Effect of the Particle Size of Al_2O_3 on the Properties of Filled Heat-Conductive Silicone Rubber

Wenying Zhou,[1] Shuhua Qi,[1] Chunchao Tu,[1] Hongzhen Zhao,[1] Caifeng Wang,[2] Jingli Kou[2]

[1]*Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an, People's Republic of China, 710072*
[2]*Xi'an Sunward Aerospace Materials Company, Limited, Xi'an, People's Republic of China, 710025*

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ABSTRACT: An elastomeric thermal pad with a thermal conductivity of 1.45 W/m K, needed for the heat dissipation of microelectronics, was obtained with hybrid alumina of different particle sizes as a filler and silicone rubber (vinyl-end-blocked polymethylsiloxane) as the matrix. The effects of the amount, particle size, and mixing mass ratio of the filler particles on the thermal conductivity and mechanical properties of silicone rubber were investigated. The results indicated that the thermal conductivity of the rubber filled with larger particles was superior to that of the rubber filled with the smaller grain size, and the rubber incorporated with a mixture of hybrid particles at a preferable mass ratio exhibited higher thermal conductivity than the rubber for which a filler with only a single particle size was used. In addition, the surface treatment of the hybrid filler with 3-methacryloyloxypropyltrimethoxysilane could increase the thermal conductivity of the composite rubber. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1312–1318, 2007

Key words: composites; silicones; thermal properties

INTRODUCTION

With the miniaturization and increasing power of microelectronics, heat dissipation has become critical to the performance, reliability, and further miniaturization of microelectronics. Heat dissipation from microelectronics is most commonly performed by thermal conduction.[1–3] For this purpose, a heat sink is used. For the heat sink to be well used, the thermal contact between the heat sink and the heat source (a substrate with semiconductor chips on it) should be very good.[4] Numerous researchers have identified the need to better understand the effects of parameters such as surface toughness, surfaces flatness, and clapping pressure on thermal interface resistance. As a result of surface irregularities, dry contact surfaces can have as little as 1–5% actual contact.[5,6] The remaining area is separated by an insulating air gap (Thermal conductivity of air, $k_{\mathrm{air}} = 0.0242$ W/m K) of varying thickness. Therefore, to reduce the thermal resistance across the interface, steps must be taken to either increase the actual contact area (e.g., by increasing the contact pressure or grinding and polishing the surface to improve flatness and roughness values) or fill the remaining air gaps with a suitable thermal interfacial material (TIM).[7–10] Because it is often impossible to increase the pressure without damaging components, surface flatness tends to be dictated by the upstream manufacturing process.[11–13] Therefore, the use of a TIM is generally required in the final packaging of most microelectronics applications.

Insulating TIMs are typically made of a polymer reinforced with highly thermally conductive but electrically insulating fillers such as aluminum nitride (AlN), boron nitride (BN), silicon carbide (SiC), and alumina (Al_2O_3). TIMs can be categorized into elastomeric thermal pads, thermal greases, solder, and phase-change materials.[1] Of all the classes of TIMs, elastomeric thermal pads are most popular for cooling low-power devices such as chip sets and mobile processors.[14] An elastomeric thermal pad, which is easy to handle and is compressible to 25% of its total thickness, consists of an elastomer (i.e., silicone rubber) filled with ceramic powder. In addition, an elastomeric thermal pad must have a low coefficient of expansion (CTE) and be easily deformed by small contact pressure to contact all the uneven areas of the mating surfaces.[15]

The thermal conductivity of pure silicone rubber is about 0.2 W/m K, whereas heat-conductive particles of Al_2O_3-filled silicone rubber with room-temperature vulcanization (RTV) exhibit a thermal conductivity ranging from 0.65 to 1.10 W/m K. Until now, much attention had been paid to heat-conductive silicone rubber with RTV, whereas studies of heat-conductive silicone rubber with high-temperature vulcanization (HTV) and the effect of the parti-

Correspondence to: W. Zhou (wyzhou2004@163.com).
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cle sizes of the filler on the properties of silicone rubber have seldom been reported.

The aim of this study was to develop an elastomeric thermal pad from HTV silicone rubber (vinyl-end-blocked polymethylsiloxane) and Al_2O_3 fillers and investigate the effects of the amount, particle size, and surface treatment of Al_2O_3 fillers on the thermal conductivity and mechanical properties of the filled silicone rubber.

EXPERIMENTAL

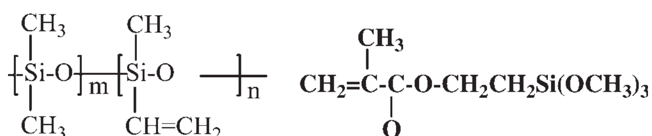
Materials

The silicone rubber was vinyl-end-blocked polymethylsiloxane (type 101B) manufactured by Chenguang Co. (Chengdu, China), whereas the curing agent was 2,5-bis(*tert*-butyl peroxy)-2,5-dimethylhexane (DBPMH), and the processing oil was hydroxyl–silicon oil, both purchased from Shanghai Xixiang Co. (Shanghai, China). The thermally conductive fillers were β-phase Al_2O_3 with a purity of 99.9% and average particle sizes of 25, 5, and 0.5 μm from Dalian Luming Co. (Dalian, China). The nanometer filler was α-phase Al_2O_3 with an average size of 50 nm, and it was supplied by Nanjing Haitai Co. (Nanjing, China). The silane coupling agent was 3-methacryloyloxypropyltrimethoxysilane (type KH-570), with a purity greater than 97.0% (batch number TMK56-02161205), from Changzhou Tianma Co. (Changzhou, China).

The chemical structures of the silicone rubber and coupling agent are shown in Scheme 1. The ethylene group at one end of the silane coupling agent molecule allows coupling to the silicone rubber matrix, and the three methoxy groups at the other end can hydrolyze in aqueous alcohol to generate hydroxy groups that react with hydroxyl groups of the filler surface. The properties of the main materials are listed in Table I.

Sample preparation

Silicone rubber was mixed with the Al_2O_3 filler and processing oil, and this was followed by the addition of DBPMH. The compounding was carried out on a two-roll mixing mill (type SK-106B, Shanghai, China), and the total mixing time for all the different concentrations was 30 min.



Scheme 1 Chemical structures of the silicone rubber and silane coupling agent.

TABLE I
Properties of Al_2O_3 and Silicone Rubber

Property	Al_2O_3	Silicone rubber
Density (g/cm^3)	3.97	1.05
CTE (10^{-6} °C)	6.9–7.4	285
Thermal conductivity (W/m K)	30–40	0.2
Electrical resistivity (Ω cm)	$\geq 10^{14}$	$\geq 10^{16}$
Dielectric constant	6.0–7.0	3.5
Mean particle size(μm)	25, 5, 0.5, and 5×10^{-2}	

The gross silicone rubber sample was placed in a stainless steel mold and was compression-molded at 165°C and a pressure of 10 MPa for 10 min in an electrically heated hot-press machine (SL-45, Shanghai, China).

The surface treatment for the Al_2O_3 particles (surface treatments were applied only to the nano-Al_2O_3 particles and the appointed mixture of Al_2O_3 particles with hybrid sizes) with 3-methacryloyloxypropyltrimethoxysilane involved the following: (1) making an aqueous ethanol solution at a 98 wt % concentration; (2) adding the silane coupling agent to the solution, stirring the mixture for 15 min with a magnetic stirrer in a flask with a reflux setting, adjusting the pH of the aqueous ethanol solution to 3–5 with dilute hydrochloric acid, and stirring for 20 min; (3) adding Al_2O_3 particles to the solution made in step 2 and stirring for 25 min; (4) heating the mixture to 70°C, refluxing it for 2 h while stirring, and then cooling it to room temperature and setting it for 3 h, (5) rinsing the mixture with ethanol by filtration; and (6) drying the mixture at 110°C for 10 h.[3]

Characterization

The thermal conductivity was calculated from the thermal diffusivity with the following equation:

$$\lambda = \alpha \rho C_p \quad (1)$$

where λ, α, ρ, and C_p are the thermal conductivity, thermal diffusivity, specific density, and specific heat capacity of the material under constant pressure.

The thermal diffusivity of the composite silicone rubber was measured by a transient method, which is closely related to laser-flash experiments. The measurement of the thermal diffusivity was conducted on a Netzsch (Selb, Germany) LFA427 system at room temperature (in air). The samples were dried for at least 2 days in a desiccator before the measurements were conducted. The sample size used for the laser flash method had dimensions of $8 \times 8 \times 1$ mm^3 with a mirrorlike, polished surface.

Specific heat capacity measurements were performed with a modulated differential scanning calo-

rimeter (modulated DSC 2920, TA Instruments, New Castle, DE). The measurements were carried out in the temperature region from −10 to 50°C at a heating rate of 5°C/min. The differential scanning calorimeter was calibrated in the same temperature region before each experiment, with a sapphire sample as a standard with a well-known specific heat capacity. Data for the heat capacity were taken at 23°C.

The specific density of the composite rubber was determined with the Archimedean principle: the density was measured by the displacement of isopropyl fluid. The weight measurements were performed with an electromagnetic balance (JS-03A, Shenzhen, China). The measurement conductions proposed in standard DIN 53479 were applied.

Morphological observations of the composite silicone rubber were performed by means of scanning electron microscopy (SEM; model KYKY-2000, China). Observations were carried out of the cross sections of the samples to study the Al_2O_3 distribution and morphology affecting the thermal conductivity of the system.

The mechanical strength tests of the samples were conducted on a screw-driven universal testing machine (model ZMGI 250, Shenzen SANS Instruments Co., Ltd., Shenzhen City, China) to determine the tensile strength with standard ISO37/1987, and the Shore A hardness was measured with a hardness tester (type Yko200, China).

RESULTS AND DISCUSSION

The thermal conductivity of Al_2O_3 (30–40 W/m K) is much larger than that of pure silicone rubber (0.2 W/m K). Therefore, the addition of Al_2O_3 to the silicone rubber matrix will increase the thermal conductivity of the rubber, and the concentration and particle size of Al_2O_3 will have effects on the thermal conductivity of the composite silicone rubber.

The effect of the concentration of Al_2O_3 with a particle size of 25 μm on the thermal conductivity is shown in Figure 1. The thermal conductivity always increases with an increasing volume fraction of Al_2O_3 up to 80%. The thermal conductivity of filled silicone rubber increases slowly with the Al_2O_3 loading when less than 40 vol %; after a loading greater than 40 vol %, the thermal conductivity increases quickly. The thermal conductivity of silicone rubber filled with 58 vol % Al_2O_3 reaches 0.88 W/m K versus 0.2 W/m K for pure silicone rubber. Because the heat-conductive particles surrounded by a rubber matrix cannot touch one another at a low loading, the thermal conductivity increases very slowly on account of high thermal contact resistance. Therefore, the conductive particles do not improve the thermal conductivity of rubber effectively when the filler concentration is less than 40 vol %. As the concentration of the filler increases, particles begin to touch one another and form a more compact packing structure. Therefore, the layer of the matrix resin between the adjacent particles becomes thinner and thinner, and the thermal conductivity is enhanced greatly because of decreasing thermal contact resistance.

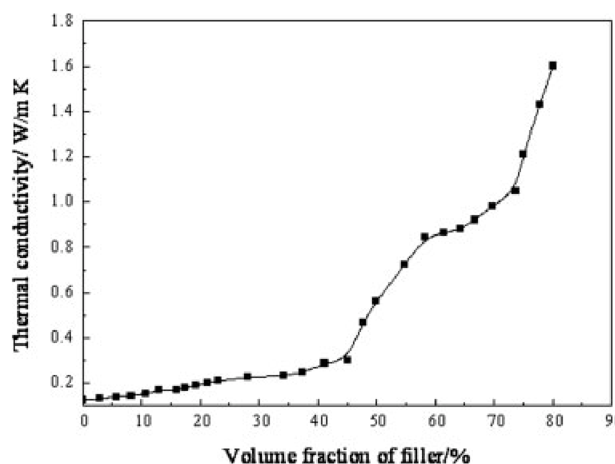


Figure 1 Thermal conductivity of silicone rubbers with different amounts of filler particles (25 μm).

When the filler loading further continues to increase from 58 to 73 vol %, the thermal conductivity increases slowly again. That can be attributed to the fact that with an increasing filler loading, the number of newly formed thermally conductive pathways shows no obvious increase because most of the particles have touched one another, and the concentration of the filler particles no longer plays an important role in enhancing thermal conductivity; whereas the packing structure of the fillers and the interfacial action between the particles and matrix become the main factors influencing the thermal conductivity. Therefore, the thermal conductivity increases rather slowly. When the concentration of the filler is above 73 vol %, the thermal conductivity increases quickly again. That is because a more compact packing structure and high packing density of the particles in the matrix can be realized. Therefore, from a theoretical point of view, increasing the concentration of the conductive fillers, that is, reducing the thickness of the rubber matrix layer between conductive particles, and trying to avoid heat flowing along the resin layer between particles are the main ways of improving the thermal conductivity. However, a high concentration of the filler easily causes a high viscosity and leads to higher hardness of the rubber. In addition, the mechanical properties worse. Therefore, the preferable concentration of the filler is 64 vol % according to the experimental results.

Different particle sizes of Al_2O_3 have an effect on the thermal conductivity and mechanical properties of the filled silicone rubber. At a low concentration

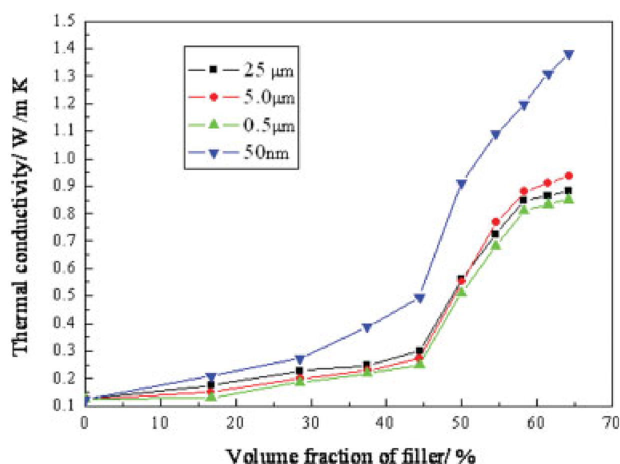


Figure 2 Effect of Al_2O_3 with different particle sizes on the thermal conductivity of silicone rubber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the filler, a larger particle (i.e., low surface area) is desired to minimize the scattering of phonons due to the lower interfacial thermal barrier. Moreover, the use of a larger particle size tends to form fewer thermally resistant junctions of the matrix layer than the smaller particle size at the same filler concentrations.[16,17] However, the concentration of larger particles must be limited under a desired level in order to not degrade the mechanical properties of the filled rubber. In this study, three micro-Al_2O_3 fillers with particle sizes of 25, 5, and 0.5 μm were used to investigate the dependence of the thermal conductivity on the particle sizes, and 50-nm Al_2O_3 was chosen for comparison also. The experimental results are shown in Figure 2.

Figure 2 shows that when the concentration of the filler is less than 50 vol %, the thermal conductivity of the rubber filled with larger filler particles is always higher than that of the rubber filled with smaller ones with the same concentration. After 50 vol %, the 5-μm-filler-filled silicone rubber exhibits higher thermal conductivity than that with the particles of 25 and 0.5 μm. The 0.5-μm- filler-filled silicone rubber always shows lower thermal conductivity than the 25- and 5-μm-filler-filled systems below a 64 vol % filler loading. That is because that under 50 vol %, the most conductive particles cannot form a compact packing structure, and some particles even are encapsulated by the rubber matrix completely. Different particle sizes will result in different interfacial areas per unit of volume in the same silicone rubber matrix fraction. As the particle size increases, the area of the interface between the particles and matrix will decrease. Therefore, there may be thinner silicone rubber layers around each particle at the same concentration of rubber. Thus, the conductive pathways can be considered more stable for the larger particles because the thicker heat-conductive pathways have less chance of being disrupted by contacting grains. This result means that the finer particles can be disadvantageous for enhancing the thermal conductivity of the composites. Therefore, the use of larger particles may be an effective way of increasing the thermal conductivity of the composites. The increase in the thermal conductivity of the composites with increasing particles size could be due to the greater stability of heat-conductive pathways for the larger particles. When the concentration of particles is greater than 50 vol %, the particles begin to touch another and basically form some heat-conductive pathways or networks in the matrix. With an increasing filler loading, the thermal conductivity increases slowly, and the formation of the compact packing structure of the particles is the main factor influencing the thermal conductivity. A higher packing density of the particles tends to lead to a higher thermal conductivity. Because the finer particles easily form a compact packing structure and high packing density, the 5-μm-particle-filled silicone rubber exhibits better thermal conductivity than that with the 25-μm particles. It can be predicted that as the loading of Al_2O_3 continues to increase, the difference between the thermal conductivities of the silicone rubbers filled with particles of different particle sizes, that is, 25, 5, and 0.5 μm, will diminish finally.

The nano-Al_2O_3-particle-filled silicone rubber shows higher thermal conductivity than microparticles because of its higher intrinsic thermal conductivity. However, at a low concentration, the filled silicone rubber almost exhibits the same thermal conductivity as the microparticle-filled systems because the nanoparticles fails to form thermally conductive pathways below a 30 vol % loading; moreover, for the nanoparticles, the hyperfine size and high surface energy make them difficult to disperse homogeneously in silicone rubber. Therefore, most nanoparticles are often separated by silicone rubber and cannot form conductive pathways in the matrix. When the concentration is over 30 vol %, nanoparticles begin to form a highly compact packing structure in the matrix and more stable and thicker heat-conductive pathways because of the very big volume fraction of nanoparticles at the same mass fraction in comparison with microparticles despite aggregation. Therefore, the composite silicone rubber exhibits high thermal conductivity. The thermal conductivity of silicone rubber filled with 64 vol % nanoparticles reaches 1.38 W/m K versus 0.8–0.9 W/m K for the micrometer-filler-filled systems.

The effects of the particle size of Al_2O_3 on the mechanical properties of silicone rubber are listed in Table II. The silicone rubber filled with finer particles exhibits better mechanical properties, such as a higher tensile strength and elongation at break, than the systems filled with larger particles at the same filler load-

TABLE II
Properties of Silicone Rubbers Filled with Al_2O_3 of Different Particle Sizes

Particle size of Al_2O_3 (μm)	Amount of Al_2O_3 (vol %)	Tensile strength (MPa)	Elongation at break (%)	Shore A hardness
25	28	0.57 ± 0.02	50 ± 3	28 ± 2
	44	1.12 ± 0.04	45 ± 2	35 ± 3
	55	0.94 ± 0.03	42 ± 2	44 ± 3
	64	0.60 ± 0.02	34 ± 2	51 ± 5
5	28	0.82 ± 0.03	80 ± 4	30 ± 3
	44	0.99 ± 0.04	106 ± 8	38 ± 2
	55	1.47 ± 0.08	94 ± 5	45 ± 3
	64	1.14 ± 0.06	78 ± 6	53 ± 4
0.5	28	0.96 ± 0.04	112 ± 12	31 ± 2
	44	1.15 ± 0.05	130 ± 11	37 ± 3
	55	1.98 ± 0.10	141 ± 12	48 ± 4
	64	1.45 ± 0.08	108 ± 9	52 ± 3
50×10^{-3}	28	1.24 ± 0.09	130 ± 10	33 ± 2
	44	1.81 ± 0.12	190 ± 17	40 ± 4
	55	3.51 ± 0.18	218 ± 20	46 ± 2
	64	2.74 ± 0.12	175 ± 15	53 ± 4

ing (whereas the latter has a lower viscosity facilitating processing). For examples, the 25-μm-filler-filled silicone rubber shows a tensile strength and elongation at break of 0.94 MPa and 42%, respectively, versus 1.98 MPa and 141% for the 0.5-μm-filler-filled system with 55 vol % filler. With a decreasing filler size, the specific surface area of the particles increases remarkably. Therefore, the interfacial area between the filler particles and rubber matrix increases significantly, and this leads to a strong interaction between the filler and matrix. Therefore, the finer particles are useful for improving the mechanical properties of filled rubber. For the same filler size, the tensile strength and elongation at break of the composites increase at a low concentration but decrease at a high concentration of the filler, and the maximum values appear at about 55 vol % filler. That is because the interaction between the filler and matrix enhances the strength of silicone rubber on account of the reinforcement effect of the filler particles, whereas with a further increasing filler loading, too many filler particles worsen the mechanical properties of the composites. Table II shows that the hardness of the composites is basically less affected by the particle size.

The nanoparticle-filled rubber shows better tensile strength and elongation at break, along with thermal conductivity, compared with the micrometer-particle-filled systems because of the hyperfine size and high surface energy.

It has been reported that a mixture of fillers of different particle sizes has advantages over a single particle size in obtaining high thermal conductivity.[18] Therefore, to achieve a high packing density, hybrid fillers of different particle sizes are suggested. The use of hybrid Al_2O_3 fillers would result in a more compact packing structure in the rubber matrix and the easy formation of random bridges or networks from conductive particles, which facilitate phonon transfer and lead to higher thermal conductivity; therefore, the thermal conductivity of silicone rubber filled with hybrid Al_2O_3 fillers of different particle sizes is higher than that of silicone rubber filled with a single particle size.[19,20] In this study, the effects of the different mass ratios of the hybrid fillers at a total volume fraction of 64% on the thermal conductivity of the composites are shown in Table III.

Table III shows that with a 2 : 5 : 1 : 1 $M_{25\mu m}/M_{5\mu m}/M_{0.5\mu m}/M_{50nm}$ mass ratio, the thermal conductivity reaches 1.45 W/m K, the highest value of all the rubbers filled in this work. This could be attributed to the fact that smaller particles easily fit into spaces that larger particles cannot occupy and form a higher packing density of the filler in the matrix (see Fig. 3); thus, the thermal conductivity increases because of the decreased resistance

TABLE III
Effect of the Weight Ratios of Different Sizes of Al_2O_3 with a Total of 64 vol % on the Properties of Silicone Rubber

$M_{25\mu m}/M_{5\mu m}/M_{0.5\mu m}/M_{50nm}$	Tensile strength (MPa)	Elongation at break (%)	Shore A hardness	Thermal conductivity (W/m K)
4 : 4 : 1 : 0	1.68 ± 0.02	68 ± 2	51 ± 2	0.98 ± 0.02
3 : 5 : 1 : 0	1.77 ± 0.03	74 ± 3	49 ± 3	1.14 ± 0.06
3 : 4 : 2 : 0	1.98 ± 0.04	87 ± 2	53 ± 2	0.93 ± 0.03
3 : 4 : 1 : 1	2.20 ± 0.05	91 ± 4	50 ± 1	1.21 ± 0.05
2 : 4 : 2 : 1	2.41 ± 0.04	98 ± 5	55 ± 4	1.13 ± 0.04
2 : 5 : 1 : 1	2.51 ± 0.07	81 ± 2	52 ± 2	1.45 ± 0.07
2 : 5 : 2 : 0	1.61 ± 0.03	77 ± 3	48 ± 2	1.01 ± 0.02
2 : 6 : 0 : 1	2.05 ± 0.05	76 ± 3	50 ± 1	1.27 ± 0.05
1 : 5 : 1 : 2	2.84 ± 0.08	102 ± 6	55 ± 3	1.38 ± 0.06
64 vol % ($M_{25\mu m}$)	0.60 ± 0.02	34 ± 2	51 ± 2	0.882 ± 0.03
64 vol % ($M_{5\mu m}$)	1.14 ± 0.04	78 ± 3	53 ± 3	0.936 ± 0.04
64 vol % ($M_{0.5\mu m}$)	1.24 ± 0.03	130 ± 7	53 ± 1	0.851 ± 0.02
64 vol % (M_{50nm})	2.74 ± 0.06	175 ± 10	53 ± 4	1.380 ± 0.09

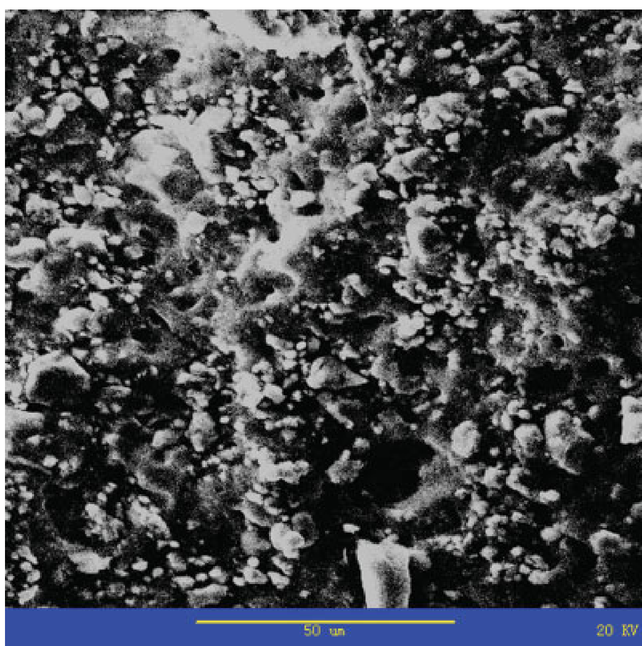


Figure 3 SEM image of the fracture surface of silicone rubber containing the Al_2O_3 hybrid with 64 vol % Al_2O_3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

among adjacent conductive fillers. Therefore, the formation of more effective conductive pathways or networks in the matrix is of great importance for enhancing the thermal conductivity. Furthermore, with a 1 : 5 : 1 : 2 $M_{25\mu m}/M_{5\mu m}/M_{0.5\mu m}/M_{0nm}$ ratio, the composites have a thermal conductivity of 1.38 W/m K, the same as that of the nanoparticle-filled system. In addition, with 3 : 4 : 1 : 1 and 2 : 6 : 0 : 1 $M_{25\mu m}/M_{5\mu m}/M_{0.5\mu m}/M_{50nm}$ mass ratios, the composite rubber also exhibits higher thermal conductivity than the case in which only micro-Al_2O_3 particles of a single particle size are used at the same total volume fraction.

Table III also shows that the hybrid-micrometer-filler-reinforced silicone rubber has better mechanical properties than those filled by micrometer fillers of a single size because of the hybrid effect. A possible reason may be that the hybrid filler could be dispersed homogeneously in the rubber matrix. After a 55 vol % filler loading, the mechanical properties of filled silicone rubber decline according to Table II, whereas the hybrid-filler-reinforced silicone rubber still keeps a higher tensile strength and elongation at break in comparison with the case in which only a filler with a single particle size is used. Furthermore, the hardness of the composites is less influenced by the filler size. Therefore, to obtain higher thermal conductivity and mechanical properties for Al_2O_3-filled silicone rubber, a hybrid filler is suggested. However, the intrinsic reason for the improvement in the mechanical properties with a mixture of fillers in silicone rubber remains unknown.

The surface treatment of Al_2O_3 particles with a coupling agent is useful for increasing the thermal conductivity of Al_2O_3-filled silicone rubber because the coupling agent improves the interfacial bonding between the filler and matrix and reduces the voids at the filler–matrix interface, and this facilitates enhanced thermal conductivity. Therefore, in this study, mixtures of Al_2O_3 particles with a 2 : 5 : 1 : 1 $M_{25\mu m}/M_{5\mu m}/M_{0.5\mu m}/M_{50nm}$ mass ratio and total volume fractions of 50, 54, 58, and 64% were surface-treated with 3-methacryloyloxypropyltrimethoxysilane with the same hybrid Al_2O_3 particles untreated for comparison, and the results are shown in Figure 4. The concentration of the coupling agent has an influence on the thermal conductivity: the thermal conductivity of the filled rubber increases at a low concentration but decreases at a high concentration of the coupling agent. The maximum values appear at about a 2.0 wt % coupling agent concentration, and the thermal conductivity reaches 1.50 W/m K versus 1.45 W/m K for the untreated system with an Al_2O_3 loading of 64 vol %. It is well known that thermal resistance is caused by various types of phonon-scattering processes, and the interfacial thermal barriers in composites are mainly due to the scattering of phonons resulting from acoustic mismatch and flaws associated with the matrix–filler interface. Adding the coupling agent to the rubber could improve the interface between the filler particle and matrix and increase the thermal conductivity.[3] Figure 5 shows SEM images of the fracture surfaces of composite rubbers reinforced with hybrid fillers without or with the surface treatment. After the treatment, the composite rubber shows relatively

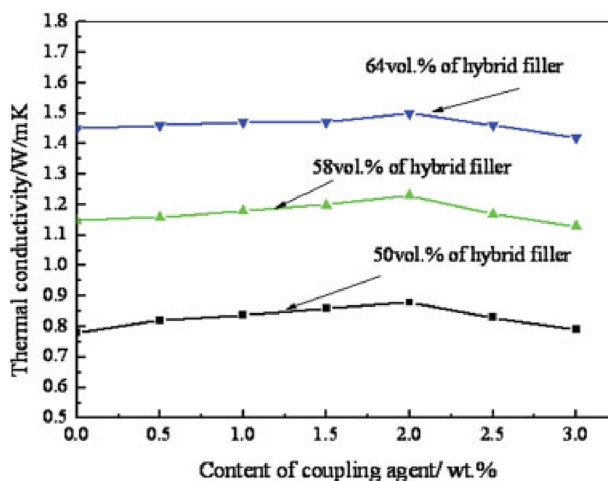


Figure 4 Thermal conductivity of silicone rubber versus the concentration of the coupling agent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

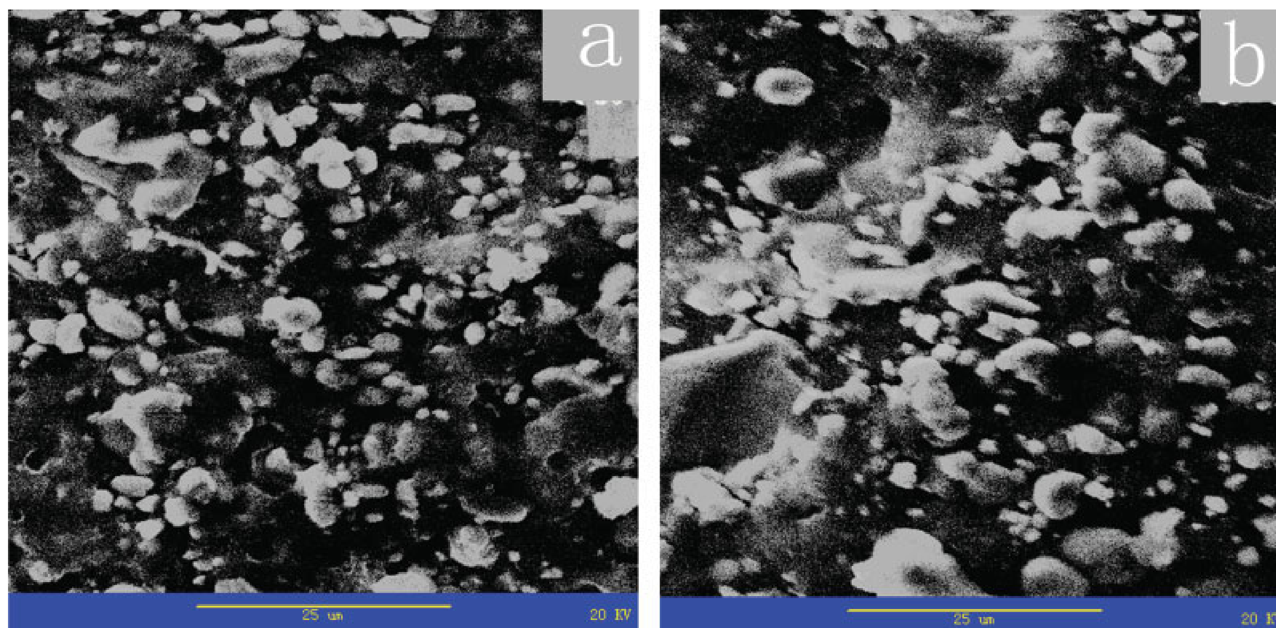


Figure 5 SEM images of the fracture surfaces of silicone rubbers containing the Al_2O_3 hybrid with 58 vol % (a) untreated Al_2O_3 and (b) treated Al_2O_3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

good filler dispersion and wetting ability versus the untreated case. However, too much coupling agent might disperse in the interface of the filler particles and matrix as a kind of low-thermal-conductivity material; the redundant coupling agent would cause phonon scattering and give rise to decreasing thermal conductivity of the composites.

CONCLUSIONS

The thermal conductivity increases with increasing Al_2O_3 concentration up to 80 vol %. However, the mechanical properties decline after 55 vol % filler. The preferable filler concentration is 64 vol %.

The size of the Al_2O_3 particles has an effect on the thermal conductivity of the composite rubber. When the filler concentration is less than 50 vol %, the silicone rubber filled with larger particles shows higher thermal conductivity than the system with small particles at the same filler concentration. At the same filler level, the thermal conductivity of the nanoparticle-filled rubber is superior to that of the rubber incorporated with microparticles. The formation of effective heat-conductive pathways is the crucial factor determining thermal conductivity.

With a 2 : 5 : 1 : 1 $M_{25\mu m}/M_{5\mu m}/M_{0.5\mu m}/M_{50nm}$ mass ratio, the thermal conductivity of the composite rubber reaches 1.45 W/m K, the highest value among all the filled rubbers of this work, in contrast to the case in which only Al_2O_3 with a single particle size is used.

The surface treatment of Al_2O_3 particles can increase the thermal conductivity of composite rubber because of the decreased thermal contact resistance at the filler–matrix interface. The composite rubber has better thermal conductivity with a 2.0 wt % concentration of the coupling agent.

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