduction appeared at much lower concentration compared to NBR and EPDM, especially when carbon fiber was used as conductive filler. Many experimental results revealed that the electrical reproducibility of the materials during heating and cooling cycles can be improved by doping different sized CBs.[12]

Silicone elastomers are often used as a polymer matrix for preparation of conductive composites because they are stable in a wide range of temperatures and have excellent weather and chemical resistance properties. In this study, flexible heaters were prepared by extruding platinum-catalyzed SR/CB/metallic filler composites. Thermoelectric switching phenomena of the composites with conductive titanium dioxide (TiO_2), zinc, copper, and aluminum powder were explored. Resistivity and thermal reproducibility of the heaters were also investigated during repeated heating and cooling cycles by periodically applying AC voltage of 110 V.

EXPERIMENTAL PROCEDURES

Materials

Platinum-catalyzed electroconductive SR (acetylene black 32 wt %, 7.62 Ω-cm, ECR 360U, Tail Chemical Co., Korea) and platinum-catalyzed SR (K-730, 2.29 $\times$ 10^{16} Ω-cm, Tail Chemical Co.) were used as received. Conductive titanium dioxide (2.5 Ω-cm, Bricem, Beijing, China) was used as received. Copper (SK-1, 95%), aluminum (SKAl1, 98%), and zinc (SK-2, 92%) powder were purchased from Sunkwang Metal

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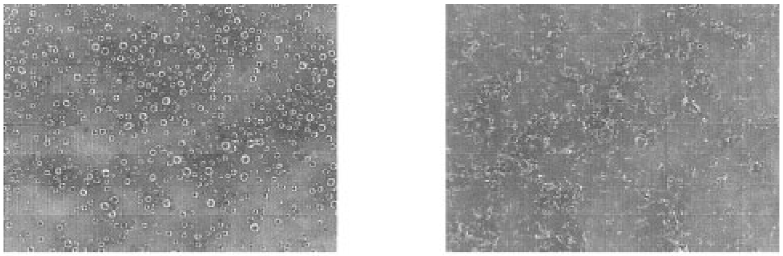
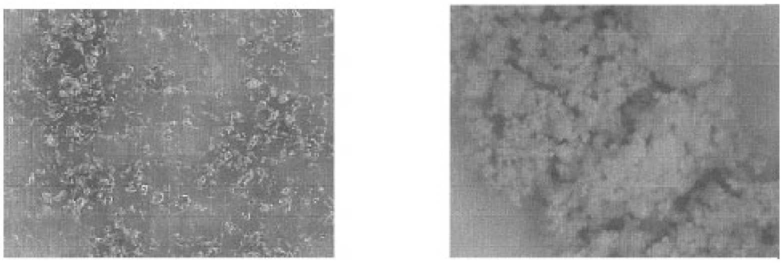
Journal of Applied Polymer Science, Vol. 95, 1122–1128 (2005)



(a) copper powder (b) aluminum powder



(c) zinc powder (d) TiO_2 powder

Figure 1 Optical photographs of the metallic powder (80×).

(Korea). The conductive fillers were dried under a vacuum at 60°C for 48 h. Other chemicals were used as received without further purification.

Instrumentation

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

Tensile properties of the conductive films were determined using a universal test machine (UTM, Model No. DECMC00, Dawha Test Machine, Korea) at a crosshead speed of 100 mm/min according to ASTM D 638 at 20 ± 2°C.

SEM (*S*-4200, Hitach, Japan) was used to observe the fractured surface morphology. Specimens were fractured in liquid nitrogen.

Measurement of volume resistivity

Conductive SR, dilute SR, and conductive fillers were compounded in a two-roll mill at room temperature for 20 min. Conductive films were made by mini roll-mixer at a fixed thickness and cured in a convection oven at 250°C for 1 h. Resistivity of the specimens was measured by wheastone bridge (2755, Portable Wheastone Bridge, Yokogawa, Japan) according to ASTM D 257 at 20 ± 1°C. Volume-resistivity (ρ_v) of the prepared conductive films was calculated using Eq. (1),

$$\rho_v = \frac{AR_v}{L}, \tag{1}$$

Where A, R_v, and L represent the sectional area of the electrode (cm^2), the measured resistance (Ω), and the distance between the electrodes (cm), respectively.

TABLE I
Volume Resistivity of the SR/CB/Conductive Filler Composites[a]

	Volume resistivity (ρ_v,Ω-cm)					
Sample code	84.0/16.0/5.0	85.0/15.0/5.0	85.5/14.5/5.0	86.0/14.0/5.0	86.5/13.5/5.0	87.0/13.0/5.0
SR/CB	647	3,400	6,050	12,110	30,100	63,840
SR/CB/Cu	120	310	490	880	1,810	53,500
SR/CB/Al	175	620	1,290	2,230	4,960	52,980
SR/CB/Zn	280	910	1,600	3,970	7,310	54,570
SR/CB/TiO_2	200	660	1,500	2,860	5,290	53,070

[a] SR/CB/conductive filler content on weight basis.

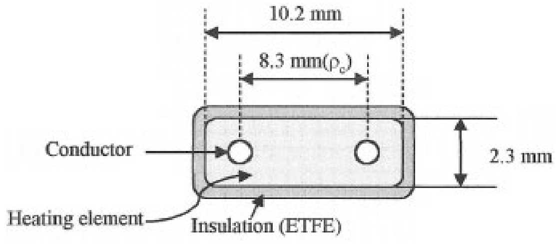


Figure A

Extrusion of PTC heater

All heating elements were extruded at 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 passage through a heating box at 500°C. The outer insulation of heating elements was extruded at 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 resistivity between the conductors of extruded heater per meter (Ω/m of heater). ρ_c was measured using a digital multimeter (HC-260TR, Hungchang Co. Ltd., Korea). As shown in Figure A 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 ρ_c versus temperature behavior were conducted in a convection oven from 20 to 250°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Figure 1 shows the optical microphotography of the conductive fillers. Copper powder was spherical in shape with diameter of ca. 50 μm. Zinc and aluminum powders were of irregular shape with approximately 50 μm length. Conductive TiO_2 particles had a granular shape with 5 to 10 μm diameter. The powder resistivity of the fillers decreased in order of TiO_2 (2.5×10^{-5} Ω-cm) > zinc (6.0×10^{-6} Ω-cm) > aluminum (2.7×10^{-6} Ω-cm) > copper (2.5×10^{-6} Ω-cm).

The conductive SR, dilute SR, and metallic powders were compounded in a two-roll mill at room temperature and cured in a convection oven at 250°C for 1 h. The logarithmic volume resistivity (ρ_v) versus the content of CB/conductive filler was measured and the results are summarized in Table I. The ρ_v of the composites decreased in order of zinc > TiO_2 > aluminum > copper powder (Fig. 2). The conductivity of the composites depends mainly on the filler type, size, shape, and orientation within the matrix. For the spherical particles and for the smaller particles the percolation threshold is lower.[12] Spherical fillers are much more conducive than fillers with irregular shape, which could be predicted intuitively.

Morphologies of the platinum-catalyzed SR/CB/metallic powder composite are shown in Figure 3. It can be seen that various conductive networks were formed depending on the filler shape. The shape of the conductive network determines the room temperature resistivity of the composites.

Table II demonstrates the tensile properties of SR/CB/metallic powder composites. When spherical copper powder was used as filler, the tensile strength increased by 25%, whereas for aluminum powder the increase in tensile strength was limited to 10%, indicating that tensile strength of the composites depended largely on the surface morphology of the filler particles. That is to say, fillers with a rough surface such as aluminum powder bring about lower tensile strength of the composites compared to fillers with a smooth surface such as copper powder. Irregularly shaped particles occupy larger effective volume than particles with a spherical shape. As a result, the composites with irregularly shaped fillers have lower elongation at break compared to the composites with spherical fillers.

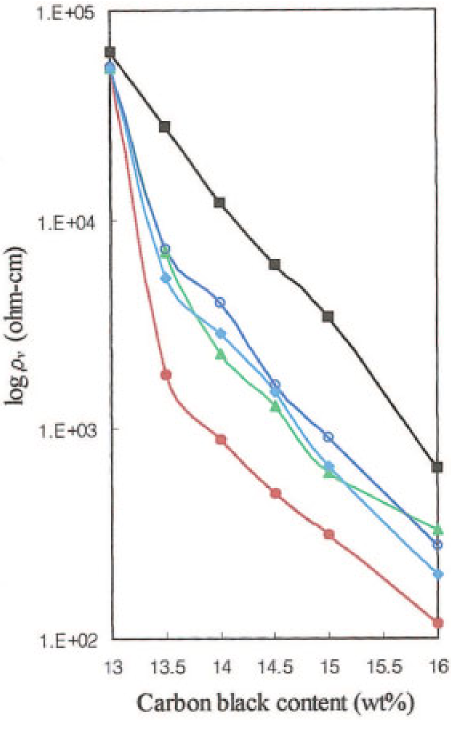
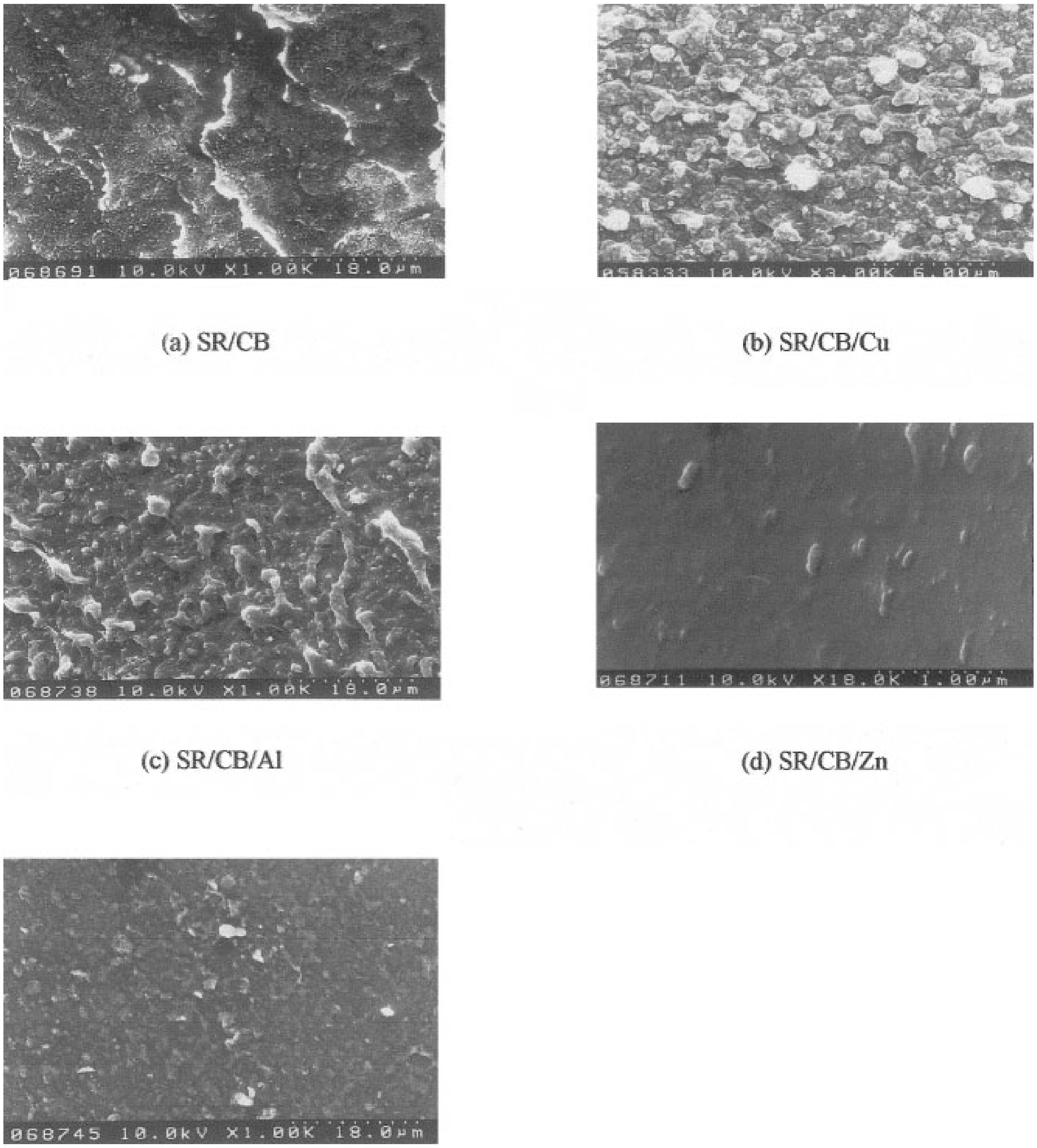


Figure 2 Volume resistivity (ρ_v) as a function of the CB content. The content of the conductive fillers was fixed at 5 parts per 100 SR/CB composite. (■) SR/CB, (○) SR/CB/Zn, (♦) SR/CB/TiO_2, (▲) SR/CB/Al, (●) SR/CB/Cu.



(a) SR/CB

(b) SR/CB/Cu

(c) SR/CB/Al

(d) SR/CB/Zn

(e) SR/CB/TiO_2

Figure 3 Scanning electron micrographs of the fractured surface of the extruded composites.

TABLE II
Tensile Properties of the SR/CB/Conductive Filler Composites[a]

Sample code	Tensile properties		
	Tensile strength (kg_f/cm^2)	Maximum load (Kg_f)	Elongation at break (%)
SR/CB	0.39 ± 0.08	3.3 ± 0.2	334 ± 24
SR/CB/Cu	0.49 ± 0.06	4.2 ± 0.3	313 ± 16
SR/CB/Al	0.43 ± 0.18	3.4 ± 0.2	263 ± 42
SR/CB/Zn	0.41 ± 0.12	3.7 ± 0.2	261 ± 26
SR/CB/TiO_2	0.52 ± 0.04	4.1 ± 0.4	320 ± 32

[a] SR/CB/conductive filler content: 85.5/14.5/5.0 on weight basis.

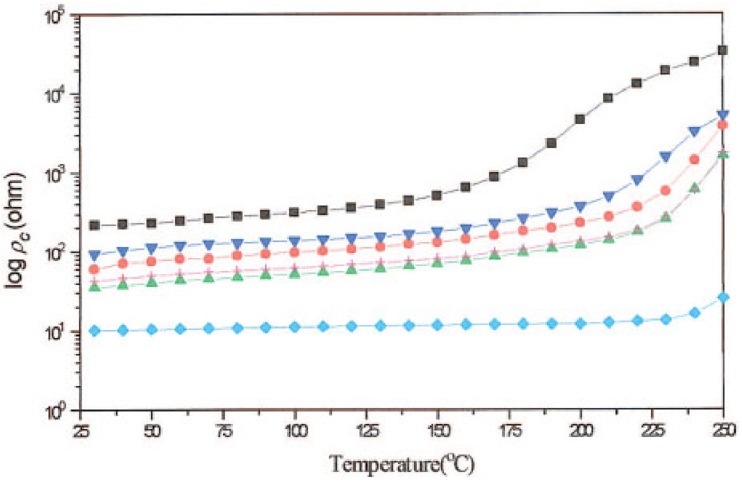


Figure 4 Resistivity–temperature behavior of the extruded heaters. (■) Heater-CB14.5, (▼) heater-TiO_2, (●) heater-Cu, (+) heater-Zn, (▲) heater-Al, (♦) heater-CB19.5.

Figure 4 reveals variation in the room temperature resistivity and PTC intensity of the extruded heaters. A significant PTC effect was observed when the CB content was 14.5 wt %. In sharp contrast, the PTC effect was almost undetectable when the CB content was 19.5 wt %. The addition of 5 parts metallic powder to 100 parts of SR/CB 85.5/14.5 composite did not decrease the PTC intensity significantly.

The PTC phenomenon is attributed to the separation of conductive pathways by thermal volume expansion that is due to the difference in the expansion coefficient between the polymer matrix and the conductive fillers.[10] At higher CB loading, the conductive networks increase and the average interparticle gap becomes smaller. Therefore, the contact pressure of particle becomes higher and the network breakdown process becomes less efficient. As a result, the rate of increase in resistivity is reduced for higher CB filled composites.

In contrast, PTC intensity was remarkably higher when 5 parts of metallic powder was added instead of CB. The threshold concentration is roughly attained by adding 25% v/v spherical metal particles, 5% v/v conductive CB, or 1% v/v metal particles with high aspect ratio or carbon fibers.[10] The PTC phenomenon was mainly controlled by the fillers with lower percolation threshold rather than those with higher percolation threshold.

Table III demonstrates conductor resistivity (ρ_c) of the extruded heater before and after postcuring at 250°C for 1 h. ρ_c is defined as the resistivity between the conductors. The decrease in ρ_c of the extruded heaters after postcuring is attributed to the decrease in resistivity between the conductors and CB particles in the composites and to the decrease in catalyst by-products. Postcuring of the heaters toughened the SR matrix, which increased the contact pressure between the conductive particles and thereby the total conductivity was increased.

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

TABLE III
Characterization of the Extruded Heaters

Sample code	SR/CB/filler content (wt %)	Conductor resistivity (ρ_c,Ω)			Output (W/m, 110 V, 25°C)	Maximum heater-output temperature (°C)
		Extruded	Postcured[a]	Thermally aged[b]		
Heater-CB19.5	80.5/19.5/0.0	10	8	10	n.d.[c]	n.d.
Heater-CB14.5	80.5/14.5/0.0	218	168	240	50	112
Heater-Cu	80.5/14.5/5.0	61	44	44	280	183
Heater-Al	80.5/14.5/5.0	33	31	76	160	141
Heater-TiO_2	80.5/14.5/5.0	91	87	128	95	152

[a] Postcured at 250°C for 1 h.
[b] Thermally aged at 250°C for 24 h.
[c] Not determined.

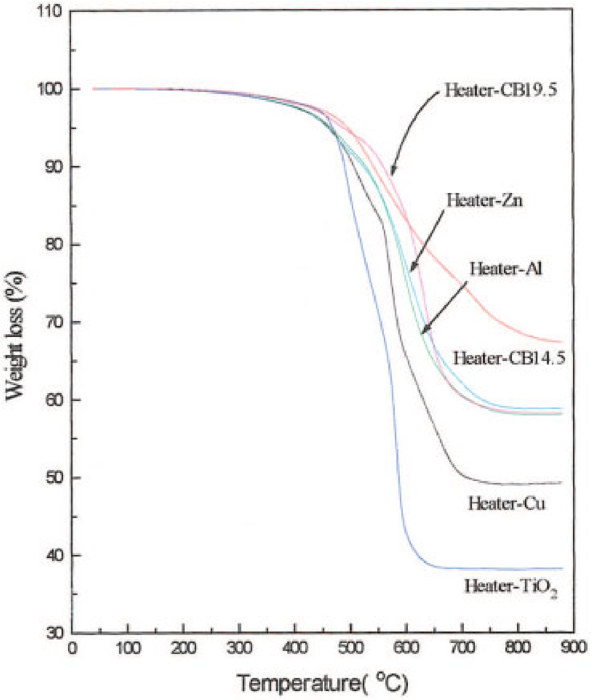


Figure 5 Thermogravimetry analysis (TGA) of the silicone rubber/CB/metallic powder composites.

Under long-term voltage applications, the heater-output reproducibility is one of the most important requirements for heating elements. Figure 6 demonstrates the reproducibility of the heater output of postcured heaters subjected to heating and cooling cycles with periodic change in applied voltage of AC 110 V. The switch was turned off after 10 min of voltage applications. When the heater cooled down to room temperature, the voltage was applied again. As shown in Figure 6, no significant difference was found for heater-Cu and heater-TiO$_2$ between the 1st and the 10th cycles. However, the decrease in heater output was significant for heater-Al as the number of the cycles increased. Resistivity changed at an early stage of the cycling test due to gradual randomization of the conductive aggregates and then approached a maximum value due to rebuilding of the conductive network, which had been destroyed previously during the heating step. The electrical hysteresis and electrical set come mainly from an irreversible change in the conductive networks during the heating and cooling cycles.

Figure 7 shows a change in the relative resistivity of the postcured heaters as a function of the heating and

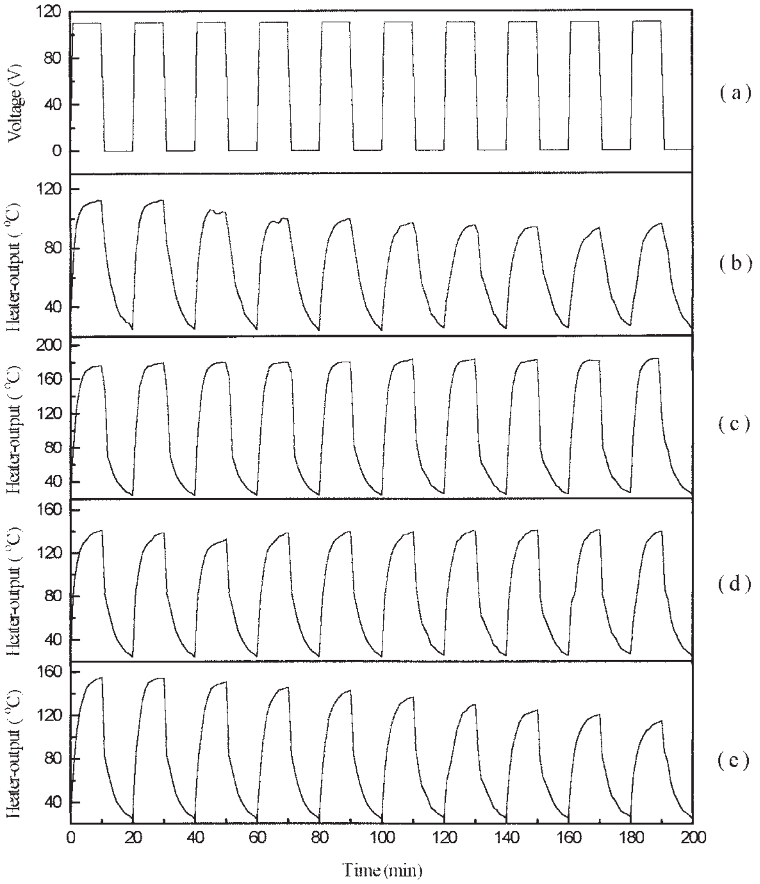


Figure 6 Cycling experiments of the postcured heaters with periodic change in applied voltage. (a) Periodic change in applied voltage AC 110 V; (b) heater-CB; (c) heater-Cu; (d) heater-TiO$_2$; (e) heater-Al.

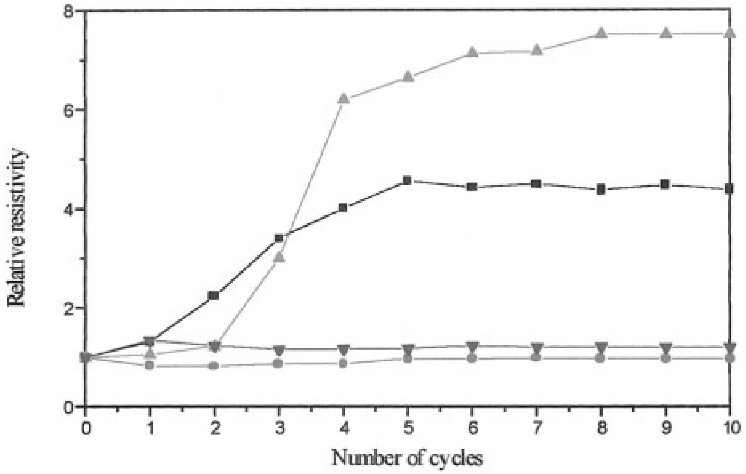


Figure 7 Change of the relative resistivity of the postcured heaters during the cycling experiments. (▲) Heater-Al, (■) heater-CB14.5, (▼) heater-TiO_2, (●) heater-Cu.

cooling cycles. Here the relative resistivity is defined as the ratio of the ρ_c value to the corresponding value of the postcured heaters at 20°C. A significant reproducibility of resistivity was exhibited for the heaters containing copper and TiO_2. The resistivity change of the heater-CB14.5 after the thermal cycles was ascribed to variation in the dispersed state of CB particles in the composites. The addition of copper and TiO_2 powder enhanced the dispersion state of CB due to the increase of the contact points between the particles without reducing the thermoelectric switching effect.

After the thermal aging process, the ρ_c of the heater-Al was significantly increased, as shown in Table III. Bigg[3,4] reviewed the development of the electrical properties of metal filled polymers and the mechanisms involved in the formation of conductive composites of polymer/metallic filler systems. Metallic powders generally suffer from oxidation and the corresponding deterioration of the electrical properties of the composite comes from the nonconductive nature of such oxide layers. Oxidation takes place more readily on aluminum powder than on copper powder. As a result, heater-Al exhibited poor thermal and resistivity reproducibility after the heating and cooling cycles.

The support of post-doc fellowship for L. W. J. is greatly acknowledged from the Brain Korea 21 project in 2003.

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