Preparation of SiO$_2$ particles with silicone-methoxy groups on surface and its co-curing hydroxyl silicone oil

Ran Zhou, Haihong Ma, Zhengfa Zhou, Weibing Xu, Fengmei Ren and Chunhui Li
School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei, 230009, People’s Republic of China
E-mail: zhengfazhou@hfut.edu.cn

Keywords: reactive SiO$_2$, co-curing, silicone rubber, composites, thermal conductivity

Abstract
SiO$_2$ particles were modified by $\gamma$-aminopropyltriethoxy silane (KH550) and $\gamma$-(2,3-epoxypropoxy)propyltrimethoxy silane (KH560) in sequence to prepare SiO$_2$ particles with silicone-methoxy groups on surface (SiO$_2$-s-Si(OCH$_3$)$_3$). X-ray photoelectron spectroscopy (XPS) and thermal gravimetric analysis (TGA) were used to characterize the modified SiO$_2$ particles. The SiO$_2$-s-Si(OCH$_3$)$_3$ particles and tetramethoxysilane were used to co-cure hydroxyl silicone oil. The strong interfacial interactions between silicone rubber and fillers, which came from hydrolyzed SiO$_2$-s-Si(OCH$_3$)$_3$ particles in situ reacting with hydroxyl silicone oil, had a great effect on the properties of composites. The mechanical properties, thermal conductivity, dielectric strength and volume resistivity of SiO$_2$-s-Si(OCH$_3$)$_3$/silicone rubber composites were considerably higher than that of pristine SiO$_2$/silicone rubber composites at the same content of SiO$_2$, while the dielectric constant and dielectric loss tangent of SiO$_2$-s-Si(OCH$_3$)$_3$/silicone rubber composites was lower than that of pristine SiO$_2$/silicone rubber composites at the same content of SiO$_2$.

Nomenclatures
- KH550: $\gamma$-aminopropyltriethoxy silane
- KH560: $\gamma$-(2,3-epoxypropoxy)propyltrimethoxy silane
- SiO$_2$-s-NH$_2$: SiO$_2$ particles with amino group on surface
- SiO$_2$-s-Si(OCH$_3$)$_3$: SiO$_2$ particles with silicone-methoxy groups on surface
- RTV: room temperature vulcanized

1. Introduction
Thermally conductive and electrically insulating silicone rubber composites act as an important role in fabrication of electronic and electric products, which express an increasing trend towards miniaturization and integration [1–3]. Usually, pure silicone rubber exhibits low thermal conductivity (0.1–0.3 W/(m$\cdot$K)), however, when filled with high thermal conductive powders, their thermal conductivities are improved greatly in broadening their applications [2]. To increase the thermal conductivity of the silicone rubber matrix, inorganic fillers such as silicon dioxide, aluminum oxide, zinc oxide, silicon nitride, silicon carbide, aluminum nitride, etc were commonly used [4, 5]. Yan et al [5] used surface modified silica as filler to study the effect of modified filler on the properties of rubber composite. But silicone rubber composites exhibit considerable thermal conductivity only when the fillers proportion was over 50 wt % with randomly dispersion [6, 7]. Feng et al [8] reported a novel fabrication method of graphite/polypropylene (PP) composites with high thermal conductivity, in which graphite flakes construct a continuous thermally conductive network. The results indicated that the thermal conductivity coefficient of the graphite/PP composites is markedly improved to be 5.4 W/(m$\cdot$K) at a graphite loading of 21.2 vol%. The high fillers content inevitably reduces the mechanical...
properties of the composites because some rigid particles act as defects in the polymer matrix. The high fillers loading also greatly affect the rheological behavior of the composites [9, 10]. Varenik et al [11] used two (hybrid) fillers with different aspect ratios, one is a plate-like filler, which sharply increases both viscosity and TC, and the other is an isotropic filler, which gradually increases these properties, to prepare silicone rubber composites with required thermal conductivity value.

Surface modification of fillers can improve the dispersion of the fillers in polymer and enhance the interfacial interaction between the fillers and polymer [12–14]. Malwela et al [15] used p-toluene sulfonic acid to treat boehmite alumina particles, and added the modified boehmite alumina to polypropylene/Polystyrene blends. The stiffness of the composites was improved to 27.5%, owing to the greatly reduced accumulation of particles by surface treatment. Jiang et al [16] grafted aminopropyltrimethoxysilane on to ground calcium carbonate (GCC) particles, the modified GCC excellently dispersed in poly(vinyl chloride) (PVC) matrix, and when the fillers content was 10 phr, the tensile strength of the PVC/GCC composites represented a 15.3% increase compared to that of the PVC filled with raw GCC particles. Kockmann et al [13] embedded modified zirconia particles in Polystyrene, cross-linkage was appeared between the fillers and the matrix. Zhong et al [17] chemically grafted vulcanization accelerator 2-benzothiazolethiol (M) onto the surface of silica to prepare silica-supported vulcanization accelerator (silica-s-M), which could be uniformly dispersed in styrene-butadiene rubber (SBR). The interfacial interaction between silica-s-M and SBR was significantly enhanced, because silica-s-M particles participated in the vulcanization of rubber chains.

The condensation silicone rubber, which owns excellent heat resistance, aging resistance, insulation and mechanical properties, can be vulcanized by silane compound with hydrolyzable polyfunctional groups under room temperature and suitably used as thermally conductive composite matrix. Han et al [18] synthesized polymethylmethoxysiloxane which could cross-link hydroxyl-terminated silicone prepolymer. Li et al [19] prepared resin modified aminopropyltriethoxysilane as a cross-linking agent. The thermal stability and mechanical properties of silicone rubber cured by resin modified aminopropyltriethoxysilane were significantly higher than that of ordinarily tetraethoxysilane. Chen et al [20] used tetramethoxysilane, tetraethoxysilane and methyltrimethoxysilane as cross-linkers to prepare a series of silicone rubbers. It could be conclude that the silicone-methoxy groups were an effective group to cross-link hydroxyl silicone oil.

The purpose of this work was to prepare modified SiO$_2$ particles with Si-methoxy groups on the surface, and use modified SiO$_2$ particles to cure hydroxyl silicone oil. As a result, condensation silicone rubber/SiO$_2$ composites were obtained. The interfaces between SiO$_2$ particles and silicone matrix were connected by chemical bonds, and the composites possess high thermal conductivity, high insulation and excellent mechanical properties at the same time.

Compared with other literature works, the advantages of the present investigation is that the modified SiO$_2$ particles with Si-methoxy groups on the surface obtained by two-step modification is introduced into the silicone rubber matrix, which can not only make the filler disperse more evenly, but also enhance the force between the filler and the matrix. More importantly, the modified silica can participate in the curing reaction of silicone rubber as a cross-linking agent, so that the thermal properties, electrical properties and mechanical properties of the obtained silicone rubber composite are significantly improved.

2. Experimental

2.1. Materials

Commercially available SiO$_2$ particles (d$_{50}$ 12 μm) were supplied by Shanghai Botong Chemical Co. Ltd, (China). The hydroxyl silicone oil was obtained from Shandong Dayi Chemical Co. Ltd, (China), the viscosity (25 °C) was 1000 mPa·s and the hydroxyl content were 0.3%. γ-aminopropyltriethoxysilane (KH-550), γ-(2,3-epoxypropoxy)propyltrimethoxysilane (KH560), tetraethoxysilane, toluene, ethanol were purchased from Aladdin Industrial Corporation (China). Dibutylsitanenanediyl diacetate was obtained from Alfa Aesar Chemistry Co. Ltd, (China). All reagents were laboratory grade chemicals and used as received without any further purification except toluene, which must be purified by removing the moisture before using. In a 250 ml round-bottom flask, 160 ml toluene, 1 g sodium, and 0.1 g benzophenone were introduced. The mixture was refluxed at 120 °C until the solution color changed to dark blue. Then the solution was heated to 130 °C and the toluene in the flask was distilled, sealed and stored for using.

2.2. Surface modification of SiO$_2$ particles

The step of the preparation of modified SiO$_2$ particles with silicone-methoxy groups at surface (SiO$_2$-s-Si(OCH$_3$)$_3$) was shown in scheme 1.

KH550 (2 wt% based on the weight of SiO$_2$ particles), water (the molar ratio of water to KH550 was 3:1) and ethanol (weight equal to KH550) were added to a glass vessel, and then the mixture was kept at 30 °C for 0.5 h to
hydrolyze KH550. SiO2 particles were added to a SHR-10C high-speed mixer (Jiangsu Zhangjiagang Bell Machinery Co. Ltd, China). When the temperature of the SiO2 particles reached 100 °C, the hydrolyzed KH550 solution was poured into the high-speed mixer uniformly and stirred for 15 min. The product was washed with absolute ethanol for three times. The modified SiO2 (SiO2-s-NH2) was dried in a vacuum oven at 80 °C for 8 h.

12.0 g of KH560 and SiO2-s-NH2 (300.0 g) obtained were added to 300 ml of anhydrous toluene in a three-necked round bottom flask equipped with a mechanical stirrer and condenser topped with nitrogen, and the mixture was stirred for 4 h at 80 °C under nitrogen atmosphere. The product was filtered and washed with absolute ethanol, and then dried in a vacuum oven at 80 °C for 8 h to get the modified SiO2 particles with silicone-methoxy groups at surface (SiO2-s-Si(OCH3)3).

2.3. Preparation of SiO2/silicone rubber composites
A certain amount of hydroxyl silicone oil and pristine SiO2 were dispersed in a commingler equipped with electric stirrer at 500 rpm for 10 min in a SG1200/750 TS-F glove box (Vigor High Purity Gas Equipment Technology (Suzhou Industrial Park) Co., Ltd, China) with nitrogen. After uniform dispersion, dibutyltin diacetate (0.1 wt% based on the weight of hydroxyl silicone oil) and a certain amount of tetramethoxysilane were added to the commingler as catalyst and crosslinking agent, respectively. After mixing, the commingler was covered with a lid, which possesses a hole with the diameter of 1 mm, and transferred into a vacuum oven within 10 s to drive away the bubbles, and then it was poured into a mold and cured at room temperature. Finally, the SiO2/silicone rubber composites were obtained. When SiO2-s-Si(OCH3)3 particles were used, the fabrication process of composites was the same as that of pristine SiO2, but the grafted silicone-methoxy groups was calculated as part of the cross-linking agent to ensure all of the composites containing equivalent amount of silicone-methoxy groups.

2.4. Characterization
2.4.1. X-ray photoelectron spectroscopy (XPS)
XPS (ESCALAB250, Thermo, USA) was employed to analyze the interaction between coupling agent and modified SiO2 particles.

2.4.2. Thermal gravimetric analysis (TGA)
TGA (TG-209-F3, NETZSCH, Germany) was used to analyze the loading of organics on the surface of modified SiO2 particles. TGA was conducted under nitrogen atmosphere at a heating rate of 20 °C min⁻¹ from 35 to 900 °C.

2.4.3. Scanning electron microscopy (SEM)
SEM (JSM-6490LV, JEOL Ltd, Japan) was used to observe the dispersion of SiO2 particles in composites. The cross-section of samples was coated with gold prior to examination.

2.4.4. Mechanical properties testing
Electronic universal testing machine (CMT4304, Shenzhen Sans, China) was used to investigate the mechanical properties of composites. The tensile strength and elongation at break were measured according to ISO 37:2005 by type II dumbbell specimen at a stretching rate of 500 mm min⁻¹. The values reported were the medians from five specimens each.

2.4.5. Thermal conductivity testing
The thermal conductivity of composites at room temperature were measured according to ASTM D5470 using Thermal analyzer (TPS 2500 S, Hot Disk, Sweden), which was based on the Transient Plane Source Method.
double helix probe of 4 mm diameter was placed between two lamellar samples of 2 mm thickness, flat on both sides.

2.4.6. Electrical resistivity measurements
The measurements were conducted on a digital high resistance test fixture PC68 (Shanghai Precision Instrument Manufacture, China) and a sample with a diameter of 60.0 mm and a thickness of 1.0 mm was used.

2.4.7. Dielectric strength measurements
The dielectric strength of composites was measured according to GB/T 1695 by a breakdown voltage tester (ZTC-50KV, Beijing Air Times Instrument Manufacture, China). The sample was cut into a circular shape with a diameter of 90 mm and a thickness of 1 mm.

2.4.8. Dielectric properties measurements
The dielectric constant and dielectric loss tangent of composites were determined by a LCR meter (TH2827C, Changzhou Tonghui, China) with frequency from 20 Hz to 1 MHz. The sample was cut into a circular shape with a diameter of 10 mm and a thickness of 1 mm.

3. Results and discussion

3.1. Preparation of SiO$_2$-s-$\text{Si(OCH}_3)_3$ particles
Figure 1 showed the XPS spectra of pristine SiO$_2$ and SiO$_2$ modified by different amount of KH550 (SiO$_2$-s-$\text{NH}_2$), and the corresponding data were provided in table 1. For pristine SiO$_2$ particles, the molar ratio of oxygen to silicon was about 2:1, which was consistent with the composition of silica particles. After SiO$_2$ particles were modified by different amount KH550 (figures 1(b)–(e)), two additional peaks of carbon and nitrogen elements appeared near 285 eV and 400 eV, respectively [21]. The content of nitrogen element on surface of SiO$_2$-s-$\text{NH}_2$ increased with the increasing content of KH550, and the content of oxygen and silicon element had a significant depletion, while the content of carbon and nitrogen element increased (table 1). Because nitrogen
element was only related to KH550, it could be concluded that amino groups exited on the surface of SiO2-s-NH2 particles.

Figure 2 showed TG curves of pristine SiO2 and SiO2-s-NH2 particles. The residual mass percent of pristine SiO2 particles was 99.41%, while that of SiO2-s-NH2 particles decreased with the increasing amount of KH550. The -OH groups on the surface of pristine SiO2 and SiO2-s-NH2, as well as organic residua of KH550 on the surface of SiO2-s-NH2, were removed at 900 °C. The amount of residual KH550 grafted on SiO2-s-NH2 could be calculated by comparing the residual mass percent deference between pristine SiO2 and SiO2-s-NH2. The residual KH550 grafted on the surface of SiO2-s-NH2 particles increased from 0.11% to 0.77% when the amount of KH550 increased from 1 wt% to 4 wt%. With the increasing content of KH550, the grafting ratio of KH550 on the surface of SiO2 increased, and the residual weight of the corresponding TG curve decreased. Meanwhile, it was found that the SiO2-s-NH2 particles agglomerated considerably after three washes with absolute ethanol and vacuum drying when the amount of KH550 was higher than 3 wt%. Therefore, the proper amount of KH550 was set at 2 wt% during the preparation process of SiO2-s-NH2 particles.

Figure 3 showed XPS spectra of SiO2-s-Si(OCH3)3 particles. KH560 amount (wt%): (c) 0; (f) 3; (g) 4; (h) 5; (i) 6.

Compared with SiO2-s-NH2 particles (sample c), the percentage of nitrogen element of SiO2-s-Si(OCH3)3 particles (sample f-i) decreased. Because a ring-opening reaction took place between the amino groups on the surface of SiO2-s-NH2 particles and the epoxy groups of KH560, and some silicone-methoxy groups were introduced on the surface of SiO2-s-Si(OCH3)3 particles. Since KH560 is free of nitrogen, the increase of element content ratios of C/N and O/N in SiO2-s-NH2 particles indicates the increase of reaction degree between.
SiO$_2$-s-NH$_2$ and KH560. Table 2 showed that the element content ratios of C/N and O/N reached the maximum value (13.05 and 11.30, respectively) when the amount of KH560 is 4 wt%. It indicated that the amino group on the surface of SiO$_2$-s-NH$_2$ particles reacted adequately with epoxy group of KH560 at this time, thus the proper amount of KH560 was set as 4 wt% of SiO$_2$-s-NH$_2$ particles.

Figure 4 showed TG curves of SiO$_2$-s-Si(OCH$_3$)$_3$ particles. The residual mass percent of SiO$_2$-s-Si(OCH$_3$)$_3$ particles (sample f-i) was lower than that of (sample c) at 900 °C. After SiO$_2$-s-NH$_2$ particles surface-treated by KH560, the residual organic chain of KH560 was attached to the surface of particles (Scheme 1), as a result, the residual mass percent of SiO$_2$-s-Si(OCH$_3$)$_3$ particles decreased at 900 °C. With the increasing amount of KH560, the residual mass percent of SiO$_2$-s-Si(OCH$_3$)$_3$ particles at 900 °C decreased at first and then increased. The organic part on the surface of SiO$_2$-s-Si(OCH$_3$)$_3$ particles reached maximum when the amount of KH560 was 4 wt%, which was the proper formulation. With the increase of reaction degree between SiO$_2$-s-NH$_2$ and KH560, the grafting ratio of KH560 on the surface of SiO$_2$-s-NH$_2$ particles increased, and the residual weight of the corresponding TG curve decreased. The reaction degree of the product corresponding to curve g in figure 4 is the largest, which is indicated in XPS analysis (table 2), so it has the smallest residual weight. Sample g was used as filler in subsequent article.

### 3.2. Proper amount of cross-linking agent

Through the silicone-methoxy groups on the surface of SiO$_2$-s-Si(OCH$_3$)$_3$ particles could cross-link hydroxyl silicone oil to prepare room temperature vulcanized (RTV) silicone composites, the amount of silicone-methoxy groups of modified particles might not enough to cure hydroxyl silicone oil. Tetramethoxysilane, which was the classical hydroxyl silicone oil cross-linking agent, was used to investigate what amount of silicone-methoxy groups is needed to cure hydroxyl silicone oil. Figure 5 showed the relationships between the mechanical properties of RTV silicone rubber and the amount of tetramethoxysilane (based on hydroxyl silicone oil mass). The proper amount of tetramethoxysilane was 4 wt%. This result may be due to the fact that moderate crosslinking can increase the tensile strength of the silicone rubber composite, so with the increase of the amount of tetramethoxysilane, the tensile strength increases first and then decreases, while the elongation at break may decrease with the increase of crosslinking degree.

| Samples | KH560 amount (wt%) | Composition (%) |
|---------|-------------------|-----------------|
| C       | 0                 | C1s 21.32, O1s 49.22, Si2p 25.66, N1s 3.80, O/N 12.95, C/N 5.61 |
| F       | 3                 | C1s 33.53, O1s 40.41, Si2p 22.38, N1s 3.68, O/N 10.98, C/N 9.11 |
| G       | 4                 | C1s 35.16, O1s 40.72, Si2p 21.00, N1s 3.12, O/N 13.05, C/N 11.30 |
| H       | 5                 | C1s 31.88, O1s 41.64, Si2p 23.30, N1s 3.18, O/N 12.75, C/N 9.78 |
| I       | 6                 | C1s 35.84, O1s 38.87, Si2p 22.05, N1s 3.24, O/N 12.00, C/N 11.10 |

Table 2. Surface element composition of SiO$_2$-s-Si(OCH$_3$)$_3$ particles.
When the SiO2-s-Si(OCH3)3 particles were used as fillers, the amount of tetramethoxysilane (m), which needed to be added to ensure all of the composites containing equivalent cross-linking agent, was calculated by the equation (3.1).

\[ m = m_1 \cdot 4\% - \frac{3m_2 \times M_1}{4M_2} \]  

(3.1) 

$m_1$ and $m_2$ were the quality of hydroxyl silicone oil and the SiO2-s-Si(OCH3)3 particles, respectively. $M_1$ and $M_2$ were molar mass of tetramethoxysilane and grafted functional group (scheme 1, -O-Si-(CH2)3-NH-CH2CH(OH)O-(CH2)3-Si(OCH3)3), respectively. $\varpi$ was the grafted functional group mass percent of SiO2-s-Si(OCH3)3 particles (sample g). By comparing the residual mass percent of pristine SiO2 particles (figures 1, 99.41%) and sample g (figures 4, 97.53%) at 900 °C, the $\varpi$ was 1.88%.

### 3.3. SiO2-s-Si(OCH3)3 particles co-curing hydroxyl silicone oil

#### 3.3.1. Mechanical properties

The tensile strength and elongation at break of composites of condensation silicone rubber filled with SiO2-s-Si(OCH3)3 and of pristine SiO2 were shown in figure 6. The tensile strength of two composites all increased at first and then decreased with the increasing content of SiO2, and the tensile strength of SiO2-s-Si(OCH3)3/silicone rubber and pristine SiO2/silicone rubber composites reached maximum value of 0.57 MPa and 0.80 MPa at 55 wt% and 50 wt% SiO2 content, respectively. The elongation at break of two composites all decreased with the increasing of SiO2 content. Wu et al. [22] reported similar conclusions.

The tensile strength and elongation at break of SiO2-s-Si(OCH3)3/silicone rubber composites were considerably higher than that of pristine SiO2/silicone rubber composites at same content of SiO2. The
reasonable explanation might be that the silicone-methoxy groups on the surface of SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub> particles participated the curing process hydroxyl silicone oil, and a Si-O-Si bond exited in the interface of SiO<sub>2</sub> and silicone rubber, which enhanced the interfacial interaction of SiO<sub>2</sub> and silicone rubber matrix. In addition, the dispersion of SiO<sub>2</sub> particles in silicone rubber matrix was also improved. Figure 7 compared the dispersion of SiO<sub>2</sub> particles in SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub>/silicone rubber and pristine SiO<sub>2</sub>/silicone rubber composites with the same content (60 wt%) of filler. The pristine SiO<sub>2</sub> particles agglomerated seriously, which could be observed clearly in figure 7(b). In contrast, the SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub> had a uniform dispersion. This may be due to the fact that SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub> particles with Si-methoxy groups on the surface participated in the curing reaction of silicone rubber, which greatly enhanced the interaction between SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub> particles and silicone rubber matrix, so as to make more uniform dispersion of the SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub> particles in the silicone rubber composite.

3.3.2. Thermal conductivity

Figure 8 showed the thermal conductivity of SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub>/silicone rubber and pristine SiO<sub>2</sub>/silicone rubber composites with different content of SiO<sub>2</sub>. The thermal conductivity of two composites increased significantly with the increasing weight fraction of SiO<sub>2</sub>. The filling of thermal conductive particles made a heat conduction loop inside the silicone rubber composites [23]. With increasing the filler amount, the heat conduction network inside the system increased, which could effectively improve the thermal conductivity of the material. In addition, compared with the pristine SiO<sub>2</sub> particles, the silicone rubber filled with SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub> particles had higher thermal conductivity with the same filler amount. The thermal conductivity of the filled composites depended on not only the content of the filler, but also the synergy of matrix and filler [24]. In this paper, in situ condensation reaction of hydrolyzed silicone-methoxy groups on the surface of SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub> particles with -OH groups of hydroxyl silicone oil strengthened the interfacial interactions between silicone rubber and SiO<sub>2</sub> particles. Figure 8 also showed that SiO<sub>2</sub>-s-Si(OCH<sub>3</sub>)<sub>3</sub> particles were more uniformly dispersed in silicone rubber, so the thermal conductive particles could touch each other more closely and heat could be transferred more easily. Many researchers [25, 26] also got the conclusion that composites
exhibited higher thermal conductivity with a better interfacial adhesion. When the content of SiO2-s-Si(OCH3)3 particles was 60 wt%, the thermal conductivity of silicone rubber reached 0.55 W/(m·K).

### 3.3.3. Electrical properties

Figure 9 showed the dielectric strength of the SiO2-s-Si(OCH3)3/silicone rubber and pristine SiO2/silicone rubber composites with different content of SiO2. The dielectric strength of the two composites decreased with the increasing content of SiO2 and the minimum value was 19.3 kV mm⁻¹. Unfilled silicone rubber has good insulation, and the dielectric strength was generally 20–30 kV mm⁻¹ [27]. It indicated that SiO2 particles could effectively improve the thermal conductivity but reduce the insulation of silicone rubber. The addition of SiO2 particles might cause the formation of electrical trees inside the silicone rubber, and thereby reduced the dielectric strength of silicone rubber. Compared with pristine SiO2/silicone rubber composites, the dielectric strength of SiO2-s-Si(OCH3)3/silicone rubber composites (the minimum value was 23.2 kV mm⁻¹) increased significantly at the same content of SiO2. It might be attributed to the strong interfacial interactions between silicone rubber and SiO2-s-Si(OCH3)3 particles suppressed electrical trees formation during breakdown voltage test.

Figure 10 showed the volume resistivity of the SiO2-s-Si(OCH3)3/silicone rubber and pristine SiO2/silicone rubber composites. The volume resistivity of pristine SiO2/silicone rubber composites increased sharply when the content of SiO2 particles was higher than 50 wt%, while that of SiO2-s-Si(OCH3)3/silicone rubber composites increased steadily. When the content of SiO2-s-Si(OCH3)3...
particles arrived 60 wt%, the volume resistivity of corresponding composites increased by one order of magnitude. It may be attributed to the reduction of chain mobility of silicone rubber by strong interfacial interaction between fillers and polymer matrix and thereby enhanced the volume resistivity. Khan et al[28] investigated the impact of mixture of micro-/nano-sized particles (micro-alumina-trihydrate and nano-silica) on electrical characteristic of silicone rubber-based composites. They found that the volume resistivity of composites increased by 690% compared with neat silicone rubber when 10 wt% micro-alumina-trihydrate and 2 wt% nano-silica were added. They also concluded that the improved volume resistivity of composites came from the enhanced interfacial interaction between fillers and polymer matrix.

The dielectric constant and dielectric loss tangent of the SiO2-s-Si(OCH3)3/silicone rubber and pristine SiO2/silicone rubber composites were shown in figure 11. The dielectric properties of fillers/silicone rubber composites were affected by not only the presence of fillers, but also the properties of the interface. The dielectric constant and dielectric loss tangent of SiO2-s-Si(OCH3)3/silicone rubber composites was lower than that of pristine SiO2/silicone rubber composites at the same content of SiO2. When the frequency is 1 MHz and the SiO2 content is 60 wt%, the dielectric constant and dielectric loss tangent of SiO2-s-Si(OCH3)3/silicone rubber composites were 4.17 pF cm⁻¹ and 0.0068, respectively, while those of the pristine SiO2/silicone rubber composites were 4.31 pF cm⁻¹ and 0.0079, respectively. Cross-linking of polymer caused a network structure formation, which effectively restricted orientation and relaxation of dipoles and thus decreased the dielectric constant and dielectric loss tangent of polymers [29, 30]. In SiO2-s-Si(OCH3)3/silicone rubber composites, the strong interfacial interactions between silicone rubber and SiO2-s-Si(OCH3)3, particles restricted orientation and relaxation of silicone rubber. As a result, the dielectric constant and dielectric loss tangent of SiO2-s-Si(OCH3)3/silicone rubber composites were lower than that of pristine SiO2/silicone rubber composites at the same content of SiO2.

4. Conclusions

In this paper, firstly, SiO2 particles with reactive silicone-methoxy groups on the surface were successfully prepared by two-step surface modifications. Then, RTV silicone rubber was prepared by co-curing as-prepared SiO2 particles with reactive silicone-methoxy groups and cross-linking agent with the hydroxy silicone oil,
which used as matrix polymer. At last, the effects of the amount of KH550 and KH560 for surface modification of SiO$_2$ powder and the amount of SiO$_2$–Si(OCH$_3$)$_3$ powder on the properties of silicone rubber were studied. It was found that the proper amount of KH550 and KH560 was 2 wt% and 4 wt%, respectively. When the SiO$_2$ content was 60 wt%, the tensile strength, elongation at break, thermal conductivity, dielectric strength, volume resistivity, dielectric constant and dielectric loss tangent at 1 MHz of SiO$_2$–Si(OCH$_3$)$_3$/silicone rubber composites were 0.76 MPa, 230%, 0.552 W/(m•K), 23.2 kV mm$^{-1}$, 1.50 $\times$ 10$^{-11}$ Ω•cm, 4.17 pF cm$^{-1}$, and 0.0067, respectively; while those of pristine SiO$_2$/silicone rubber composites were 0.48 MPa, 164%, 0.521 W/(m•K), 19.4 kV mm$^{-1}$, 1.07 $\times$ 10$^{-11}$ Ω•cm, 4.31 pF cm$^{-1}$ and 0.0079, respectively. The dispersion of fillers in SiO$_2$–Si(OCH$_3$)$_3$/silicone rubber composites was more uniform than that of pristine SiO$_2$/silicone rubber composites. The mechanical, thermal conductive and electrical properties of SiO$_2$–Si(OCH$_3$)$_3$/silicone rubber composites improved a lot compared with that of the SiO$_2$/silicone rubber composites, which was mainly attributed to the strong interfacial interactions existing between silicone rubber and fillers.

The as-prepared SiO$_2$ particles with reactive silicone-methoxy groups can react with many groups, when this kind of modified fillers is introduced into silicone rubber matrix, the dispersion of the fillers in the matrix is more uniform, at the same time, the interaction between the fillers and the matrix is enhanced, which makes the thermophysical and electrical properties of the composite improved obviously. This surface modification technology presented a strategy to prepare conductive composites having high thermal conductivity simultaneously with low dielectric loss.

Acknowledgments

The authors are grateful for the support and funding from Anhui Science and Technology Department, China (17030901076).

ORCID iDs

Zhengfa Zhou @ https://orcid.org/0000-0002-3846-4105

References

[1] Chiu H T, Sukachonnakul T, Kuo M T, Wang Y H and Wattanakul K 2014 Appl. Surf. Sci. 292 928–36
[2] Gao B Z, Xu Z J, Peng J J, Kang F Y, Du H D, Li J, Chiang S W, Xu C J, Hu N and Ning X S 2015 Thermochim. Acta. 614 1–8
[3] Li L Y, Zhang D, Liu J H and Li Y G 2019 Mater. Res. Express 6 125210
[4] Peng W Y, Huang X Y, Yu J H, Jiang P K and Liu W H 2010 Compos. Part A Appl. Sci. Manufac. 41 1201–9
[5] Yan L, Han B Y, Wen S P, Liu Y L, Yang H B, Zhang L Q and Liu L 2014 Compos. Part A Appl. Sci. Manufac. 62 52–9
[6] Wu K, Lei C, Huang R, Yang W X, Chai S G, Geng C Z, Chen F and Fu Q 2017 ACS Appl. Mater. Interfaces 9 76357–47
[7] Yin D Z, Zhang Q Y, Zhang H P and Yin C J 2010 J. Polym. Res. 17 689–96
[8] Feng C P, Ni H Y, Chen J and Yang W 2016 ACS Appl. Mater. Interfaces 8 19732–8
[9] Zhao M, Ren Z Z, Yang M B and Yang W 2019 J. Polym. Res. 26 28
[10] Lakshay D, Sateep B, Seung C L and Umesh V W 2019 Mater. Res. Express 6 124006
[11] Vareni AV, Radhakrishnan AV, Selvendran S and Regev O 2017 ACS Appl. Mater. Interfaces 9 7556–64
[12] Ghaemi F, Yumus K, Saleh M A M, Rashid S A and Lim H N 2015 RSC Adv. 5 28022–31
[13] Kockmann A, Porsiel JC, Siaudt R and Garnweitner G 2018 RSC Adv. 8 11199–18
[14] Gokuldas R and Ramesh R 2018 Mater. Res. Express 5 055302
[15] Malwela T, Khumalo V M, Salehiyan R and Ray S S 2018 J. Appl. Polym. Sci. 135 46376
[16] Jiang Z, Wang J W, Ge R K and Wu C J 2017 Polym. Bull. 75 1123–39
[17] Zhong B C, Jia Z X, Hu C D, Luo Y F, Jia D M and Liu F 2017 Compos. Part A Appl. Sci. Manufac. 96 129–36
[18] Han Y M, Zhang J Y, Yang Q Y, Shi L, Qi S C and Jin R G 2010 J. Appl. Polym. Sci. 107 3788–95
[19] Li Q G, Huang X J, Liu H, Wang B, Song Z Q and Song J 2017 ACS Sustainable Chem. Eng. 5 10002–10
[20] Chen D Z, Yi S P, Fang P F, Zhong Y L, Huang C and Wu X J 2011 React. Funct. Polym. 71 302–11
[21] Acers R G, Ellis A V, Alvino J, Lenehan C E, Khodakov D A, Metha G F and Andersson G G 2012 J. Phys. Chem. C. 116 6289–97
[22] Wu L F, Wang X M, Ning L, Han J J and Wan Z 2016 J. Appl. Biomater. Funct. Mater. 14 S11–4
[23] Chatterjee S, Nafezareh E, Tai H N, Schleifenbaum L, Nuesch F A and Chu BT T 2012 Carbon 50 5380–6
[24] Mao L, Han J B, Zhao D, Song N, Shi L Y and Wang J H 2018 ACS Appl. Mater. Interfaces 10 33556–63
[25] Chen J L, Jia Z X, Tang Y H, Wu L H, Luo Y F and Jia D M 2017 Compos. Sci. Technol. 144 1–7
[26] Shang J J, Zhu Y M and Li Z H 2017 Appl. Surf. Sci. 394 169–77
[27] He S J, Hu J B, Zhang C, Wang Q J, Chen L, Bian X M, Lin J and Du X Z 2018 Polym. Test. 67 295–301
[28] Khan H, Amin M, Ahmad A and Yasin M 2017 J. Elastomers Plast. 50 501–19
[29] Delighez O, Gorgues S, Yaziciyiu T, Yildirim S, Deger D and Ulutas K 2005 Polymer 46 3720–9
[30] Zhao S, Xie S C, Liu X L, Shao X M, Zhao Z, Xin Z X and Li L 2018 J. Polym. Res. 25 225