

CROSSLINKED ORGANOSILOXANE HYBRID MATERIALS PREPARED BY CONDENSATION OF SILANOL AND MODIFIED SILICA: SYNTHESIS AND CHARACTERIZATION*

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Abstract Hybrid materials based on polymethylphenylsiloxane (PMPS) and organic functionalized silica were synthesized via condensation reaction between silanol and alkoxyethyl groups in the presence of quaternary ammonium hydroxide. The structure of prepared materials was investigated by FTIR and NMR, which indicate that the products have incorporated modified silica into the polymer matrix. The prepared hybrid materials show a satisfactory thermal resistance because the initial decomposition of typical product occurred at nearly 100 K higher than that of the pure polymer according to the thermogravimetric analysis (TGA) results. Differential thermogravimetric analysis (DTGA) data confirm that the thermal degradation of prepared hybrid materials comprises of two steps, of which the first one could be controlled by adjusting the content of silica particles and the ratio of surface groups on the particles. The coating films obtained from hybrid products exhibit good thermal mechanical properties. Therefore, the materials are hoped to be used for the application in thermal resistant coating.

Keywords: Hybrid material; Crosslinked polysiloxane; Condensation polymerization; Thermal stability.

INTRODUCTION

Thermal resistant polymers hold an important role in the development of modern aerospace and military industry. Among these useful polymers, highly crosslinked polymethylphenylsiloxane (PMPS) shows great thermal stability because its backbones comprised of silicon and oxygen atoms with high bond dissociation energy (453.6 kJ/mol). However, the application for this type of binders is limited because the polysiloxane can still thermally degrade owing to flexibility of Si—O—Si molecular chains^[1]. Because the current nuclear and space industries set high requirements to the properties of these materials to satisfy the specific application, an improvement on the thermal stability of PMPS is necessary.

Two major approaches are generally used to improve the conventional organosilicone polymers. First, large-volume groups such as 1,4-phenylene^[2] and carborane^[3, 4] are combined onto the backbones for enhancing thermal stability by strengthening the rigidity of polymer chains. In addition, another component can be integrated into polysiloxane to produce copolymers and composites. Organic-inorganic hybrid technology^[5] is one of the most effective methods to produce polymer composites, which show advanced performance that cannot be obtained by physical blending. In the case of hybrid materials, the inorganic components inherently distribute on molecular scale and contribute to the improvement of material properties. In the field of coating applications, hybrid technology is significantly beneficial to enhance the thermal stability of polymer matrix,

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because inorganic particles retard the thermal motion of molecular chains^[6, 7]. Hybrid coatings are also accepted to strengthen corrosion resistance of materials^[8–12], owing to the barrier effect of inorganic particles distributed on molecular scale.

In situ formed SiO₂, TiO₂ and other inorganic oxide particles are generally used in various polymer matrices, in which SiO₂ is more accessible because of low cost. Generally, these composites are prepared *via* Sol-Gel process using metallic alkoxides, especially tetraethoxysilane (TEOS) as precursors. The process is generally facile to be realized in the case of polysiloxane-based hybrid materials. Yan *et al.*^[13] developed a PMPS/SiO₂ hybrid material, which exhibited satisfied thermal resistance and showed that the inorganic particles imported to polysiloxane enhanced the thermal stability and hardness. Duo^[14] and Hu^[15] found that polydimethylsiloxane (PDMS)/SiO₂ hybrid material starts to decompose at 350 °C, which is 200 K higher than the initial decompose temperature of pure polymer. Wang *et al.*^[16] obtained a hybrid glass coating which not only showed more excellent thermal stability than common organic glass, but possessed a good hydrophobicity. The mechanical properties of PDMS/SiO₂ and PDMS/TiO₂ have been studied in detail by McCarthy, revealing that the mechanical strength of these composites was improved by interpenetrating polymer network structure^[17, 18]. This type of composites also displays a good anti-corrosion property, because inorganic component modifies the interface between substrate and coating film^[19].

However, crosslinked PMPS, different from linear polysiloxane, is mostly obtained by co-hydrolysis and condensation of various chlorosilanes. The preparation process uses organic solvents and brings high concentration of hydrochloric acid into reaction system, where conventional sol-gel process is impossible to be employed successfully. Hence, other approaches, in order to form chemical bonds on the surface of two moieties, should be considered to assure the compatibility of prepared materials. We have tried to use the homo-condensation between silicon hydroxyl groups in previous researches, but the poor reactivity of hydroxyl groups on silica particles cannot permit to obtain a homogeneous product.

In order to obtain compatible hybrid materials, hetero-condensation between different silicon functional groups deserves to be noticed, especially the reaction between Si—OH and Si—OEt, which distribute in the silanol oligomer obtained from chlorosilanes hydrolysis and silica particles, respectively. The modified silica (MQ silicone resin) comprises SiO₂ units and methyl-terminated groups *via* acid-catalytic process, but contains —Si—OEt groups to provide sufficient opportunities of hetero-condensation reactivity. This hetero-condensation reaction was first applied on highly crosslinked polysiloxane due to relatively mild operating condition^[20]. Without using expensive alkoxysilanes, the cost of starting materials was controlled. According to the research of the thermal resistance and mechanical properties in detail, the prepared hybrid material is expected to lay a foundation for further development of thermal resistant coatings.

EXPERIMENTAL

Reagents and Materials

Phenyltrichlorosilane and diphenyldichlorosilane were supplied by Hefei Yabang Chemical CO. LTD. Methyltrichlorosilane was purchased from Tianjin Shentai Chemical Reagent CO. LTD. Dimethyldichlorosilane, hexamethyldisiloxane (MM) was obtained from Huafeng Silicon Works. TEOS was purchased from Beijing Chemical Works. All reagents above were distilled before use in our synthesis. Xylene, acetone, sulfuric acid and sodium bicarbonate are of AR grade and were obtained from Beijing Chemical Works.

Preparation of Organically Modified Silica

TEOS (41.6 g, 200 mmol) and MM were mixed in a tetra-necked 250 mL round-bottomed flask with a dropping funnel, a condenser, a thermometer and a mechanical stirrer. The mixture was immersed into a water bath at the temperature of 15–20 °C. Into the flask was slowly dropped 0.5 g (5 mmol) of sulfuric acid. Water (5.4 g, 300 mmol) was fitted in dropping funnel, and was introduced into the reaction mixture within 20 min under strong stirring, during which the temperature of the reactants should not be over 20 °C. Then the water bath was heated to 78 °C and the reaction mixture was stirred for 2.5 h. The system was neutralized *via* addition of

excessive NaHCO_3 (2.0 g). After a large part of ethanol was distilled, a proper amount of xylene (50 mL) was added. The liquid was continued to be distilled to 140 °C for dehydration by azeotrope, and was filtered to obtain a clear sol.

Hydroxylation of Chlorosilanes

Into a three-necked 1000 mL round-bottomed flask with a dropping funnel and a condenser, the chlorosilane monomers: methylchlorosilane (11.83 g, 79 mmol), dimethylchlorosilane (19.09 g, 148 mmol), phenyltrichlorosilane (36.15 g, 171 mmol) and diphenyldichlorosilane (25.82 g, 102 mmol), and xylene (212 mL) were added. The solution of chlorosilane mixture was immersed into a water bath heated to 60 °C. A mixture of water (158 mL) and acetone (118 mL) was fitted in the dropping funnel, and was dropped slowly into the reaction mixture within 1.5 h. The reaction mixture was stirred at 60 °C for another 2.5 h and was placed until a phase separation, from which the organic layer was washed with an aqueous solution of NaHCO_3 (0.4 g in 100 g) and water (2×100 g) and was distilled at 140 °C for dehydration. This procedure yielded a turbid liquid, which was a silanol solution in xylene.

Preparation for Hybrid Materials

The resulting solution was mixed with silica sol obtained from the procedure described above, and Et_4NOH was added into the mixture. The liquid mixture was stirred overnight. At a pressure of 29.33 kPa, the mixture was heated to 100 °C to distill a majority of solvent within 0.5 h. The residual liquid was heated to 160 °C, stirred at 0.67–1.33 kPa for a period of 1 h. A resin-like solid was obtained *via* this process.

Measurements

FTIR was measured on a Bruker Vector22 infrared spectrophotometer. Specimens were prepared on the KBr pellet and were scanned at a wave number range of 4000–400 cm^{-1} at 25 °C. The ^1H - and ^{29}Si -NMR spectra were taken on Bruker AV400 and AV300 instruments in deuterated chloroform (CDCl_3) at ambient temperature respectively. Molecular weights and molecular weight distributions of the polymers were determined by a WATERS-515 Gel Permeation Chromatograph at 30 °C, where THF was used as the eluent at flow rate of 1.0 mL/min. Thermogravimetric analysis (TGA) was realized on a Shimadzu TGA-50 instrument at a heating rate of 10 K/min under nitrogen atmosphere.

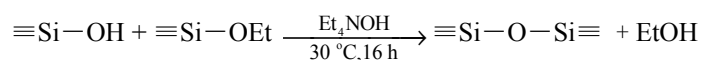
The solution of product was painted on tin plates (120 mm $\times$ 50 mm $\times$ 0.03 mm). The substrates with coating films were dried at room temperature for 24 h, and were heated at 180 °C for 2 h. After the coating samples were cooled, the tests for coating films could be executed.

The adhesion power, impact resistance and flexibility of the coating film were measured based on standards GB/T 1720-79, GB/T 1732-1993 and GB/T 1731-1993, respectively.

RESULTS AND DISCUSSION

Preparation of Hybrid Materials

In this work, methyl modified silica was imported into prepared hybrid materials as shown in Fig. 1. The stages of reaction reveal that this component was synthesized by cohydrolysis and condensation of TEOS and MM at the presence of H_2SO_4 . Herein, the methyl modified silica particles mainly comprise a core of SiO_2 and terminal units $\text{Me}_3\text{SiO}_{0.5}$, in order to stably distribute in organic solvents. However, a small amount of $-\text{Si}-\text{OH}$ and residual $-\text{Si}-\text{OEt}$ groups still link with the modified silica particles due to the equilibrium effect. These residual functional groups could provide linkages with polymer segments. Sauvet *et al.*^[20] indicated that no reactions happened between silanol and $-\text{Si}-\text{OEt}$ groups without catalyst, while acidic catalysts promoted homo-condensation, and organometallic catalysts such as compounds of tin and aluminum also could lead to side reaction. This work introduced a type of alkali catalyst, quaternary ammonium hydroxide (Et_4NOH), to realize grafting reaction:



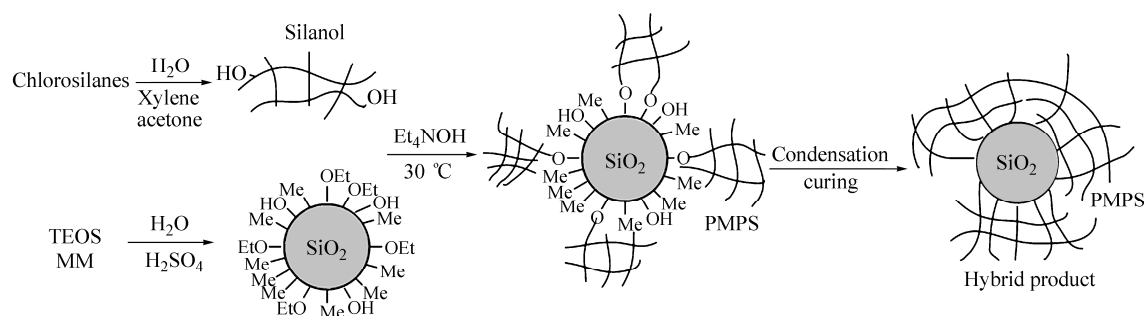


Fig. 1 Synthesis of PMPS/modified silica hybrid materials

Jost *et al.*^[21] synthesized functionalized polyhedral oligomeric silsesquioxanes (POSS) *via* this type of reaction using RSi(OR)_3 and trisilanol as starting materials at ambient temperature, where quaternary ammonium hydroxide was also used as catalyst. Jost's reaction reveals the feasibility of such hetero-condensation at room temperature. Similarly, a considerable amount of linkages could generate between polymer matrix and modified silica, in order to enhance their compatibility. Introducing quaternary ammonium hydroxide brings about another advantage: this organic alkali catalyst can be deprived from the reaction mixture by thermal decomposition without additional separation.

The Influence of Catalyst Content on Grafting Reaction

The alkali catalyst solution initially induced the reaction mixture into turbid. The reaction mixture was soon found to become transparent gradually, reflecting the change in the extent of condensation reaction. Table 1 lists the state of product using varying amount of catalyst. As shown in Table 1, the reaction was rather sensitive to the concentration of catalyst: when the catalyst was added by 2 wt% of silanol, a white, turbid product was obtained; on the contrary, the amount up to 2.4 wt% led to translucency; more than 2.5 wt% of catalyst permitted to obtain a transparent solution, but the crosslinking system tended towards fast transforming to gel. These different states probably correspond to the compatibility of final mixtures, suggesting the efficiency of linkages forming between two moieties. The amount of 2 wt% could not assure sufficient new bonds forming, leading to phase separation, which contains independent polymer molecules and modified particles. In contrast, More than 2.5% of catalyst resulted in forming sufficient Si—O—Si bonds to assure a homogeneous phase, but yielded gels with irreversible networks. As indicated in Table 1, 2.4 wt% could be considered as an appropriate amount of catalyst.

Table 1. Influence of Et_4NOH amount on state of products

$\text{Et}_4\text{OH/silanol}$ (W/W)	State of reaction mixture
0.020	Turbid
0.022	Turbid
0.024	Translucent
0.025	Transparent, but viscous
0.030	Transform to gel rapidly

Structural Characterization

The methyl-modified silica was quantitatively characterized by $^1\text{H-NMR}$. The spectra show the existence of $-\text{CH}_3$ ($\delta = 0.17$) and $-\text{OEt}$ ($\delta = 1.28$ and 3.89) as described in Fig. 2. In addition, every spectrum curve shows a broad, weak signal corresponding to the $-\text{OH}$ groups. Because of the satisfied quantitative function for $^1\text{H-NMR}$ spectra, the relative amount of substituted groups in modified silica was obtained according to peak areas, which are listed in Table 2. As indicated in Table 2, the modified silica is combined with sufficient Si—OEt groups, which produce a potential tendency to induce a hetero-condensation in the presence of Et_4NOH . With an increasing ratio of methyl groups/ SiO_2 units (M/Q), the relative amount of $-\text{OEt}$ and $-\text{OH}$ groups exhibits a significant tendency to reduce.

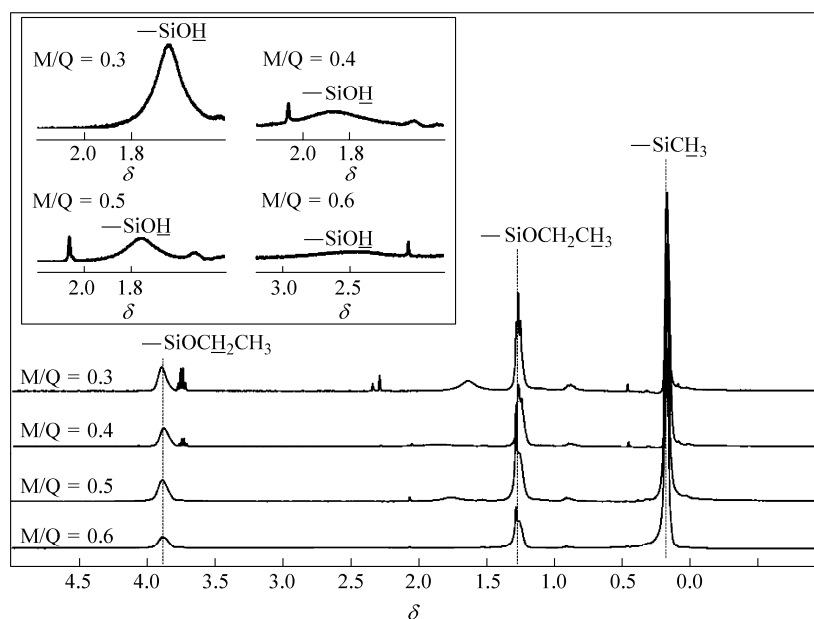


Fig. 2 ^1H -NMR spectra of modified silica with varying values of M/Q

Table 2. Influence of M/Q on the number of substituted groups of silicone resin*

M/Q	—OEt/—Me (mol/mol)	—OH/—Me (mol/mol)
0.3	0.706	0.759
0.4	0.507	0.363
0.5	0.357	0.214
0.6	0.275	0.231

*The relative amount of functional groups is calculated by using NMR peak areas.

Figure 3 displays FTIR spectra of hybrid product, neat PMPS and modified silica. In the case of modified silica particles, the important absorptions show peaks at 2963, 1250, 1100 cm^{-1} , which are assigned to $-\text{CH}_3$, $-\text{Si}-\text{CH}_3$ and $\text{Si}-\text{O}-\text{Si}$ respectively. Herein, the latter absorption exhibits a strong and sharp peak, which is quite in agreement with typical silica samples. In addition, the existence of $\text{Si}-\text{O}-\text{Et}$ is able to be confirmed due to the absorption at 970 cm^{-1} , which disappears in the FTIR spectrum of PMPS/modified silica hybrid material, because such groups probably transform into $\text{Si}-\text{O}-\text{Si}$ bonds *via* homo and hetero-condensation reaction. The FTIR data of crosslinked PMPS hybrid materials are similar to neat PMPS, from which only a few differences could be observed. As Fig. 3 shows, the peaks at 1265, 810, 845 cm^{-1} reflect the existence of $\text{Si}-\text{CH}_3$, while those at 2000–1600, 1590, 1120, 740, 720 and 700 cm^{-1} exhibit the vibrations of benzene rings next to silicon atoms. The relative intensity of such two groups of peaks is only related to the organic component, showing no differences between hybrid material and neat PMPS. However, the absorption of hydroxyl in the region between 3300 and 3600 cm^{-1} is weakened in the case of prepared hybrid product, which results from the consumed hydroxyl groups during the condensation between two components. In addition, the asymmetrical stretching vibration absorption of $\text{Si}-\text{O}-\text{Si}$ bonds corresponding to the range of 1000–1100 cm^{-1} in the spectrum of prepared hybrid material is obviously enhanced, suggesting the Q units of modified silica is imported to polymer matrix along with the new-formed $\text{Si}-\text{O}-\text{Si}$ bonds.

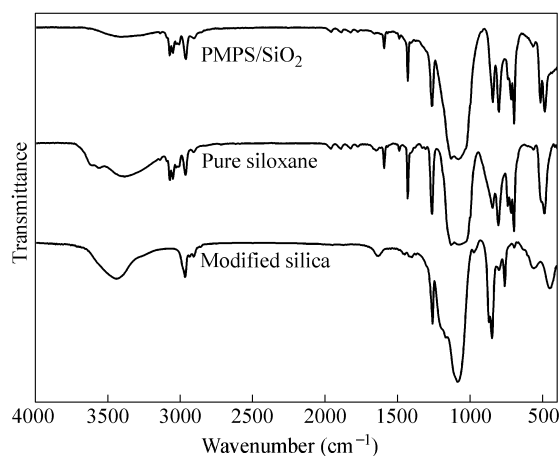


Fig. 3 FTIR spectra of prepared hybrid material, pure siloxane and modified silica

Figure 4(A) displays ^{29}Si -NMR spectrum of the hybrid material, showing signals of organosilicon units: $\delta = -15$ ($(\text{CH}_3)_2\text{SiO}$), -42 (Ph_2SiO), -62 ($\text{CH}_3\text{SiO}_{1.5}$), -78 ($\text{PhSiO}_{1.5}$); and those of modified silica particles: $\delta = 12$ ($(\text{CH}_3)_3\text{SiO}_{0.5}$, M mers), -109 (SiO_2 , Q mers). The NMR data prove the existence of PMPS and methyl-terminated silica in prepared hybrid material. The ^{29}Si -NMR spectrum of modified silica is shown in Fig. 4(B). On the spectrum the signal of $-\text{Si}-(\text{OSi}-)_3-\text{OH}$ or $-\text{Si}-(\text{OSi}-)_3-\text{OEt}$ (Q^3) can be observed at $\delta = -102$. But almost no signal of Q^3 mers at that chemical shift is presented on the spectrum of prepared hybrid material, revealing that the residual reactive groups transformed into $\text{Si}-\text{O}-\text{Si}$ bonds to form stable linkages between two moieties. Consequently, the feasibility of condensation reaction between PMPS and modified silica is confirmed according to the structural characterization.

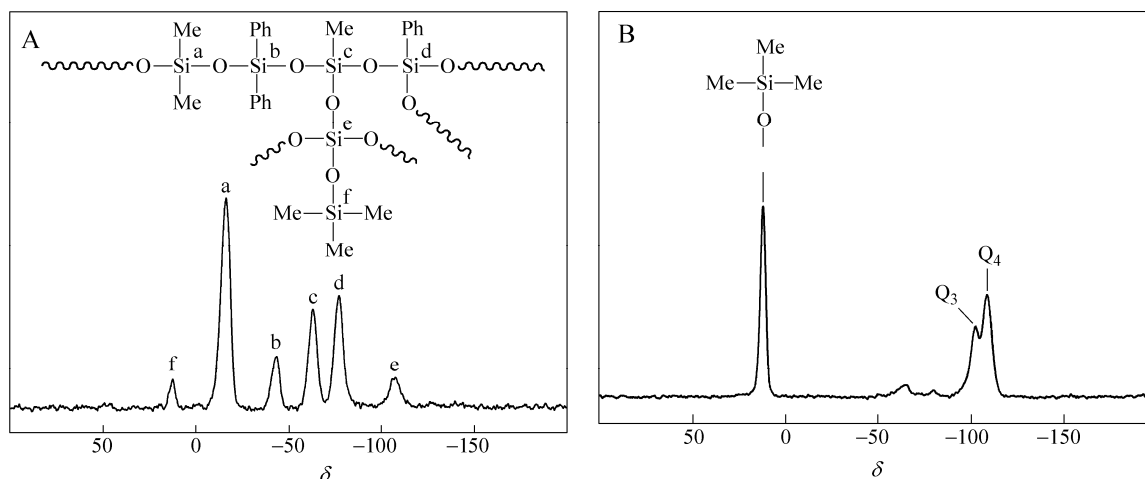


Fig. 4 ^{29}Si -NMR spectra of prepared hybrid material (A) and modified silica (B)

We have compared the molecular weight of prepared hybrid material, modified silica and silanol prepolymer obtained from GPC analysis described in Fig. 5. From the GPC curves, a number average molecular weight (M_n) of 1600, as well as a distributional coefficient of 7 can be detected in the case of prepared hybrid material, which is slightly crosslinked and soluble in non-polar solvents, and has not been undergone thermal curing. But silanol prepolymer has only relatively low M_n of 650. In addition, the typical product exhibits a continuous, wide molecular weight distribution without showing significant trace of modified silica. These results suggested that a large part of polymer molecules has been combined with modified silica particles. The

grafting ratio varies, which could be influenced by equilibrium and steric effect. This type of molecular weight distribution leads to a satisfactory rheological property, therefore the hybrid product is suitable as the binder of coatings.

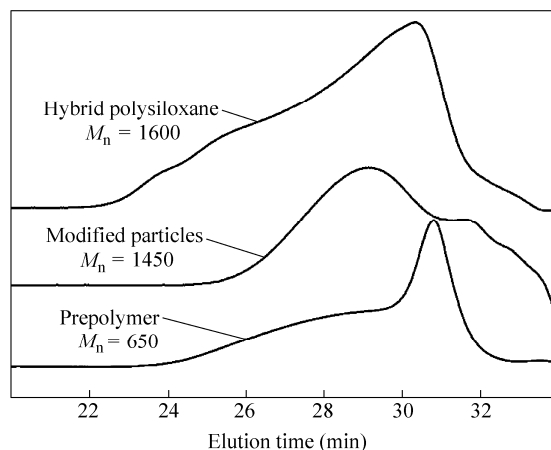


Fig. 5 GPC curves of prepared hybrid material (PMPS/10 wt% modified-silica), modified particles and prepolymer

Thermal Performance

The thermal stability is one of the most important advantages of organosilicone polymers. Figure 6 provides the information on the degradation of hybrid crosslinked polysiloxane, pure PMPS as well as modified silica. TGA curves reveal that the initial decomposition temperature, which is defined as the temperature of 5% weight loss, reaches 377 °C, while the value of compared pure polymer is at 283 °C. After being heated to 750 °C, the typical hybrid material in our research yields approximately 70 wt% of residual ratio, while pure sample yields only 55 wt% of that. Therefore, the prepared hybrid material shows better thermal stability after the modified silica was imported. It can be clearly found that because of the functional groups linked with SiO₂ core, the modified silica slightly loses weight by deprivation of condensation products, including ethanol and water, but shows the lowest residual ratio. After the functional groups transform into linkages in hybrid system, the modified silica provides great enhancement to hybrid product. According to thermal degradation mechanism^[22], generally, the backbones of polysiloxane initially transform their conformation, then the terminal —OH groups bite back to nonadjacent units, eliminating six or eight-membered rings. Moreover, at relatively high temperatures (> 450 °C), the molecular chains could rupture by concerted reactions and radical reactions. The increased initial degradation temperature suggests that the thermal stability of organosilicone polymers could be enhanced by rigid silica particles since the transform of conformation was prohibited by steric hindrance. Consequently, the terminal —OH groups are blocked to coordinate with non-adjacent unit, resulting in restraining the effect of releasing small molecules. Based on the explanation, highly crosslinking polymer structure imported with the silica particles could retard the former degradation step, in order to show great improvement in thermal stability compared with pure PMPS.

Differential thermogravimetric analysis (DTGA) curves indicate clearly the mentioned two steps of degradation, which were separated at about 500 °C: when the temperature was below such critical value, the weight loss of hybrid material is retarded compared with pure sample, which could be attributed to the steric hindrance of silica particles; in contrast, their tendencies of degradation above 500 °C were similar, indicating that the steric effect of silica cannot play an prominent role at that temperature. In fact, when the temperature is over 500 °C, the polymer matrix undergoes large quantities of bond ruptures, which also result in the weight loss due to the deprivation of small molecules. In fact, the local bond ruptures are closely related to bond energy, and are rarely affected by steric hindrance. Consequently, DTGA curves in Fig. 6 confirm that the import of modified silica only effectively restrains the first step of degradation. It could be predicted that the structure and

morphology of modified particles will greatly influence thermal degradation of hybrid material: complicated morphology and high specific surface area may improve its inherent steric effect. The modified process will be reported in other studies.

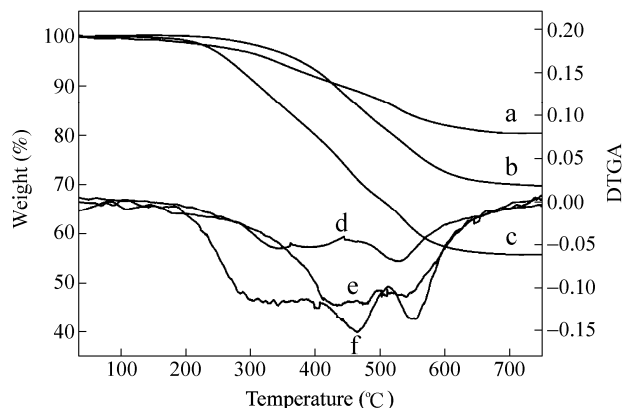


Fig. 6 TGA curves of modified silica (M/Q = 0.5) (a), PMPS/10 wt% modified-silica (b) and pure PMPS (c); DTGA curves of modified silica (M/Q = 0.5) (d), PMPS/10 wt% modified-silica (e) and pure PMPS (f)

Figure 7 displays the isothermal weight loss of prepared materials for different modified silica contents in order to demonstrate their relative thermal stability. In this work, the products were calcinated at 350 °C for 2 h, and then their thermal weight loss was recorded. As shown in Fig. 7, the weight loss reduces with increasing the content of modified silica, but it reaches a constant level after such particles surpasses a critical amount. The reduced weight loss can be explained by steric effect among modified silica. An appropriate amount of silica would influence the tendency of molecules shifting, but excessive addition of the modified silica particles cannot enlarge that effect. From the observation of weight loss at high temperature (Fig. 7), a further increasing amount of imported modified silica over 7 wt% fails to enhance the thermal stability continuously.

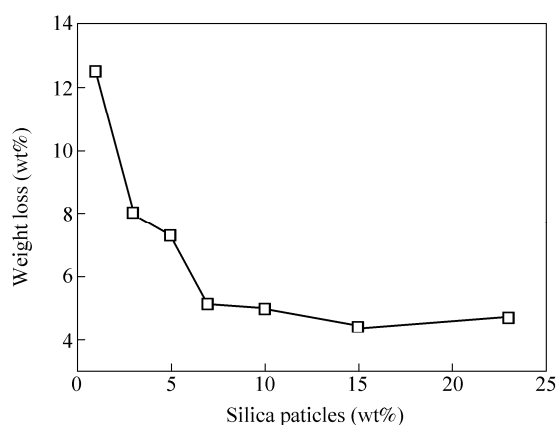


Fig. 7 Influence of modified silica amounts on the isothermal weight loss of products

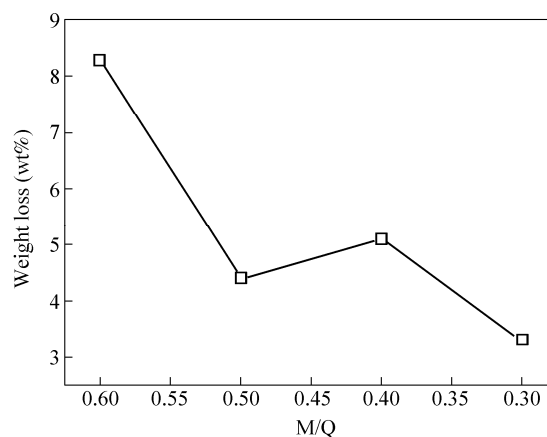


Fig. 8 Influence of M/Q on the isothermal weight loss of products (PMPS/10 wt% silica)

The thermal properties are also influenced by the number of methyl groups on modified silica particles. The terminal groups (methyl), beneficial to the dispersibility in organic solvent, are linked to the core of SiO₂ as the ratio of M/Q. The data on isothermal weight loss with varying M/Q are also recorded in Fig. 8, indicating that a decrease in M/Q provides better thermal stability. The tendency for weight loss suggests that lower value of M/Q restrains the thermal motion of polymer molecules more effectively. Provided less terminal groups can lead to more structural units (Si—O—Si) contained in one silica particle, the particle inherently could take up more

space and produce more significant steric effect on polymer matrix. Thus, the thermal degradation was retarded by the enhanced restraints among the polymer backbones.

Mechanical Properties of Coating Films

The investigated hybrid product is applied in the domain of thermal resistant coating, so their mechanical performance, including adhesion, impact resistance and flexibility, should be preserved at high temperatures. Two main factors are investigated in this paper: the M/Q value of modified silica particles and the content of such component. Table 3 lists mechanical properties of the samples heated at 350 °C for 2 h. These hybrid samples are mostly found to have good properties although they have suffered so high temperature, especially in adhesion and flexibility, while the impact resistance of the investigated samples is significantly influenced by the content and the ratio of M/Q of particles. For neat PMPS samples, obviously, the advanced mechanical properties cannot be held after calcination. The enhancement of impact strength at lower M/Q values is also attributed to more effective restraint of modified silica on PMPS matrix. In addition, an increase in modified silica particles content could promote the coating films to show sufficient impact resistance. However, when the amount reaches 20 wt% (HM07), the film sample exhibits an impact resistance rapidly reduced to 10 kg·cm, with showing poor adhesion and flexibility, probably because excessive inorganic particles induce incompact agglomeration, leading to a sharp increase in brittleness of prepared products. As indicated in Table 3, the introduction of 10 wt%–15 wt% of inorganic particles into polymer matrix provides a satisfactory thermal mechanical performance onto the coating films.

Table 3. Thermal mechanical performance of prepared hybrid product membranes after calcinating at 350 °C for 2 h

Sample	Description	Adhesion* (grade)	Impact strength (kg·cm)	Flexibility (mm)
HM01	PMPS/15 wt% silica, M/Q = 0.5	1	45	1
HM02	PMPS/15 wt% silica, M/Q = 0.4	1	45	1
HM03	PMPS/15 wt% silica, M/Q = 0.3	1	50	1
HM04	PMPS/15 wt% silica, M/Q = 0.6	1	40	1
HM05	PMPS/1.0 wt% silica, M/Q = 0.5	1	35	1
HM06	PMPS/10 wt% silica, M/Q = 0.5	2	40	1
HM07	PMPS/20 wt% silica, M/Q = 0.5	5	10	2
	Neat PMPS	1	25	1

* On the basis of the standard GB/T 1720-79, the measurement was performed by carving series of circles on coating films using a needle, and the results were reflected by the extent of film stripping. No film stripping indicates the adhesion level is grade 1.

CONCLUSIONS

The prepared crosslinked PMPS hybrid materials containing modified silica particles are reported in this paper. Using Et₄NOH as catalyst, the organosilicone matrix can grafted onto modified silica particles *via* heterocondensation between —OH and —OEt groups to obtain homogeneous hybrid products. The polymer matrix and modified silica are incorporated into a hybrid system. The prepared hybrid products show good thermal stability. The temperature of initial weight loss was significantly elevated compared with neat polymer. Such results reveal that the importation of modified silica retards the degradation *via* restraining thermal motion among polymer chains, which is attributed to the steric hindrance produced by modified silica. An increase in modified silica amount in hybrid products enhanced the thermal stability, but an excess of silica particles cannot continue to produce lower weight loss at high temperatures. When 10 wt%–15 wt% of silica particles was introduced, the prepared coating films show the best thermal mechanical properties. Therefore, the PMPS/modified silica hybrid product is expected as a selectable binder of thermal resistant coatings.

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