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# Experimental and theoretical studies of effective thermal conductivity of composites made of silicone rubber and $Al_2O_3$ particles

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ABSTRACT

In this study, effective thermal conductivities of composite materials were investigated both experimentally and theoretically. The composites made of silicone rubber and spherical $Al_2O_3$ particles of four mean diameters were prepared with various volume fractions. Experimental results indicate that the effective thermal conductivity increases nonlinearly with increasing particle volume fraction and is higher for larger particles, indicating its dependence not only on conductivities and volume fraction, but also on the materials' interfacial geometry. The experimental results were used to evaluate the performance of theoretical models. It was found that the models by Deissler and Boegli and by Maxwell that contain no parameter for interfacial effects were unable to predict the experimental results. On the other hand, the models by Hsu et al. and by Agari and Uno that provide interfacial contact parameters fit very well with the data over the whole ranges of the present experiment.



## 1. Introduction

Polymer composite materials are widely used as electronic packaging materials for their high thermal conductivity, high modulus, high electrical insulation, low thermal expansion and low dielectric constant. Polymer composites with ceramic fillers, such as boron nitride, aluminum nitride, aluminum, and aluminum oxide [1–5], were demonstrated to have high thermal conductivity, low thermal expansion and excellent insulation properties. A number of polymers, such as epoxy-resin, polyethylene, and silicone rubber [6–8], used as matrix materials, have been reported to improve not only thermal conductivity, but also mechanical properties and thermal stability of the composites. Silicone rubbers, because of their stability and flexibility over a wide range of temperature, as well as superb properties in weather and chemical resistances, are most commonly used as polymer-matrix for the preparation of thermal pads, thermal grease, and others [9]. Usually, pure silicone rubbers have poor thermal conductivity (0.1–0.3 W/m K); however, when filled with high thermal conductive ceramic powders, their corrosion resistance and thermal conductivities are improved greatly in broadening their applications. Up to now, $\alpha$-$Al_2O_3$ is the most widely used ceramic filler as electronic packaging materials in industry for its high thermal conductivity (30–40 W/m K), excellent electric insulation property, good corrosion resistance, and most importantly moderate price.

Although there are few literatures reported the variations of effective thermal conductivity of composites, there seems to have no systematic investigation on the dependence of effective thermal conductivity on volume fraction and particle morphology, and sometimes the existing results are inconsistent [10,11]. In this study, experiments were conducted systematically to measure the effective thermal conductivities of composite materials made of silicone rubber and spherical $Al_2O_3$ particles with various volume fractions and of four mean particle diameters. Experimental results were compared with predictions from existing models to reveal the dependence of effective thermal conductivity on volume fraction, as well as on particle geometry. Mechanisms of model parameters responsible for the agreement between measured results and model predictions were also discussed.

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## 2. Experiments

### 2.1. Materials characterization

The silicone rubber was vinyl terminated polydimethylsiloxane ($[(CH_3)_2SiO]_m[CH_3SiCH_2=CHO]_n$) manufactured by Shin–Etsu Chemical Corporation, Japan. The curing agent was hydroxyl–silicone oil and the catalytic agent was platinum catalyst, both purchased from Shuotai Technology Company (Shenzhen, China). The silicone coupling agent was vinyl trimethoxy silane ($CH_2=CHSi(OCH_3)_3$) purchased from Jitu Biological Technology Company (Shanghai, China).

The thermal conductive fillers were spherical $\alpha$-$Al_2O_3$ particles with purity of 99.9% and mean particle diameters of 3 μm, 10 μm, 35 μm, and 75 μm, purchased from Electrical Chemical Corporation, Japan. The de-airing mixer was the planetary gravity mixer (Sinomix mixer VM 300SA, Sinomix Co. Ltd. Mianyang, China). The materials properties of $Al_2O_3$ and silicone rubber as provided by the suppliers are listed in Table 1.

The morphologies of $Al_2O_3$ particles were examined on a field emission scanning electron microscope (FE-SEM, HITACH S4800) at 5.0 or 10 kV. The stereo-scan photographs of $Al_2O_3$ particles as obtained by FE-SEM are shown in Fig. 1. Note that higher resolution was used for smaller particles. From these photos, it is seen that the particle surfaces are very smooth and the particle shapes are very spherical, in consistent with the specification for experiments.

Size distributions of $Al_2O_3$ particles were measured by a laser particle size analyzer (Mastersizer 2000E, Malvern Instruments Ltd.), using water as dispersing agent, and the refractive index of $Al_2O_3$ particle is 1.765. The distributions of particle size are shown in Fig. 2(a–d) for the four different mean particle diameters, respectively.

The logarithmic scale in the abscissa reveals that for each mean diameter of $Al_2O_3$ particle, the particle size is distributed over a range of a factor of 10, for example, from 4 to 40 μm as shown in Fig. 2b. In the present experiments, the separations of mean particle diameters were sufficiently larger than the standard deviations of the particle distribution to meet measurement uncertainty requirement. It should be noted that if the property of the composite depends on particle size of fillers, the measured property should be interpreted as the result averaged over particle size distribution. This is the case for the effective thermal conductivities measured in this study.

As to be illustrated later, heat transfer in composites is governed by volumetric and interfacial process of silicone rubber and $Al_2O_3$ particles. For reference purpose, the specific area and average particle diameters based on distributions of particle surface area (D[3,2]) and of particle volume (D[4,3]) are also obtained from particle size analysis; they are given in Table 2.

### 2.2. Synthesis of composites

The $Al_2O_3$ particles were firstly surface-treated by using silicone coupling agent. Typically, a small amount of silicone coupling agent was added into an ethanol–$H_2O$ mixture with 98% ethanol, which was subjected further to ultrasonic agitation for 20 min to obtain a uniform solution. The $Al_2O_3$ powders were then added into the solution. The mixture was stirred with an ultrasonic mixer for 30 min, and dried at 80 °C for 24 h to obtain surface-treated $Al_2O_3$ powders.

A typical test sample of composite consisting of 70 vol% silicone rubber and 30 vol% 3 μm $Al_2O_3$ powder was prepared as follows. The surface-treated $Al_2O_3$ powders of 85.28 g and curing oil of 1.8 g were added into methyl vinyl silicone rubber of 50 g, which were further mixed uniformly in a de-airing mixer, and then cooled to room temperature in a refrigerator. A catalytic agent was added into the above cooled compound, followed by further stirring in de-airing mixer for 1 min to achieve a completely mixed state. At last, the mixed compound was poured evenly into a mold, which was placed into a muffle furnace maintained at 120 °C for 3 h. The composite removed from the mold yields the test sample of a square plate, with a cross sectional area of 31 mm × 31 mm and thickness of 5 mm.

By properly changing the weight compositions of $Al_2O_3$ powder and silicone rubber, composites of different volume fractions of $Al_2O_3$ powder were obtained following the above same procedure, also the same for preparing test samples of different mean particle diameters.

Fig. 3 shows the typical SEM images at different resolutions for the synthesized composite corresponding to a volume fraction 0.4 of particle of mean diameter of 35um. It is clear that particles are well dispersed in composites. As compared to Fig. 1c, the interface between silicone and $Al_2O_3$ is not as vivid as that of Fig. 1c, i.e., $Al_2O_3$ particles are well immersed in silicone rubber.

**Table 1**
Properties of $Al_2O_3$ and silicone rubber.

| Property | $Al_2O_3$ | Silicone rubber |
|---|---|---|
| Density (g/cm$^3$) | 3.90 | 0.98 |
| Thermal expansion coefficient ($10^{-6}$/°C) | 6.9–7.4 | 285 |
| Thermal conductivity (W/m K) | 30 | 0.15 |
| Electrical resistivity (Ω cm) | $\geq 10^{14}$ | $\geq 10^{16}$ |
| Dielectric constant | 6.0–7.0 | 3.5 |
| Mean particle diameter (μm) | 3, 10, 35, 75 | |

### 2.3. Measurements of effective thermal conductivity

In this sub-section, fundamental theories of heat conduction in pure substance materials and in composites are reviewed briefly to justify the use of steady method for measuring effective thermal conductivity of composites in this experiment. For pure substance materials, transient heat conduction equation can be obtained by conservation of thermal energy as given by (see Holman [12]):

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (\vec{q}^{\rightarrow}) = 0 \tag{1}$$

where $T$ represents the temperature, $\rho$ the mass density, $C_p$ the specific heat capacity and $\nabla$ the gradient operator ($\nabla = \frac{\partial}{\partial x}\vec{i}^{\rightarrow} + \frac{\partial}{\partial y}\vec{j}^{\rightarrow} + \frac{\partial}{\partial z}\vec{k}^{\rightarrow}$). For materials with isotropic thermal conductivity $k$, heat flux $\vec{q}^{\rightarrow}$ as given by the Fourier law is:

$$\vec{q}^{\rightarrow} = -k\nabla T \tag{2}$$

The substitution of Eq. (2) into Eq. (1) gives:

$$\rho C_p \frac{\partial T}{\partial t} = k\nabla^2 T \tag{3}$$

which is the three-dimensional heat conduction equation.

For heat conduction of one-dimension in $x$, Eqs. (2) and (3) reduce to:

$$q_x = -k\frac{\partial T}{\partial x} \tag{4}$$

$$\rho C_p \frac{\partial T}{\partial t} = k\frac{\partial^2 T}{\partial x^2} \tag{5}$$

which are equations commonly used to measure thermal conductivity. Based on Eq. (4), heat flux and temperature gradient are measured and the thermal conductivity is determined. In practice, it is more convenient to measure the total heat rate $Q_x$