Highly Thermally Conductive Room-Temperature-Vulcanized Silicone Rubber and Silicone Grease

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Received 27 February 2002; accepted 16 November 2002

ABSTRACT: In this study, the effects of thermally conductive filler type (α-Al_2O_3, SiC), volume fraction of the filler, and filler particle size distribution on the thermal conductivity and viscosity of room-temperature-vulcanized (RTV) silicone rubber and silicone grease were investigated. We were interested to find that silicone grease (or the RTV silicone rubber) had a maximum thermal conductivity (~1.48 W/mK) and a minimum viscosity (~3.4×10^4 mPa s), with a definite total volume fraction of the filler (0.55) when the distribution of filler sizes (the number ratio of two different particles sizes, i.e., 0.8 and 6 μm) was 600–700. We were able to increase the thermal conductivity of the RTV silicone rubber and silicone grease beyond 2 W/mK by increasing the total volume fraction of the filler with adequate filler size distributions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2397–2399, 2003

Key words: silicones; fillers; particle size distribution; viscosity

INTRODUCTION

Typical pure silicone rubber and methyl silicone oil usually have poor thermal conductivities (0.165 W/mK). However, when filled with inorganic thermally conductive fillers, such as α-Al_2O_3, SiC, BN, and ZnO, they can be made into silicone rubber and silicone grease with excellent thermal conductivities. Such thermally conductive silicone rubber and silicone grease are widely used in aviation, electronic devices, and so on. The thermal conductivity of high-temperature vulcanizable silicone rubber has been reported to reach 1.5–2.5 W/mK,[1,2] with some even reaching over 3 W/mK, whereas the thermal conductivity of room-temperature-vulcanized (RTV) silicone rubber or silicone grease is much lower, usually only about 0.3–0.6 W/mK.[3,4] Although one can add more a larger quantity of filler to improve the thermal conductivity of RTV silicone rubber and silicone grease, too much filler increases the viscosity of the RTV silicone rubber composition and silicone grease at the same time, which makes processing and application more difficult. There is a contradiction between high thermal conductivity and good processing behavior, which should be solved. In this study, we chose a proper thermally conductive filler (SiC) having different particle sizes and then chose the optimum filler particle size distribution to make the particles closely packed in the RTV silicone rubber and silicone grease. We could then obtain RTV silicone rubber and silicone grease that not only had high thermal conductivity but also good fluidity and processing performance.

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Journal of Applied Polymer Science, Vol. 89, 2397–2399 (2003)

EXPERIMENTAL

Materials

Methyl silicone oil ($(CH_3)_3Si{-}O{-}[Si(CH_3)_2{-}O]_n{-}Si(CH_3)_3$; Beijing Second Chemical Plant, China; viscosity = 500 mPa s), terminal hydroxyl polydimethysiloxane (Beijing Second Chemical Plant, China; viscosity = 2700 mPa s), SiC (Institute of Chemistry and Metallurgy, Chinese Academy of Sciences, Beijing, China; particle sizes = 12, 6, 3, and 0.8 μm), and α-Al_2O_3 (Zizhou Special Mold Plant, Shandong, China; particle sizes = 12, 6, 3, and 0.8 μm) were all industrial chemicals. Ethyl silicate and dibutyltin dilaurate (Beijing Chemical Agent Company, China) were AR (analytically pure).

Preparation of the samples

The inorganic thermally conductive fillers were incorporated into the terminal hydroxyl polydimethysiloxane or methyl silicone oil. This composition was mixed in a three-roll mill at 25°C twice, heated in the baking oven at 140°C for 4 h, and was milled again in the three-roll mill at 25°C twice after cooling. Thus, the thermally conductive RTV silicone rubber composition or thermal conductive silicone grease was obtained.

TABLE I
Thermal Conductivity of RTV Silicone Rubber or Silicone Grease

Type	Sample no.	Type of thermally conductive filler	Volume fraction of filler*[a]	Tensile strength (MPa)	Thermal conductivity (W/mK)
RTV silicone rubber	1	α-Al_2O_3	0.47	2.6	0.9
	2	α-Al_2O_3	0.64	2.4	2.1
	3	SiC	0.47	3.2	1.2
	4	SiC	0.64	2.8	2.7
Silicone grease	5	α-Al_2O_3	0.47	—	1.0
	6	α-Al_2O_3	0.64	—	2.2
	7	SiC	0.47	—	1.3
	8	SiC	0.64	—	2.6

*[a]Volume fraction of filler = the Real volume of filler/(Real volume of filler + Real volume of silicone oil).

Vulcanization

We mixed the RTV silicone rubber composition (100 parts by weight) with ethyl silicate (crosslinking agent; 2 parts by weight) and dibutyltin dilaurate (catalyst; 1 part by weight) and then cured the mixture at room temperature for 3 days to obtain thermally conductive RTV silicone rubber.

Determination of the properties

The thermal conductivities of the RTV silicone rubber by size (10 × 4 × 1 cm) and the silicone grease were tested with a thermally conductive probe instrument (Puyang Radio Plant, Anhui, China) by the transient-state method.[5] The viscosity was determined with a rotary viscometer (Haake Viscotester VT-02, New Jersey). The tensile strength of the RTV silicone rubber was measured as described in the literature.[6]

RESULTS AND DISCUSSION

Effect of thermally conductive fillers (Al_2O_3 and SiC) on the thermal conductivity of RTV silicone rubber and silicone grease

As shown in Table I, the particle size distributions of SiC and α-Al_2O_3 were the same. The data in Table I shows that SiC improved the thermal conductivity of the sample more efficiently when the volume fraction of the filler was equal, which indicates that the thermal conductivity of the sample was related to the thermal conductivity of the thermally conductive filler. As the volume fraction of the filler increased, the thermal conductivity of the RTV silicone rubber and silicone grease increased. As shown in Table I, the RTV silicone rubber and silicone grease had thermal conductivities as high as 2.7 W/mK; the RTV silicone rubber also had a high tensile strength (>2 MPa). The RTV silicone rubber and silicone grease had the same thermal conductivities when the type, quantity, and particle size distribution of the fillers were the same. This indicates that the crosslinking density of the samples had little effect on their thermal conductivities.

Effect of the particle size distribution of the filler on the thermal conductivity

In Figure 1, the two curves show that the thermal conductivity of the samples (RTV silicone rubber) increased as the volume fraction of the filler increased. In addition, the thermal conductivities of the samples, which were filled with mixed particles, were higher than those of the samples filled with a single particle size. As shown in Figure 2, all of the samples (silicone grease) had the same total quantity of filler (the total volume fraction of the filler was 0.55), and the particle size of the fillers (0.8 and 6 μm) did not change. The data in Figure 2 show that thermal conductivity reached a maximum as the quantity of the small-size filler changed. The regular patterns of the curves were similar to each other no matter whether the filler was SiC (1.48 W/mK) or Al_2O_3 (1.31 W/mK).

For a polymer filled with particles, many bulk properties, such as the modulus and dielectric constant, also change according to the particle size distribution.[7] In highly filled polymers, the form of the effect of the particle size distribution on the polymer's bulk property is the maximum packing fraction (Φ_m; Φ_m = Real volume of the filler/Apparent volume of the filler),

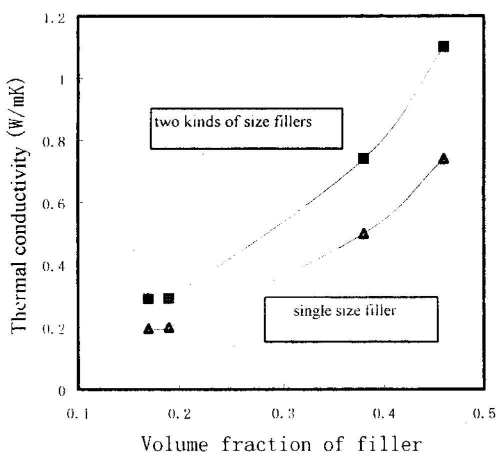

Figure 1 Thermal conductivity of different packing RTV silicone rubbers (the filler was SiC).

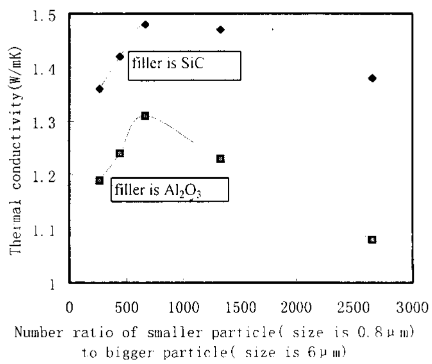

Figure 2 Effect of filler size distribution on the thermal conductivity of silicone grease.

which means Φ_m will change as the particle size distribution of the filler changes. The general approach for obtaining a high packing fraction is to use small-size particles to fill in the pores in the packed structure obtained from large-size particles. When the two kinds of differently sized fillers are packed closely enough, when Φ_m can reach a maximum, some of the bulk properties of the polymer will also reach some extreme value. As shown in Figure 2, the thermal conductivity, as one of the RTV silicone rubber and silicone grease's bulk properties, changed as the particle size distribution did. So, we conclude that it is the optimum particle sizes of the filler and the optimum quantities of the two sizes of fillers that made the filler packing closer, which thus led to more rapid heat elimination. RTV silicone rubber and silicone grease with the best thermal conductivities were obtained.

Effect of the particle size distribution on the viscosity of silicone grease (the RTV silicone rubber composition)

In Figure 3, the total quantity of the filler and the particle size of fillers are as the same as in Figure 2. As shown in Figure 3, when the total quantity of the filler and the particle sizes did not change, the viscosity was increased if the quantity of the small-size filler was too great or too little. So, if the quantity of the large-size filler and the small-size filler was optimized (600–700), we could obtain an RTV silicone rubber composition and silicone grease with minimum viscosities (3.4×10^4 mPa s).

According to these results (shown in Figs. 2 and 3), we obtained a maximum thermal conductivity and the lowest viscosity when the particle size ratio and the quantity of the two kinds of fillers were optimized.

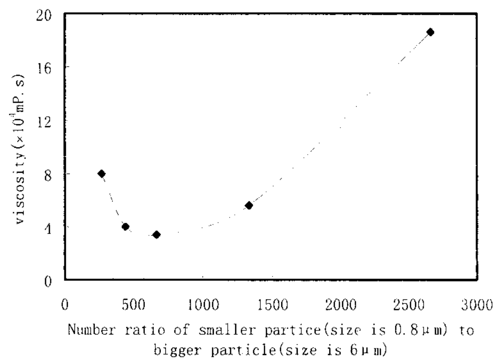

Figure 3 Effect of filler particle size distribution on the viscosity of silicone grease.

The closest packing of the filler simultaneously increased the sample's thermal conductivity and reduced the viscosity. It was instructive to solve the contradiction between the thermal conductivity and the processing behavior of the RTV silicone rubber and silicone grease. Although the viscosity and the thermal conductivity were the bulk properties of the RTV silicone rubber and silicone grease, Φ_m had different effects on them. We think that the thermally conductive filler broke the fluidity of the sample and improved the thermal transfer in the RTV silicone rubber and silicone grease.

CONCLUSIONS

This study showed that the quantity of two kinds of differently sized fillers had a significant effect on the thermal conductivity and the viscosity when we used differently sized thermally conductive fillers. The thermal conductivity and viscosity of the RTV silicone rubber and silicone grease changed with changes in the filler particle-size distribution. Both a high thermal conductivity (>2 W/mK) and a good processing behavior were acquired when the filler particle size distribution was optimized.

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