Novel Heat-Conductive Composite Silicone Rubber

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ABSTRACT: The silicone rubber with good thermal conductivity and electrical insulation was obtained by taking vinyl endblocked polymethylsiloxane as basic gum and thermally conductive, but electrically insulating hybrid Al_2O_3 powder as fillers. The effects of the amount of Al_2O_3 on the thermal conductivity, coefficient of thermal expansion (CTE), heat stability, and mechanical properties of the silicone rubber were investigated, and it was found that the thermal conductivity and heat stability increased, but the CTE decreased with increasing Al_2O_3 fillers content. The silicone rubber filled with hybrid Al_2O_3 fillers exhibited higher thermal conductivity compared with that filled with single particle size. Furthermore, a new type of thermally conductive silicone rubber composites, possessing thermal conductivity of 0.92 W/mK, good electrical insulation, and mechanical properties, was developed using electrical glass cloth as reinforcement. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2478–2483, 2007

Key words: silicone rubber; alumina; elastomeric thermal pads; thermal conductivity

INTRODUCTION

In recent years, thermally conductive materials with high thermal conductivity, low coefficient of thermal expansion (CTE), and high electrical resistance attracted more and more attentions because of their important uses in many occasions.[1] Recent advancement in electronics technology has resulted in the miniaturization of transistors, allowing more transistors to be crammed and integrated into a single device, resulting in a higher performance device.[2–5] Nevertheless, integration and cramming of transistors has resulted in the escalation of power dissipation as well as an increase in heat flux at the devices. So, the heat dissipation problem is of great importance to the lifespan of the higher performance device, since it is well known that the reliability of devices is exponentially dependent on the operating temperature of the junctions, whereby a small difference in operating temperatures (in the order of 10–15°C) can result in a two times reduction in the lifespan of a device.[6–8] Therefore, it is essentially crucial for the heat generated from the devices to be dissipated as quickly and effectively as possible, to maintain the operating temperatures of the device at a desired level.[9]

The various methods employed to dissipate heat accumulated from the devices include the attachment of a high thermal conductivity and low CET heat sink on the devices.[10] However, without good thermal contacts the performance of a high thermal conductivity heat sink to dissipate heat is limited because of interfacial thermal resistance arising from nonsurface flatness and surface roughness of both the devices and heat sink. Nonsurface flatness is commonly observed in the form of convex, concave, and wavy surfaces, resulting in as much as 99% of the interfaces being separated by air gaps.[11] Interstitial air gaps trapped due to improper mating of the surfaces significantly reduce the capability to dissipate heat, due to the low thermal conductivity value of air ($k_{\text{air}} = 0.026$ W/mK). One method that is commonly used to reduce the thermal contact resistance between the two surfaces is to include an additional material, commonly referred as thermal interface material (TIM), to provide an effective heat path,[12–14] as shown in Figure 1.

TIMs are typically made up of polymer or silicone matrix reinforced with highly thermally conductive but electrical insulating fillers such as alumina, aluminum nitride, boron nitride, and silicon carbide. An ideal TIM should have both high thermal conductivity and low CTE. In addition, the material must be easily deformed by small contact pressure to contact all the uneven areas of the mating surfaces.[1]

As one of the TIMs, the elastomeric thermal pads, which are mainly made of rubber filled with thermally conductive fillers, are popular for cooling of low-power devices, such as chip sets and mobile processors.[15,16]

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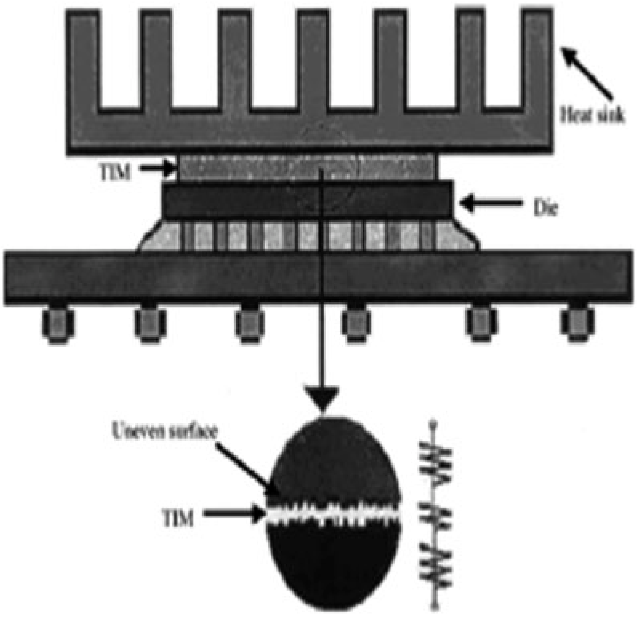

Figure 1 Surface roughness between heat sink and device filled with TIM.

The advantage of elastomeric thermal pads is that they are easy to handle, in addition to being compressible to 25% of their total thickness, enabling the pads to absorb tolerance variances in assemblies.[17]

The elastomeric thermal pad made of silicone rubber filled with alumina (Al_2O_3) fillers has been seldom studied before. So, the purpose of this study was to develop elastomeric thermal pad from vinyl endblocked polymethylsiloxane and hybrid Al_2O_3 fillers, and investigate the effects of the content of Al_2O_3 on the thermal conductivity, curing behavior, and thermal stability of the silicone rubber. Further, based on the developed elastomeric thermal pad, the attempt was made to develop a new type of reinforced elastomeric thermal pad using electrical glass cloth as reinforcement.

EXPERIMENTAL

Materials

Silicone rubber is vinyl endblocked polymethylsiloxane (type: 101B) manufactured by Chenguang Chemical Co., Chengdu, China, while the curing agent used is 2,5-bis(*tert*-butyl peroxy)-2,5-dimethylhexane, and processing oil is dimethyl hydroxy silicone oil emulsion, both purchased from Northwest Research Academy of Rubber, China. The thermal conductive fillers are α-phase alumina (Al_2O_3) with purity of 99.9% and average particle size of 3 and 20 μm, respectively, from Pengda Powder Co., China. The other fillers are calcium carbonate ($CaCO_3$) and gaseous phase white carbon black (SiO_2) with purity of 99.5%, supplied by Shenyang Chemical Co., China. The reinforcement is electrical glass cloth with the type of 2116 supplied by Gongkong Glass-Fiber Co., China. The properties of the materials used are shown in Table I.

Sample preparation

The recipe of composite silicone rubber is shown in Table II. Silicone rubber was first mixed with SiO_2, $CaCO_3$, and processing oil, followed by the addition of Al_2O_3 fillers and curing agent. The compounding was carried out on a two-roll mixing mill (Type: S K-106B, China), and the total mixing time for all the different concentrations was kept at 30 min.

The gross silicone rubber was dissolved in the distilled gasoline, and the viscosity of dissolved gross silicone rubber was adjusted to 0.5–0.8 Pa s. Then, the electrical glass cloth treated with silane coupling agents was placed in the silicone rubber bath; after finishing impregnation, the impregnated reinforcement was dried in oven.

A stainless steel mold was used, and the filled silicone rubber samples with or without reinforcement were compression molded at 165°C and a pressure of 10 MPa for 10 min in an electrically heated hot press (Type: SL-45, China).

Characterization

The differential scanning calorimeter (DSC), Model MDSC2910, was used to analyze the effect of filler on the curing reaction of Al_2O_3-filled silicone rubber. Measurements were conducted in a nitrogen atmosphere, from room temperature to 300°C, at a heating rate of 2°C/min.

Weight loss of the composite silicone rubber upon heating was measured using the Thermogravimetric analyzer, Model Q50. Measurements were conducted in an air atmosphere, from room temperature to 800°C, at a heating rate of 10°C/min. Then, the observed weight loss was analyzed.

CTE measurement was measured using the linear expansion apparatus (Model: AXT200, China) accord-

TABLE I
Properties of Al_2O_3 and Silicone Rubber

Properties	Al_2O_3	Silicone rubber
Density (g/cm^3)	3.98	1.05
CTE (10^{-6}) (°C)	7.2	285
Thermal conductivity (W/mK)	33	0.2
Volume resistivity (Ω cm)	$\geq 10^{14}$	$\geq 10^{16}$
Dielectric constant	7.0	3.5
Mean particle size (μm)	3 and 20	

TABLE II
The Recipe of Composite Silicone Rubber

Raw materials (g)	Content
Silicone rubber	100
Al_2O_3	Variant
White carbon black	15
$CaCO_3$	5
Curing agent	0.5–1
Processing oil	1–1.5

ing to Standard GB1036-89. The samples for CTE measurements are 6 mm × 6 mm × 20 mm in size and were prepared from the hot pressed panels. CTE was determined from the slope of thermal expansion versus temperature.

Thermal diffusivity of the composite silicone rubber was measured on Netzsch system (LFA427, German). Then, the thermal conductivity was calculated from thermal diffusivity by the following equation:

$$\lambda = \alpha\rho C_p$$

where λ, α, ρ, C_p are the thermal conductivity (W/mK), thermal diffusivity (cm^2/s), density (g/cm^3), and specific heat capacity (J/kg K)of the material under constant pressure. The thermal diffusivities of samples were measured at room temperature (in air) and elevated temperature (in argon). Samples were dried for at least 2 days in a desiccator before measurements were conducted.

Morphological observations on the composite silicone rubber were done by means of the scanning electron microscope (SEM), Model KYKY-2000. Observations were carried out on the cross section of the composite silicone rubber to study the Al_2O_3 distribution and morphology.

Volume resistivity measurement was performed on an ultrahigh electric resistor apparatus (Model: ZC-36, China) according to the standard GB/T1410-1989. Dielectric constant measurement was measured on a Dielectric Constant Apparatus (Model: S914, China) following the standard GB/T1410-1989, and breakdown voltage measurement was conducted with the apparatus (Model: TNC, China) adopting the standards GB/T1408-1999.

The mechanical strength tests of the samples were conducted on a screw-driven universal testing machine (Model:ZMGI250, China) at a cross-head speed of 10 mm/min to determine tensile strength, adopting China standards GB/T1040-1992, and the tearing strength was measured on a Dynatup Instrument. In addition, Shore hardness was measured with hardness tester (Type: Shore A, China), and the viscosity of the dissolved filled rubber was measured on a rotational viscosimeter (DNJ-1, Shanghai, China) according to GB 7193-1987.

RESULTS AND DISCUSSION

Thermal conductivity

It is well known that the transport of heat in polymers occurs by the flow of phonons or lattice vibrations.[18] The most polymeric materials exhibit very poorer heat conduction because the transport of heat occurs only by phonons resulting from their very low crystallinity compared with some ceramics materials.[19] Since the intrinsic high thermal resistance of polymers is caused by various types of phonons scattering processes, to maximize the thermal conductivity, these phonons scattering processes must be minimized. The interfacial thermal barriers in polymer composites are mainly due to the scattering of phonons resulting from acoustic mismatch and flaws associated with the filler–matrix interface. So, there are two main methods of improving the thermal conductivity of composites, namely (a) forming conductive networks through appropriate packing of the fillers in the matrix, and (b) decreasing the amount of thermally resistant junctions involving a polymer layer between adjacent filler units by using large filler units with little or no defects.[18]

The thermal conductivity of Al_2O_3 filler is much larger than that of silicone rubber. Therefore, the addition of Al_2O_3 into silicone rubber would increase the thermal conductivity, and the content and particle size of Al_2O_3 have obvious effect on the thermal conductivity. To obtain high thermal conductivity, the hybrid fillers with different particle sizes are suggested. The thermal conductivity of silicone rubber filled with hybrid Al_2O_3 fillers is higher than that of silicone rubber filled with the filler of single particle size.[19,20] As seen from viewpoint of bridging, the use of hybrid Al_2O_3 fillers with different particle sizes would result in the highly compact packing structure in silicone rubber and the more formations of random bridges or networks from conductive particles, which facilitates phonon transfer and leads to high thermal conductivity. So, in this study, to obtain maximum thermal conductivity of silicone rubber through the two ways mentioned earlier, two kinds of Al_2O_3 with different average particle sizes (20 μm, 3 μm) were employed at the mass ratio of 3:2, and the effect of the content of hybrid fillers on the thermal conductivity of the composite silicone rubber is shown in Figure 2.

It can be seen from Figure 2 that the thermal conductivity increased slowly with increasing Al_2O_3 loading below 37 wt %. When the loading was greater than 37 wt %, the thermal conductivity increased quickly, and reached 0.92 W/mK at the loading of 55 wt %, compared with 0.2 W/mK for the unfilled silicone rubber. Since the conductive particles surrounded by silicone rubber can not touch another at low loading of filler, the thermal contact resistance is

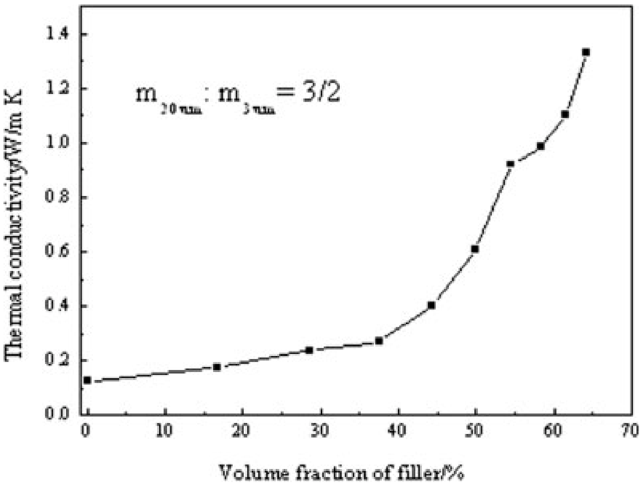

Figure 2 Thermal conductivity of silicone rubber versus amount of hybrid Al_2O_3 particles.

high. Therefore, the addition of conductive particles does not improve thermal conductivity of the system effectively. While, as increasing the filler content, conductive particles begin to touch each other and form more highly compact packing structure. So, the layer of silicone rubber between the particles becomes thinner and thinner, and the thermal contact resistance decreases quickly. Moreover, the use of larger particle size tends to form fewer thermally resistant junctions of the silicone rubber layer than the smaller particle size at the same filler content. Therefore, the mixture of large and small particle size at the mass ratio of 3 : 2 is advantageous over sole particle size used alone. This could be attributed to the fact that small particles easily occupy the space where large particles can not occupy, and the more conductive pathways are formed in silicone rubber (as seen from Fig. 3). In addition, the mechanical properties of the composites were not worsened obviously by use of hybrid fillers. As for the content of filler, it had better not exceed 58 wt % because the viscosity of filled silicone rubber increased sharply, making it very difficult for the filled silicone rubber to be solved in gasoline. Moreover, mechanical properties became deteriorated. So, the preferable content of Al_2O_3 was 55 wt % according to the experimental results. The mechanical properties and the strain–stress curve of the silicone rubber filled with different content of filler are shown in Table III and Figure 4, respectively.

Thermal stability

Figure 5 shows the TGA results of silicone rubber filled with 44 and 55 wt % of Al_2O_3 filler, respectively, with an unfilled silicone rubber as a comparison. It can be seen from Figure 5 that the addition of Al_2O_3 into silicone rubber improved its thermal stability, as at 200°C, a relative weight loss of 2.10 wt % was observed for the unfilled rubber compared with 0.62 and 0.50 wt % for the 44 and 55 wt % of Al_2O_3-filled rubber, respectively. When further heated to 300°C, a relative weight loss of 4.08 wt % was observed for the unfilled rubber compared with 0.68 and 0.56 wt % for the 44 and 55 wt % of Al_2O_3-filled rubber, respectively. It was also found that the initial decomposition temperature of the filled rubber was enhanced greatly compared with the pure silicone rubber, and the inclusion of Al_2O_3 in silicone rubber improved remarkably the thermal stability. That could be explained by the interaction between the filler and silicone rubber, which leads to the increase in physical and chemical crosslinking points, and the thermal-stable Al_2O_3 filler, which limited the segmental movement of silicone rubber.[1] Therefore, the filled silicone rubber has good high-temperature resistance, being very suitable for use in TIMs.

Effect of filler on curing behavior

The effect of Al_2O_3 filler on the curing behavior of silicone rubber was investigated by DSC, and the ex-

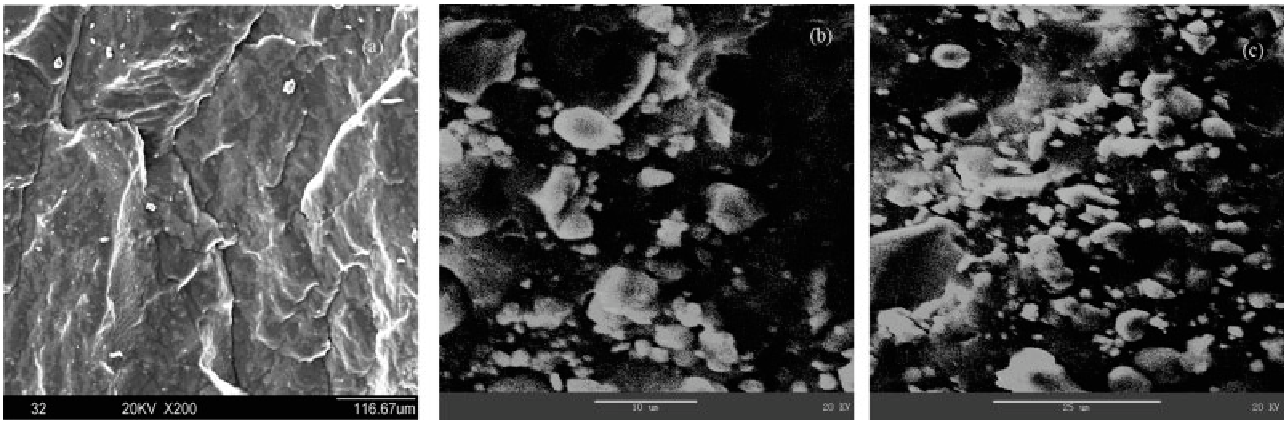

Figure 3 Micrograph of the cross section of silicone rubber filled hybrid Al_2O_3 (a) 0 wt % (b) 44 wt %, and (c) 55 wt %.

TABLE III
Effect of Content of Hybrid Micro-Al_2O_3 Particles on Mechanical Properties of Silicone Rubber

Mass fraction of Al_2O_3 (%)	Tensile strength (MPa)	Elongation at break (%)	Shore A hardness
44	1.56	123	45
50	1.43	101	50
55	1.27	86	65
58	1.06	78	74

perimental result is shown in Figure 6. From Figure 6, it was obvious that the curing curve of the pure silicone rubber is nearly same with that of the 55 wt % of Al_2O_3-filled silicone rubber, and the locations of the initial reaction temperature and peak temperature of filled silicone rubber have shifts of 2°C and 5°C toward low temperature compared with pure silicone rubber. It was indicated that the Al_2O_3 filler serves as a catalyst for curing reaction of rubber and quickens slightly the vulcanization reaction, implying that the curing behavior of silicone rubber is basically less affected by the Al_2O_3 filler.

Coefficient of thermal expansion

It was observed from Figure 7 that CTE of filled silicone rubber decreased with increasing filler content. At a filler content of 55 wt %, CTE of Al_2O_3 filled silicone rubber is 90×10^{-6} °C^{-1}, compared with 285×10^{-6} °C^{-1} of the unfilled silicone rubber. This clearly indicated that the use of filler reduced CTE of the silicone rubber matrix. The probable reason may be that there exists mechanical interaction between the filler and silicone rubber matrix which binds the matrix together and prevents it from expanding as much as it would on its own. When used as elastomeric thermal pad, the composite silicone rubber is subjected to a predetermined number of cycles of heating and cooling to test its reliability during temperature cycle. If the CTE of silicone rubber is high, it is expected to contract more than the copper heat spreader due to the CTE mismatch between the two materials.[21–23] So, the silicone rubber filled with 55 wt % of Al_2O_3 is more suitable for use in TIMs because of its lower CTE.

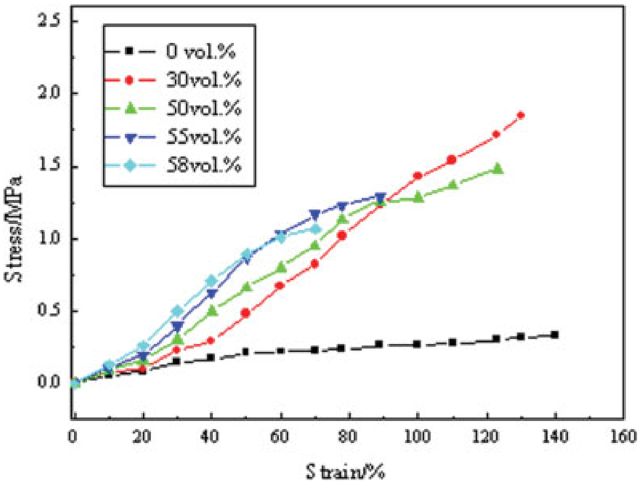

Figure 4 The strain–stress curve of the silicone rubber filled with different content of filler. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

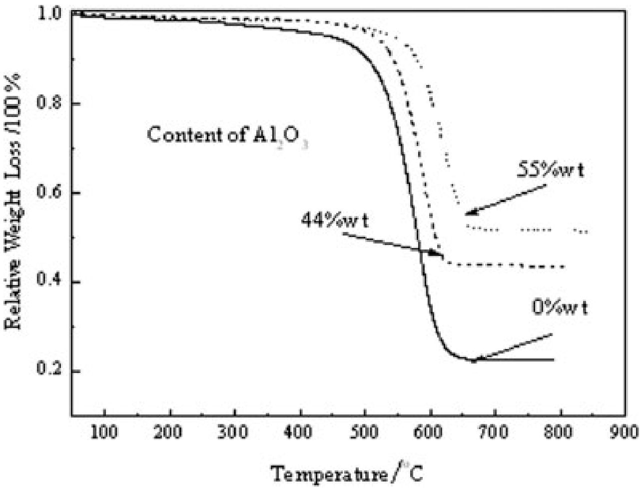

Figure 5 TGA of the filled silicone rubber composites.

Properties of reinforcement-reinforced composite silicone rubber

The prepared silicone rubber pad filled with 55 wt % of filler has higher thermal conductivity (0.92 W/mK),

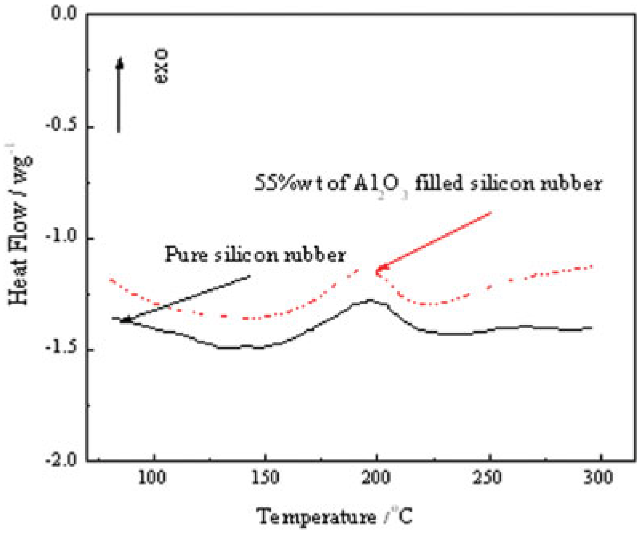

Figure 6 DSC comparison between silicone rubber and filled silicone rubber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lower CTE (90×10^{-6} °C^{-1}), and high temperature resistance. However, the low tearing strength of silicone rubber limits its many applications. For this purpose, the electrical glass cloth treated with silane coupling agent was used as reinforcement, imparting the silicone rubber good tearing resistance property, and thus a new type of composite elastomeric thermal pad was developed. The reinforced silicone rubber pad not only has good thermal conductivity and mechanical properties, but also has good electrical properties and soft, smooth surface which make the silicone rubber pad easily deformed by small contact pressure to compact all the uneven areas of the mating surface, which improves the heat dissipation efficiency of the device. In addition, it is innoxious and solvent resistant, and can be processed to different shapes as designed. The overall properties of reinforced composite silicone rubber are shown in Table IV.

TABLE IV
Properties of Thermally Conductive Silicone Rubber Reinforced with Electrical Glass Cloth

Physical properties	Value
Thickness (mm)	0.24
Breaking strength (MPa)	18
Shore A hardness	80
Continuous use temperature (°C)	−60 to +180
Thermal conductivity (W/mK)	0.92
Thermal resistance (°C/W)	0.62
Breakdown voltage (kV)	4.5
Dielectric constant	5.0
Volume resistivity (Ω m)	2×10^{12}

CONCLUSIONS

The elastomeric silicone rubber thermal pad was successfully prepared from silicone rubber and heat-conductive Al_2O_3 filler. The inclusion of Al_2O_3 into rubber increases both thermal conductivity and thermal stability, while decreases the CTE. The use of hybrid Al_2O_3 fillers with different particle sizes is advantageous over the use of filler with single particle size, because the hybrid fillers could improve the packing density of particles in silicone rubber, and form more heat-conductive pathways along heat-flow, which is crucial for improvement of thermal conductivity of composites.

Moreover, considering the low tearing strength of filled silicone rubber, a new type of thermally conductive silicone rubber composites, which possesses thermal conductivity of 0.92 W/mK, good electrical insulation, and mechanical properties, was obtained using electrical glass cloth as reinforcement. This composite silicone rubber pad, with a small pressure applied to it ensure good conformity at the interfaces, is an ideal thermal interfacial material for heat dissipation of higher performance electronic device.

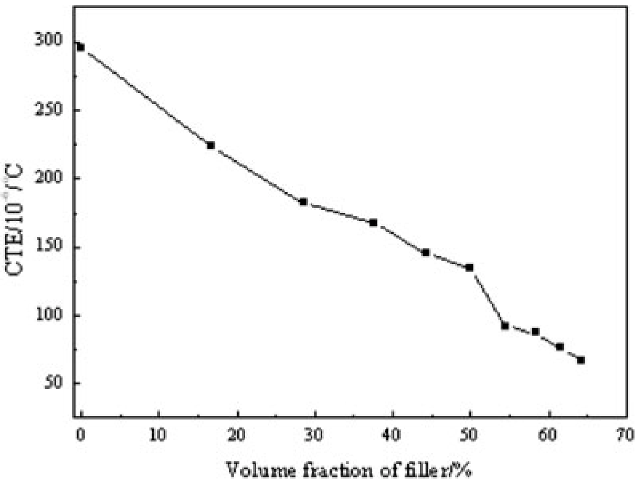

Figure 7 Effect of the content of Al_2O_3 on CTE of filled silicone rubber.

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