

Synthesis of Poly(methylphenylsiloxane)/Phenylene-Silica Hybrid Material with Interpenetrating Networks and Its Performance as Thermal Resistant Coating

Dahai Gao, Mengqiu Jia

State Key Laboratory of Chemical Resource Engineering, and Key Lab. of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China

Correspondence to: M. Jia (E-mail: jiamq@mail.buct.edu.cn)

ABSTRACT: In this study, poly(methylphenylsiloxane) (PMPS) and phenylene-silica based hybrid material with interpenetrating networks was prepared by a two-step sol-gel process. Firstly, in the presence of H_2SO_4 , the phenylene-silica was formed as sol particles with high branching degree by cohydrolysis and condensation of phenylene-bridged monomer, tetraethoxysilane (TEOS), and hexamethyldisiloxane (MM). Then, the intermediate transformed into gel framework in polymer matrix using alkali catalyst, in order to produce a homogenous hybrid material with interpenetrating networks. The structure of prepared hybrid material was characterized by FTIR and NMR, suggesting that phenylene-silica framework was imported into polymer matrix and the hybrid products have a much higher network chain density than neat PMPS. The thermogravimetric analysis (TGA) shows that the prepared materials start to degrade at around 490°C. The results of tensile test indicate that the typical PMPS/phenylene-silica hybrid material has a tensile strength up to 26 MPa and demonstrate a certain degree of flexibility. An increase of phenylene content in phenylene-silica particles tends to produce hybrid materials with improved thermal stability and tensile strength. The hybrid coating films after calcinating at 350 and 400°C for 2 h exhibit a good mechanical performance on adhesion, impact strength and flexibility. Electrochemical impedance spectroscopy (EIS) measurements show that the investigated films have an extremely high electric resistance (10^{10} Ohm·cm²) and a satisfied impermeability to 3.5 wt % sodium chloride solution. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 3619–3630, 2013

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INTRODUCTION

Poly(methylphenylsiloxane) (PMPS) within highly crosslinking structure is often used as an important component in coating applications because of the advantages in thermal resistance, anticorrosion, and low dielectric properties as well as excellent miscibility with most organic solvents. The PMPS-based coatings are widely applied in numerous industrial fields for resisting high temperature and environmental corrosion. However, the neat PMPS is difficult to satisfy the increasingly strict requirements in modern aerospace and nuclear industry. So an improvement in the thermal resistance and the mechanical properties of the crosslinked polysiloxane is necessary.

Two approaches have generally been used to improve the thermal stability of organosilicone polymer. One way is that the polymer chains could incorporate some rigid groups, such as arylene,¹ carborane cage,² or some larger rigid groups,^{3–5} which produce huge steric hindrance to transfer the conformations in case of

decomposition caused by molecular thermal motion, and lead to an improved performance on thermal stability compared with pure Si—O—Si chains. Although these silicon-containing polymers can resist sufficient high temperature up to 500°C, complicated synthesis procedures and high cost of monomers and polymers hampered their general applications. Another approach is to use inorganic particles, especially silica, which can distribute in many polymer matrices in molecular scale via sol-gel process to form hybrid materials, in order to optimize thermal,^{6–11} mechanical,^{12–14} and corrosion^{15–18} resistant properties. Organic-inorganic hybrid technology, which is available for most polymer systems, has become one of the most widely used approaches to improve the performance of neat polymer.

The hybrid systems based on organic polysiloxane and silica via conventional sol-gel process has frequently been reported.^{19–22} In these studies, tetraethoxysilane (TEOS) was widely used as silica source. Duo¹⁹ used two precursors TEOS and silanol-

terminated PDMS to fabricate a PDMS/SiO₂ hybrid material and has proved that the silica component can improve the decomposition temperature to 350°C and show an enhanced atom oxygen resistance. Yan²⁰ synthesized a SiO₂/organosilicone copolymer, which demonstrated improved thermal stability and hardness. Park et al.²¹ designed a polyimide-polysiloxane/SiO₂ hybrid material and indicated that inorganic silica component could promote the separation of certain gas. Chen²² also found that organosilicone hybrid coating containing in-situ SiO₂ has a good barrier property against the corrosion process. However, this *in-situ* formed silica particles have always been obtained with a cage-type structure, which is likely to lead to microphase separation from polymer matrix. Consequently, the inorganic components only provide a limited enhancement to thermal stability, and the obtained hybrid products often show brittleness in comparison with neat polymer.

Functionalization with organic groups on silica particles is an important approach to strengthen interfacial combination, in order to improve their compatibility between silica and organic component. Generally, silica is often functionalized with mono-functional organic groups via cocondensation with single substituted alkoxy silanes. This modification assures the dispersity of inorganic particles in hybrid materials, but cannot change the cage-type core of the inorganic framework. The separated inorganic phases fail to significantly retard thermal degradation of hybrid materials, because the thermal motion is still likely to occur for most of free molecules.

We have paid more attention to silica functionalized with arylene groups originated from TEOS and arylene-bridged precursors. The incorporated arylene groups distributed in silica framework could induce the high branching dispersity instead of compact cage-type structure owing to their large volume. Furthermore, the arylene-silica will produce more significant steric hindrance because of the high branching framework. In recent years, some researchers have integrated several alkylene-bridged groups into silica framework to fabricate functionalized hybrid particles and membranes via sol-gel process of TEOS and bridged monomers.^{23–25} However, rare investigations focused on the system containing both organic polysiloxane and such phenylene-modified silica containing arylene-bridged structure. Ohtani et al.²⁶ first designed a phenylene-silica-polyimide hybrid film, in which phenylene-silica shows an ordered mesoporous structure. The poly(amic-acid) precursor trapped in the pores could transform into polyimide to produce a self-standing hybrid film, which shows thermal stability up to 450°C and good flexibility.

In this article, we prepared PMPS/phenylene-silica based hybrid material via a two-step sol-gel process. The phenylene-silica, which is facile to form a three-dimensional gel with high branching degree because of the rigid configuration and great volume for phenylene groups, was imported into polysiloxane matrix for the first time. Therefore, the hydroxyl terminated polysiloxane molecules can crosslink among the gel framework to produce interpenetrating networks, which show positive effect to the performance of prepared hybrid materials because of the homogeneous system. In such hybrid system, stable chemical crosslinking and ordered physical entanglement coexist

for enhancing the thermal stability and mechanical strength of organic polymer.

EXPERIMENTAL

Reagents and Materials

Dimethyldichlorosilane, phenyltrichlorosilane and diphenyldichlorosilane (Hefei YaBang Chemical) and methyltrichlorosilane (Tianjin Shentai Chemical Reagent) was purified by distillation at the protection of drying tube. Methyltriethoxysilane (MTES, Zhangjiagang Guotai-Huarong New Chemical Materials), Hexamethyldisiloxane (Huafeng Silicon Works) and TEOS (Beijing Chemical Works) was redistilled. Xylene, acetone, sulfuric acid, and sodium bicarbonate (Beijing Chemical Works) were of AR grade and were used directly. THF (Beijing Chemical Works, AR) was dried with CaH₂ for 24 h and distilled with sodium and benzophenone. Magnesium powder (Sinopharm Chemical Reagent Beijing) was washed by HCl (1.5 wt %), deionized water, ethanol and acetone successively. 1,4-dichlorobenzene (Sinopharm Chemical Reagent Beijing) was recrystallized with methanol (1,4-dichlorobenzene: methanol = 1 : 1, w : w). Et₄NOH (35 wt % aqueous solution) was provided by Hangzhou Yanshan Chemical.

Preparation of 1,4-Bis(diethoxymethylsilyl)benzene

Magnesium powder (12.6 g, 0.525 mol) was placed in a tetra-necked round-bottomed flask equipped with a thermometer, condenser, mechanical stirrer, and a nitrogen supply. The system was stirred at above 100°C for 30 min under nitrogen flow, and then was cooled down to ambient temperature. Then the flask were added 1,4-dichlorobenzene (22.0 g, 0.150 mol), methyltriethoxysilane (89.2 ml, 0.450 mol) and THF (26.8 ml, 0.330 mol). The reaction mixture was immersed in oil bath, which was then heated to 130°C. The reaction was initiated by two iodine crystals under stirring and was maintained for 48 h. After cooling, the mixture was filtered to eliminate magnesium salt. The yellow filtrate was distilled under vacuum, and the product was collected at 170–180°C (2.0 kPa) to provide 36.0 g of 1,4-bis(diethoxymethylsilyl)benzene (70%). ¹H-NMR (400 MHz, CDCl₃) δ 0.39 (s, 6H, Si-CH₃), 1.27 (t, 12H, Si-OCH₂CH₃), 3.85 (q, 8H, Si-OCH₂CH₃), 7.66 (s, 4H, Si-C₆H₄-Si).

Preparation of Phenylene-Silica Sol

TEOS and 1,4-bis(diethoxymethylsilyl)benzene (0.050 mol in total), hexamethyldisiloxane were mixed in a tetra-necked 100 mL round-bottomed flask with a dropping funnel, a condenser, a thermometer and a mechanical stirrer. The mixture was immersed into water bath of 15–20°C. Sulfuric acid (0.125 g, 1.25 mmol) was slowly dropped to the flask within 20 s. Deionized water (1.80 g, 0.100 mol) was fitted in dropping funnel, and was introduced into the reaction mixture within 20 min, while the temperature of the reactants was maintained below 20°C. Then the reaction mixture was heated to 78°C, stirred for 2.5 h. The system was neutralized by excessive amount of NaHCO₃ (0.500 g). After injecting xylene (15.0 mL), the mixture was centrifuged to yield a clear sol. The molar ratios of TEOS and 1,4-bis(diethoxymethylsilyl)benzene were set to 1 : 10 and 1 : 8, to obtain Sol A and Sol B, respectively. The molar ratio under 1 : 8, which induce gelation within several hours, should be avoided.

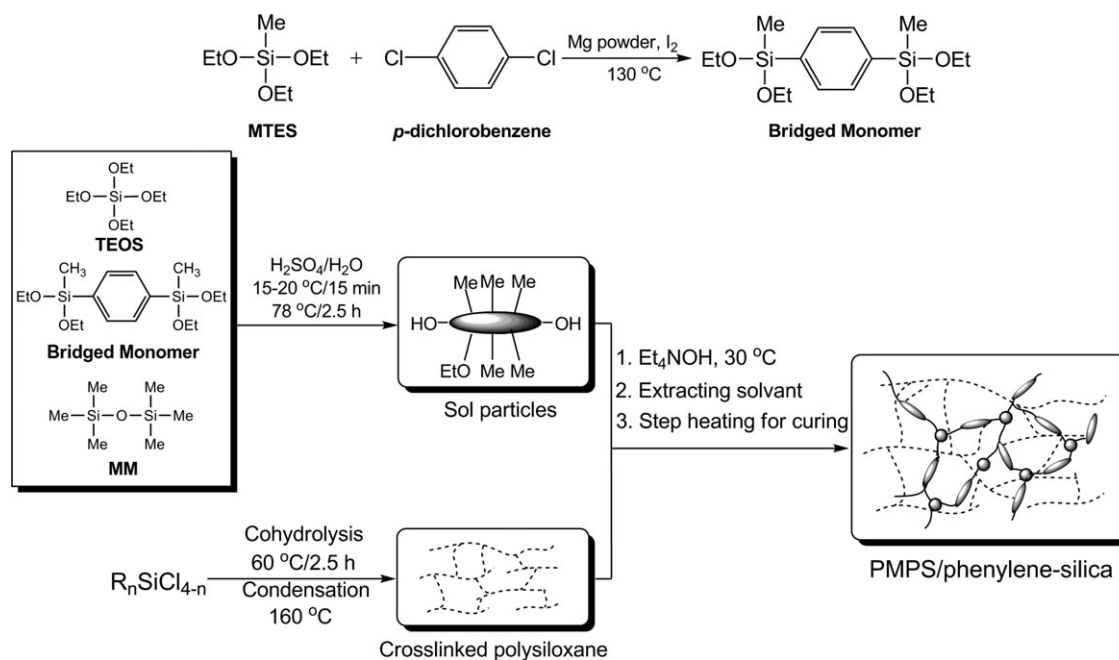


Figure 1. Scheme for synthesis of PMPS/phenylene-silica hybrid materials.

Preparation of Poly(methylphenylsiloxane), PMPS

The tetra-necked 1000 mL round-bottomed flask was equipped with a dropping funnel and a condenser. To this flask was added a mixture of the chlorosilanes monomers: methyltrichlorosilane (11.8 g, 79.0 mmol), dimethyldichlorosilane (19.1 g, 148 mmol), phenyltrichlorosilane (36.2 g, 171 mmol) and diphenyldichlorosilane (25.8 g, 102 mmol), and xylene (212 mL). The flask was immersed into a water bath heated to 60 °C. A mixture of water (158 mL) and acetone (118 mL) were dropped slowly into the mixture within 1.5 h under stirring. The reaction mixture was stirred at 60 °C for another 2.5 h and was placed for a phase separation, in which the organic layer was washed with an aqueous solution of NaHCO₃ (0.400 g in 100 g) and water (2 × 100 g). This procedure yielded silanol solution in xylene.

The silanol solution was placed in three-necked bottomed equipped with vacuum system and mechanical stirrer. After most of solvent was distilled at 2.0–3.0 kPa, the temperature was raised up to 160 °C and the slow stirring rate was maintained for 6–8 h. Then a resin-like product (95%) was obtained, which was soon dissolved in a mixture of xylene and ethanol (1 : 1, v : v). The number average molecular weight (\bar{M}_n) and polydispersity (PDI), measured by Gel Permeation Chromatography (GPC), was 1800 and 6.4, respectively.

Preparation for PMPS/Phenylene-Silica Hybrid Materials

The PMPS solution was placed in three-necked round bottom equipped with mechanical stirrer and vacuum system. The aqueous solution of Et₄NOH (35 wt %) was added into the PMPS solution, and the sol of prepared phenylene-silica was dropped slowly at 30 °C within 1 h. Then the mixture was continued to stir for 0.5 h. At a pressure of 29.3 kPa, the mixture was heated to 70 °C to distill most of solvent within 0.5 h. A viscous hybrid sol was obtained via the process.

The hybrid sol was placed at ambient temperature for 48 h and was heated at 120 °C for 1 h. After the complete gelation, the samples were heated at 180 °C for crosslinking of PMPS.

All the steps in the preparation of hybrid products were shown in Figure 1.

Characterization

FTIR was measured on a Bruker Vector22 infrared spectrophotometer. Specimens were prepared on the KBr pellet and were scanned at wave number range of 4000–400 cm⁻¹ at 25 °C, with a resolution of 2 cm⁻¹. The liquid-state ¹H spectrum was taken on a Bruker AV400 instrument in deuterated chloroform (CDCl₃) at ambient temperature, while solid-state ²⁹Si-NMR spectra were tested on a Bruker AV300 instrument. Molecular weights and molecular weight distributions of the polymers were determined by a WATERS-515 Gel Permeation Chromatography at 30 °C, where THF was used as the eluent at flow rate of 1.0 mL/min. Thermogravimetric analysis (TGA) was realized on STA449 instrument from ambient temperature to 750 °C at a heating rate of 10 °C/min under constant flow of argon. TGA coupled with FTIR spectroscopy (TGA-FTIR) was recorded by the Mettler TGA/DSC 1 thermogravimetric analyzer coupled with the Thermofisher Nicolet 6700 infrared spectrophotometer. The samples were heated from ambient temperature at a scanning rate of 10 °C/min under a constant flow of Nitrogen (24 mL/min). Scanning electron microscope (SEM) is studied by an S-4700 instrument.

The tensile measurement, according to the standard ASTM D 882, was proceeded on a Instron 5567 machine at a strain rate of 5 mm/min by using 50 mm × 4 mm specimens, which were molded in Teflon plates. For each repetition, five specimens were tested.

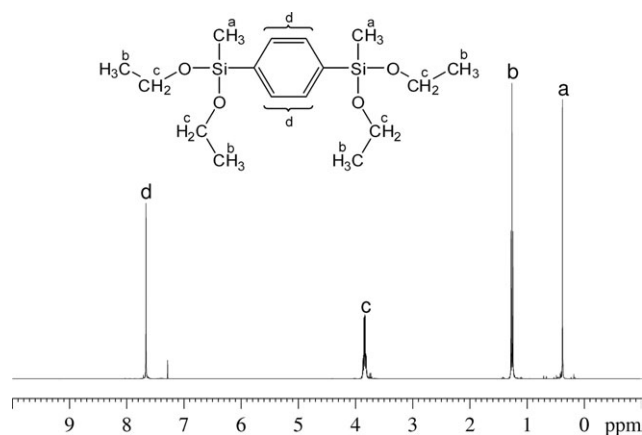


Figure 2. $^1\text{H-NMR}$ spectrum of 1,4-bis(diethoxymethylsilyl)benzene.

The hybrid coating films was fabricated on tinned steel sheets (120 mm \times 50 mm \times 0.03 mm), on which the tin coating had been polished away. The substrates with coating films were dried at ambient temperature for 24 h, and were heated at 180°C for 2 h. Then, the films were calcinated at 350°C for 2 h in order to investigate the thermal mechanical performance. After the samples were cooled, the tests for coating membrane could be executed. The adhesion of coating films, based on standards GB/T 1720-1993, was evaluated by carving a group of circles on coating films using a needle, and the results were reflected by the film stripping. The impact strength, based on GB/T 1732-1993, was carried out using a 1 kg of heavy punch with conical surface to impact onto the coating film, and the results were recorded by the maximum height of heavy punch (≤ 50 cm) producing no failure on the films. The flexibility, based on GB/T 1731-1993, was revealed by bending the painted sheet along metal sticks with different diameters. The minimum stick diameter of yielding no crack on the films was considered as the parameter of flexibility.

The Electrochemical Impedance Spectroscopy (EIS) was recorded by IM6e electrochemical workstation and was realized in aqueous 3.5 wt % NaCl medium equipped a conventional three electrode electrochemical cell with a saturated calomel electrode as reference, platinum as counter-electrode and a working electrode with an area of 3 cm². The coating films were fabricated on polished 45 steel plates, and the same curing steps with samples on tinned steel sheets were applied.

RESULTS AND DISCUSSION

Hybrid Material Synthesis

As shown in Figure 1, the first step was carried out via acid-catalyzed cohydrolysis and condensation of bridged-monomer and TEOS as the ratio of 1 : 10, and 1 : 8 to obtain the samples Sol A and Sol B, respectively. The structure of bridged-monomer is confirmed by $^1\text{H-NMR}$ (Figure 2). MM was used as a terminated agent for assisting the product to distribute in organic reaction system and preventing the rapid gelation. Therefore, the resulting intermediates are linked with abundant $-\text{Si}(\text{CH}_3)_3$ as terminated groups as well as a small amount of hydroxyl and ethoxy groups. Provided the phenylene-bridged monomer pos-

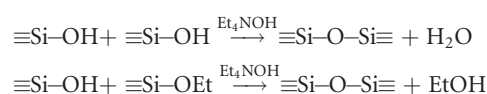
sesses grand volume and high rate of condensation compared with TEOS,²⁷ the co-hydrolysis and condensation in our case tend to produce a network framework with high branching degree.

The PMPS matrix terminated by silicon hydroxyl was obtained from the hydrolysis and condensation process of chlorosilanes. After the phenylene-silica sol obtained from the first step was added into the solution of PMPS, and the branching sol could continued to grow via condensation under the effect of strong alkaline catalyst Et_4NOH . The phenylene-silica framework was finally formed after eliminating the solvent via heating. The polymer molecules were trapped among the gel framework, and their crosslinking reaction produced interpenetrating networks.

Influence of Catalyst

The components in the interpenetrating networks are inherently fixed by the crosslinks, often yielding a homogeneous product that exhibits transparency because any small segregated phase will lead to light dispersion.²⁸ But phase segregation probably occurs during the preparation process. The key of successfully obtaining uniform hybrid material is to control the reaction condition to assure a homogeneous phase during the process of condensation. Quaternary ammonium base, which exhibits high catalytic activity, is miscible with our reaction system and was chosen to promote the formation of silica framework. Furthermore, that catalyst can be eliminated by thermal decomposition below the curing temperature of neat PMPS.

Table I shows the state of products synthesized with varying catalyst content, revealing that the quaternary ammonium base, indeed, makes it promising to obtain homogeneous hybrid materials. When the catalyst content attains above 2 wt %, the products present a sufficient degree of transparency. This fact suggested that new chemical bonds formed between phenylene-silica framework and PMPS via homo- and hetero-condensation, which is beneficial to the compatibility of such two components:



Herein, a certain amount of silicon hydroxyl and ethoxy groups are distributed on the phenylene-silica sol, and the polymer

Table I. Influence of Catalyst Amount on the Morphology of Products

Catalyst amount ^a	Morphology of product	Weight loss (wt) ^b
0.010	Turbid	-
0.015	Turbid	-
0.020	Transparent	2.92
0.030	Transparent	2.66
0.050	Transparent	2.67
0.100	Transparent	2.51

^aCatalyst/theoretical yield (w/w).

^bThe test was carried out at 350°C for 2 h.

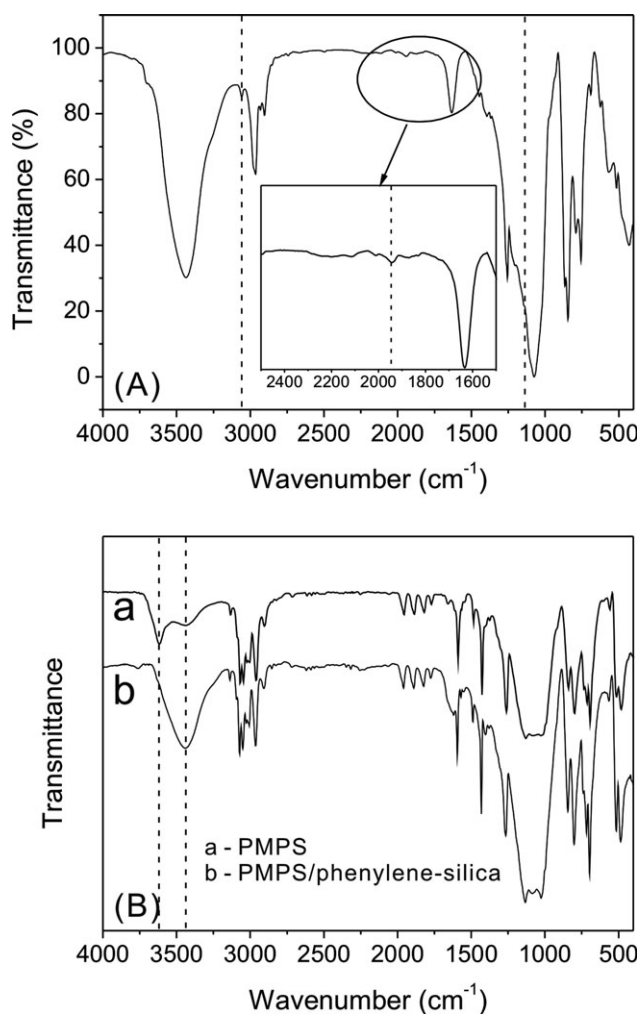


Figure 3. Infrared spectra of (A) phenylene-silica and (B) neat PMPS and PMPS/phenylene-silica hybrid material. The phenylene-silica was prepared from Sol B.

matrix was terminated by silicon hydroxyl groups. Some researchers have reported the condensation of silanol and alkoxy-silane with the catalysis of basic compounds^{29,30} and reveal the hetero-condensation reaction can take place under mild conditions. This fact indicates that linkages could be founded between PDMS and phenylene-silica domains to overcome the difficulty of microphase separation. The increasing catalyst content will induce the formation of graft interpenetrating networks, contributing to the increasing degree of transparency and slight decreasing weight loss at high temperature. Further increase in the catalyst content will continue to promote the prepared materials into homogeneous state. However, significant color change was observed when the catalyst content was above 5 wt %, probably caused by side reactions. Therefore, 3 wt % of catalyst content has been fixed as an optimal amount.

Structural Characterization

The structure of phenylene-silica and hybrid product has been characterized by FTIR and ²⁹Si-NMR. Figure 3(A) shows the FTIR spectrum of phenylene-silica, and Figure 3(B) shows the spectrum of hybrid product, with the one of pure PMPS as a

source of reference. From Figure 3(A), the absorption of aryl C—H bonds in phenylene at 3054 cm⁻¹ reveals that phenylene groups have been linked into the silica network. The peaks between 1000 and 1100 cm⁻¹ are assigned to the asymmetric stretch vibration of Si—O—Si bonds. The small peak at 1942 cm⁻¹ was especially shown in a partial enlarged detail, which is the contribution of 1, 4-phenylene.

As shown in Figure 2(B), the absorptions of C—H in —CH₃ and —C₆H₅ can be seen in the regime of 3136–2908 cm⁻¹, and —C₆H₅ groups show their coupling vibrations and overtone bands at 1959, 1894, 1824, 1774 cm⁻¹. Those peaks, which are only related to the organic substituted groups in the siloxane backbone, were set as the equal intensity. In the case of hybrid product, the absorption of Si—O—Si at 1000–1100 cm⁻¹ was found to be enhanced owing to the imported phenylene-silica providing abundant Q units (SiO₂ mers) into the hybrid system. The absorption of free —OH at 3622 cm⁻¹ disappears in comparison with that of neat PMPS, while the wide band corresponding to associated —OH at 3300–3600 cm⁻¹ is strengthened. That fact indicates that all the free —OH groups in pure PMPS transform into associated types, which is mostly attributed to stable links or hydrogen bonds forming between PMPS and phenylene-silica.

The solid state ²⁹Si-NMR spectroscopy was used to investigate the structural units in phenylene-silica and hybrid products as shown in Figure 4. For comparison, the spectra of compared silica (without phenylene groups) and the neat PMPS are also presented. Both spectra of Figure 4(A) shows peaks of —Si—CH₃, —Si(O—Si)₃O— (Q³), and —Si(O—Si)₄ (Q⁴), respectively. For phenylene-silica, the silicon atom directly linked with phenylene shows chemical shift at —32 ppm. The ²⁹Si-NMR spectrum of hybrid material in Figure 4(B) shows signals of four basic structural units of crosslinked polysiloxane and the signals of phenylene-silica component even though the ratio of modified silica/PMPS (w/w) was only 0.02. The spectrum data mentioned above suggested that the phenylene-silica framework have been imported into the hybrid product.

Evaluation of Thermal Stability

The thermal stability of PMPS/phenylene-silica hybrid materials and neat PMPS are measured by TGA under inert atmosphere. The satisfied thermal stability has been observed from TGA data as seen in Figure 5, and Table II reports the parameters derived from TGA and DTGA curves (Figure 6). As depicted in Figure 5, it is obviously seen the retarded degradation process of PMPS/phenylene-silica hybrid products compared to pure PMPS. Herein, the initial decomposition temperature (*T*_{d5}) was defined as the temperature at 5 wt % of weight loss. The parameters in Table II indicate that for prepared hybrid material *T*_{d5} reaches around 490°C, whereas for neat PMPS *T*_{d5} is only 409°C. On the other hand, the neat PMPS experienced a slow and broad step from 200 to 520°C followed by a rapid degradation step. In general, polysiloxanes start to decompose with the removal of six or eight-membered ring oligomers at high temperature.³¹ This process is induced by molecular thermal motion and conformational flipping in the backbone. In the hybrid system, new formed restraints on molecular mobility contribute to an

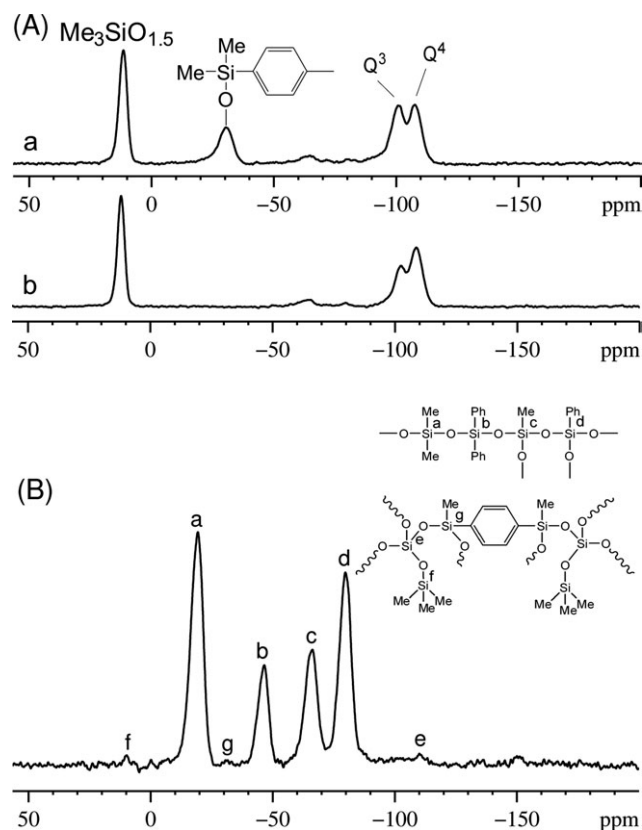


Figure 4. ^{29}Si -NMR spectra: (A) phenylene-modified silica (a) and comparable silica unmodified by phenylene bridge (b); (B) PMPS/phenylene-silica hybrid sample. The phenylene-silica was prepared from Sol B.

enhanced thermal stability of PMPS/phenylene-silica hybrid materials compared to neat polymer.

Compared with the silicone polymer containing silarylene groups in backbones,^{32,33} the prepared hybrid materials in our work also realize high initial degradation temperature close to 500°C with low cost in preparation. In addition, in the case of crosslinked silicone resin with silphenylene units, which was reported in previous work of our research group, the T_{d5} was up to 510°C,³⁴ but the preparation of this product is difficult to control and induces gelation, whereas PMPS/phenylene-silica system is more facile to be prepared, with no gel particles during synthetic process. Therefore, the approach to the enhancement in thermal stability using rigid arylene-silica framework has a considerable potential in practical application. Furthermore, the hybrid system obtained via two-step sol-gel process has special advantage over the systems via one-step sol-gel process from alkoxy silanes.^{22,35–38} The reason is that in the latter case, silica component generally exist as separated particles or dual-continuous phases with polymer matrix, whereas in our hybrid system the polymer backbones are “fixed” among rigid framework, which contributes to significant restraint to polymer chains, leading to a considerable improvement in initial degradation temperature.

The degradation steps of PMPS/phenylene-silica hybrid materials and neat PMPS could be investigated in detail by differential

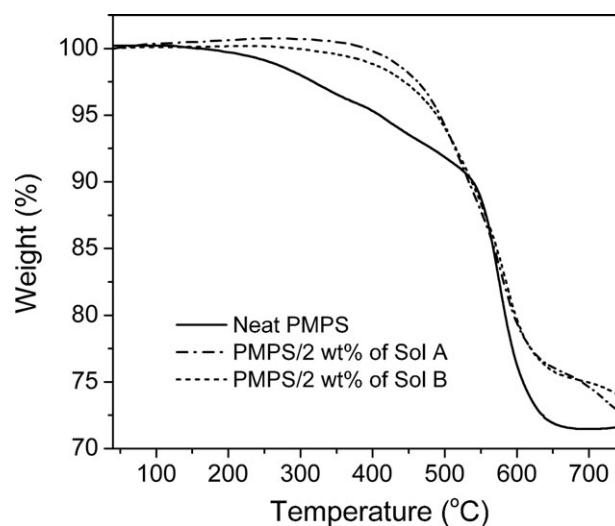


Figure 5. TGA curves of prepared hybrid materials and neat PMPS in inert atmosphere.

thermal analysis (DTGA), of which the results are shown in Figure 6. In the case of PMPS/phenylene-silica, the DTGA curves were treated by multiple peak fitting, indicating two main overlapped steps of their degradation. The first step, with the maximum degradation rate at 500°C, was related to the degradation of eliminating ring oligomers; while the second step centered at 580°C is attributed to the random rupture of bonds in the polymer backbone.³¹ All PMPS/phenylene-silica hybrid materials exhibit similar trends in TGA and DTGA curves. According the observation on degradation rate, the improvement on thermal stability by phenylene-silica satisfies the trend Sol A < Sol B, which reflects the extent of steric effect produced by phenylene-silica. In this way, the increase of phenylene content in phenylene-silica contributes to the higher branching degree among the hybrid system, and then the thermal stability was significantly enhanced.

In order to determine the effect of imported phenylene-silica framework, it is necessary to investigate the thermal degradation mechanism, which could be detected using FTIR connected to TGA analyzer. The results were shown as 3D FTIR spectra in Figure 6, which were recorded by collecting the eluting molecules of the decomposition under inert atmosphere. Figure 7(A) shows the 3D FTIR spectra recorded on the thermal degradation of pure PMPS. The peaks at 3060 cm^{-1} and 670 cm^{-1} , which indicate the existence of benzene ring, show maximum intensity

Table II. Degradation Parameters of Hybrid Products and Pure PMPS Under Inert Gas Flow

Sample	T_{d5} (°C)	Temperature at maximum rate of weight loss (°C)	Residue at 750°C (wt %)
Pure PMPS	409	560	71.7
PMPS/2 wt % Sol A	493	578	73.8
PMPS/2 wt % Sol B	489	586	72.5

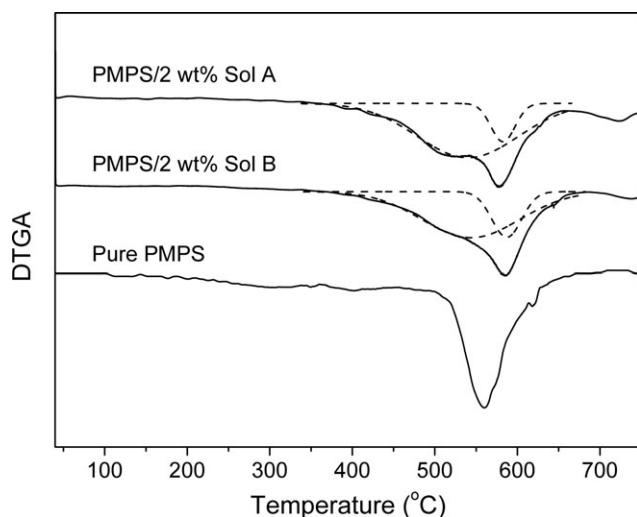


Figure 6. DTGA curves of prepared hybrid materials and neat PMPS in inert atmosphere.

at 50.0 min (530°C). Such two peaks started at 24 min (270°C) disappear at 62 min (650°C). Therefore, the PMPS dominantly degrade via deprivation of phenyl groups in the range 460–650°C. In the range 59–82 min (620–850°C), the FTIR signals of methyl (at 3050 and 1300 cm^{-1}) were detected. This process probably belongs to radical reaction, which is in agreement with the literatures on degradation of siloxanes.³⁹ It should be noted that the evolved products in the range below 620°C derived from 3D FTIR spectra show benzene is predominant product, indicating the degradation process belongs to concerted reaction, but not radical reaction, because the latter could yield multiple products by radical termination, such as biphenyl and benzene homologues, which could not be detected from the 3D spectra.

Figure 7(B) demonstrates the 3D FTIR spectra on thermal degradation of prepared hybrid material. The onset of FTIR signals corresponding to phenyl groups occurred at higher temperature than those of pure PMPS. In detail, the absorptions of phenyl

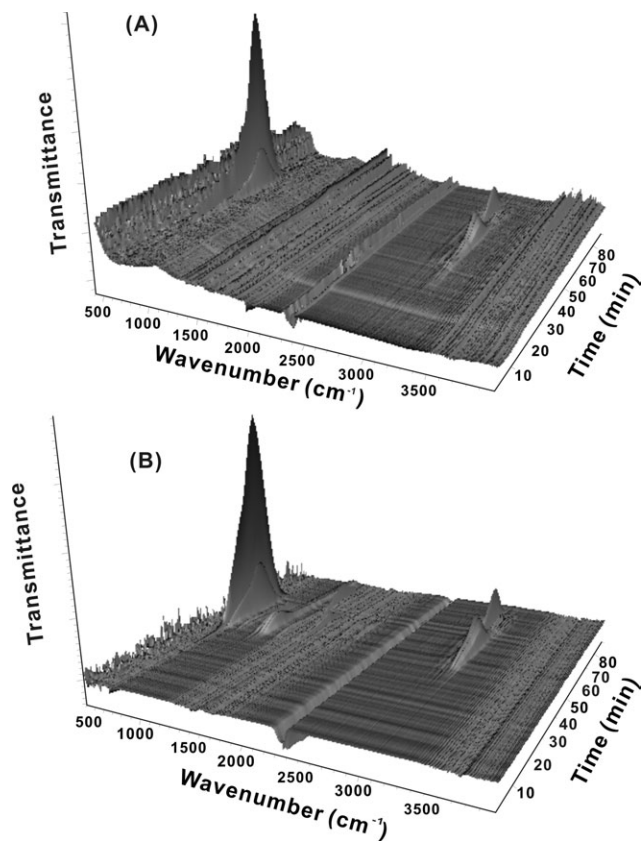


Figure 7. 3D FTIR spectra recorded simultaneously with thermal degradation using TGA-FTIR analysis: (A) Neat PMPS; (B) PMPS/phenylene-silica.

at 3060 cm^{-1} and 670 cm^{-1} start to show at 40 min (430°C). This could be explained by a restraint of phenylene-silica framework on PMPS segments. Under the steric effect of imported rigid framework, these segments probably exhibit lower tendency for chain mobility. For that reason, the degradation reactions are blocked, which induce the emission of oligomers and small molecules until the elevated temperature.

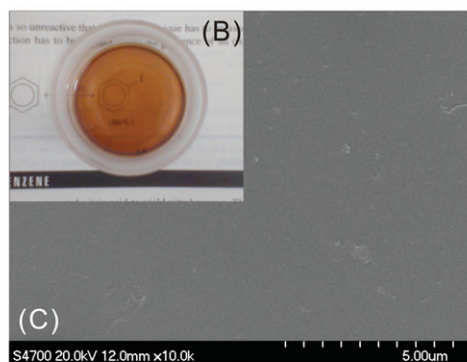
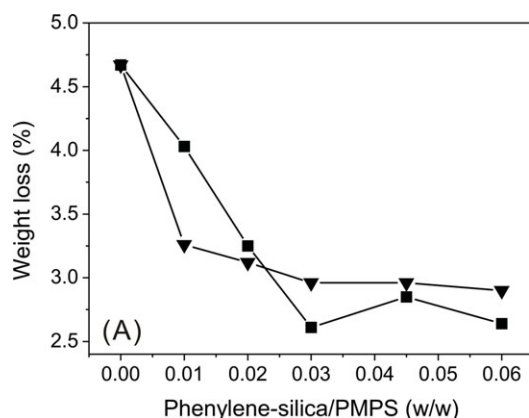


Figure 8. (A) Iso-thermal weight loss of PMPS/phenylene-silica with varying phenylene-silica content: (■) PMPS/Sol A; (▼) PMPS/Sol B. (B) Photography of prepared hybrid materials after calcinating (Sol B 3.0 wt %). (C) SEM image of prepared hybrid materials after calcinating (Sol B 3.0 wt %). All the samples are calcinating at 350°C for 2 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermal Mechanical Properties of Coating Films Fabricated by Prepared Hybrid Materials

Film sample		Adhesion (grade)		Impact strength (kg/cm)		Flexibility (mm)	
Sol sample ^a	Content ^b	350°C ^c	400°C	350°C	400°C	350°C	400°C
Sol A	0.010	1	1	45	40	1	1
Sol A	0.020	1	1	50	50	1	1
Sol A	0.030	1	1	50	45	1	1
Sol A	0.045	1	1	50	35	1	2
Sol A	0.060	1	1	50	40	1	1
Sol B	0.010	1	1	50	50	1	1
Sol B	0.020	1	1	50	50	1	2
Sol B	0.030	1	1	50	50	1	1
Sol B	0.045	1	1	50	50	1	1
Sol B	0.060	1	1	50	50	1	1
Neat PMPS		1	<3	20-30	<5	3	>5

^aIndicated sol was applied in the preparation of the hybrid coating sample.

^bRatio of sol to polymer matrix (w/w).

^cTest was carried out after calcinating the sample at the indicated temperature for 2 h.

The isothermal weight loss was investigated by calcinating the samples at 350 °C for 2 h, which is shown in Figure 8(A), in order to compare the hybrid materials with varying phenylene-silica amount. An increasing amount of phenylene-silica in PMPS/phenylene-silica hybrid materials initially results in the reduction of weight loss, but once the amount surpasses a critical value (3 wt%), the isothermal weight loss almost reaches a constant. Figure 8(A) also indicates the more rapid decrease tendency for weight loss with the increase in the content of phenylene groups, which is another evidence for higher branching degree in gel framework prepared from Sol B, because the framework will generate more significant steric effect in that case. Figure 8(B) demonstrates the photography of typical calcinated hybrid product investigated in isothermal weight loss. It was found that the hybrid product still exhibits a homogenous, transparent state, with no cracking and blistering. Figure 8(C) shows the SEM image taken from the calcinated hybrid product, showing an essentially flat surface. These facts reflect that no significant damage occurred in the hybrid system which has been calcinated at 350°C for 2 h.

Thermal Mechanical Performance of Hybrid Films

Thermal mechanical performance of PMPS/phenylene-silica films after calcinating at 350 and 400°C for 2 h is investigated as listed in Table III, where the advantage of increasing the phenylene content in modified silica is also observed by comparing the results of adhesion, impact strength and flexibility. As a comparison, the performance data of pure PMPS reported in our previous works⁴⁰ are also listed along with those of hybrid products, indicating the importation of rigid framework is greatly beneficial to increase the application temperature of coating films. Most of the investigated hybrids coating samples show excellent adhesion and flexibility. However, prepared coating films incorporating the gel framework prepared from Sol B gave the best impact strength of all samples, which is also attributable to highest branching degree in the phenylene-silica

sample, even though the films have been calcined at 400°C for 2 h. As the prepared materials can tolerate high temperature up to 400°C, the application temperature range of crosslinked PMPS binder could be enlarged.

Tensile Test

In general, composites containing silica as an intensifier usually present improved tensile strength whereas their flexibility reduces because silica is generally of compact cage-type structure without sufficient interface interaction with polymer phase. However, phenylene-silica has a great superficial area because of high branching degree and is facile to form a three-dimensional network even though very low solid concentration in the sol. In the way, the polymer chains could be trapped among the gel framework and cure under suitable conditions to produce tough membrane with interpenetrating networks, which allows the prepared materials into homogeneous product with satisfactory

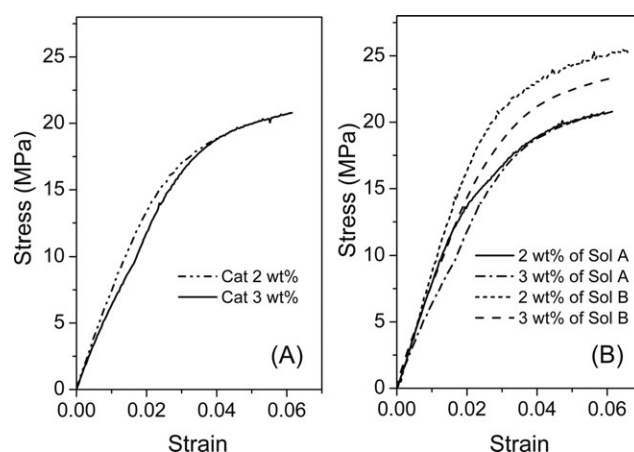


Figure 9. Stress–strain curves of hybrid samples. A: Influence of catalyst amount on hybrid system (w/w). B: Influence of phenylene content on modified silica and phenylene-silica amount hybrid membranes (cat 3 wt %).

Table IV. Tensile Properties of Hybrid Samples

Cat (wt %)	Sample		Tensile strength (MPa)	Tensile modulus (MPa)	Elongation to break (%)
	Sol sample	Sol (wt %)			
2	A	3	18.7 ± 0.3	747 ± 93	4.20 ± 0.36
3	A	2	20.0 ± 1.2	877 ± 50	5.97 ± 1.02
3	A	3	20.7 ± 1.2	878 ± 75	5.08 ± 1.03
3	B	2	25.9 ± 1.7	888 ± 79	6.16 ± 0.33
3	B	3	22.3 ± 0.6	681 ± 83	5.51 ± 0.22

mechanical strength. The stress–strain curves of tensile strength in this work are shown in Figure 9, and the data and their standard deviations are listed in Table IV.

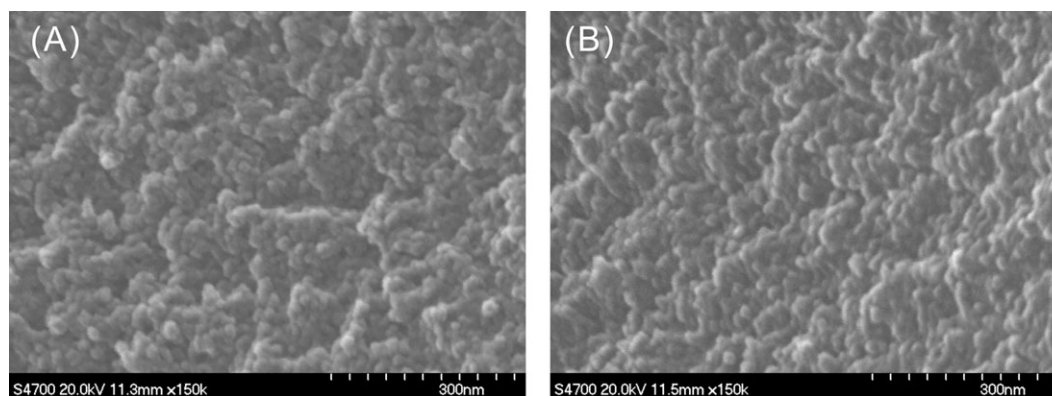
The influence of catalyst content on the tensile performance of hybrid samples is described in Figure 9(A). From these data in stress–strain curves, 3 wt % of catalyst content is more beneficial because the corresponding tensile sample presented more elongation at break. The catalyst content of 2 wt % resulted in an approximate transparent product, but may still induce to form tiny dispersed phases, which are unfavorable to mechanical strength. Figure 9(B) reveals that high content of phenylene groups in silica network contributes to both good tensile strength and elongation at break. Specially, the sample modified with phenylene-silica originated from Sol B realized elongation at break of nearly $6.16 \pm 0.33\%$ as well as a tensile strength of 25.9 ± 1.7 MPa from observing from Table IV. Furthermore, a certain level of yield behavior has been observed on the stress–strain curve, suggesting that the flexibility of the typical product is improved by the framework of modified silica, especially with high phenylene content.

The tensile properties of highly crosslinked organosilicone polymers are rarely reported in research papers, probably because of their poor tensile behavior produced by weak interaction among the molecules. In some current patents,^{41–43} the tensile strength of such polymers can reach 7–12 MPa. In our case, the pure PMPS is so brittle that it could not even be fabricated as tensile sample. In fact, some polysiloxanes can exhibit sufficient high tensile strength if they possess well-defined structure, for exam-

ple, polysilsesquioxanes³¹ and some heterochain polysiloxanes,⁴⁴ obviously as a result of organized chain distribution. Herein, interestingly, the phenylene-silica framework exhibits an ordered meso-structure,²⁶ which permits the polymer backbones to obstruct in such framework, and therefore is beneficial for enhancement in mechanical properties. The SEM images depicted in Figure 10 furthermore show the meso-structure of dried phenylene-silica. A pearl string-like morphology is observed, in which the string diameter is 10–30 nm. For Sol B, the distribution of pear strings shows more ordered meso-structure, which results in the more advanced performance of the hybrid system prepared from Sol B.

Electrochemical Impedance Spectroscopy Analysis

Electrochemical impedance spectroscopy (EIS) analysis is one important approach to measure the corrosion resistance of coating films. The polymeric binders are generally considered as an isolation layer on the metal substrate with huge electrical resistance. When the coating films are exposed in liquid medium, the impedance $|Z|$ could decrease as the films are invaded by the liquid molecules. The penetrating rate of liquid medium into polymeric films is related to branching and cross-link density of the polymer materials. Figure 11 displays the typical Bode plots of prepared hybrid films immersed in 3.5 wt % sodium chloride solution for 1 day, 15 days, and 30 days as well as the tendency of R_c with immersion time. The coating resistance (R_c) was obtained according the equivalent circuit in Figure 12, which was quite well correlated with the EIS data. The Bode plots in Figure 11(A) indicate a linear relationship

**Figure 10.** SEM images of dried phenylene-silica: (A) Sol A; (B) Sol B.

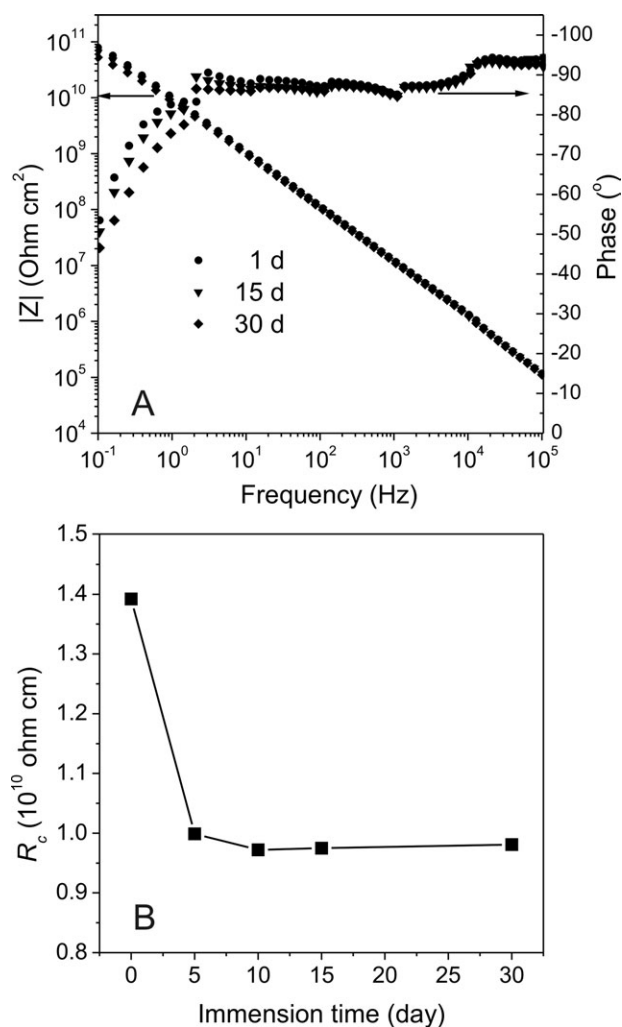


Figure 11. Evolution of EIS diagram (A) and coating resistance (R_c) (B) of cured coating film which was prepared by R0208, with no thermal treatment. Working electrode with an area of 3 cm^2 is used, and the average film thickness is $228 \mu\text{m}$.

between $\log|Z|$ of prepared film and logarithm of frequency during immersion. The maximum of impedance data could remain $10^{10} \Omega \text{ cm}$ and show almost no signs of decrease, while phase angles at low frequency reduced slowly during 30 days. According to Figure 11(B), the value of R_c reduced at initial immersion time probably because of liquid diffusion into the

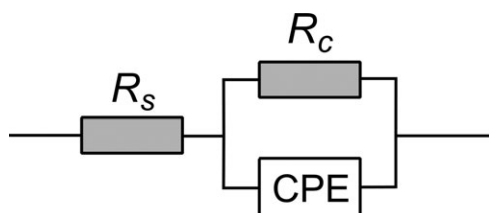


Figure 12. Equivalent circuit used for modeling data of Electrochemical Impedance Spectroscopy (EIS). CPE, constant phase element; R_c , coating resistance; R_s , solution resistance.

membrane. Subsequently, the value of R_c reduced to a stable level after the film was immersed for 10 days, suggesting that the diffusion of liquid medium come to saturation. The coating resistance was still maintained at the level of $10^{10} \text{ Ohm}\cdot\text{cm}^2$ in such case. As observed from EIS data, the prepared hybrid film shows a satisfied impermeability to 3.5 wt % sodium chloride solution.

Figure 13 also provides the similar EIS information with Figure 11, but these data are related to the calcinated coating film. The thermal treatment at 350°C for 2 h has not provided any defects into the investigated coating film. In contrast, the results indicated that the calcinated hybrid film shows higher impedance and more stable performance on the evolution of corrosion resistance. Especially in Figure 11(A), the phase angles at all the scanning region are nearly 90° during 30 days. The plots at low frequency are parallel to each other with only a slight reduction. The samples calcinated at 350°C have higher

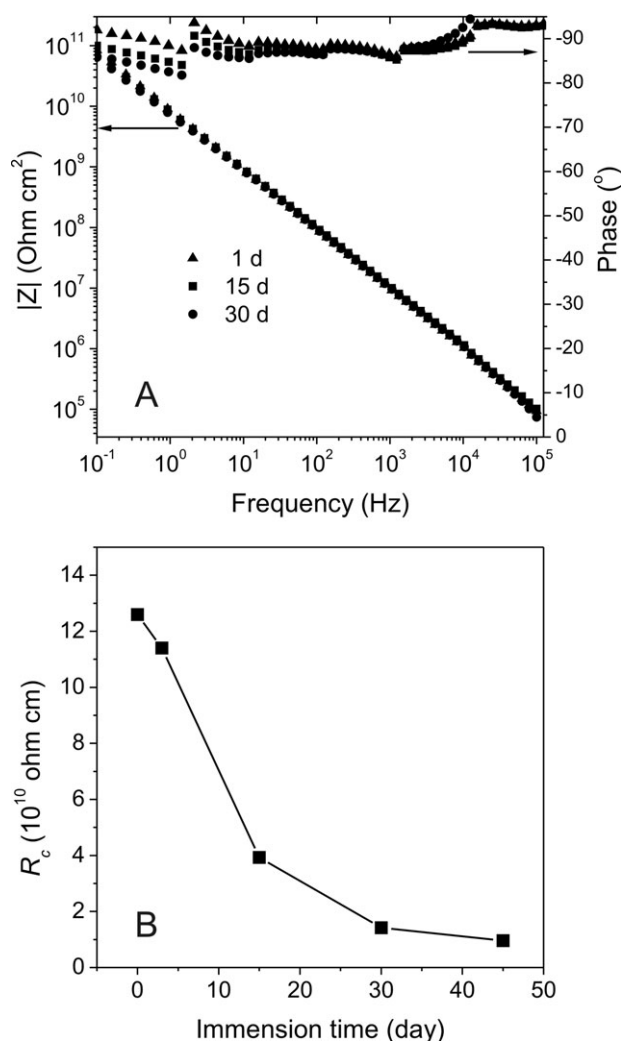


Figure 13. Evolution of EIS diagram (A) and coating resistance (R_c) (B) of prepared coating film. The coating film (R0208) has cured and was subjected to a thermal treatment at 350°C for 2 h. Working electrode with an area of 3 cm^2 is used, and the average film thickness is $237 \mu\text{m}$.

resistance than coatings without thermal treatment as the crosslinking density increased considerably at high temperature. According to the evolution of R_c recorded in Figure 13(B), which was calculated based on the same model circuit (Figure 10), the corrosion of prepared film became stable when the immersion time exceeded 15 days, because the diffusion rate of liquid medium into coating film was further limited due to thermal crosslinking.

CONCLUSIONS

The hybrid materials based on PMPS and phenyl-silica were successfully obtained via a two-step sol-gel process. The phenylene-silica, prepared from cohydrolysis and condensation of TEOS and phenylene-bridged monomer, exhibits high branching degree and is well compatible with polymer matrix, leading to the formation of graft interpenetrating networks under the effect of the alkaline catalyst. The structural characterization including FTIR and NMR indicates that the phenylene-silica framework has been incorporated into the hybrid system. The prepared hybrid materials can be fabricated to homogeneous, tough films with satisfactory tensile strength. The results of TGA showed a good thermal stability for prepared hybrid materials, especially when the imported phenylene-silica was synthesized with high proportion of phenylene-bridged monomer. In that case, the phenylene-silica possesses highest branching degree in its framework, which shows the most effective steric effect and leads to most significant restrictions on chain mobility. Through the investigation on thermal mechanical properties, excellent adhesion, flexibility, and impact strength were observed for the film samples containing the phenylene-silica prepared from Sol B, even after the samples were calcinated at 400°C. From the EIS measurement results, the hybrid films showed a satisfactory corrosion resistance, which is even enhanced after calcinating the film at high temperature.

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REFERENCES

- Jia, M.; Wu, C.; Li, W.; Gao, D. *J. Appl. Polym. Sci.* **2009**, *114*, 971.
- Patel, M.; Swain, A. C.; Cunningham, J. L.; Maxwell, R. S.; Chinn, S. C. *Polym. Degrad. Stab.* **2006**, *91*, 548.
- Hattori, Y.; Miyajima, T.; Sakai, M.; Nagase, Y.; Nemoto, N. *Polymer* **2008**, *49*, 2825.
- Imai, K.; Sasaki, T.; Abe, J.; Kimoto, A.; Tamai, Y.; Nemoto, N. *Polym. J.* **2009**, *41*, 584.
- Otomo, Y.; Nagase, Y.; Nemoto, N. *Polymer* **2005**, *46*, 9714.
- Cumurcu, A.; Erciyas, A. T. *Prog. Org. Coat.* **2010**, *67*, 317.
- Ivanković, M.; Brnardić, I.; Ivanković, H.; Huskić, M.; Gajović, A. *Polymer* **2009**, *50*, 2544.
- Jadav, G. L.; Singh, P. S. *J. Membr. Sci.* **2009**, *328*, 257.
- Karataş, S.; Kayaman-Apohan, N.; Demirer, H.; Güngör, A. *Polym. Adv. Technol.* **2007**, *18*, 490.
- Yang, P.; Wang, G.; Xia, X.; Takezawa, Y.; Wang, H.; Yamada, S.; Du, Q.; Zhong, W. *Polym. Eng. Sci.* **2008**, *48*, 1214.
- Yeh, J. M.; Yao, C. T.; Hsieh, C. F.; Yang, H. C.; Wu, C. P. *Eur. Polym. J.* **2008**, *44*, 2777.
- Ahmad, Z.; Al Sagheer, F.; Al Arbash, A.; Ali, A. A. M. *J. Non-Cryst. Solids* **2009**, *355*, 507.
- Khalil, M.; Saeed, S.; Ahmad, Z. *J. Appl. Polym. Sci.* **2008**, *107*, 1257.
- Wang, Z.; Suo, J.; Li, J. *J. Appl. Polym. Sci.* **2009**, *114*, 2388.
- Huang, K.-Y.; Weng, C.-J.; Lin, S.-Y.; Yu, Y.-H.; Yeh, J.-M. *J. Appl. Polym. Sci.* **2009**, *112*, 1933.
- Radhakrishnan, S.; Siju, C. R.; Mahanta, D.; Patil, S.; Madras, G. *Electrochim. Acta* **2009**, *54*, 1249.
- Weng, C.-J.; Huang, J.-Y.; Huang, K.-Y.; Jhuo, Y.-S.; Tsai, M.-H.; Yeh, J.-M. *Electrochim. Acta* **2010**, *55*, 8430.
- Yeh, J.; Weng, C.; Liao, W.; Mau, Y. *Surf. Coat. Technol.* **2006**, *201*, 1788.
- Duo, S.; Li, M.; Zhu, M.; Zhou, Y. *Mater. Chem. Phys.* **2008**, *112*, 1093.
- Yan, W.; Li, W.; Chen, J. *Huagong Xuebao* **2002**, *53*, 45.
- Park, H. B.; Kim, J. K.; Nam, S. Y.; Lee, Y. M. *J. Membr. Sci.* **2003**, *220*, 59.
- Chen, G.; Liu, G.; Yao, J.; Du, N. *Biaomian Jishu (in Chinese)* **2008**, *37*, 47.
- Díaz-Morales, U.; Bellussi, G.; Carati, A.; Millini, R.; Parker W. O. N., Jr.; Rizzo, C. *Microporous Mesoporous Mater.* **2006**, *87*, 185.
- Yang, D. J.; Xu, Y.; Zhang, L.; Zhai, S. R.; Wu, D.; Sun, Y. H. *Huaxue xuebao* **2005**, *63*, 1461.
- Zhang, Y.; Jin, Y.; Yu, H.; Dai, P.; Ke, Y.; Liang, X. *Talanta* **2010**, *81*, 824.
- Ohtani, O.; Goto, Y.; Okamoto, K.; Inagaki, S. *Mater. Lett.* **2006**, *60*, 177.
- Shea, K. J.; Loy, D. A. *Acc. Chem. Res.* **2001**, *34*, 707.
- Ganachaud, F.; Boileau, S.; Boury, B., Eds. *Silicon Based Polymers: Advances in Synthesis, Supramolecular Organization*; Springer: Berlin, **2008**; p 19.
- Guibergia-Pierron, M.; Sauvet, G. *Eur. Polym. J.* **1992**, *28*, 29.
- Jost, C.; Kuhnle, A.; Cornelis, H.; Abbenhuis, L. U. S. Patent 10/494,043, (**2002**).
- Jones, R. G.; Wataru, A.; Chojnowski, J. *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications*; Kluwer Academic Publisher: Dordrecht, Netherlands, **2000**.
- Kawakita, T.; Oh, H. S.; Moon, J. Y.; Liu, Y.; Imae, I.; Kawakami, Y. *Polym. Int.* **2001**, *50*, 1346.
- Otomo, Y.; Nagase, Y.; Nemoto, N. *Polymer* **2005**, *46*, 9714.

34. Wu, C. B.; Jin, Y. H.; Li, W.; Gao, D. H.; Jia, M. Q. *High Perform. Polym.* **2010**, *22*, 959.
35. Prado, L. A. S. A.; Sforça, M. L.; de Oliveira, A. G.; Yoshida, I. V. P. *Eur. Polym. J.* **2008**, *44*, 3080.
36. Zaisheng, Z.; Weiping, T.; Jianqing, H. *J. Chin. Cer. Soc.* **2011**, *39*, 334.
37. Wu, K.; Chao, C.; Yeh, T.; Chang, T. *Surf. Coat. Technol.* **2007**, *201*, 5782.
38. Lei, H.; Qiuyu, Z., *Mater. Prot. (in Chinese)* **2008**, *40*, 7.
39. Camino, G.; Lomakin, S. M.; Lageard, M., *Polymer* **2002**, *43*, 2011.
40. Wu, C.; Li, W.; Gao, D.; Jia, M. *Polym.-Plast. Tech. Eng.* **2009**, *48*, 1094.
41. Kashiwagi, T. U.S. Patent 12/973,534, (**2009**).
42. Bahadur, M.; Nelson, R.; Strong, M. Patent 13/257,659, (**2012**).
43. Kashiwagi, T. U.S. 7,553,915, (**2009**).
44. Smith, M. A.; Zhu, B. EP Patent 1,814,952, (**2009**).