

# The effect of hollow glass microspheres on the properties of high silica glass fiber fabric/liquid silicone rubber composite sheet<sup>\*)</sup>

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**Abstract:** In this study, high silica glass fiber fabric/liquid silicone rubber (HSGFF/LSR) composite sheet filled with hollow glass microspheres (HGM) was prepared. The effects of HGM content on the mechanical, thermal insulation and dynamic mechanical properties of the composite sheet were investigated. The results showed that the compatibility and interfacial properties between HGM and the matrix were improved after the HGM was treated with a silane coupling agent, KH550. Composite, in which the HGM content was 7 % by weight, shows the most advantageous mechanical, insulating and damping properties.

**Keywords:** composite sheet, hollow glass microspheres, liquid silicone rubber, dynamic mechanical properties, thermal conductivity.

## Wpływ dodatku mikrosfer szklanych na właściwości kompozytów tkaniny z włókna kwarcowego z ciekłym kauczukiem silikonowym

**Streszczenie:** Na bazie tkaniny z włókien kwarcowych (HSGFF) nasyconej ciekłym kauczukiem silikonowym (LSR) otrzymano kompozyty napełniane mikrosferami szklanymi (HGM). Badano wpływ dodatku mikrosfer na właściwości mechaniczne, izolacyjność cieplną i właściwości dynamiczno-mechaniczne kompozytowych arkuszy. Stwierdzono, że modyfikacja mikrosfer szklanych za pomocą silanowego czynnika sprzęgającego KH550 poprawiła kompatybilność i oddziaływania międzyfazowe cząsteczek HGM i nasyconej ciekłym kauczukiem tkaniny z włókien szklanych. Najkorzystniejsze właściwości mechaniczne, izolacyjne i tłumiące wykazywał kompozyt, w którym zawartość HGM wynosiła 7 % mas.

**Słowa kluczowe:** arkusz kompozytowy, mikrosfery szklane, ciekły kauczuk silikonowy, właściwości dynamiczno-mechaniczne, przewodność cieplna.

Silicone rubber is an important silicone product, as its main chain is composed of Si-O-Si bonds. Compared with the general rubber, it has excellent resistance to high and low temperature, weather resistance, electrical insulation, chemical resistance, and physiological inertia [1, 2]. It is widely used in the aerospace, electrical and electronic, medical and health, and machinery industries and in everyday applications in various fields [3]. Hollow glass microspheres (HGM) are an excellent inorganic non-metallic filler [4]. The unique closed-cell structure makes it light weight, with high specific strength, good heat insu-

lation, and excellent mechanical damping properties [5]. These features make HGM irreplaceable in many areas, especially for light high-strength foam, buoyancy and aerospace materials [6, 7], and so on.

Researches have been extensively reported on polymer composites filled with hollow glass microspheres. Gao [8] prepared silicone rubber foam material filled with hollow glass microspheres by compression molding. Compared with silicone rubber foams filled with silica, HGM filler has a higher degree of foaming, lower thermal conductivity and lower hardness. Hu [9] filled silicone rubber with different proportions of intact HGM and broken HGM and investigated the effect of broken HGM on the density, mechanical properties and thermal conductivity of composites. The results showed that these properties increased with the increase of the ratio of broken HGM. Li [10] prepared poly(butylene succinate)/hollow glass microsphere (PBS/HGM) composites and discussed the effect of different HGM contents on its properties. The re-

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sults showed that the introduction of HGM significantly reduced the density of the composites. With increasing HGM content, the storage modulus and viscosity of the composites increased.

The influence of HGM on the properties of polymer matrix composites has been reported in many studies. However, HGM-filled polymer-based composites reinforced with fibers have been less studied (especially fiber-reinforced silicone composites). The coating is composed of silicone material as a matrix, to which a variety of functional fillers, widely used in high temperature thermal insulation and heating field, are added. However, due to the low strength of silicone materials and their poor adhesion to substrates, these coatings are easy to crack and may even fall off during service. Furthermore, most of the coatings contain organic solvent, harmful to the environment, which limits its use. However, this issue can be improved by introducing fiber mesh reinforcement: on the one hand, fiber mesh can enhance the composite material properties, on the other hand, in high temperature environments, the surface of fiber fabric forms a melting film. It can adsorb the  $\text{SiO}_2$ , which is decomposition product of silicone rubber and plays a role in supporting the skeleton to improve the structural integrity of the composite material.

In this paper, HGM/HSGFF/LSR composite sheet was prepared by addition of HGM to LSR subsequently reinforced with HSGFF. The mechanical, thermal insulation and dynamic mechanical properties of the composite sheet with various HGM contents were investigated. The aim of the study was to improve and supplement the theoretical basis of HGM-filled polymer matrix composites.

## EXPERIMENTAL PART

### Materials

Liquid silicone rubber (LSR) and curing agent were purchased from Wuhan Silicone Material Co. Ltd. Hollow glass microspheres (HGM) with an average particle size of 110  $\mu\text{m}$  and density of 0.125  $\text{g}/\text{cm}^3$  were obtained from Shanghai Xiang Lan Chemical Co., Ltd. The silane coupling agent KH550 (3-aminopropyl triethoxysilane) was obtained from Silicone Co., OSI. High silica glass fiber fabric (HSGFF) with a surface density of 160  $\text{g}/\text{m}^2$  was purchased from Shaanxi Huate New Material Co., Ltd.

### Surface treatment procedure

HGM surface treatment: sulfuric acid with a concentration of 98 % and 30 % hydrogen peroxide, in accordance with the volume ratio of 3 : 1, were mixed to form a powerful etch solution and then the HGM was added and left to soak for 40 min to remove surface impurities from the HGM and increase the hydroxyl content on the surface. After being washed with distilled water until the solution was neutral, the treated HGM was placed in an oven at 100 °C for 2 h to dry. Then 3 g of dried HGM was added to 100  $\text{cm}^3$  of an aqueous ethanol solution (the volume ratio of absolute ethanol to distilled water was 9 : 1), and pH was adjusted to the range of 4 to 5 by adding glacial acetic acid. After that the HGM was uniformly dispersed by ultrasonics. The KH550 (3 wt %) was added to the mixture, then stirred at 40 °C for 3 h before filtering. The HGM then was washed with distilled water and placed in an oven at 80 °C for 5 h.

High silica glass fiber fabric surface treatment: the high silica glass fiber fabric was put in the muffle furnace at 350 °C for heating for 30 min, to remove oil and impurities from the surface. Then it was soaked in 1  $\text{mol}/\text{dm}^3$  hydrochloric acid solution for 1 h at 80 °C (in order to form grooves on the surface of the fiber cloth and increase the contact area with the silicone rubber), rinsed with distilled water to neutral pH, and dried.

### Sample preparation procedure

Liquid silicone rubber was taken in amount of 100 parts by weight, and 3, 5, 7 and 9 parts of surface-modified HGM was added to liquid silicone rubber, respectively, and then 5 parts of curing agent was added. The mixture was scraped onto the high silica glass fiber fabric and a mold was used to control the thickness of composite layer at 2 mm. Then, the composite was cured at room temperature for 2 to 3 hours. Finally, the composite sheet was obtained. Table 1 shows the basic formulation of composite sheet.

### Methods of testing

#### Mechanical properties

The tensile strength and elongation at break of the composite sheet were tested according to GB/T528-2009 using

**Table 1.** The basic formulation of composite sheets

Sample	Content, wt %			Volume fraction of HGM, vol %
	LSR	HGM	Curing agent	
LSR-0	100	0	5	0.00
LSR-3	100	3	5	21.34
LSR-5	100	5	5	31.13
LSR-7	100	7	5	38.76
LSR-9	100	9	5	44.86

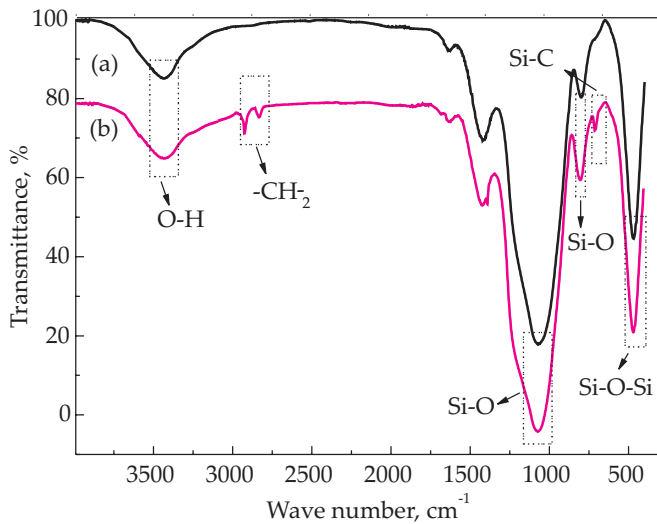


Fig. 1. FT-IR spectra of HGM before (a) and after modification (b)

the universal material testing machine (RGM 4100, Shenzhen Reger, China). The testing speed was 500 mm/min. Five specimens were tested for each sample.

#### Thermal conductivity

The thermal conductivity of the composite sheet was determined using the thermal conductivity tester (QTM-500, Kyoto, Japan) according to GB/T10297-2015. The specimen size was 100 mm × 100 mm × 10 mm, the measurement temperature was 23 °C, and the relative humidity was 38–46 %.

#### Dynamic mechanical properties

The storage modulus and loss factor of the composite sheet were measured using the dynamic thermal mechanical analyzer (DMA8000, PE, United States) in stretch mode, in the temperature range from -110 °C to

250 °C at heating rate of 5 °C/min at 1 Hz. The specimen size was 2 mm × 5 mm × 50 mm.

#### Scanning electron microscopy

The tensile-fractured and HGM surface morphologies were observed using the scanning electron microscope (JMS0-IT300, Japanese electronics co., Ltd., Japan). The samples were coated with gold before observation.

#### FT-IR

The condition of the HGM before and after modification was analyzed using Fourier transform infrared spectroscopy (Nexus 6700, Thermo Nicolet, USA) with resolution of 4 cm<sup>-1</sup> and scanning range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

### FT-IR analysis of HGM treated with the silane coupling agent

The infrared spectra of HGM before and after KH550 modification are presented in Fig. 1. Absorption peaks are evident at 460 cm<sup>-1</sup>, 794 cm<sup>-1</sup> and 1056 cm<sup>-1</sup>, which corresponded to the bending vibration of the Si-O-Si bonds and symmetric stretching vibration and asymmetric stretching vibration of the Si-O bonds [11, 12], respectively, which indicated that the main component of HGM was SiO<sub>2</sub>. After treatment with KH550, the infrared spectra of the HGM showed three new absorption peaks at 2830 cm<sup>-1</sup>, 2927 cm<sup>-1</sup> and 703 cm<sup>-1</sup>. The first two corresponded to the stretching vibrations of methylene group and the latter corresponded to the stretching vibration of the Si-C bond. The presence of new absorption peak indicated that the silane coupling agent KH550 had been attached successfully to the surface of the HGM (Fig. 2), which effectively reduced the surface free energy

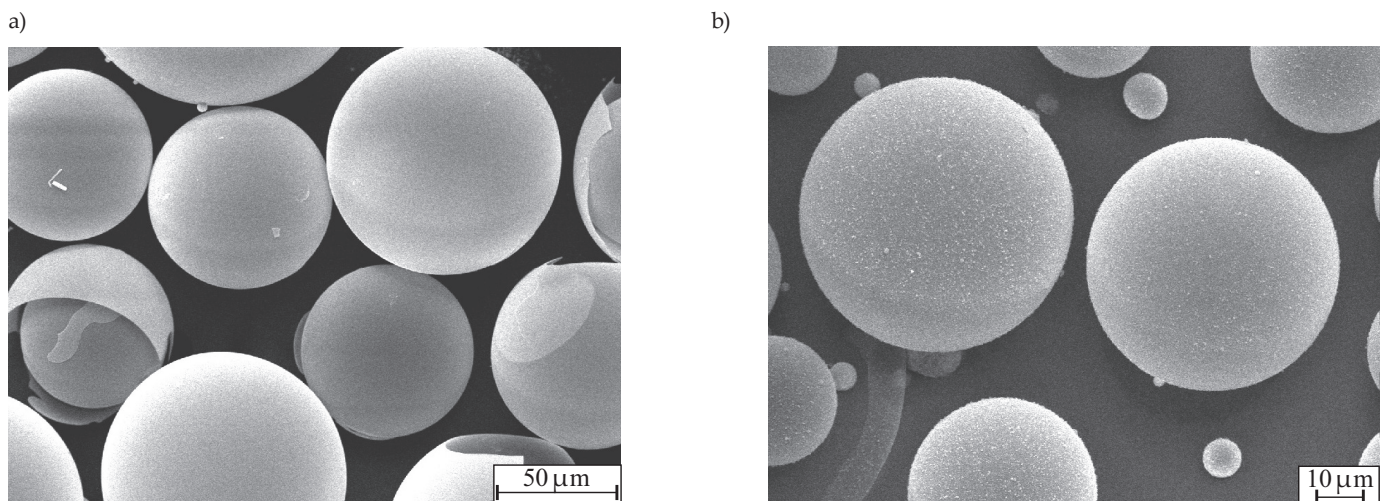


Fig. 2. Microscopic morphologies of the HGM surface: a) before, b) after modification



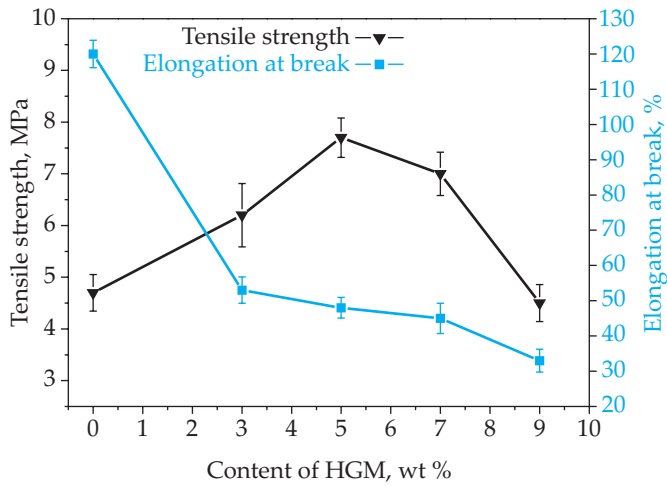


Fig. 3. Effect of HGM content on the tensile strength and elongation at break of the composite sheet

of the HGM, increased its hydrophobicity and improved its compatibility with matrix.

**Mechanical properties analysis of composite sheet**

The effect of different HGM contents on the mechanical properties of the composite sheet and their standard deviation are illustrated in Fig. 3.

It can be observed that the tensile strength of the composite sheet firstly increased and then decreased with increasing HGM content. When the content of HGM was less than 5 wt % there was a good interface between HGM and matrix. When the composite sheet was subjected to a load, the matrix and bonded interface could absorb energy effectively [13, 14], so the tensile strength of the composite sheet was increased. However, when the content of HGM exceeded 5 wt %, the decreased content of the matrix material per unit volume resulted in the lower thickness of the interfacial layer, which became unable to withstand effectively the stress delivered from the rubber matrix to the microspheres [15]. At the same time,

due to the smaller distance between the filler particles, as well as the agglomeration effect, volume fraction of the internal voids and non-infiltration regions of the composite sheet increased [16]. When the load was applied to the material, the HGM filler was liable to disbond from the matrix (Fig. 4) until the composite was destroyed. In addition, Fig. 3 shows that the elongation at breaking load of the composite sheet decreased as the HGM content increased. This was because addition of the filler particles increased the rigidity of the composite sheet. Moreover, at a rapid tensile loading rates, the material would break before it had yielded.

**Thermal insulation properties analysis of composite sheet**

The heat flow in the composite sheet was transmitted in three ways: a) heat transfer between solid and gas, b) convection of gas in the HGM, c) HGM surface radiation transfer [17, 18] (Fig. 5). For porous materials, convective heat transfer and radiant heat transfer usually were

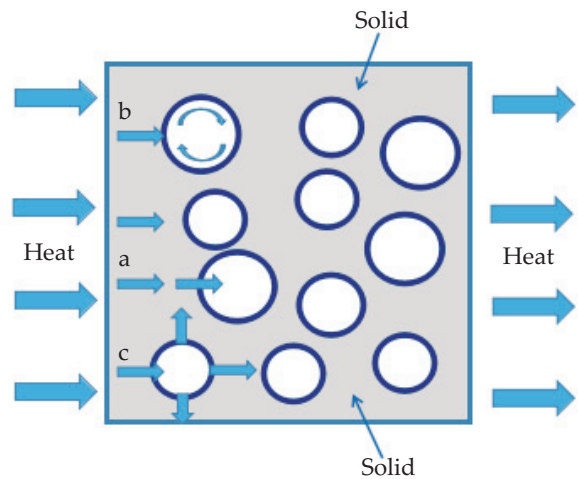


Fig. 5. Model of heat transfer in composite sheet

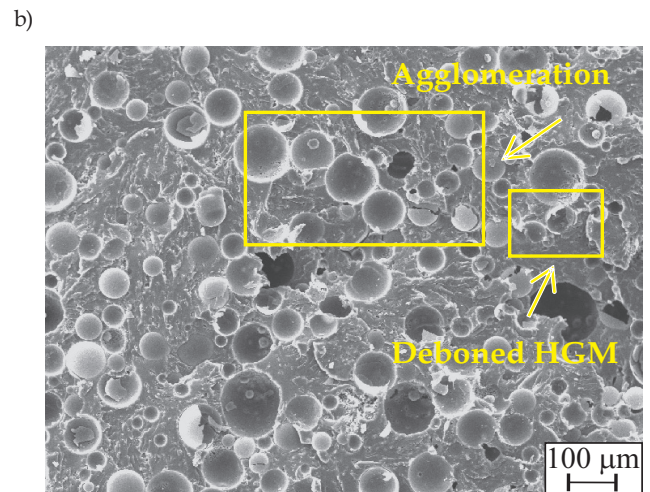
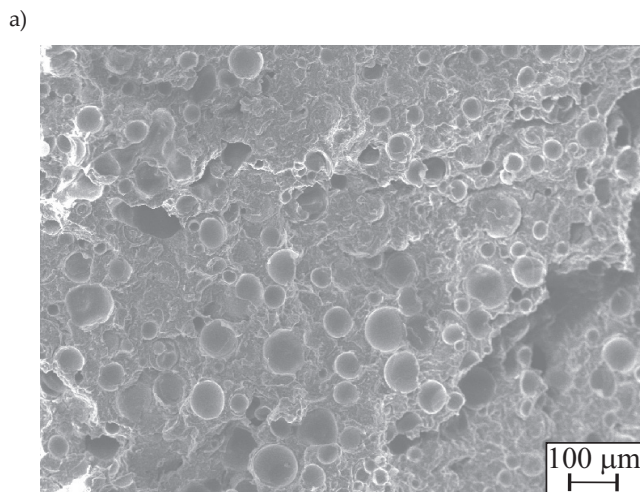


Fig. 4. Tensile fracture surface of the composite sheet with various contents of HGM: a) 7 wt %, b) 9 wt %

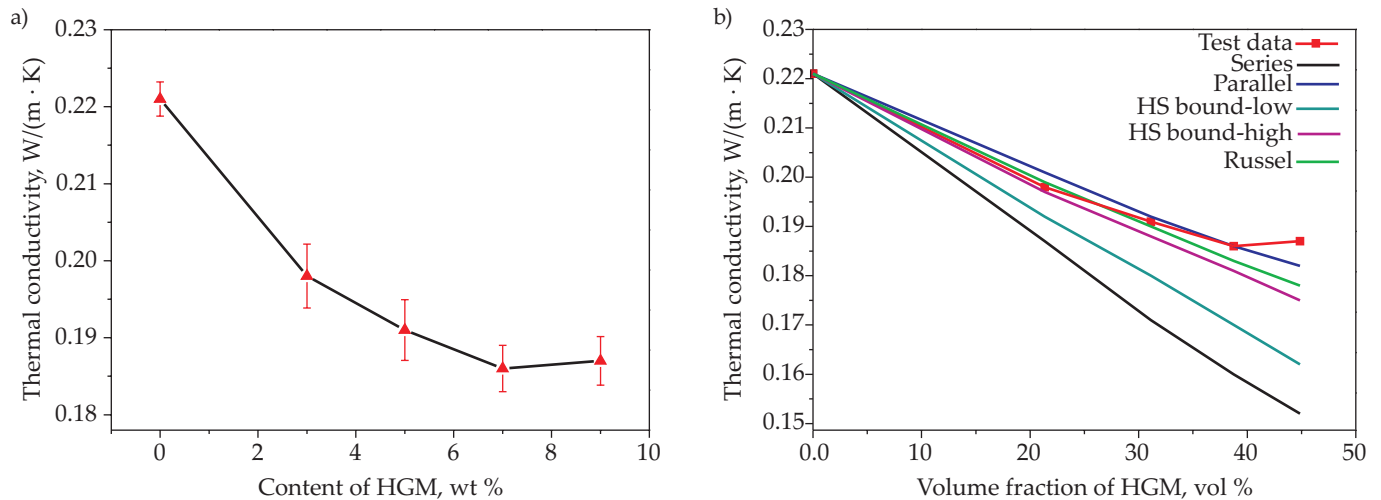


Fig. 6. Thermal conductivity of the composite sheet with different HGM contents: a) with various mass ratios, b) with various volume fractions

neglected when the pore size was small [19]. Thus, the heat transfer between the solid and the gas was the primary heat transfer mechanism of the composite sheet.

It can be seen from Fig. 6 that the thermal conductivity of the composite sheet decreased with increasing HGM content and reached the minimum value when the content of HGM was 7 wt % (38.76 vol %). The reason of this was the increase of the proportion of spherical pores per unit volume with increased HGM content. As the thermal conductivity of HGM itself was very low, the increase of the proportion of spherical pores hindered the heat transfer path in the solid phase resulting in the decrease in thermal conductivity. Subsequently, however, there was a slight rebound rise when the HGM content continued to increase to 9 wt % (44.86 vol %). This may be because the distance between the HGM microspheres decreased and it was difficult to disperse them well in the matrix. In consequence, local agglomeration occurred and the HGM spheres with thin walls contacted with each other, forming a fast passage of heat transfer (see Fig. 4b), so that the thermal conductivity of the composite sheet increased slightly.

Several models were used for thermal conductivity predictions, these were mainly the parallel model, the series model, the Hashin bounds-high model, the Hashin bounds-low model and the Russell model [20]. Figure 6 illustrates the comparison of thermal conductivity between the five effective thermal conductivity models and experimental results for two-phase systems. The series model and the Hashin bounds-low model did not match the actual filling structure of the material so the thermal conductivity predicted by the models was quite different than observed during the experiments. When the content of the HGM was low, the test data was close to other prediction models. However, when the HGM volume fraction exceeded 25 vol %, the experimental results began to deviate from the Hashin bounds-high model and Russell model and approached the parallel model. This was because all the models were based on

the fact that there was no interaction between the filled particles and uniform dispersion in the continuous phase. When the HGM content increased, the HGM was unevenly dispersed in the matrix and the agglomeration phenomenon became very evident. Since HGM spheres were in contact with each other, the spherical voids within the material were close to each other so that the structure of the material tended to be more consistent with the parallel model [21].

#### Dynamic mechanical properties analysis of composite sheet

The storage modulus and loss factor of the composite sheet with various contents of HGM are shown in Fig. 7. It was confirmed from Fig. 7a that the storage modulus of composite sheet with different HGM contents decreased with increasing temperature. In the glass transition temperature range, due to the synergistic effect of the molecular segments of the silicone rubber [22], the storage modulus decreased rapidly and when the temperature rose above  $-30^{\circ}C$  the storage modulus was low and substantially constant. In the low-temperature glassy zone, when the HGM content was increased to 7 wt %, the storage modulus of the composite sheet reached a maximum value. This was because the increase in HGM content resulted in more interfaces between HGM and silicone rubber matrix. The high interfacial bonding force limited the movement of the matrix silicone rubber molecular chains and, in consequence, the storage modulus of the composite sheet increased [23]. When the content of HGM increased to 9 wt %, the interface between the HGM and the silicone rubber decreased as a result of accumulation of HGM, which decreased the storage modulus of the material. It was evident from Fig. 7b that when 5 wt % of HGM was added, the glass transition temperature ( $T_g$ ) of the composite sheet was shifted from  $-47^{\circ}C$  to  $-33^{\circ}C$ , compared with composite sheet

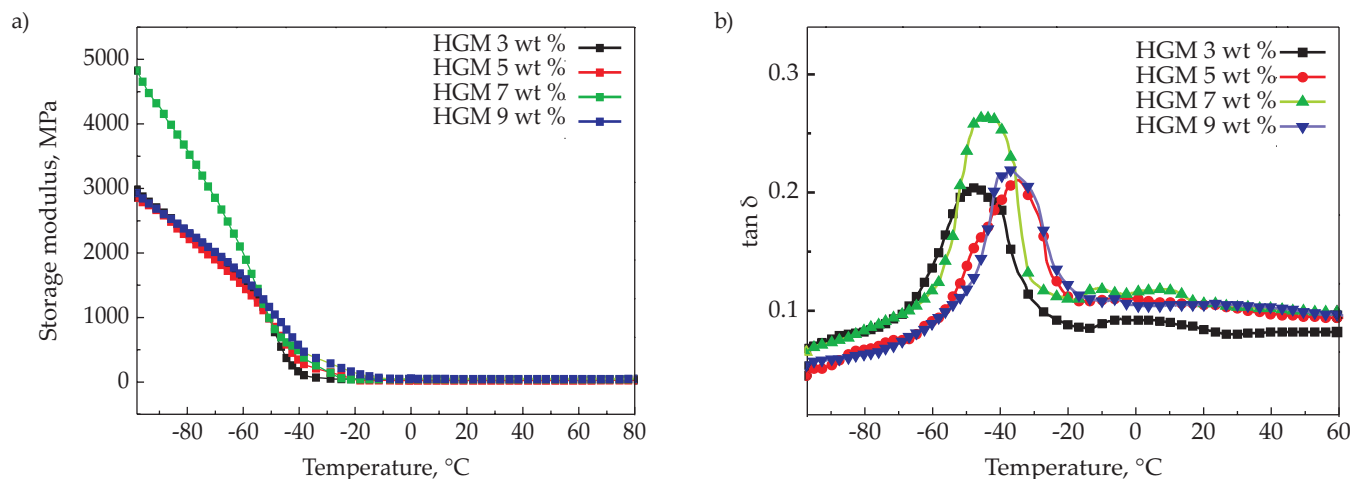


Fig. 7. a) Storage modulus, b) loss factor of the composite sheets with various contents of HGM

in which the content of HGM was only 3 wt %. This was because the increase in HGM content increased the rigidity of the composite sheet and hindered the movement of the silicone rubber molecular segments. Then, as the HGM content continued to increase, the  $T_g$  did not change significantly. At the same time, it could be seen that the loss factor,  $\tan \delta$ , of the composite sheet increased with the increase in HGM content and reached a maximum of 0.264 when the HGM content was 7 wt %. This was because the internal friction of the composite sheet increased with an increase in HGM content consequently the energy absorption of the composite sheet increased so the loss factor,  $\tan \delta$ , increased [24]. When the HGM content reached 9 wt % the accumulation of the HGM reduced the internal friction of the composite sheet and in consequence the loss factor,  $\tan \delta$ , decreased [25].

## CONCLUSIONS

- FT-IR and SEM results demonstrated that the compatibility and interfacial properties between HGM and the matrix were improved after the HGM was treated with the silane coupling agent, KH550.

- With increase in the HGM content, the tensile strength of the composite sheet firstly increased and then decreased, and the elongation at break was decreased.

- Due to the addition of HGM, the thermal conductivity of the composite sheet decreased from a value of 0.221 W/(m · K) for pure silicone rubber to 0.186 W/(m · K) for silicone rubber with HGM content of 7 wt %.

- The glass transition temperature ( $T_g$ ) of the composite sheet increased with increase in the HGM content. When 7 wt % of HGM was added, the loss factor,  $\tan \delta$ , of the composite sheet was maximal and the damping performance of the composite material was improved.

- The comprehensive analysis of the performance of the composite sheet revealed that the ideal HGM content was 7 wt %.

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