Improving properties of ceramic silicone rubber composites using high vinyl silicone oil

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ABSTRACT: Reactive high vinyl silicone oil (HVSO) was selected to prepare the ceramic silicone rubber composites. The effects of HVSO on the mechanical properties and thermal stabilities of ceramic silicone rubber composites were investigated. The structures of the cross-linked network of silicone rubber with or without HVSO were studied. The intermolecular space of silicone rubber was enlarged, and the cross-linked point was concentrated by addition of HVSO, which was demonstrated by cross-linking densities, scanning electron microscope (SEM) images, and dynamic mechanical analysis (DMA). The cross-linked network model was formed with the slipping of the cross-linked points along with the silicone rubber chain. Mechanical properties of composites were enhanced by the formation of this cross-linked network. The tear strength, tensile strength, and elongation at break of the composites were increased by 18.5%, 13.2%, and 37.4% by the adding of 2 phr HVSO, respectively. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41864.

INTRODUCTION

Ceramic silicone rubber composites with a polymeric matrix are widely used in thermal protection systems for space vehicles and civilian electrical equipments,[1–3] owing to its good ablation resistance, low cost, low density, and high electrical insulation properties. Silicone rubber–based ceramic composite is a heat insulation material for wire and cable insulation coating material.[4] This kind of material has outstanding capability to withstand oxidative environments at fire.[5] After being burned or heated, the relicts play an important role in reducing the temperature rise and act as an insulating protective layer.

Many ceramic silicone rubber composites have been reported.[6,7] Silicone rubber flame-retardant cable products were developed by German chemical company WACKER, which can continue to work for a period of time when confronted with fire with the formation of a ceramic layer.[8] The effects of silicone rubber, silica,[9–12] silicone oil,[13] montmorillonite,[14,15] zirconia,[16] carbon fibers,[17] and alumina[18,19] on the mechanical and ablation properties of the silicone rubber composites have been investigated in details. But the studies on mechanical properties of most ceramic silicone rubber composites are poor.[20–23] Yang *et al.*[24]

studied the effects of zirconia on silicone rubber–based ablative composite, the tensile strength and elongation at break of which ranged from 3.9–4.5 MPa and 78.7–158.5%, respectively.

HVSO is a kind of silicone oil contenting large amount of vinyl groups. The introduction of HVSO into ceramic silicone rubber composites was seldom reported. In this study, a promising method to enhance the mechanical properties and stability properties was studied. Silicone rubber composites containing different contents of HVSO were prepared, and the mechanical properties and thermal stabilities were investigated by universal testing machine (UTM), thermal analysis, respectively. The strengthening mechanism of HVSO on ceramic silicone rubber composites was proposed.

EXPERIMENTAL

Materials

Polydimethylsiloxane (PDMS 110-2) was commercially supplied by Shanghai Resin Co., China, with the weight-average molecular weight of about 550,000 and the vinyl content 0.15 mol %. Fumed SiO_2 (A-380 Shenyang Chemical Co., Ltd. China) with a BET surface area of 380 m^2g^{-1} was used. High vinyl silicone oil (210) was provided by Zhejiang Quzhou Chun Shun Silicone

Table I. Formulations of the Silicone Rubber Composites

	Silicone rubber (g)	Fumed SiO$_2$ (g)	Hydroxy silicone oil (g)	Methyl hydrogen silicone oil (g)	MgO (g)	ZrO$_2$(g)	HVSO(g)	HMDS(g)	DBPMH(g)
HVSO-0	100	60	8	0.6	10	10	0	18	2
HVSO-1	100	60	8	0.6	10	10	1	18	2
HVSO-2	100	60	8	0.6	10	10	2	18	2
HVSO-4	100	60	8	0.6	10	10	4	18	2
HVSO-8	100	60	8	0.6	10	10	8	18	2

Co., Ltd. China with the vinyl content of 10 mol %. 2,5-Bis(-tert-butylperoxy)-2,5-dimethylhexane(DBPMH), a peroxide as vulcanizator, was purchased from Jing Hui Chemical Co., Ltd. ZrO$_2$ powder and MgO(light) powder were supplied by Sinopharm Chemical Reagent Co., China and Shanghai Lingfeng Chemical Reagent Co., Ltd., respectively. Hydroxy silicone oil (209-3) and methyl hydrogen silicone oil (202) were obtained from Silicon Industry Co., Ltd. Laizhou Jintai (China) and Shanghai Yi Chu Silicone Material Co., Ltd. (China), respectively. HMDS was obtained from Shanghai Puzheng Biological Technology Co. Ltd. (China).

Composites Preparation
Formulations of the silicone rubber composites are shown in Table I. The composites were prepared in a HAAKE torque rheometer (HAAKE PolyLab System THERMAL instruments) at 60°C for 35 min. In order to get the uniform modification of the fumed SiO$_2$, fumed SiO$_2$ and HMDS were continuously added to silicone rubber, then the MgO, ZrO$_2$, HVSO, methyl hydrogen silicone oil were added. In order to avoid the hydroxyl reacting with HMDS, the hydroxy silicone oil was introduced into the composite as the last component. Then, the composites were mixed in a two-roll laboratory model of an open mixing mill (length 600 mm diameter 230 mm) and the vulcanizing agent DBPMH added. The mix was operated at room temperature for 15 min. Then, the composites were vulcanized in a mold at 165°C, 15 MPa for 15 min. The secondary vulcanization was carried out at 200°C for 2 h in an airflow drier.

Tear Properties
Tear strength of the samples was measured by using a computer-controlled electronic tensile testing machine (Shenzhen sans Materials Testing Limited, China). The specimens were prepared according to the GB/T 529-1999. The cross-head speed was 500 mm min^{-1}, and the results of five specimens were averaged.

Cross-Linking Density
The cross-linking densities of the samples were measured by the equilibrium solvent swelling method. A certain amount of sample (about 0.5 g) was put into excess N-heptane in a sealed vessel at $25.0 \pm 0.1°C$.[25] After being immersed in N-heptane for 7 days, the swelling equilibrium was achieved, and the samples were taken out and weighed. The molecular weight between cross-linking points of silicone rubber (M_c) is calculated from the Flory–Rehner relation as shown in eq. (1):[26]

$$M_c = \frac{\rho_2 v_1 \left(\frac{v_2}{2} - v_2^{\frac{1}{3}} \right)}{[\ln(1 - v_2) + v_2 + \chi_1 v_2^2]} \tag{1}$$

Where v_1 is solvent molar volume (100.2 cm^3 mol^{-1} for N-heptane), ρ_2 is the measured density of silicone rubber composites, v_2 is the measured equilibrium volume fraction of silicone rubber composites and χ_1 is the polymer–solvent interaction parameter which was 0.49 for silicone rubber N-heptane at 20°C. The results of five specimens were averaged.
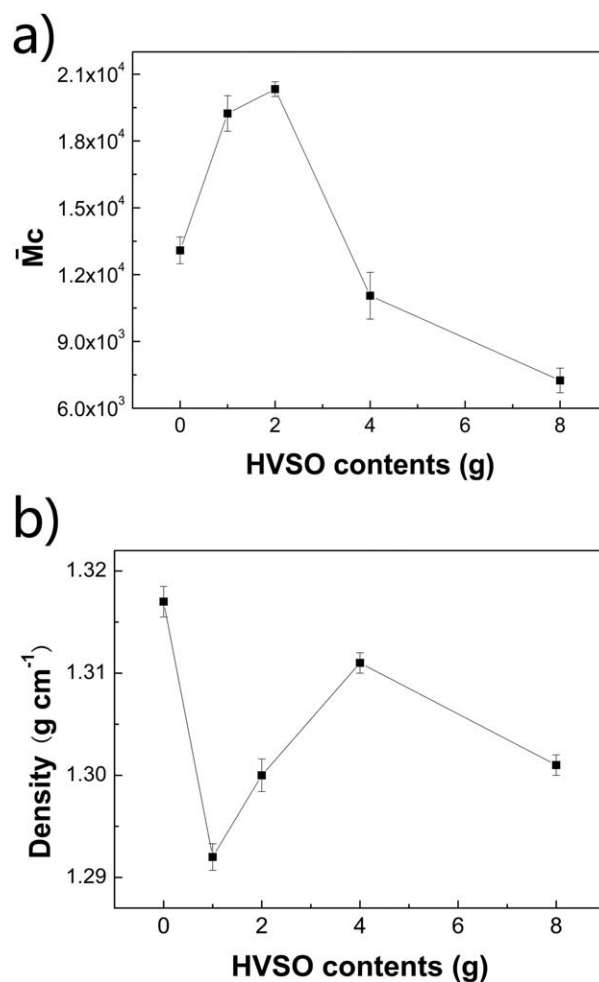

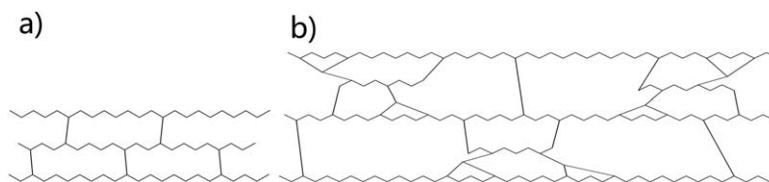**Figure 1.** (a) The molecular weight and, (b) the densities of composite materials depend on the content of HVSO.

Figure 2. (a) Cross-linked networks of composites without HVSO, (b) cross-linked networks of composites with HVSO.

Thermal Properties

Thermal gravimetric analysis (TGA) was performed on a NETZSCH STA 409 equipment. About 10 mg samples was heated in a platinum crucible from room temperature to 650°C under nitrogen, with heating rate of 10°C min^{-1}.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed on vertical mode using a dynamic mechanical analyzer (DMA Rheogel-E4000, UBM Instruments). The storage modulus (E') and mechanical loss factor (tan δ) of the samples were measured at a fixed frequency of 11 Hz. The sample dimensions were 25 mm $\times$ 6 mm $\times$ 2 mm. The samples were tested with a temperature ranging from -70°C up to -10°C at atmospheric pressure and a heating rate of 3°Cmin^{-1}.

Morphological Characterization

Morphological observations of the ceramic silicone rubber composites were done using the scanning electron microscope (SEM S3400N HITACHI Instruments), obtained from tear fracture in tensile testing machine, and subsequently coated with a thin gold layer using a scanning electron microscopy (SEM) coating machine.

RESULTS AND DISCUSSION

Structure of the Cross-Linked Network

The M_c and the densities of the silicone rubber depending on the content of HVSO are shown in Figure 1. M_c is calculated from the Flory–Rehner relationship in eq. (1). As shown in Figure 1a, the $\overline{M_c}$ of silicone rubber increased firstly and then descended with the increase in HVSO. $\overline{M_c}$ for 0, 1, 2, 4, and 8 phr of HVSO-modified
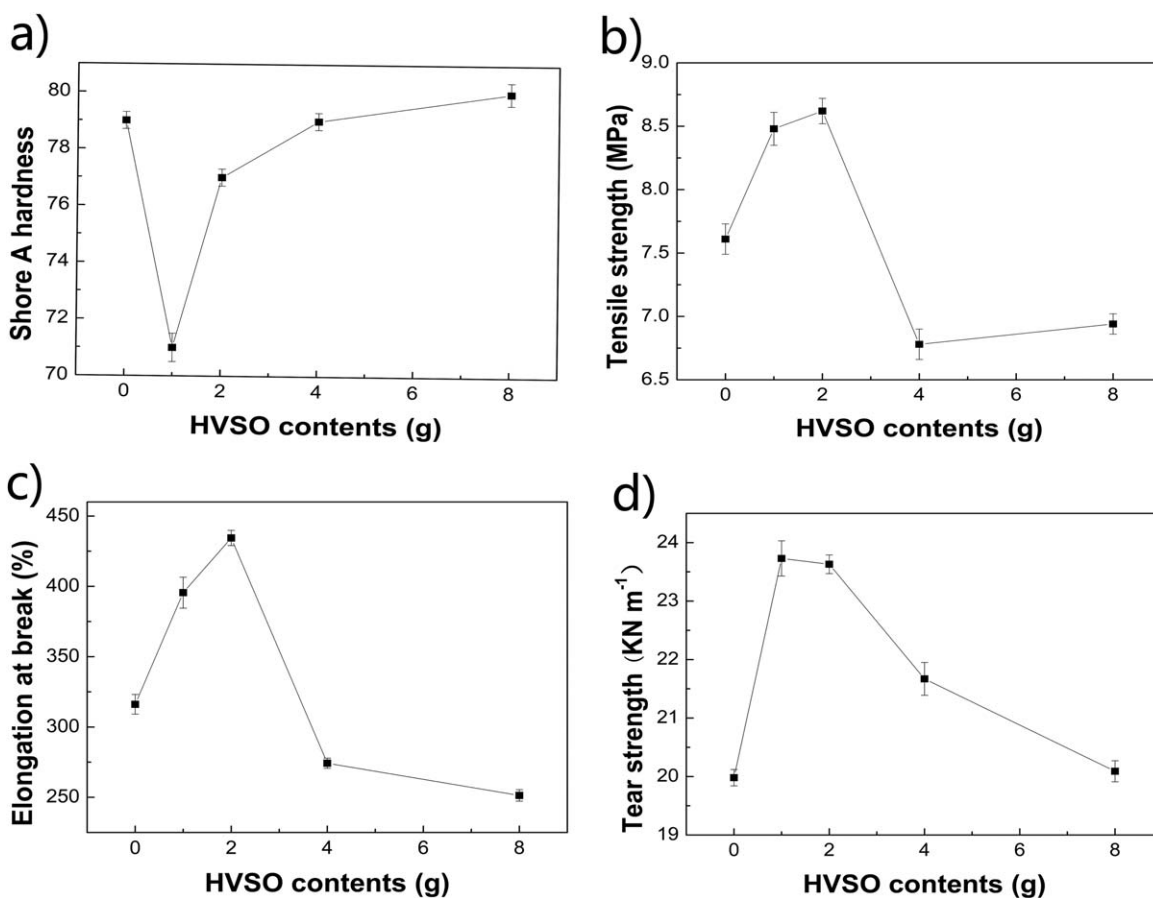

Figure 3. The properties of composites depend on the content of HVSO: (a) shore A hardness, (b) tensile strength, (c) elongation at break, (d) tear strength.
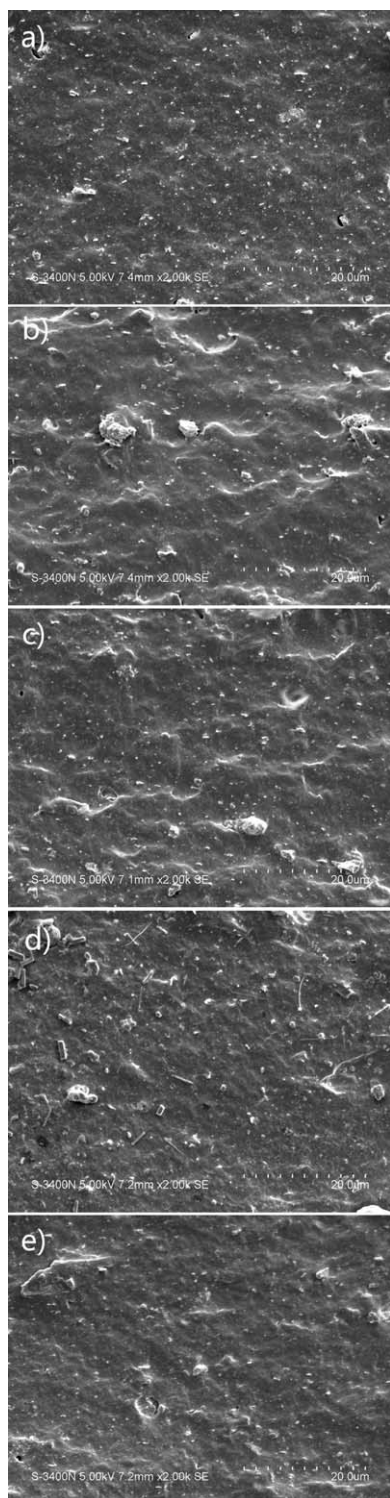
Figure 4. Tear fractographs of composites: (a) HVSO-0, (b) HVSO-1, (c) HVSO-2, (d) HVSO-4, (e) HVSO-8.

et al.[25] and Zhao et al.[27] have established a cross-linked structure model of silicone rubber. As a small molecule, HVSO changed the materials cross-linked structure and the structure is similar to them. However, with the increase in HVSO, the cross-linking densities improved. The space for solvent reduced, resulting in less solvent be absorbed into composites and there be a diminutive $\overline{M_c}$ with eq. (1).

The densities of the composites were measured and the changes of densities with the increase in HVSO are displayed in Figure 1b. It is clear that with the increasing of HVSO, the densities of the composites descended firstly, then increased and eventually dropped. As a small molecule, HVSO existed between the silicone rubber chains makes the cross-linked point concentrated, which increased the intermolecular space and decreased the composites densities. But HVSO can increase the cross-linking density of silicone rubber and make the uniform distribution of cross-linked points at some dosages. Four phr of HVSO has the higher density than other contents of HVSO. While more than 4 phr of HVSO, the density of composites decreased.
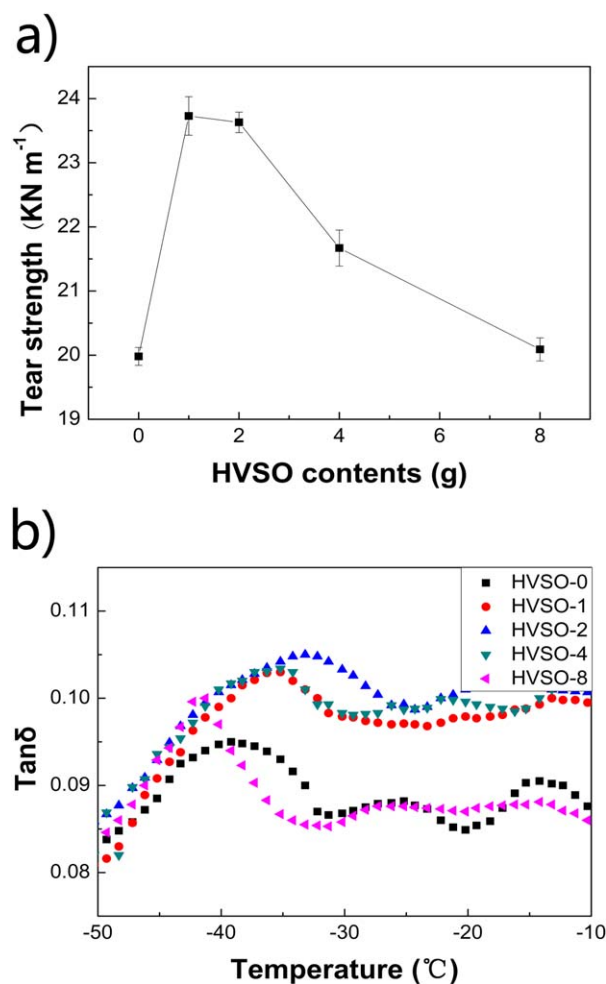

Figure 5. (a) Storage modulus E' and (b) tan δ of the composites versus temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

silicone rubber samples were $1.3 \times 10^4, 1.9 \times 10^4, 2.0 \times 10^4, 1.1 \times 10^4$, and $7.2 \times 10^4 \mathrm{g\ mol}^{-1}$, respectively. The composite with 2 phr of HVSO has the maximum value of $\overline{M_c}$ which means that it has the lowest cross-linking density. It is owing to the distance between silicone rubber molecules increased by the existence of HVSO [Figure 2(a,b)] and more solvent was absorbed. Xu
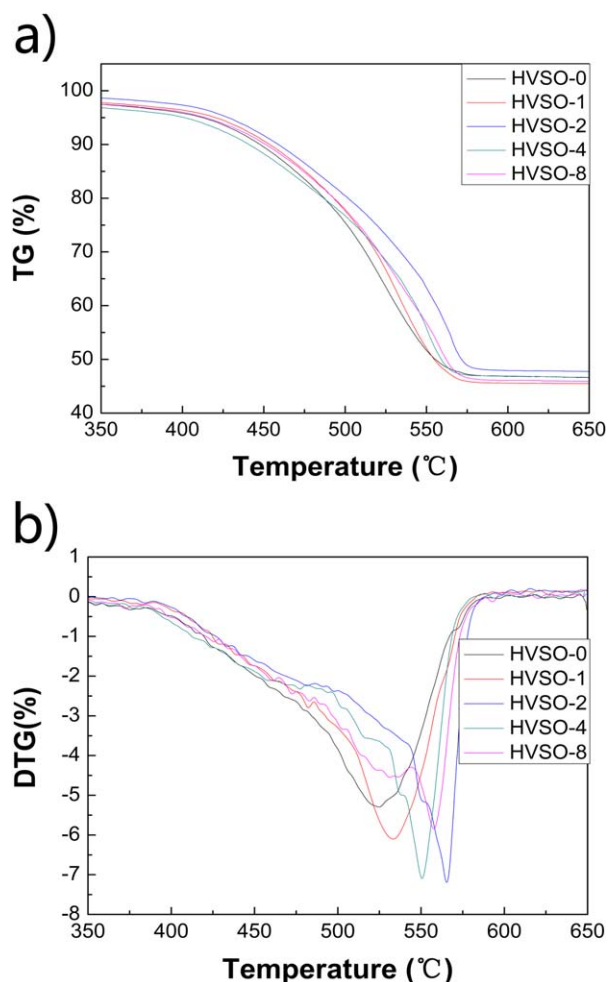
Figure 6. (a) TG and (b) DTG of the composites in nitrogen versus temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical Properties

The tensile strength, elongation at break, tear strength and Shore A hardness of these composite materials were measured, and the results were shown in Figure 3. The tensile strength, elongation at break, tear strength, and Shore A hardness of these materials are related with the content of HVSO. The variation of Shore A hardness exhibits a different trend from those of the tensile strength, tear strength, and elongation at break. During the measuring process, the needle of the detector makes the rubber molecule move.[9] In the case of intact rubber mole-

cule, by virtue of HVSO existence between the rubber cross-linked networks, the resistance against the move is much smaller. Consequently, HVSO weaken the Shore A hardness. However, an excess of HVSO can improve the Shore A hardness. Figure 3a shows the Shore A hardness of the composite with 4 phr of HVSO was 79, which was equal to the one that without HVSO. With more HVSO, the value of Shore A hardness was higher.

From Figure 3(b–d), we can learn that HVSO would enhance the mechanical properties of the composites. The mechanism of HVSO enhancing the mechanical properties is the change of cross-linked network structure of matrix. An increase in HVSO increased the cross-linking densities and the intermolecular space. Thus, the interaction, physically or chemically, changed, which brought better mechanical properties to the composite materials.

The variation of tensile strength of silicone rubber with the amount of HVSO is shown in Figure 3b. The tensile strength graph shows an optimum amount of HVSO (8.6 MPa for 2 phr), and the tensile strength is 7.6 MPa for silicone rubber composites without HVSO. This is because that 1 or 2 phr of HVSO can enhance the ductile behavior, which makes the stress concentrated on the dense cross-linked points and increases the tensile strength. While the content of HVSO is more than 2 phr, the cross-linked network of the rubber will become excessively tighter and the flexibility of the rubber will diminish. This leads to less ductile behavior and low tensile strength. The elongation at break is well correlated with the tensile strength. As shown in Figure 3c, the elongation at break decrease steadily from 434% to 251% with the content of HVSO increased from 2 phr to 8 phr. But the elongation at break with low content of HVSO is higher than that of the sample without HVSO.

The tear strength of samples with HVSO is higher than that of the sample without HVSO (Figure 3d). The tear strength for 0, 1, 2, 4, and 8 phr HVSO-modified silicone rubber samples were 20.0, 23.8, 23.7, 21.7, and 20.1 KNm^{-1}, respectively, which demonstrated that the tear strength of composites was improved by the addition of HVSO. The improvement of tear strength is due to the tear strength failure mechanism has changed after the addition of HVSO as described below.

Figure 4 are the images of tear fractographs of samples with various content of HVSO. The tear fractograph of HVSO-0 is shown in Figure 4a. The smooth fracture surface means that it is brittle rupture and has poor tear strength, which is correlated to the above results and Agarwal[13] et al. study. Owing to the largest tear strength

Table II. Characteristic Temperatures for the Degradation of Silicone Rubber Composites TGA Tested in N_2 Atmosphere

Sample	Initial degradation temperature (°C)	Inflection point temperature (°C)	Final temperature (°C)	Residual (wt. %)
HVSO-0	460.4	524.9	560.9	46.6 ± 1.1
HVSO-1	497.4	540.8	568.8	46.2 ± 0.3
HVSO-2	493.3	568.2	573.2	47.1 ± 1.1
HVSO-4	485.2	550.4	566.4	46.4 ± 0.7
HVSO-8	472.3	560.3	565.3	46.0 ± 0.8

of sample HVSO, its fracture surface is the more coarser and shows good interaction (Figure 4b). The coarse fracture surface absorbed much energy during the tear processing that leads to a higher tear strength. HVSO-2 also shows a coarse fracture surface (Figure 4c), but it is smoother than HVSO-1. With the increase in HVSO, the fracture surface is more and more smooth [Figure 4(d,e)]. All these features of Figure 4d and e support a marked fall in tear strength with the increase in HVSO. It is obvious that the addition of HVSO has changed the tear failure mechanism from brittle fracture to ductile fracture and then back to brittle fracture. Thus, by the addition of the HVSO, higher mechanical properties of the ceramic silicone rubber can be obtained.

Dynamic Mechanical Properties

The dynamic mechanical properties of the composites were measured, and the results were shown in Figure 5. Figure 5a shows the samples storage modulus E' of HVSO content as a function of temperature. It can be found that the log E' value of HVSO-0 sample is relatively higher than those containing HVSO samples. For the HVSO existed between the silicone rubber chains improved the chains slipping abilities, the HVSO weaken effect for storage modulus is remarkable. However, with the increment of HVSO from 2 phr to 8 phr, the cross-linking densities improved and the chains slipping abilities reduced, and thus, the storage modulus E' was increased. The results also demonstrate that the flexibility of silicone molecular chains is increased at low level of HVSO, while with high content of HVSO the composites become stiff.

The tan δ versus temperature curves of HVSO-modified silicone rubber composites are shown in Figure 5b. The plots for different content HVSO show peaks located at -37.9, -35.2, -32.6, -36.5, and -41.3, respectively. It can be seen that the addition of HVSO in silicone rubber composites considerably affected the T_g and the peak of tan δ. After adding HVSO, the cross-linking points of the composites were increased and concentrated, so the T_g improved. While HVSO existing between the silicone rubber chains increased the friction, so the tan δ peaks of composites with HVSO were higher than without HVSO.[28,29]

Thermal Gravimetric Analysis

The TGA results of the composites from 350°C to 650°C in nitrogen are shown in Figure 6. Figure 6a shows TG curves of the samples. The residue of HVSO-0 at 650°C was 46.6 ± 1.1 wt. % of the initial weight as shown in Table II, which mainly be composed of MgO, ZrO_2, SiO_2, and siliconoxycarbide[16] ($SiOxCy$, $x < 2$, $y > 0$). It can be seen that the silicone rubbers decomposed with the increase in temperature, while the initial degradation temperature was improved by the addition of HVSO.[30]

The DTG results of the silicone rubber composites from 350°C to 650°C in nitrogen are shown in Figure 6b. In the temperature range between 400°C and 600°C, the decomposition of silicone rubber took place quickly. Slow weight decrements of samples with 1, 2, 4, and 8 phr HVSO were observed in the DTG curves compared with the sample without HVSO. It is owing to the increment of cross-linked densities with the existence of HVSO. However, with the increase in the HVSO, the

degradation temperature dropped but still higher than the sample that without HVSO, which tally to the tear strength.

CONCLUSIONS

The influence of HVSO on mechanical properties of ceramic silicone rubber composites was studied. The tear strength, tensile strength, and elongation at break of composite materials were improved by the addition of HVSO. Owing to HVSO increased the silicone rubber cross-linking densities and the intermolecular space, a special cross-linked network structure was formed. By contrasting the mechanical properties, thermal stabilities and physical properties, it turns out that HVSO is useful in improving the properties of silicone rubber composites. Two phr HVSO is the best choice.

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