

Preparation and Performance of HGM/PPENK-based High Temperature-resistant Thermal Insulating Coatings

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Abstract Novel high temperature-resistant coatings with high mechanical strength and thermal-insulating performance were prepared with poly(ether nitrile ketone) (PPENK) resin as matrix and hollow glass microspheres (HGMs) as thermal-insulating filler. The corresponding mechanical and thermal-insulating study indicated that the mechanical properties of the coatings decreased with the increase of HGM content, and were improved after surface modification of HGM by KH570 resulting in enhancement of interaction between HGM and PPENK resin. The thermal conductivity of HGM/PPENK thermal-insulating coating decreased with the increase of HGM content and coating thickness, along with the decrease of the true density. It also showed slight increase trend due to HGMs surface modification. The HGM/PPENK coating filled with modified HGMs showed better thermal resistance than that of unmodified HGM/PPENK coating. The thermal decomposition temperature at 5% weight loss of the coating containing modified HGMs was 10 °C lower than that of pure PPENK, and 40 °C higher than that of neat HGM/PPENK coating. The coating exhibited commendable appearance after 400 °C for 30 min. The merits of HGM/PPENK-based thermal coatings obviously demonstrated promising prospect in thermal protection fields.

Keywords Coatings; Temperature-resistant; HGM/PPENK; Thermal conductivity; Mechanical properties

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INTRODUCTION

With the development of modern industry, especially the industries of metallurgy, aerospace, and militaries, the thermal protection of some components and substrates is becoming increasingly important. Thermal protection has been an effective means to protect materials from damage and maintain its initial function. It is simultaneously the most convenient way to modify materials towards several new properties.^[1]

Currently, there are two kinds of thermal protection methods. One is loading high-temperature alloys (e.g., Al and Ti) during the material preparation process to resist destruction resulted from high temperatures.

Unfortunately, such strategy usually involves high cost and complicated technology. There is a contradiction between improvement of temperature resistance and mechanical properties. The other one is introducing thermal-resistant coatings on the substrate.^[2] Such method is proved more economical and practical with the help of thermal-insulating coatings rather than developing new high temperature-resistant composites.^[3] Hence, high temperature-resistant coatings have increasingly caught the attention of researchers.

Generally, high temperature-resistant coatings can reduce internal temperature of substrate by coating on the surface. It could meanwhile be conducive to maintain normal functioning of basic material under harsh service environment.^[4,5] Compared with other surface decorating techniques, high temperature-resistant coating is more promising due to several advantages, such as low cost, facile fabrication and high efficiency. Especially with assistance of modern spraying techniques, thermal-resistant coating technique has become the most attractive thermal protection technology.

Based on properties of film-forming materials, thermal-resistant coatings could be divided into organic and inorganic types. Organic coatings generally consist of resin matrices, pigments and additives. Thermoplastic resin matrices include organic silicon, organic fluorine, ferrocene-containing polymers, aromatic polyimide, polysulfone, poly(phenylene oxide) and poly(ether ether ketone). Thermosetting resin matrices include phenolic resin, epoxy resin, bismaleimide resin, and polyimide, etc. Organic silicon is celebrity as film-forming matrix for thermal-insulating coatings,^[6] because of its higher bonding energy (Si—O, 443 kJ·mol⁻¹) than that of the C—C covalent bond (347 kJ·mol⁻¹), usually resulting in high thermal stability. However, several drawbacks still should be taken into account towards practical applications, such as long time curing, inconvenient operation in large scale, poor solvent resistance and low surface tension. There are many

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studies on the modification of silicone resin with common polymer materials, such as epoxy resin,^[7] poly(acrylic acid),^[8,9] or polyester^[10,11] resin. Unfortunately, such materials inevitably lead to decrease of thermal stability.

As typical high performance resins, heterocyclic polymers possess outstanding comprehensive properties such as high thermal stabilities, excellent mechanical and chemical inertia, including aromatic polyimide, polysulfone, poly(phenylene oxide) and poly(ether ether ketone). They have been widely used in high-tech fields, like aerospace, energy, automobile and marine. Our team introduced twisted, non-coplanar, three-dimensional phthalazinone moiety into poly(aryl ether) backbone, resulting in a series of novel resins with high thermal resistance (T_g), good solubility and prominent mechanical performance, such as poly(aryl ether sulfone) (PPES), poly(aryl ether ketone) (PPEK) and poly(aryl ether sulfone ketone) (PPESK), poly(ether nitrile ketone) (PPENK).^[12] Such unique promising polymer system could be prepared with simple synthesis process and low cost, which has already been successfully applied as enameled wires,^[13] light-curing paint, insulating paint^[14] and thermal-resistant adhesive.^[15]

PPENK contains cyano and ketone groups in backbone. Due to strong polarity of cyano functional group, PPENK exhibits great adhesion on matrix. Furthermore, cyano group could provide potential crosslinking point, when disposed under high temperature, further improving its heat resistance. However, the thermal conductivity of PPENK is slightly higher for thermal insulation. Hollow glass microspheres (HGMs) was utilized for blend to meet the thermal insulation requirement.

HGMs consist of outer stiff glass and inner inert gas, resulting in excellent performances, such as low density, low thermal conductivity, excellent dispersion, chemical stability and high compressive strength. They have been widely used in the fields of aerospace,^[16,17] deep-sea diving,^[18,19] micro-electronics,^[20,21] building materials,^[22,23] coatings.^[24–26] Li *et al.*^[27] studied the effect of particle size of HGM on heat insulation performance for waterborne coatings. Hu^[28] filled different concentrations of broken HGM into SR together with intact HGM, and the results showed that the broken HGM increased the thermal conductivity of the composites but weakened the thermal insulation properties. Ozkutlu *et al.*^[29] prepared PMMA syntactic foams by dispersing different types of HGMs into poly(methyl methacrylate) (PMMA) and studied effects of HGM density and surface modification on the mechanical and thermal properties of PMMA. Vahtrus *et al.*^[30] compared the influence of hydrophobic aerogels (SiO_2) and hollow glass microspheres (HGM) on the thermal conductivity of epoxy composites. They pointed out that the thermal

conductivity of the composites filled with SiO_2 is lower than that of HGM because aerogel pores are filled with epoxy adhesive.

Many studies on HGM applications have been reported recently, however, there are relatively few studies focusing on the diversity of high performance polymers and their high temperature (more than 400 °C) insulation behaviors. Herein, PPENK/HGM high temperature-resistant thermal-insulating coatings were prepared with HGM featured with different contents or parameters. The surface of HGM was modified by silane coupling agent to enhance dispersion and interfacial interaction between PPENK and HGM. Different HGM contents (0 vol%–60 vol%) of PPENK/HGM coatings were prepared and their thermal, mechanical properties, and morphologies were further investigated as well.

EXPERIMENTAL

Materials

The PPENK matrix was purchased from Dalian Polymers New Materials Co., Ltd. with intrinsic viscosity $[\eta]$ of 0.46 dL/g. *N*-methyl-2-pyrrolidone (NMP) was purchased from Mitsubishi Chemical Corporation, and silane coupling agents, KH-560 and KH-570, were purchased from the Xiang Fei Institute of Chemistry, Nanjing. Silane additive BYK310, BYK354 were purchased from BYK Additives and Instruments, Germany. HGM were provided by 3M Hong Kong Ltd. and Ma'an Shan New Material Technology Co., Ltd. The properties of microspheres were listed in Table 1.

Preparation of PPENK Varnish and HGM/PPENK Coatings

The refined PPENK powder was dissolved in NMP and the contents in the solution were 18 wt% and 22 wt%, respectively. Then, coupling agent KH560 (0.5 wt%–1 wt% based on the weight of resin) was added into the solution, and stirred for 10 min. Subsequently, dispersant BYK310 (0.08 wt% based on the weight of total mass) and BYK354 (0.5 wt% based on the weight of total mass) were separately added into the above PPENK solution, stirred by a high-speed mixing machine for 30 min to form uniformly mixtures. Stand still for a while to remove the air bubbles.

Modified HGMs with different contents were respectively added to 22 wt% PPENK varnish, stirring for 30 min in high speed mixer. The content of HGM was 9.6 vol%, 19.9 vol%, 30.0 vol%, 41.5 vol%, 47.0 vol%, 51.6 vol%, 55.4 vol%, 58.7 vol% and 61.5 vol%, respectively. The coatings containing different HGMs are marked as VS5500/PPENK, S15/PPENK, XLD3000/PPENK and T40/PPENK, respectively.

Table 1 Parameters of hollow microspheres.

Type of HGM	Compressive strength (MPa)	True density ($\text{g}\cdot\text{cm}^{-3}$)	Particle size				Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)
			10 th %	50 th %	90 th %	Max	
S15	2.07	0.15	25	55	90	95	0.055
XLD3000	20.67	0.23	15	30	40	95	0.078
VS5500	37.90	0.38	15	40	75	85	0.127
T25	5	0.25	30	65	106	110	0.051
T40	28	0.40	20	45	70	75	0.065

Procedure for HGM/PPENK Thermal Insulation Film Preparation

Spraying operation was achieved in the fume hood with an air humidity below 30%. Firstly, 18 wt% PPENK varnish was sprayed on the surface of substrate, moved into Muffle furnace and dried to form a film as pre-programmed after leveling. Then, HGM/PPENK coating was sprayed on the drying PPENK film surface several times to prepare films with different thicknesses. The dried HGM/PPENK film thicknesses were 0.2, 0.4, 0.6 and 0.8 mm, respectively.

Surface Modification of HGM

Firstly, an ethanol aqueous solution was prepared with a volume ratio of water to ethanol 15:1. Then, acetic acid was added to adjust pH to around 2. Afterwards, appropriate amounts of KH-570 were added (10 wt% based on the weight of HGM) to the solution and stirred strongly for 10 min by magnetic stirrer until hydrolysate of KH570 was formed. HGMs were then added to the solution, stirred at 70 °C for 3–4 h. Extra KH570 was added during the process. The system was allowed to cool to room temperature. Finally, HGM was filtered out and dried at 120 °C for 12 h. The modified HMG was marked as m-HMG, the unmodified HMG as u-HMG.

Characterizations

The flow viscosity of coating was measured by T-4 cup according to ISO 2431-1993. The adhesion of the PPENK film was assessed via a circle-drawing tester according to GB/T 1720-79. The adhesion of the HGM/PPENK coating was assessed via a grid-drawing tester according to ISO 2409. The resistance to impact was measured using a QCI impact tester according to GB/T 1732-93. Differential scanning calorimetry (DSC) analyses were performed on Mettler DSC822 under a nitrogen atmosphere of 50 cm³·min⁻¹ at a heating rate of 10 °C·min⁻¹ from room temperature to 400 °C.

Thermal gravimetric analysis (TGA) was performed on a TGA/SDTA851 thermal analyzer at a heating rate of 20 °C·min⁻¹ under nitrogen purge of 50 cm³·min⁻¹ from room temperature to 800 °C. In order to study the interface state between HGM filler and PPENK matrix, the images of fractured surface were monitored by field emission scanning electron microscope (SEM, QUANTA 450, FEI). The samples with fractured surface were coated with gold before SEM observation. The thermal conductivity of the HGM/PPENK coatings at room temperature was carried out using a Thermal Properties Analyzer (Xiotech TC3000, Xi'an Xiayi Electronic Technology Co., Ltd.) according to GB/T 10297-2015. The measured samples were coated on the substrate covered by aluminum foil. Tear the film off the foil and tailor it to a size of 50 mm × 50 mm × 0.1 mm. Thermal diffusion diffusivity of the HGM/PPENK coatings was measured using Nanoflash® analyzer. (LFA447, Netzsch, Germany) at room temperature, 100 and 200 °C. The samples were disk shaped with 12.7 mm in diameter, and 0.5–0.8 mm in thickness. The actual heat insulation effect was measured with self-constructed equipment. The HGM/PPENK thermal-insulating coating samples were coated on the tinplate with a size of 120 mm × 50 mm × 0.8 mm. The surface of HGM/PPENK coatings was marked as "a" side, and the other as "b" side. When temperature of furnace reached up to 400 °C, put the "a" face to the inside of the furnace, monitoring the temperature of "b" side with thermocouple, as shown in Fig. 1.

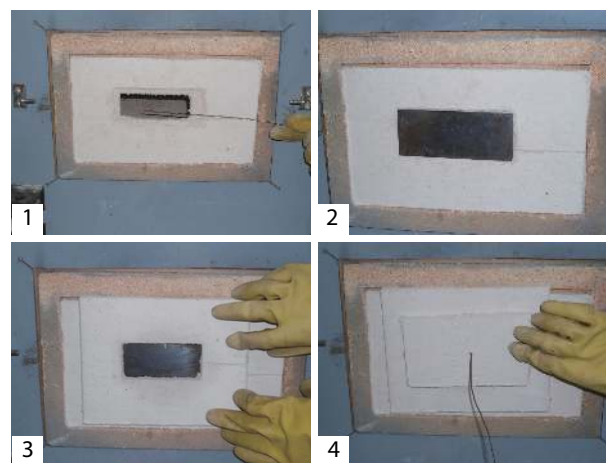


Fig. 1 Schematic diagram of heat insulation performance of PPENK/HGM coatings.

RESULTS AND DISCUSSION

Viscosity of HGM/PPENK Thermal Insulation Coatings

"Coating viscosity" refers to flow viscosity in industry. Flow viscosity is a critical rheological parameter associating with fluidity, which could be measured conveniently and quickly by T-4 cup. The content of HGM filler in the HGM/PPENK thermal-insulating coating has a great influence on the fluidity of the coating. The performances of coating directly associate with thickness of coatings, that is, related to the volume of fillers. So, the content of HGM is represented here by volume fraction (vol%). The HGM/PPENK coatings were heated to 100 °C to obtain good liquidity. The variation of T-4 viscosity of HGM/PPENK coatings filled with modified VS5500, S15, XLD3000, T40 with the volume fraction of HGM at 100 °C are shown in Fig. 2.

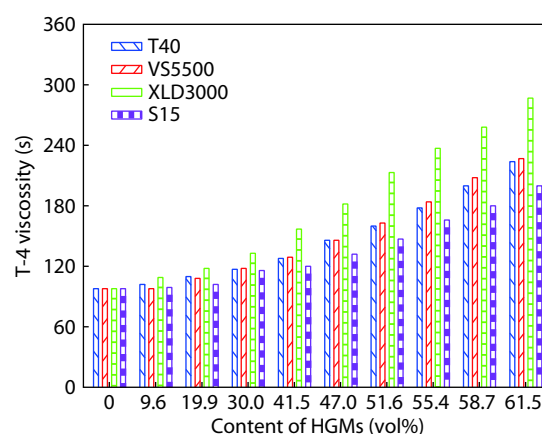


Fig. 2 Effect of HGM contents on T-4 viscosity of coatings.

It can be seen that the T-4 viscosity of all coatings increase with the increase of HGM content and the decrease of HGM particle size. With the increase of m-HGM content, the more adsorption and entanglement of resin solution on HGM surface, the less fluidity of resin solution in the gap of the HGM, resulting in higher flow resistance and T-4 viscosity. The T-4

viscosity of coating containing XLD3000 is the highest and possesses the most rapid increase rate among the samples, while S15 sample shows the lowest viscosity, which is attributed to the particle size and distribution of HGM. For XLD3000, it has smaller particle size and the narrower distribution, which means larger surface area that can adsorb more resin solutions on the surface leading to higher viscosity. Accordingly, larger particle size and smaller specific surface area for S15 could only accompany with less resin solutions on surface. It can also be seen that the T-4 viscosity of HGM/PPENK coatings increased slowly with less content of HGM. And it increased rapidly with the increase of HGM volume fraction. This may be due to the critical volume fraction of HGM. In practical application, the HGM/PPENK coatings can be sprayed with T-4 viscosity below 150 s.

Mechanical Properties of HGM/PPENK Thermal Insulation Coatings

The adhesion and impact strength tests of the coatings were always conducted on the substrate. The adhesion between the coatings and the substrate would influence the impact strength of the coatings. The impact strength would essentially reflect the balance between the adhesion to substrate and the cohesion within the film, and thus impact strength and adhesion as a function of the VS5500 content with and without modification are shown in Fig. 3.

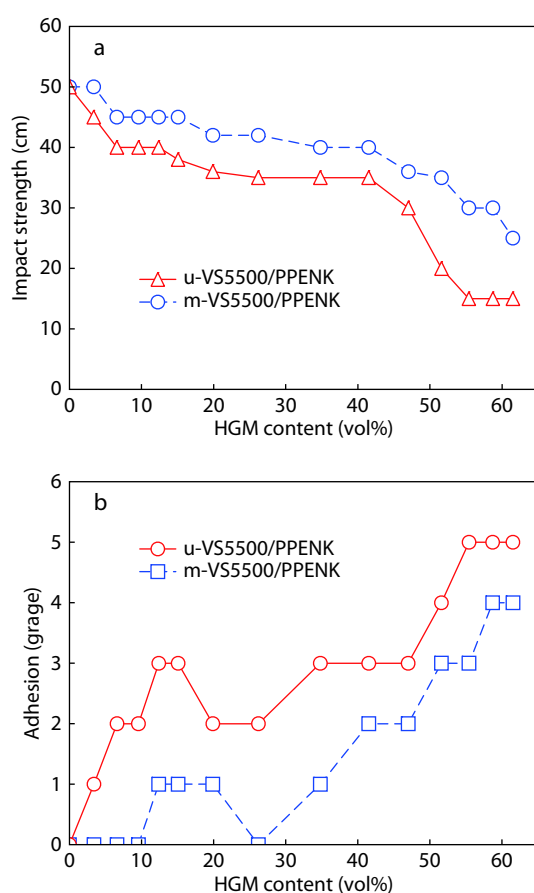


Fig. 3 Effect of HGM contents on impact strength (a) and adhesion (b) of coatings.

It can be seen that the impact strength and the adhesion decreased with the increase of HGM loading (vol%). When the content of HGM is less than 41.5 vol%, the impact strength gradually decreased and declined rapidly with the content of HGM above 40 vol%. The adhesion showed the same trend. It is indicated that the content of HGM reached the critical volume fraction (CPVC) at 41.5 vol%. Void defects were formed as a result of the lack of resin filling the voids among HGMs when content is above CPVC. Accordingly, mechanical properties of the film greatly reduced. The impact strength of the m-HGM/PPENK coating is more than 40 cm, and the adhesion is greater than 1 grade when the content is below 41.5 vol%.

Fig. 3 also demonstrates that the impact strength and adhesion of HGM/PPENK coatings containing m-HGM were significantly improved compared to those of the coatings containing u-HGM ones. When u-HGMs were filled into coatings, an distinct interspace between the HGM and the PPENK matrix existed, resulting in stress that could not distribute continuously in the film under external impact stress, which lead to weak adhesion and poor impact stress. After modification with KH570, PPENK resin tightly adhered to the surface of HGMs which led to improved compatibility between HGM and resin matrix. The participation of m-HGM facilitated the stress to be uniformly distributed on the coatings. Therefore, the mechanical properties of the coating were enhanced accordingly.^[31,32]

The HGMs/PPENK coatings have to be dried at high temperature for a long time to form the thermal insulation film. In previous studies,^[33] PPENK will crosslink at high temperature which may result in change of mechanical properties. So, the appearance and the mechanical properties of PPENK film, cured at subsequent process, were studied as shown in Table 2.

Table 2 Parameters of hollow microspheres.

Drying program	Color of film	Gel content (%)	Flexibility	Adhesion	Impact stress (cm)
a	Yellow	0	Flexible	Peeled	—
b	Light yellow	77.2	Flexible	1	45
c	Tan	91.4	Flexible	0	50
d	Brown	94.8	Flexible	0	50
e	Brown	99.5	Brittle	2	45

(a) 220 °C for 60 min; (b) 280 °C for 5 min; (c) 280 °C for 30 min; (d) 280 °C for 30 min and 330 °C for 15 min; (e) 30 °C for 24 h.

It was observed that the PPENK film became darker and the gel content increased as cured at higher temperatures, which indicated that crosslink within PPENK resin indeed happened. The adhesion and impact strength gradually increased when cured with curing program a, b, c and d, while decreased with curing program e. This illustrates that both temperature and time have a great influence on the performance of the film. When the PPENK resin was cured at 280 °C for 5 min, as shown in curing program b, the adhesion of the film increased from peeling to grade 1, and impact strength increased to 45 cm. These can be attributed to the movement of PPENK macromolecular chain segment at 280 °C, close to its T_g (275 °C), enabling it to chemically bind to the substrate. When the PPENK resin was cured at programs c and d, the adhesion and impact strength were grade 0 and 50 cm, and gel

content were 91.4% and 94.8%, respectively. The film was still flexible, indicating that improvement of mechanical properties of PPENK film are due to partially cross-linking at high temperature. When the film underwent process e, it exhibited the darkest color and relative brittleness. The gel content increased to 99.5%, the adhesion and impact strength were reduced as well, suggesting that higher degree of thermal curing at 330 °C for 24 h caused the volume shrinkage of film in turn to result in deterioration of mechanical properties.

Microstructure of the Coatings

As the interface state between filler and resin plays an important role for the properties of the film, the fracture morphologies of HGM/PPENK films were analyzed by SEM. Fig. 4 shows the cross-sectional SEM images of HGM/PPENK films with the content of VS5500 for 41.5 vol%.

It was seen from Fig. 4 that the dispersion of HGMs in the PPENK matrix were uniform and almost no aggregation. Figs. 4(a) and 4(c) show that certain amount of u-HGMs were completely peeled from the matrix to leave holes. The surface of HGMs exposed on the fracture surface was clean without any residual resin. When the magnification of the images was improved, obvious interspace was observed between HGMs and the PPENK resin, which means that no chemical bond was formed between them.

Figs. 4(b) and 4(d) show that the gap between HGM and PPENK disappeared after modifying the surface of HGM with KH570, as discussed above. HGMs were embedded in the matrix and almost no complete pulling out happened. The surface of HGMs exposed on the fracture section was not clean but adhered certain amount of residual PPENK resin, indicating that the PPENK molecules were strongly bonded to the surface of the HGMs and a strong chemical interaction was formed. These results proved that the strong interaction is beneficial for properties of the coatings. In Fig. 4(b), an irregular hole can be observed (less than 20 μm), which is due to small solvent bubbles enclosed in high viscosity HGM/PPENK coatings and left in the films.

Figs. 4(e) and 4(f) show the cross-section images of u-HGM/PPENK coatings cured at 220 °C for 1 h and 330 °C for 24 h, respectively. The PPENK resin became rough due to the formed gel particles by crosslink when comparing Figs. 4(a), 4(e) and 4(f). The surface of HGM was smooth without any residual resin matrix, in other words, without any interaction between HGMs and PPENK resin. It proved that curing crosslink only played a weak role for the improvement of mechanical properties of HGM/PPENK coatings.

Thermal Insulating Properties of HGM/PPENK Coatings

The thermal conductivity of HGM/PPENK coatings filled with VS5500 and S15 was measured as a function of HGM content. As shown in Fig. 5, it was easily found that thermal conductivity decreased gradually with the increasing HGM content. HGM is one kind of hollow, spherical and lightweight inorganic functional powder, bearing gas in the core, which endow HGM with low thermal conductivity. The preserved pores in the materials were the most significant physical factor in determining the thermal conductivity of the composites.^[34] Thus, the thermal conductivity of the coatings decreased with increasing HGM content and tended to be stable when the content was above 41 vol% for VS5500 and above 51 vol% for S15. These results implied that the HGM content reached critical volume fraction. At this time, the thermal conductivities of the coating filled by m-VS5500 and m-S15 were 0.149 and 0.109 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively, much lower than that of pure PPENK (0.287 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$).

When using the same type of HGM, m-HGM filled coatings have higher thermal conductivity than u-HGM filled coatings at all HGM contents. The thermal conductivity of coatings containing VS5500 with and without modification decreased to 0.122 and 0.115 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively, and containing S15 were 0.109 and 0.096 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for m- and u- HGMs, respectively, when the content is 51 vol%. As mentioned in Fig. 4, the surface modification of HGM by KH570 could effectively lower down the gap between HGM and PPENK matrix, which

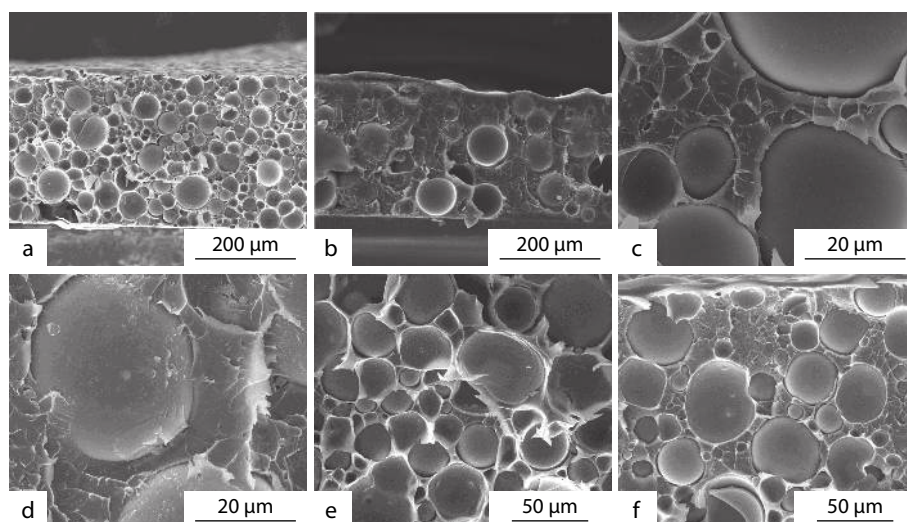


Fig. 4 SEM images of fracture surface of HGM/PPENK coatings filled with (a) u-HGM, (b) m-HGM, (c) u-HGM, (d) m-HGM, all cured at 280 °C for 30 min, (e) u-HGM cured at 220 °C for 1 h, (f) u-HGM cured at 330 °C for 24 h.

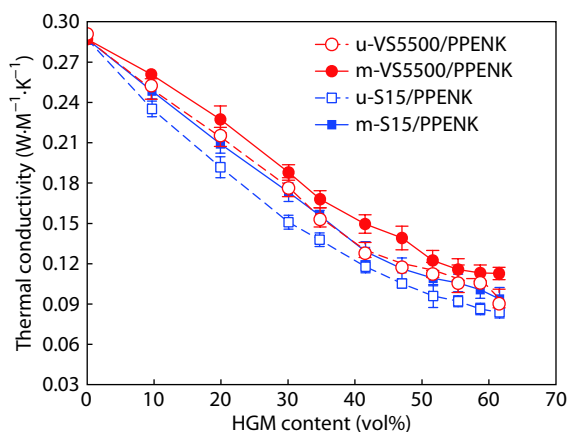


Fig. 5 The thermal conductivity of the HGM/PPENK coatings as a function of HGM content.

significantly brought down the phonon scattering, and thus enhanced the thermal conductivity of the coatings.^[35]

At the same volume fraction of HGM filler, it can be seen that the coatings filled with S15 showed higher thermal conductivity than that filled with VS5500. The S15 had a larger diameter and smaller wall thickness, leading to more gas which contributed to insulation as a result of lower thermal conductivity.

Thermal conductivity of the fillers significantly affected the thermal insulation performance of composites. The thermal conductivity coefficients of the fillers are related to their physical parameter.^[36] Fig. 6 evaluate thermal conductivity of HGM/PPENK coatings as a function of HGM true density. It can be seen that the thermal conductivity of the HGM/PPENK thermal-insulating coating gradually increased with the increase of HGM true density. The basic heat transfer generally includes conduction, convection and radiation according to heat transfer mechanism.^[27] According to the theory of Skochdopole,^[37] the natural convection would not occur when bubble diameter was less than 4 mm for porous materials. So convective heat transfer can be neglected since the diameter of HGM was less than 100 μm as shown in Table 1. Thermal radiation is usually significant only when temperat-

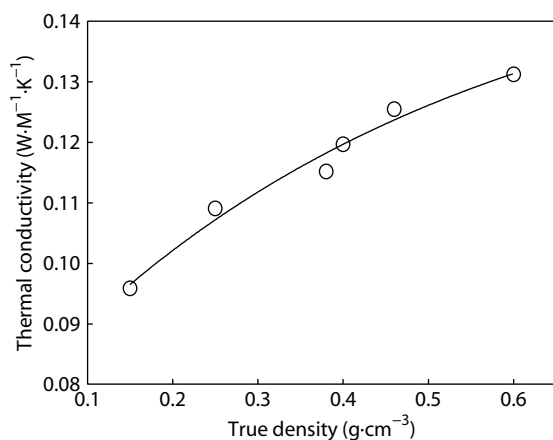


Fig. 6 Effect of real density of HGM on thermal conductivity of coatings.

ure is higher than 770 K^[38] and can be neglected when temperature is lower than 573 K.^[39]

In conclusion, thermal conduction is the main mechanism of heat transfer for HGM.^[40] The heat mainly transferred *via* solid phase of the HGM rather than *via* gas.^[41] So, the HGM thermal conductivity and the thermal insulation coating system both increased with the increase of the HGM true density, which endowed the HGM with smaller d/D and more solid phase.

Fig. 7 presents the thermal diffusivity of the VS5500/PPENK and S15/PPENK coatings as a function of the temperature with HGM content of 51 vol%. Thermal diffusivity is an index of the capability to transmit temperature through material which is more intuitive than thermal conductivity. It can be found from Fig. 7 that thermal diffusion diffusivity of the thermal insulation coating decreased with the increase of temperature. The thermal diffusivity of VS5500/PPENK coating was $0.389 \text{ mm}^2\cdot\text{s}^{-1}$ at R.T. and reduced to $0.226 \text{ mm}^2\cdot\text{s}^{-1}$ at 300 °C. Therefore, the coating exhibited better thermal insulation performance at high temperature. The thermal diffusivity of VS5500/PPENK coatings was always larger than that of S15/PPENK at the same volume fraction. This is attributed to the smaller true density and larger inner gas volume for S15. Therefore, the thermal diffusivity of coatings reduced by increasing the ratio of internal diameter and external diameter of HGM.

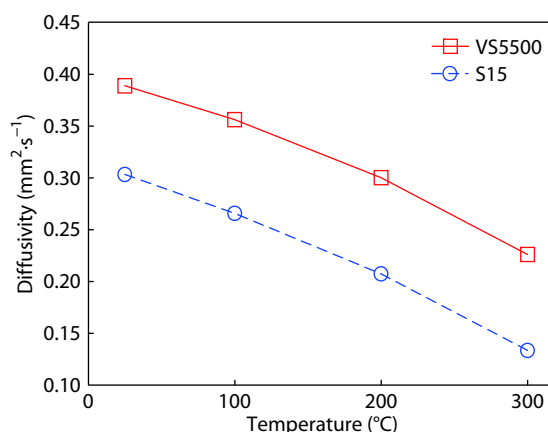


Fig. 7 Effect of temperature on thermal diffusivity of coatings.

The Actual Thermal Insulation Effect

The actual thermal insulation performance of HGM/PPENK coating were expressed by testing the temperature of the back of the sample plate. The surface of the sample was coated with VS5500/PPENK thermal insulation coatings. The changes in temperature at the back of the sample plate were measured as a function of coating thickness and the volume fraction of HGM as shown in the Figs. 8 and 9, respectively.

From Fig. 8, it could be observed that the temperature at the back of the sample plate decreased obviously with the increase of coating thickness. When the Muffle furnace internal temperature reached 400 °C, that was, the surface coated with HGM/PPENK thermal insulation coating subjected to 400 °C thermal shock, the temperatures at the back of the sample were 125, 110, 89 and 71 °C, respectively with the

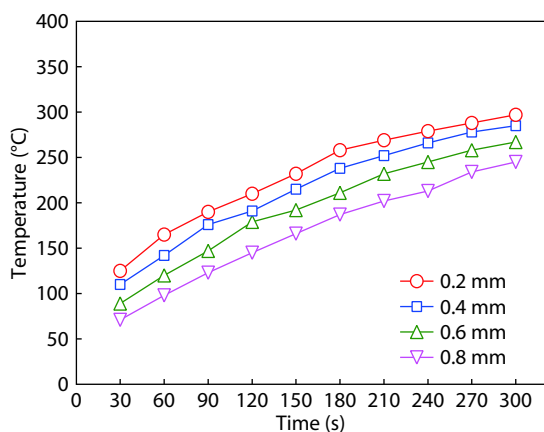


Fig. 8 Effect of coating thickness on thermal insulation performance.

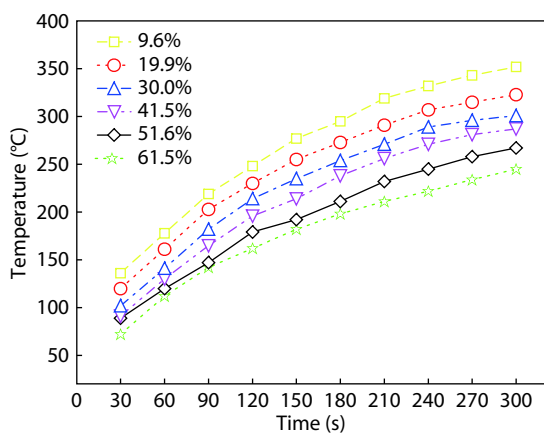


Fig. 9 Effect of HGM content on thermal insulation performance.

thickness of 0.2, 0.4, 0.6 and 0.8 mm after 30 s. The corresponding temperatures were 165, 142, 120 and 98 °C, respectively when the time surpassed 60 s. This indicated that the increase of coatings thickness could effectively improve the thermal insulation performance. The surface temperature of sample with a thickness of 0.8 mm was lower (54 °C) than that with a thickness of 0.2 mm. Hence, great thermal-insulating performance can be obtained with thick thermal insulation coating.

Fig. 9 presents the changes in temperature at the back of the sample plate with volume fraction of HGM. The thickness of the measured coating was 0.6 mm. With the increase of HGM content, the back temperature of sample plate decreased, which was consistent with thermal conductivity regulation against HGM content. A large number of HGM accumulated together to form a thermal buffer layer, which had a strong effect on blocking heat transfer. The temperature at the back of the sample plate was 89 °C with the content of HGM 51 vol% after 30 s.

Fig. 10 shows the changes in temperature at the back of the sample plate as a function of true density of HGM. The samples were coated with S15 and VS5500, with the HGM content of 41.5 vol% and the thickness of HGM 0.6 mm. The back temperature of sample plate coated with S15/PPENK in-

sulation coating was lower than that coated with VS5500/PPENK insulation coating, consistent with the effect of HGM density on thermal conductivity. The back temperature of the two samples plate were 91 and 80 °C, respectively, at 30 s. With a longer time, the temperature difference increased and was gradually stabilized. The difference of temperature for the back temperature of the two samples plate was 11 °C, increasing to about 30 °C at 120 s.

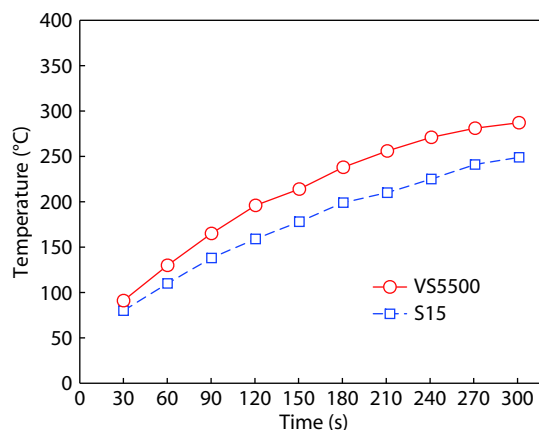


Fig. 10 Effect of the true density of HGM on the thermal insulation performance.

Thermal Stability of HGM/PPENK Coatings

The TGA and differential thermogravimetry (DTG) curves of PPENK film and HGM/PPENK coatings containing m-HGM and u-HGM under N₂ atmosphere are shown in Fig. 11.

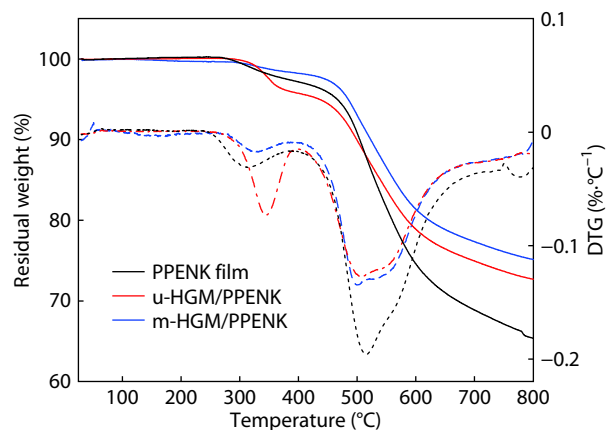


Fig. 11 TGA and DTG curves of PPENK and m-HGM/PPENK coatings.

The thermal stability of HGM/PPENK coatings was evaluated by the 5% weight loss temperatures ($T_{5\%}$). It can be seen clearly that all the coatings show good thermal stability with $T_{5\%}$ s of 480, 470 and 430 °C, respectively, for PPENK film, m-HGM/PPENK coatings and u-HGM/PPENK coatings. The thermal stability of the coating was improved by adding m-HGM due to the increase of interface interaction with PPENK, which agreed well with the SEM results. From the DTG curves, the thermal degradation processes of all samples were composed of two main steps. The first weight loss of temperature sample occurred at about 200–400 °C due to the removal of

residual solvent NMP.^[42] It seems that the residual solvent in the film containing m-HGM is easier to be removed than that containing u-HGM. This phenomenon may be due to the decreased interaction between m-HGM surface and solvent NMP after being modified by coupling agent. Then, the solvent is easier to be removed from the coating. The main weight loss of the sample occurred between 400 and 600 °C attributed to the degradation of PPENK molecular chain.

Heat Resistance of HGM/PPENK Coatings

In practical application of thermal insulation coating, good heat resistance is very necessary for coating at high temperature. So the thermal insulation coating has to maintain a good surface condition when subjected to high temperature.

Fig. 12 shows the photos of VS5500/PPENK insulation coating when ablated at 400 °C for 30 min in Muffle furnace. It can be seen that the color of the coating darkened as a result of PPENK crosslinking. At the same time, a small amount of tiny bubbles appeared at the edge of coatings, which might be caused by the volatilization of residual solvent in the film. Secondly, the high temperature resistance test was carried out in Muffle furnace. The center temperature of the Muffle furnace chamber was calibrated to be 400 °C before the test. However, the temperature in the furnace is not uniform, near the inside of the furnace is higher, and the outside is slightly lower. Therefore, the side of the sample near the inside furnace was subjected to higher temperature resulting in some small bubble defects. There was no distinct surface defect such as big bubbles and ablation on the surface of the coating, indicating excellent stability of surface quality at high temperature.

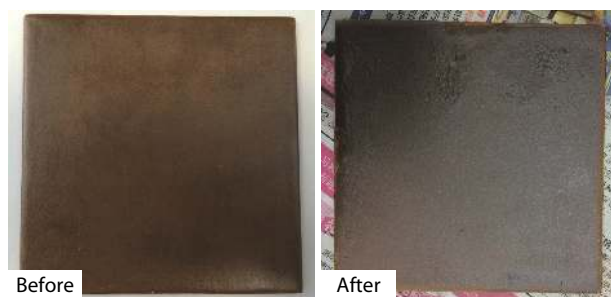


Fig. 12 Photos of HGM/PPENK coatings before and after ablation at 400 °C for 30 min.

CONCLUSIONS

High temperature-resistant thermal insulation coatings with high mechanical and thermal-insulating performance were prepared with PPENK resin and HGM fillers. The addition of the surface-modified HGMS greatly enhanced the mechanical performance and barely reduced the thermal resistance of the coating. However, the addition of m-HGM led to the increase of thermal conductivity for the coatings. The thermal conductivity of HGM/PPENK coatings decreased with increasing content and true density of HGM. When the external temperature was 400 °C, the internal temperature of substrate coated with HGM/PPENK coatings was less than 100 °C after 60 s, which showed excellent thermal insulation effect.

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