Ceramifiable and mechanical properties of silicone rubber foam composite with frit and high silica glass fiber

J Q Song[1, a], Z X Huang[1], Y Qin[1], G Y Yang[1] and X Wang[1]

[1] School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, 430070, China

[a] Corresponding author: songjq9@126.com

Abstract. In this paper, ceramifiable silicone rubber foam composite was prepared by silicone rubber, fumed SiO_2, talc, frit, high silica glass fiber, foaming and vulcanizing agents. Thermal property, micromorphology, phase transformation and compressive strength of pyrolysis residues at different temperatures were discussed. Thermogravimetric analysis (TGA) results indicated that the amount of ceramic residues increased from 34.5% to 41.1% at 1000℃ with the increase of frit content, whereas T_5 and T_{max} decreased by 43℃ and 103℃, respectively. SEM images showed that pore size became well-distributed by adding frits to the silicone rubber. And after pyrolysis at 1000℃, bridged structure was formed well, which made the structure of residues be coherent and integrated. XRD tests indicated that new crystalline phase, $MgSiO_3$, was appeared at above 1000℃. The effect of frit on compressive strength of composite at room temperature was little, but there was a great improvement after being treated at high temperature, especially at 1000℃.

1. Introduction

With the rapid development of science and technology, silicone rubber composites have lots of applications in human life because of its excellent performance. The silicone rubber foam composites not only have the properties of silicon rubber, but also the characteristics of lightweight, high strength, sound insulation, shock absorption and shock resistance of foam materials [1]. The studies about the matching of vulcanization and foaming in high temperature vulcanized silicone rubber foaming process and the cellular structure of foamed materials have been reported in many literatures [2-6]. However, fire-resistance of silicone rubber foam composite is being paid more and more attention in recent years. So ceramifiable silicone rubber foam composite through adding silicate minerals, metallic oxide and others as ceramifiable additives has become an important research direction [7, 8].

Generally, the ceramifiable silicone rubber foam composite is comprised of silicone rubber matrix, refractory fillers, fluxing agents, foaming agents and other additives. Montmorillonite, muscovite and talc are usually used as refractory fillers to improve the strength of ceramifying residue [9-11]. Frits [12], zinc borate and APP [13] can usually reduce the ceramifying temperature, which is conducive to the formation of ceramic structure. The formation and the strength of ceramic structure and properties of silicone rubber have attracted much attention in the process of ceramization. Some researchers are also working hard to improve the mechanical properties of ceramifiable silicone rubber foam composite [14-17]. However, there was few reports on the ceramifying property of silicone rubber foam composite. It is very necessary to improve the property of ceramifying residues for some stringent application environment.

Therefore, this paper focused on the application of silicone rubber foam materials in special extreme conditions and obtained a kind of ceramifiable silicone rubber foam composite which could form ceramic structure to prevent fire and heat transmission under high temperature. At the same time, compared with the ceramifiable silicone rubber, ceramifiable silicone rubber foam composite has the advantages of small density and light quality and plays a very important role in the lightweight materials.

2. Experimental

2.1. Materials
Commercial methyl vinyl silicone rubber (abbreviated to VMQ) was produced by Chengdu Zhonghao Chenguang Technology Co. Ltd., China. The average molecular weight was about 550000. The vinyl content of the silicone rubber was about 0.15% per mole. Fumed silica and talc were purchased from Shanghai Jingchun Bio-Chem Technology Co. Ltd., China. 2,5-Dimethyl-2,5- di(tert-butylperoxy)-hexane (abbreviated to DBPH) was also from Shanghai Jingchun Bio-Chem Technology Co. Ltd., China. Frits were provided by Gaoyao Chanlong Technology Co. Ltd., China. The chemical compositions of the frit, determined by X-Ray Fluorescence (XRF), were given in Table 1. Foaming agent was purchased from Matsumoto Yushi-Seiyaku Co.,Ltd., Japan.

Table 1. Chemical compositions of frit.

Components	Na_2O	MgO	Al_2O_3	SiO_2	CaO	K_2O	ZnO	BaO	others
wt%	10.65	1.29	5.51	31.94	8.75	1.44	33.41	3.05	3.96

Table 2. Chemical compositions (wt.%) of ceramifiable silicon rubber foam composites.

Sample code	VMQ	Fumed SiO_2	Talc	Frit	Foaming agent	DBPH
F3-1	100	10	40	0	6	1
F3-2	100	10	40	5	6	1
F3-3	100	10	40	10	6	1
F3-4	100	10	40	15	6	1
F3-5	100	10	40	20	6	1

2.2. Sample preparation
All of the ingredients were mixed on a two-roll mill with a gear ratio of 1:1.2 at room temperature. The silicone rubber was first softened, and then the fumed silica, talc and frits were added until a homogeneous batch was obtained. The foaming agent and curing agent (DBPH) were added and processed until a visually good dispersion was achieved. The total mixing time was about 30min. The samples were foamed and vulcanized for 40min at 160℃. Then the samples were put into air-dry oven at 180℃ for 2 hours for additional vulcanization. The formulations of ceramifiable silicon rubber foam composites were given in the Table 2.

2.3. Sample pyrolysis
Pyrolysis of samples (φ30mm×10mm) was performed in a muffle furnace. Samples were heated from 50℃ to 600℃, 800℃, 1000℃ and 1200℃ at the heating rate of 10℃/min and kept at each temperature for 30 min, and then cooled to room temperature with the muffle furnace to obtain the pyrolysis residues at different temperatures.

2.4. Characterization

Thermal gravimetric analysis (TGA, STA449C/3/G, NETZSCH, Germany) was conducted to investigate the thermal stability of the samples under the air. Then a series of samples were heated at a rate of 10℃/min. The relative mass loss and heat change of the samples were recorded from room temperature to 1000℃. The crystal phases of the samples were identified by an X-ray diffraction (XRD) with a D8 ADVANCE diffractometer (Bruker) with Cu Kα (λ=0.1542 nm) radiation at a generator voltage of 40 kV and a generator current of 400mA. The scan was conducted from a 2θ angle of 5° to 80° with a step interval of 4°. The morphologies of the composite after ceramifying process was characterized by scanning electron microscopy (SEM, JSM-5610LV/*, JOEL, Japan). Chemical compositions of frit were studied with X-ray fluorescence spectrometer (ESCALAB 250Xi, USA) by X-ray fluorescence technique. Universal mechanical testing machine (Instron 5967) was used to evaluate the compressive strength of ceramic residues, according to GB/T 7757-2009 and GB/T 1964-1996.

3.   Results and discussion

3.1. Thermal gravimetric analysis (TGA)

Figure 1 shows the TG and DSC curves of ceramifiable silicone rubber foam composite with different content of frit, and the thermal decomposition parameters are shown in Table 3. As shown in Figure 1, there was a little mass loss of about 2% from 280℃ to 290℃, which might be that the polymer shell of the foaming agent decomposed. The pyrolysis of silicone rubber occurred between 400℃ and 600℃. It can be seen from table 3 that the initial decomposition temperature (T_5) and the maximum thermal decomposition temperature (T_{max}) of silicone rubber decreased by 43℃ and 103℃ with the addition of frit, respectively. However, the amount of ceramic residue increased from 34.5% to 41.1% at 1000℃. Studies have shown that metal ions can catalyze and accelerate depolymerization of the polyolefin polymers, reducing the thermal stability of the composites. So the metal ions in frit accelerated the thermal decomposition of silicone rubber composites, which decreased the decomposition temperature and improved the thermolysis rate. As the amount of frit increased, during the pyrolysis process, the frit was melted and liquid phase was formed. Then eutectic reaction happened between the liquid phase and fillers, forming porous ceramic layer to prevent thermal transmission and pyrolysis of composite.
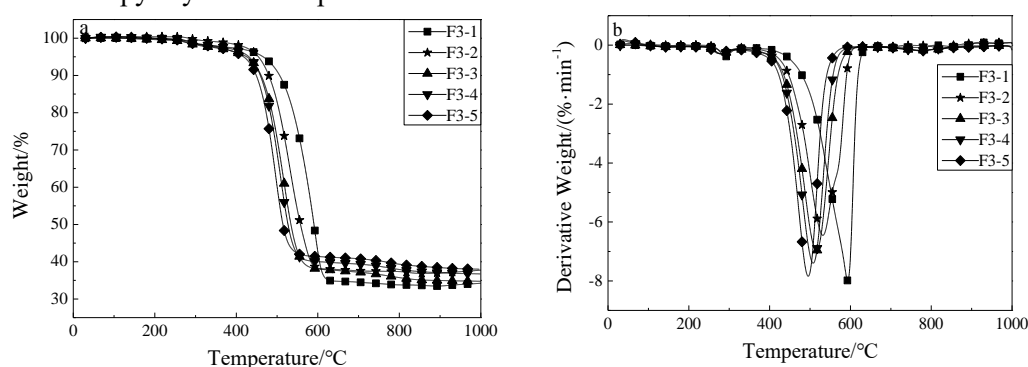

Figure 1. TG (a) and DTG (b) curves of samples with different content of frit under air atmosphere.

Table 3. Thermal decomposition parameters of samples.

Samples	T_{m1} (℃)	T_5 (℃)	T_{max} (℃)	Residual rate (%)
F3-1	289	406	596	34.5
F3-2	286	389	541	37.6

F3-3	283	384	523	38.3
F3-4	284	374	512	40.1
F3-5	281	363	493	41.1

3.2. Microstructure analysis of the residues

Figure 2 shows micromorphology of silicone rubber foam composite before and after adding frit (sample F3-1 and F3-5). After adding frit, the microstructure of the foam composite did not change significantly, but the pore size was more uniform. The frit was evenly distributed in the silicone rubber matrix, forming three-dimensional network structure with some other fillers, which restricted the free expansion of microspheres. Whereas the stability of the three dimensional structure was lower without frit, the compressive stress of microspheres was smaller in the process of free expansion and the expansion deformation of the silicone rubber matrix was larger. So there were lots of microcapsules with large diameter. Meanwhile, the squeezing of microcapsules resulted in a smaller diameter of the microcapsules, which influenced pore size distribution.

The micromorphology of the ceramifiable silicone rubber composite (F3-5) after being treated at 600℃, 800℃, 1000℃ and 1200℃ are shown in Figure 3. It can be seen that, at 600℃, the original cell structure was filled with powdery filler, and the amount of liquid phase formed by the frit melting was few. With the increase of temperature, the structure of the ceramic residues became clear at 800℃, and the original cell structure of the silicone rubber foam composite could be seen. The amount of liquid phase in the residues increased, and the liquid phase cooled to form spherical particles with larger size, attaching to the surface of the pyrolysis products of silicone rubber foam composite. At 1000℃, the liquid phase had been joined to form liquid phase bridge, and the skeleton structure with smooth surface was wrapped up by the liquid phase. The pore structure of the silicone rubber foam composite was well maintained. When the temperature rose to 1200℃, the low melting frit was completely melted, forming continuous liquid phase to cover the whole pyrolytic products and fillers. However, some of the liquid phase vaporized at high temperature, resulting in larger pores on the matrix skeleton. The density of the structure decreased.
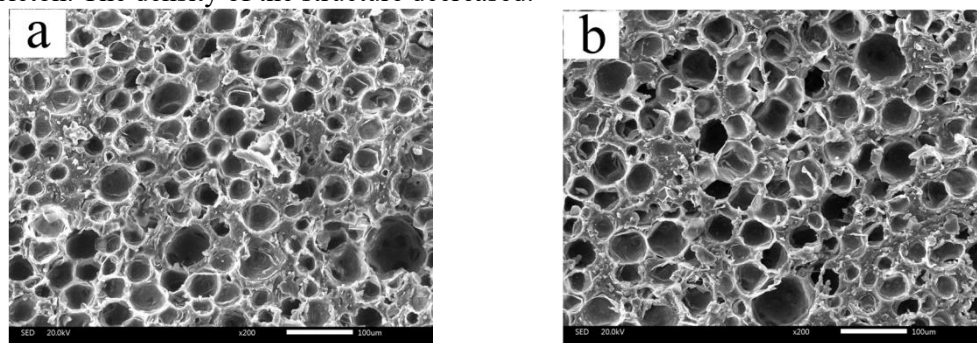

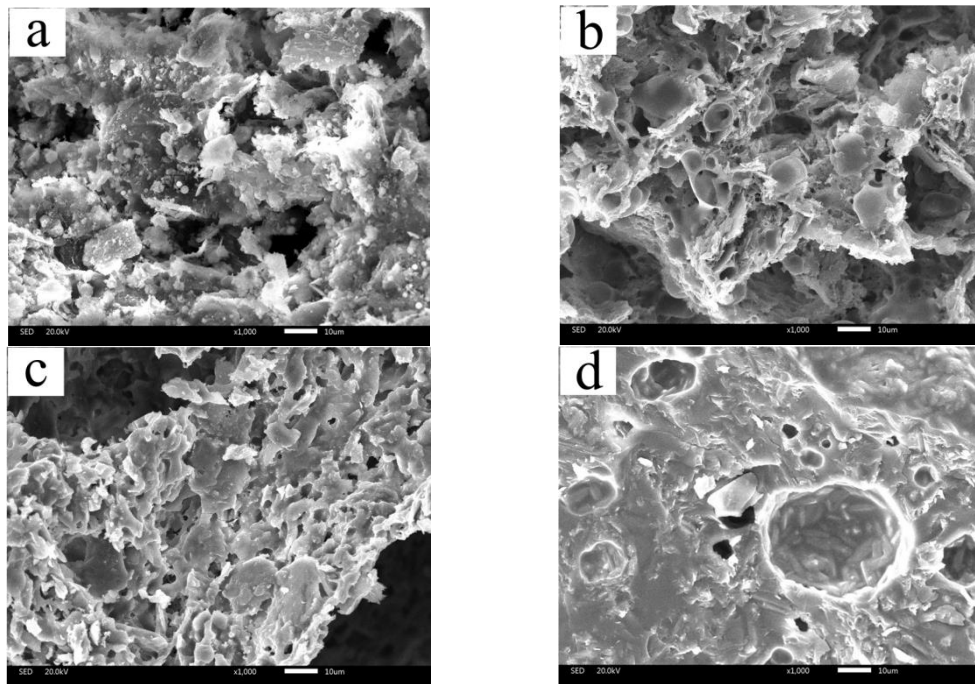Figure 2. Micromorphology of silicone rubber foam composite before and after adding frit.

Figure 3. Micromorphology of pyrolysis products at different temperatures.
(a-600℃; b-800℃; c-1000℃, d-1200℃).

3.3. XRD analysis

As shown in Figure 4, the phases of pyrolysis products changed with the increase of pyrolysis temperature. When the samples (F3-5) were pyrolized at 600℃ and 800℃, respectively, the peaks marked at 19.4°, 28.6°, 34.6°, 36.1° and 62.1° were the characteristic peaks of talc, and an obvious "hump" appeared at 15-30°, confirming the presence of amorphous SiO_2. With the increase of temperature, the characteristic peaks of talc disappeared due to its decomposition. At 1000℃, obvious characteristic peaks of SiO_2 appeared, marking at 23.2°, 28.4°, 31.8° and 35.8°. With the temperature up to 1200℃, the new peaks marked at 46.06° and 61.96° were regarded as the characteristic peaks of $MgSiO_3$, which indicated that the decomposition of talc resulted in the formation of $MgSiO_3$.
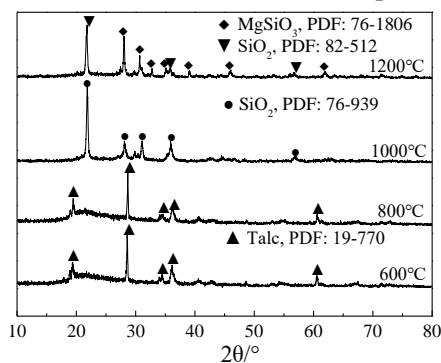

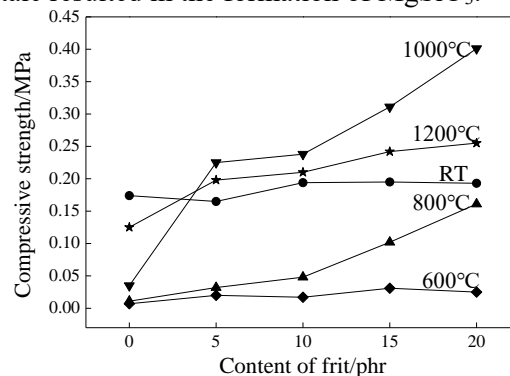Figure 4. The XRD patterns of residues at different pyrolysis temperatures.

Figure 5. The compressive strength of pyrolysis products at different temperatures.

3.4. Compressive strength

The compressive strength of pyrolysis products at different temperatures is shown in Figure 5. With the increase of frit content and temperature, the compressive strength of ceramifiable silicone rubber

foam composites increased. The compressive strength of the residues at 600℃ and 800℃ was very low. However, with temperature up to 1000℃ and 1200℃, the compressive strength was obviously improved. In addition, the compressive strength of residue at 1000℃ was higher than that of 1200℃. The softening point of the frit was 560℃ in this paper. When the composite was heat treated at 600℃ and 800℃, little liquid phase formed and the structure of residues was incompact, resulting in low compression strength. With the increase of the temperature and frit content, the effect of the frit became more and more obvious. The liquid phase increased gradually and wrapped around the decomposition products of the matrix, forming compact ceramic skeleton structure. So the compressive strength increased. However, at 1200℃, some of the liquid phase volatilized due to the high heat-treatment temperature, resulting in the formation of the porous skeleton structure and reduction of the density of the skeleton structure, which reduced the density of the residue, decreasing the compressive strength.

4.   Conclusions

With the addition of frit, the ceramic structure was formed during the heat treatment of the silicone rubber foam composite. The pore structure of the silicone rubber foam was maintained and the compressive strength of the composite increased greatly. At 1000℃, the ceramic structure was a lot compact and compressive strength of residue was high. The volatilization of liquid phase in the system made the density of the ceramic structure decrease, which decreased the strength of the residue. With the increase of frit content, the amount of liquid phase in the system increased, which improved the adhesion among filler particles, resulting in the high strength. The addition of frit reduced the decomposition temperature of silicone rubber, whereas increased the pyrolysis residual rate of silicone rubber foam composite. In the heat treatment process of 600 to 1200℃, the phase changed in the system. At 600 and 800℃, the diffraction peak of talc was the most obvious. At 1000℃, the diffraction peak of silicon dioxide could be seen in the system. The diffraction peaks of SiO_2 and $MgSiO_3$ could be observed at 1200℃, which indicated that the decomposition of talc resulted in the formation of $MgSiO_3$.

Reference

[1]   Song L X, Lu Z Y, Lu A and Feng P J 2014 *Mater. Lett.* **121** 126-8.
[2]   Gao J, Wang J B, Xu H Y and Wu C F 2013 *Mater. Design.* **46** 491-6.
[3]   Bai J W, Liao X, Huang E B, Luo Y, Yang Q and Li G X 2017 *Mater. Design.* **133** 288-98.
[4]   Park E S 2008 *J. Appl. Polym. Sci.* **110** 1723-29.
[5]   Amdt K 2000 *Macromol. Mater. Eng.* **284-285** 70-5.
[6]   Yao W, Lei W H, Che L X, Zhou A W, Ding G F 2013 *Mater. Rev.* **Z1** 249-51.
[7]   Shi Y G, Lei W H, Zhang C S, Xu Z G, Luo S K 2008 *Silic. Mater.* **6** 373-76
[8]   Hanu L G, Simon G P and Mansouri J 2004 *J. Mater. Pro Tech.* **153-154** 401-7.
[9]   Wang J H, Ji C T, Yan Y T, Zhao D and Shi L Y 2015 *Polym. Deg. Stab.* **121** 149-56.
[10]   Hanu L G, Simon G P and Cheng Y B 2005 *Mater. Sci. Eng.* A. **398** 180-7.
[11]   Anyszka R, Bieliński D M, Dzich Z P and Szumera M 2015 *J. Therm.Anal. Calorim.* **119** 111-21.
[12]   Kim E S, Kim E J, Shim J H and Yoon J S 2008 *J. Appl.Polym.Sci.* **110** 1263-70.
[13]   Hu S, Chen F, Li J G, Shen Q, Huang Z X and Zhang L M 2016 *Polym. Deg. Stab.* **126** 196-203.
[14]   Guo J H, Gao W, Wang Y, Liang D, Li H J and Zhang X 2017 *Polym. Deg. Stab.* **136** 71-9.
[15]   Yang D, Zhang W, Jiang B Z 2013 *Ceram. Int.* **41** 1575-81.
[16]   Cao E P, Cui X Q, Wang K, Li Y Y and Guo W H 2015 *J. Appl. Polym. Sci.* **132** 41864
[17]   Imiela M, Anyszka R, Bieliński D M, Pędzich Z, Zarzecka-Napierała M and Szumera M 2016 *J. Therm.Anal. Calorim.* **124** 197 - 203