Effects of French Chalk/Hollow Glass Beads on the Flame Retardation of Silicone Foams

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ABSTRACT

Low-density (0.18–0.31 g/cm^3), flame-retardant closed cell silicone foams (SiFs) were successfully obtained through dehydrogenation at room temperature. Moreover, a flame-retardant system for SiF composites was obtained through a synergistic combination of French chalk (FC)/hollow glass beads (HGB). The mechanical properties, flame retardancy, and thermal stability of SiF composites with FC and HGB were tested using the tension test, limiting oxygen index (LOI), UL-94 test, cone calorimeter, and thermogravimetry. The mechanical properties of SiFs could be significantly improved by interfusing FC. The fire retardancy of the SiFs could be prominently improved by adding FC and HGB. With 50 wt% FC, the SiF achieved the UL-94-V0 rating with the LOI value of 41.6%. Remarkably, the addition of 30 wt% FC and 1 wt% HGB significantly reduced the peak heat release rate by 59.9%, total heat release by 40.9%. TG test showed that FC and HGB can promote the char formation in the degradation process of SiFs. The initial decomposition temperature of SiF with 30 wt% FC and 1 wt% HGB was 445.0 °C and the residue at 900.0 °C was 81.0%, which were noticeably higher than that of pure SiF. Through the analysis of the results of this experiment, it was a promising strategy for preparing flame retardant SiFs with improved mechanical performance and thermal stability by adding FC and HGB.

KEYWORDS: Silicone foams, flame retardancy, thermal stability, mechanical properties.

INTRODUCTION

Flexible silicone foams (SiFs) are a series of cellular polymer materials with –Si–O–Si– comprising their main chains [1]. As a high-performance type of material, SiFs exhibit many outstanding characteristics, including good biological compatibility, nontoxicity, antiaging, strong sound absorption, chemical stability, light weight, ozone resistance, high and low-temperature resistance, electrical insulation, etc. [2–5]. Therefore, they are widely applied in aerospace, national defence, medicine, electrical, transportation, construction industries, etc. [6–9].

However, belonging to the abundant hydrocarbon groups on its side-chain, SiFs can smoulder, combust, and release choking smoke once ignited, which becomes a bottleneck restricting their rapid popularization and application. To improve the flame retardancy and mechanical behavior of SiFs, Deng et al. [10] fabricated SiFs with seven bilayers of chitosan/ammonium polyphosphate coatings; the limiting oxygen index (LOI) increased from 20.2% to 23.8%, the peak heat release rate (PHRR) decreased by 27.6%, and the total smoke production decreased by 42%. Chruściel et al. [11] prepared flame-retarded SiFs whose content was 30% melamine and expanded graphite and whose limiting oxygen index (LOI) was 41–43%. Verdejo et al. [12] examined the fire resistance of silicone-based foams with carbon nanotubes, the limiting oxygen index of the composite increased

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as a function of carbon nanotube content, attaining the self-extinguishing grade even at low mass fraction of the carbon nanotubes (0.5 wt%). Additionally, inorganic fillers such as carbon black, asbestos, kaolin, and artificial fibres are widely applied in flame-retardant SiFs [13–19]. Other designs of flame-retardant SiFs have been rarely reported.

Superfine French chalk (FC) is a naturally occurring hydrated magnesium sheet silicate, $3MgO_4SiO_2H_2O$. It can be used as semi-reinforcing and flame retardancy filler for silicone rubber. Moreover, hollow glass beads (HGB) can improve the fire retardancy capabilities and thermal stability of composites effectively. The heat release rate (HRR) of ethylene-vinyl acetate (EVA) composites with 1.0 wt% HGB reduced by 37% and show higher thermal stability at high temperature when compared with EVA composites without HGB [20]. Additionally, the weight of hollow glass beads-filled composites can be effectively decreased compared with the initial composition [21].

In this study, low-density (0.18–0.31 g/cm^3), flame-retardant closed cell SiFs were prepared through condensation dehydrogenation. The flame retardancy, mechanical properties, and thermal stability of SiFs with FC and HGB as flame-retardant filler were tested using the LOI, UL-94 test, cone calorimeter, tension test, and thermogravimetry.

MATERIALS AND METHODS

Materials

The base gum comprised 75 wt% vinyl terminated siloxane (viscosity: 10,000 MPa·s) and 25 wt% fumed silica, which was kindly donated by Salirone New Materials Co. (Huizhou, China). Hydroxy silicone oil (viscosities: 20–30 MPa·s and 1500 MPa·s), hydrogen-containing silicone oil, and Pt compounds (3000 ppm) were produced by Shenzhen Osbang New Materials Co. (Shenzhen, China). The hydrogen content of the hydrogen-containing silicone oil was 0.7 mol%. Methylbutynol was obtained from Shaoguan Koya Fine Chemicals Co. (Shaoguan, China). French chalk was produced by Guangfu Institute of Fine Chemical Engineering (Tianjin, China). Hollow glass beads (particle size: 37.4 µm) was obtained from Sunda Chemical Co. (Dongguan, China).

Preparation of samples

The condensation dehydrogenation method was used to synthesize SiF composites. In detail, a combination of hydroxy silicone oil (viscosities: 20–30 MPa·s and 1500 MPa·s), base gum, methylbutynol, Pt compounds, and flame retardant were placed into a beaker with a mechanical stirrer and stirred for 10 min. Thereafter, hydrogen-containing silicone oil was added, followed by stirring for 3 min. Then poured the mixture carefully into a mould (150 × 150 × 10 mm^3). Afterwards, it foamed and cured at room temperature after approximately 2.0–4.0 min. Finally, the mixture was dried in an oven at 80.0 °C for 3 min. Subsequently, the white closed cell SiFs with smooth surface were finally obtained. The specific formulations are summarized in Table 1.

In this experiment, vinyl terminated siloxane, fumed silica, hydroxy silicone oil, and methylbutynol were used as crosslinking agent, reinforcing filler, vesicant, and inhibitor, respectively. Hydrogen-containing silicone oil was taken as vesicant and crosslinking agent. Pt compounds was used as catalyst, FC and HGB were used as flame-retardant fillers.

Characterisation

The mechanical properties were performed on a HZ-1009C universal tensile testing machine (Shanghai Hengzhun, Shanghai, China) with a drawing speed of 100 mm/min. The specimens were prepared in accordance with the ISO 37-2005. For each sample, five measurements on different surface locations were averaged.

The density of SiFs were measured according to ASTM D1622-2008, and each specimen was 150 × 100 × 10 mm^3. The density of SiFs were calculated by the weight and the volume of the specimen. All specimens were tested three times, and then the average values were reported.

Table 1. Formulation and characteristics of flame retardant SiF composites

Foam	FC/wt%	HGB/wt%	Density (g/cm^3)	LOI (%)	UL-94
SiF0	0	0	0.26	28.8	V1
SiF1	10	0	0.27	31.5	V0
SiF2	20	0	0.28	33.8	V0
SiF3	30	0	0.29	36.6	V0
SiF4	40	0	0.30	39.1	V0
SiF5	50	0	0.31	41.6	V0
SiF6	0	1	0.23	29.2	V1
SiF7	0	2	0.21	29.6	V1
SiF8	0	3	0.20	29.9	V1
SiF9	0	4	0.19	30.4	V1
SiF10	0	5	0.18	30.8	V0
SiF11	30	1	0.26	36.7	V0
SiF12	30	3	0.22	36.9	V0
SiF13	30	5	0.20	37.2	V0

The LOI value was determined using a JF-3 oxygen index instrument (Jiangning, Nanjing, China) in accordance with the ISO4589 standard. The dimensions of all samples were 150 × 10 × 10 mm^3.

The UL-94 vertical flame test was conducted using a CZF-3 horizontal and vertical combustion tester (Jiangning, Nanjing, China) in accordance with the UL-94 test standard. The specimens were 127.0 × 12.7 × 3.0 mm^3 in accordance with the ASTM D3801-2010 test standard.

The experiments were conducted using a cone calorimeter (Fire Testing Technology, London, UK) at an external heat flux of 35 $\mathrm{kW/m}^2$ in accordance with the ISO 5660 standard. All specimens (100 × 100 × 5 mm^3) were tested three times, and the results were reproducible within ±10%.

Thermogravimetry (TG) was performed using a Netzsch TG209F1 (Netzsch, Bavaria, Germany) thermal analyser. At a heating rate of 10 °C/min, 10 mg of the sample was heated from 40 to 900 °C in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Mechanical properties

Mechanical properties are vital factors that affect the performance of polymer materials. To investigated the effects of FC and HGB on the mechanical properties of the SiFs, the tensile strength and elongation at break of SiFs are shown in Fig. 1.

The results for the samples containing only FC indicated that the tensile strength and elongation at break of SiFs first ascended and then descended by increasing FC content from 0 to 50 wt%. When FC content was 30 wt%, the SiFs exhibited highest tensile strength and elongation at break. SiF11 (30 wt% FC, 1 wt% HGB) exhibited higher tensile strength and elongation at break than pure SiF.

Furthermore, the tensile strength and elongation at break of SiF11 (30 wt% FC, 1 wt% HGB), SiF12 (30 wt% FC, 3 wt% HGB), and SiF13 (30 wt% FC, 5 wt% HGB) were higher than the SiFs with the same content of HGB but without FC. Notably, FC can significantly improve the mechanical properties of SiFs, while the tensile strength and elongation at break of SiFs decreased markedly with the increasing content of HGB. For instance, when the HGB content increased from 1 to 5 wt%, the breaking strength and elongation at break of SiFs declined from 80 KPa, 172% to 45 KPa, 125% (i.e., a decrease of approximately 44% and 27%, respectively). This phenomenon may contribute to the unsatisfactory compatibility between HGB and SiFs.

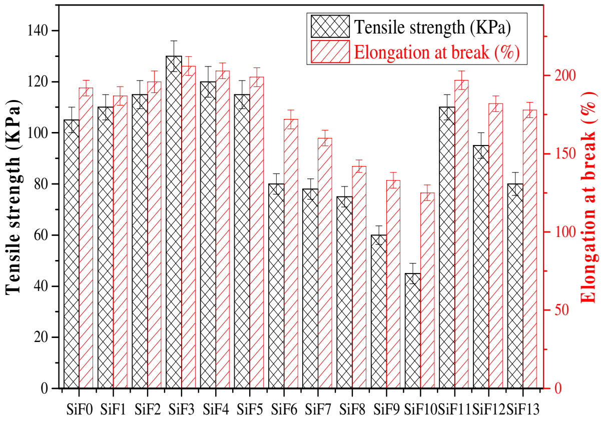

Fig.1. Tensile strength and elongation at break of SiF composites.

Density

As expected, the additon of HGB had a positive effect on the density of the SiF composites. From Table 1, we could plainly see that the density of SiFs increase with the increasing content of FC, while it dramatically decrease with the increasing content of HGB. Compared with SiF0, the density of SiF10 with 5 wt% HGB significantly reduced by 30.8%. In addition, SiF11 (30 wt% FC, 1 wt% HGB) could keep the same density as SiF0.

Flame retardancy

The LOI values and UL-94 tests were used to determine the flammability of the flame-retardant materials. LOI, which is the minimum oxygen concentration by volume required to maintain the burning of a material, is critical for evaluating SiF flame retardancy [22]. The LOI and UL-94 test results for the SiFs were recorded in Table 1. Notably, we could conclude that the LOI values of SiFs rose with the increasing content of FC and HGB. With 50 wt% FC, SiF5 achieved the UL-94-V0 rating with the LOI value of 41.6%. Meanwhile, all the SiFs with no less than 10 wt% FC could achieve the UL-94-V0 rating, which indicated that FC apparently improved the LOI value of SiFs. Moreover, SiFs with only 5 wt% HGB could achieve the UL-94-V0 rating, and the LOI values of SiF11 (30 wt% FC, 1 wt% HGB), SiF12 (30 wt% FC, 3 wt% HGB), and SiF13 (30 wt% FC, 5 wt% HGB) were obviously higher than SiF3 (30 wt% FC) . According to Table 1, SiF0 and SiF11 possessed the same density, however, SiF11 significantly increased the LOI by 27.4% after added 30 wt% FC and 1 wt% HGB. In summary, SiF composites with FC/HGB exhibited excellent flame retardancy.

Fire hazard analysis

The cone calorimeter test is a universal method for investigating the combustion behavior of polymer materials, especially for evaluating the heat release behavior in a real fire [23, 24]. The

HRR and total heat release (THR) of SiF0, SiF1, SiF3, SiF6, SiF10, and SiF11 are delineated in Fig. 2. The main parameters, including time to ignition (TTI), PHRR, and time to PHRR (TPHRR) of the SiF composites, are listed in Table 2. Moreover, the fire growth index (FGI) and the fire performance index (FPI) for SiF composites were shown in Fig. 3.

It could be seen from Fig. 2 (a) and Table 2 that the Pure SiF burned very fast after ignition, and a sharp PHRR of 132.61 kW/m^2 was obtained at 45 s. The PHRR of the SiF composites with FC or HGB was much lower than that of pure SiF, and the PHRR values of SiF1, SiF3, SiF6, SiF10, and SiF11 were as follows: 60.14 kW/m^2, 60.89 kW/m^2, 71.22 kW/m^2, 53.18 kW/m^2, 50.64 kW/m^2. Remarkably, SiF11 with 30 wt% FC and 1 wt% HGB significantly reduced the PHRR by 59.9%. Furthermore, the TTI of pure SiF were only 20 s, while the TTI of SiF11 were 123 s. Compared with SiF3 (30% FC), SiF11 (30 wt% FC, 1 wt% HGB) had a more excellent flame retardant ability.

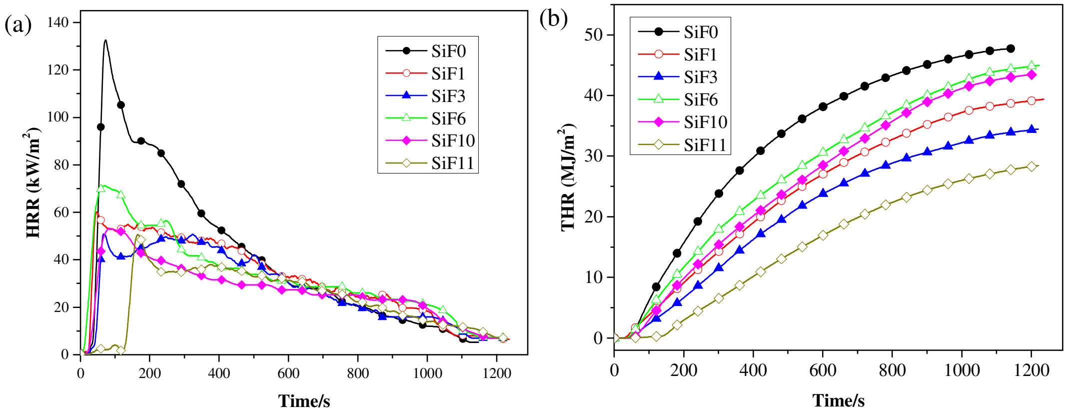

Fig. 2. (a) HRR and (b) THR curves of SiF composites.

Table 2. Cone calorimeter data of SiF composites

Sample	TTI (s)	TPHRR (s)	PHRR (kW/m^2)	THR (MJ/m^2)
SiF0	20	45	132.61	47.79
SiF1	27	49	60.14	39.38
SiF3	40	68	60.89	34.46
SiF6	24	72	71.22	44.98
SiF10	47	87	53.18	43.50
SiF11	123	166	50.64	28.42

Figure 2 (b) presented the THR of SiF composites. It could be seen that the THR value (47.79 MJ/m^2) of pure SiF was obviously higher than that of other SiF composites. The THR of pure SiF was 47.79 MJ/m^2, while the THR of SiF1, SiF3, SiF6, SiF10, and SiF11 were 39.38 MJ/m^2, 34.46 MJ/m^2, 44.98 MJ/m^2, 43.50 MJ/m^2, and 28.42 MJ/m^2, respectively. Compared with SiF0, SiF11 with 30 wt% FC and 1 wt% HGB significantly reduced the THR by 40.9%. It was reported that the gradient of THR curve can be assumed as representative of flame spread [25, 26]. From Fig. 2 (b), we could see that the flame spread rate was considerably reduced. The reason was that there was a much compact char residue forming on the surface of the sample to restrict flames spread.

The FGI was the ratio of PHRR to TPHRR, and the FPI was the ratio of TTI to PHRR. The FGI and FPI are parameters directly reflect the safety rank of samples directly. A lower FGI and higher FPI indicate a greater safety rank. [27, 28] The FGI and FPI of SiF11 were 0.31 kW/(m^2·s) and 2.43 m^2·s/kW, which were the lowest FGI value and highest FPI value among the SiF composites, which indicated that SiF11 possessed relatively higher safety rank than other SiF composites.

The above phenomena can be illustrated in the following. Firstly, after the SiFs is ignited, a lot of heat can be absorbed during the pyrolysis process of FC. Secondly, FC and HGB can form compact char residue on the surface of the SiF composites and improve the weight of char residue. At last, the SiFs with HGB have poor thermal conductivity, which can count against the heat transfer on the surface of the SiF composites.

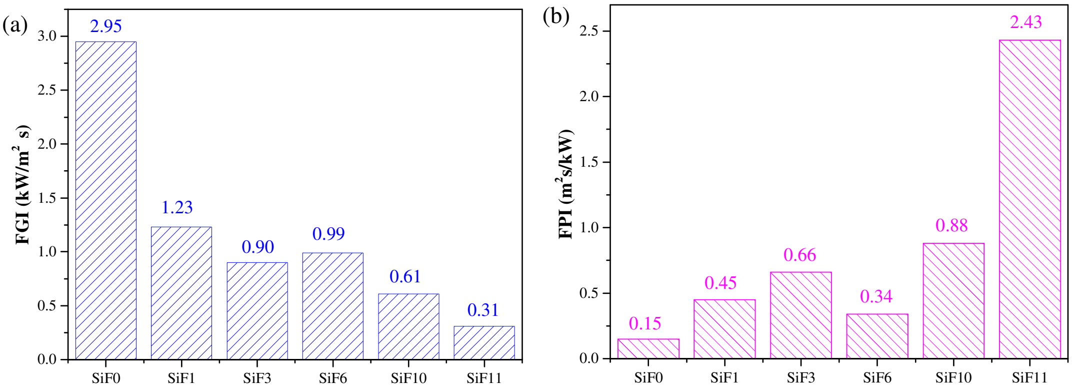

Fig. 3. Cone calorimeter (a) fire growth index and (b) fire performance index for SiF composites.

Thermal stability

The thermal stability of SiF has a bearing on the decomposition products and char formation, which can reveal the flame retardant mechanism [29, 30]. The curves of TG and derivative TG (DTG) for the SiF composites are presented in Fig. 4, and the key parameters are summarized in Table 3. The data clearly indicate that SiF0 started to decompose gradually at 399 °C. Two-stage decomposition of SiF0 was observed from T_{1max} and T_{2max} of 454 and 649 °C, respectively. Ultimately, 63.1% of the char residue remained at 900 °C. The occurrence of the first stage was mainly attributed to the cleavage of Si–C bonds and side organic groups, whereas the occurrence of the second stage was ascribed to the decomposition of the main chains (Si–O–Si).

Compared with pure SiF, the fire retardancy and thermal stability of the SiFs could be prominently improved by adding FC and HGB. The initial decomposition temperatures (T–1 wt%) of SiF1, SiF3, SiF6, SiF10, and SiF11 was 468 °C, 466 °C, 431 °C, 454 °C, and 445 °C, respectively, which were noticeably higher than that of pure SiF. Usually, the thermal degradation of SiF1, SiF3, SiF6, SiF10, and SiF11 comprises three stages, and the extra stage was attributed to the decomposition of FC and HGB. When the temperature was higher than 588 °C, the residual masses of SiF1, SiF3, SiF6, SiF10, and SiF11 were heavier than that of pure SiF. In particular, the residual masses of SiF1, SiF3, SiF6, SiF10, and SiF11 at 900 °C were 80%, 80%, 74.9%, 75%, and 81.0%, respectively, which were significantly higher than that of pure SiF (63.1%).

It was easy to come to a conclusion that the thermal stability of SiF composites were increased by FC and HGB so that they started decomposing later than pure SiF, and the residual masses were higher than that of pure SiF. The decomposition rates of SiF1, SiF3, and SiF11 were generally lower than pure SiF, and the time to reach the peak value of DTG were longer than that of pure SiF. It was obvious that FC contributed more to the char forming progress than HGB. The formed carbon layer delayed the thermal degradation process, and reduced the fire risk of SiF composites.

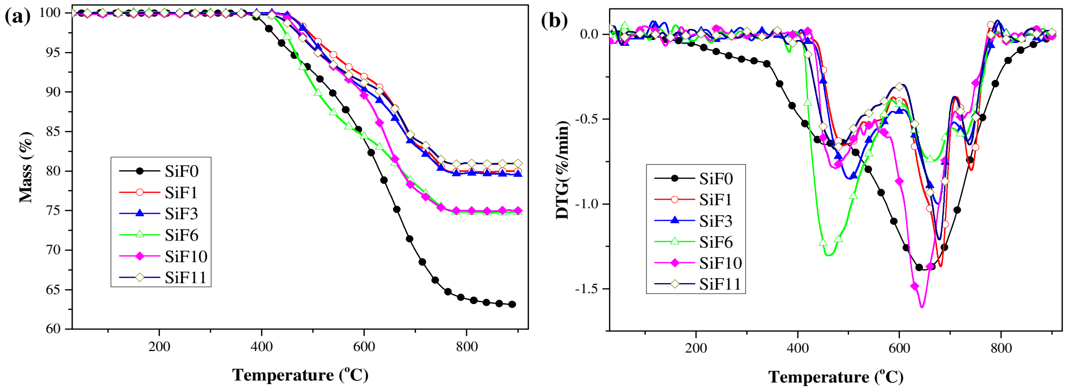

Fig. 4. (a) TG and (b) DTG curves of SiF composites at a heating rate of 10.0 °C/min in N_2.

Table. 3. TG parameters of SiF composites

Sample	$T_{-1wt\%}$ (°C)	T_{1max} (°C)	T_{2max} (°C)	T_{3max} (°C)	Residue at 900 °C (%)
SiF0	399.0	454.0	649.0	–	63.1
SiF1	468.0	489.0	681.0	741.0	80.0
SiF3	466.0	503.0	675.0	733.0	80.0
SiF6	431.0	461.0	668.0	722.0	74.8
SiF10	454.0	474.0	644.0	726.0	75.0
SiF11	445.0	474.0	678.0	738.0	81.0

CONCLUSIONS

In this study, low-density (0.18–0.31 g/cm^3) environmentally friendly flame-retardant closed cell SiFs were successfully prepared at room temperature. The detailed conclusions for the SiF composites tested for mechanical properties, LOI, UL-94, cone calorimeter, and TG were as follows. First, FC could significantly improve the mechanical properties of SiFs. Second, the fire retardancy and thermal stability of the SiFs could be prominently improved by adding FC and HGB. Furthermore, the SiF with 30 wt% FC and 1 wt% FC exhibited optimal flame retardancy, mechanical properties, and thermal stability. In summary, the FC/HGB synergistic flame-retardant system for SiF composites was effective.

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