Modification of Fe_2O_3 and Its Effect on the Heat-Resistance of Silicone Rubber

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ABSTRACT: By means of the wet chemical surface modification, the surface of Fe_2O_3 was modified by vinyltrimethoxysilane (VTMS). Infrared spectroscopy (IR) was used to investigate the structure of the modified Fe_2O_3, and the result showed that VTMS has been attached onto the surface of Fe_2O_3. Effect of VTMS concentration on the active index of the modified Fe_2O_3 was also studied, and the result indicated that the active index of the modified Fe_2O_3 increases with the increase of VTMS concentration and the optimal concentration of VTMS is 12 wt %. The effect of the modified Fe_2O_3 on the tear strength of silicone rubber before and after aging was studied and it was found that in comparison with the unmodified Fe_2O_3 the addition of the modified Fe_2O_3 results in the significant increase of the tear strength before ageing because of the increase of the crosslinking density of silicone rubber. The tear strength of silicone rubber filled with the modified Fe_2O_3 after ageing is higher than that with the unmodified Fe_2O_3, indicating that the modification of Fe_2O_3 can improve the heat-resistance of silicone rubber owing to the fine dispersion of the modified Fe_2O_3 in silicone rubber. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3202–3206, 2009

Key words: silicone rubber; Fe_2O_3; surface modification; heat-resistance

INTRODUCTION

Silicone rubber is one of the most important types of synthetic rubbers with excellent thermal stability, low-temperature toughness, and electrical-insulting properties and has been widely used in various areas.[1] Although the heat-resistance of silicone rubber is better than that of conventional rubbers, it is still not sufficient in some high temperature circumstances.[2] Therefore, it is necessary to improve the heat-resistance and prolong the life time of silicone rubber.

Among various modification methods, adding heat-resistant additives is an efficient way to improve the heat-resistance of silicone rubber. Metal oxides,[3–5] such as ferric oxide (Fe_2O_3) and cerium oxide (CeO_2), can be used as heat-resistant additives and suppress the oxidative degradation of side chains of polysiloxane to improve the heat-resistance of silicone rubber. However, metal oxides are easy to agglomerate because of their high surface energy. Furthermore, the poor compatibility between metal oxides and silicone rubber results in the bad dispersion of metal oxides in silicone rubber and the poor dispersion affects the heat-resistance of the modified silicone rubber. The major challenge is to find novel methods to improve the dispersion of metal oxides in silicone rubber.

Fortunately, this problem can be resolved by using some special techniques, such as, adding surface modifying agents.[6] VTMS is a surface modifying agent having methoxy group and unsaturated vinyl group. The methoxy group in VTMS could hydrolyze to form hydroxy and react with active groups on the surface of Fe_2O_3. On the other hand, vinyl in VTMS may take part in the crosslinking of methylvinylsilicone gum and is beneficial for a good interfacial bonding between Fe_2O_3 particles and silicone rubber. As a result, VTMS modified Fe_2O_3 could prevent its aggregation, increase the interfacial compatibility between silicone rubber and Fe_2O_3, and improve properties of silicone rubber.[7,8] In the present work, Fe_2O_3 was used as a heat-resistant additive and VTMS modified Fe_2O_3 was prepared using the surface modification method. The structure of the modified Fe_2O_3 was investigated with infrared spectroscopy (IR). The dispersion of VTMS modified Fe_2O_3 in silicone rubber, and the effect of the modified Fe_2O_3 on the tear strength of silicone rubber before and after ageing were also studied.

EXPERIMENTAL

Materials

Methylvinylsilicone gums including GP300 and GP700 and VTMS (Z-6300) were purchased from

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Dow-Corning Corporation. Fe_2O_3 and 2,5-bis(*tert*-butyl peroxy)-2,5-dimethyl hexane (DBPMH) were obtained from Zhejiang Zhengqi Chemical Corporation and Tianjian Akzo Nobel Peroxide Corporation (China), respectively. The reagents used in the experiments, such as heptane, etc., were analytically pure, and commercially available. No further treatment was needed before use.

Surface modification of Fe_2O_3

Heptane and VTMS were mixed under stirring, and an appropriate amount of Fe_2O_3 was added. The mixture was heated to 70°C under vigorous stirring for 4 h. The suspension was then filtered and the precipitate was rinsed thoroughly with alcohol to remove VTMS that has not attached onto the surface of Fe_2O_3. The precipitate was dried in a vacuum oven for 24 h. A white powder of the modified Fe_2O_3 was obtained. By changing the concentration of VTMS a series of samples were prepared.

Preparation of heat-resistant silicone rubber

Methylvinylsilicone gum (GP300 and GP700), Fe_2O_3 and DBPMH (1.5 wt %) were mixed at room temperature in a two-roller mixer (SK-160B, Shanghai Rubber Machinery Plant) and vulcanization was carried out at 170°C for 10 min under 8 MPa using a rubber compression machine. The vulcanizate samples were postcured at 200°C for 4 h.

Apparatus and measurement

IR analysis of the modified Fe_2O_3 was carried out on a PE-200 FT-IR spectrometer.

The active index was used to reveal the modification effect of Fe_2O_3. Certain amount of the modified Fe_2O_3 in water (Fe_2O_3 content was 10 wt %) was added into a 100 mL test beaker and stirred for 30 min. After keeping stationary for 1 h, the Fe_2O_3 powder that floats in the upper layer of water was taken out and then dried and weighed. The active index was analyzed in terms of the amount of Fe_2O_3 powder that floats in the upper layer of water per gram of the total Fe_2O_3.

A Philips 505 SEM was used to observe the dispersivity of Fe_2O_3 in silicone rubber.

Swelling measurements were made by gravimetric method. The cross-linked silicone rubber was immersed in toluene at 25°C, then the swollen silicone rubber was taken out at an appropriate time interval, and the toluene adhered to the surface of the silicone rubber was removed with filter paper, and quickly weighed on a Mettler analytical balance (Model AL 204), and then replaced into toluene immediately. This procedure was repeated until the sample attained constant weight.

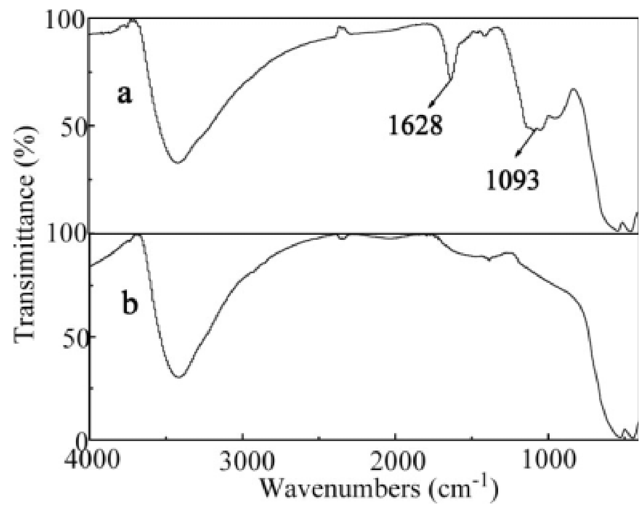

Figure 1 FTIR spectrum of Fe_2O_3 ((a) modified Fe_2O_3 (b) unmodified Fe_2O_3).

The ageing of silicone rubber was conducted at 300°C for 30 min in an ageing oven (Hangzhou Lantian Instrument). The weight loss of silicone rubber was studied by a thermogravimetry (Perkin-Elmer Pyris 1 TGA) under air atmosphere. The samples were heated from 25 to 600°C at a heating rate of 10°C/min and the change of the weight loss of silicone rubber with temperature were recorded.

The tear strength test before and after ageing was carried out on a Zwick/Roell Z202 tester (Germany) at a crosshead speed of 500 mm/min according to GB/T529-1999.

RESULTS AND DISCUSSION

Surface modification of Fe_2O_3

The structure of VTMS modified Fe_2O_3 were characterized by IR and the results were showed in Figure 1. It was found that the peaks at 550 and 470 cm^{-1} are the characteristic peaks of the unmodified Fe_2O_3. In comparison with the unmodified Fe_2O_3, the peak at 1628 cm^{-1} is ascribed to the stretching vibration of C=C bond and the wide peak at 1093 cm^{-1} shows the stretching vibration of Si—O bond, indicating that the hydrolysate of VTMS has reacted with hydroxy on the surface of Fe_2O_3.[8,9] However, the appearance of peak at 3430 cm^{-1} shows that hydroxy on the surface of Fe_2O_3 has not reacted with VTMS completely.

Unmodifed Fe_2O_3 is a polar substance and its density is high in comparison with water, therefore, it sinks naturally in water. After modification by VTMS the surface of Fe_2O_3 becomes nonpolar, therefore, the VTMS modified hydrophobic Fe_2O_3 can float and don't sink in water. The active index was

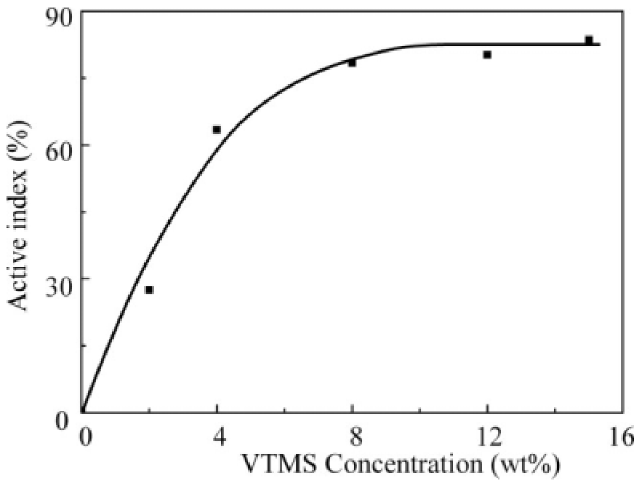

Figure 2 Change of the active index of modified Fe_2O_3 with VTMS concentration.

used to characterize the modification effect of Fe_2O_3.[10] Figure 2 shows the effect of VTMS concentration on the active index of the modified Fe_2O_3 in water. It was found that the active index of the unmodifed Fe_2O_3 in water is 0, indicating the poor hydrophobic properties. With the increase of VTMS concentration, the active index of the modified Fe_2O_3 in water increases significantly, which indicates that a modified hydrophobic layer exists on the surface of Fe_2O_3 and the suspension becomes more stable. When VTMS concentration is about 12 wt %, the active index of the modified Fe_2O_3 in water is 80.2% and almost remains constant, indicating that the optimal VTMS concentration is 12 wt %.

Effect of the modification and content of Fe_2O_3 on the tear strength of silicone rubber before and after ageing

Effect of the modification and content of Fe_2O_3 on the tear strength of silicone rubber before and after ageing was studied and the results were shown in Table I. It was found that before ageing the tear strength of silicone rubber increases significantly with the increase of the modified Fe_2O_3 content,

TABLE I
Effect of the Modification and Content of Fe_2O_3 on the Tear Strength of Silicon Rubber before and after Ageing ($kN\ m^{-1}$)

Fe_2O_3 content (wt %)	Silicone rubber with unmodified Fe_2O_3		Silicone rubber with modified Fe_2O_3	
	Before ageing	After ageing	Before ageing	After ageing
0	29.9	17.9	29.9	17.9
0.5	30.6	22.5	34.1	24.4
1.5	30.8	25.4	35.2	31.9

TABLE II
The Swelling ratio, Molecular Weight Between crosslinking points, crosslinking Density of Silicone Rubber Filled with 1.5 wt % Unmodified and Modified Fe_2O_3

Species of Fe_2O_3	Q_m (%)	M_c ($g\ mol^{-1}$)	$D \times 10^{-4}$ ($mol\ g^{-1}$)
Unmodified Fe_2O_3	183	2708	1.85
Modified Fe_2O_3	176	2517	1.99

whereas the tear strength of silicone rubber filled with the unmodified Fe_2O_3 almost does not change.

To elucidate the reason why the tear strength increases after the addition of the modified Fe_2O_3, the crosslinking behavior of silicone rubber was studied.[11] Swelling properties of silicone rubber in toluene were measured. The equilibrium swelling ratio (Q_m) for the silicone rubber is calculated according to eq. (1) and the result was shown in Table II.

$$Q_m = \frac{w_s - w_0}{w_0} \quad (1)$$

where, w_0 and w_s are the weights of the silicone rubber before and after swelling in toluene, respectively.

On the basis of Flory-Rehner equation [eq. (2)], the molecular weight between crosslinking points (M_c) can be estimated and the crosslinking density of silicon rubber (D) is calculated according to eq. (3).

$$-\left[\ln(1-v_r) + v_r + \chi v_r^2\right] = \rho \frac{V_1}{M_c}\left(v_r^{1/3} - \frac{v_r}{2}\right) \quad (2)$$

$$D = \frac{1}{2M_c} \quad (3)$$

where, v_r is the volume fraction of silicone rubber after swelling, ρ is the density of silicone rubber ($g\ cm^{-3}$), χ is the interaction parameter between silicone rubber and solvent and V_1 is the molar volume of solvent ($cm^3\ mol^{-1}$).

It was found that the equilibrium swelling ratio of the silicone rubber filled with the modified Fe_2O_3 is low in comparison with that of the silicone rubber filled with the unmodified Fe_2O_3. Correspondingly, M_c of silicone rubber filled with the modified Fe_2O_3 is low, whereas D is high compared to those of the silicone rubber filled with the unmodified Fe_2O_3. The decrease of the equilibrium swelling ratio and the molecular weight between crosslinking points of silicone rubber filled with the modified Fe_2O_3 is probably ascribed to the increase of the crosslinking density of silicone rubber after the introduction of VTMS modified Fe_2O_3, indicating that vinyl groups in VTMS take part in crosslinking of silicone rubber. Therefore, it can be concluded that the modified

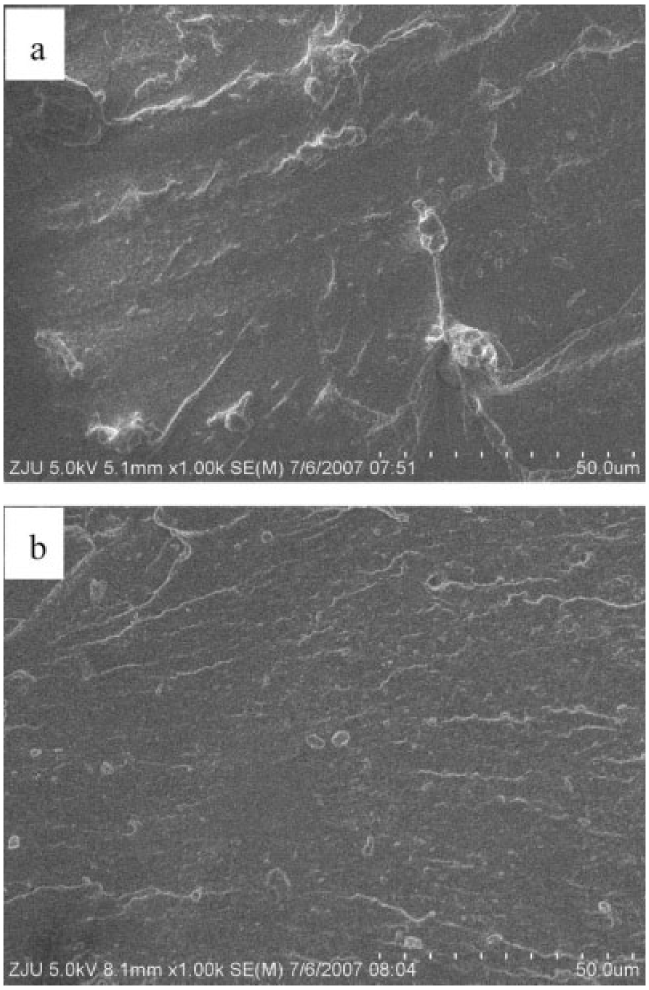

Figure 3 SEM of silicone rubber filled with (a) 1.5 wt % unmodified Fe_2O_3, (b) 1.5 wt % modified Fe_2O_3.

Fe_2O_3 particles become the concentrated crosslinking points and results in the increase of the tear strength of silicone rubber.

It was also found from Table I that the tear strength of silicone rubber after ageing increases significantly with the increase of Fe_2O_3 content whether the unmodified or modified Fe_2O_3, indicating that Fe_2O_3 can be used as a heat-resistant additive of silicone rubber. Feng[1] indicated that the side chain of polysiloxane during the ageing was oxidized and the radical was formed. Fe_2O_3 can quench the radical formed during the oxidation of the side chain and improve the heat-resistance of silicone rubber based on the following equation.[12]

$$Fe^{3+} + R\cdot \rightarrow R^{+} + Fe^{2+}$$

The tear strength of silicone rubber filled with the modified Fe_2O_3 after ageing is higher than that with the unmodified Fe_2O_3, indicating that the modification of Fe_2O_3 can improve the heat-resistance of silicone rubber.

The dispersion of Fe_2O_3 particles in silicone rubber was carried out by using SEM. Figure 3 shows SEM images of the unmodified and modified Fe_2O_3 particles in silicone rubber. It can be seen from Figure 3(a) that some of the unmodified Fe_2O_3 particles are seriously aggregated and overlapped. It was found from Figure 3(b) that in comparison with the unmodified Fe_2O_3, the modified Fe_2O_3 particles disperses well in silicone rubber. These results confirm that the phenomena of Fe_2O_3 particles agglomeration decreases effectively by the surface modification layer of VTMS and the fine dispersion of the modified Fe_2O_3 can improve significantly the heat-resistance of silicone rubber.

Thermal weight loss behavior of silicone rubber filled with Fe_2O_3

The effect of Fe_2O_3 on the thermal weight loss behavior of silicone rubber was studied by means of TG, and the results are shown in Figure 4. It was found that both the weight retained at the same temperature and the initial weigh loss temperature of silicone rubber filled with Fe_2O_3 are higher than those of silicone rubber without Fe_2O_3, indicating that Fe_2O_3 can improve the heat-resistance of silicone rubber. Furthermore, the weight retained of silicone rubber filled with the modified Fe_2O_3 is high in comparison to that of silicone rubber filled with the unmodified Fe_2O_3, which demonstrated that the heat-resistance of the silicone rubber filled with the modified Fe_2O_3 is better than that of silicone rubber filled with the unmodified Fe_2O_3 because of the improved dispersion of the modified Fe_2O_3 in silicone rubber. On the other hand, the modifying agent of Fe_2O_3, that is, VTMS takes part in the crosslinking of methylvinylsilicone gum, resulting in the increase of the steric hindrance of the main chain

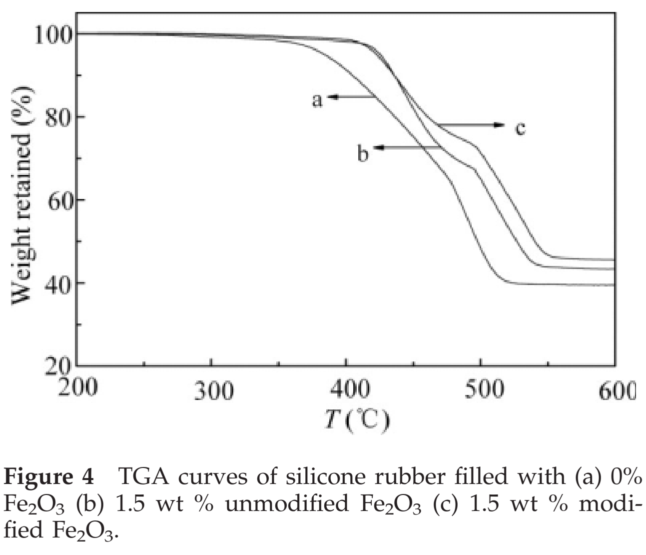

Figure 4 TGA curves of silicone rubber filled with (a) 0% Fe_2O_3 (b) 1.5 wt % unmodified Fe_2O_3 (c) 1.5 wt % modified Fe_2O_3.

degradation. Therefore, the heat-resistance of silicone rubber was improved greatly after introducing the modified Fe_2O_3.

CONCLUSIONS

The modified Fe_2O_3 was prepared by a chemical surface modification method, and IR result indicated that VTMS has been attached onto Fe_2O_3 surface. The optimal concentration of VTMS is 12 wt %. After the addition of the modified Fe_2O_3 the tear strength of silicone rubber before ageing increases significantly due to the increase of the crosslinking density of polysiloxane. The tear strength of silicone rubber filled with the modified Fe_2O_3 after ageing is higher than that with the unmodified Fe_2O_3. Therefore, the modification of Fe_2O_3 can improve the heat-resistance of silicone rubber due to the good dispersion of the modified Fe_2O_3.

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