

Preparation and Properties of Organic–Inorganic Hybrid Composites Based on Polystyrene and an Incompletely Condensed Polyvinylsilsesquioxane Oligomer

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ABSTRACT: An incompletely condensed polyvinylsilsesquioxane (PVSQ) oligomer containing abundant silanol groups was synthesized and characterized by FTIR, ¹H-NMR, ²⁹Si-NMR, and MALDI-TOF-MS. Polystyrene/polyvinylsilsesquioxane (PS/PVSQ) hybrid composites were prepared by an *in situ* bulk polymerization. The hybrid composites showed higher T_g , T_d , and char yield than PS homopolymer and without mechanical loss. The improvements in the properties of PS/PVSQ hybrid composites can be ascribed to the crosslinking function of PVSQ by silanol condensation in later processing. The hybrids

showed different morphology from discrete microstructure to continuous network depending on the concentration of PVSQ. Because of the surface enrichment, a PVSQ protection layer was formed, which made the hybrid surface more hydrophobic. The structure and the reaction mechanism of PS/PVSQ hybrid composites were also investigated. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2497–2505, 2010

Key words: polystyrene; hybrid composites; thermal properties; polysilsesquioxane

INTRODUCTION

Organic–inorganic hybrid composites have attracted considerable interest as this class of materials can combine the advantages of inorganic compounds with those of organic polymers.¹ Polysilsesquioxanes (PSQ) are important organic–inorganic hybrid compounds with an empirical formula of $(\text{RSiO}_{3/2})_n$, where R is methyl, vinyl, or other substituted organic groups. The inorganic molecular skeleton (Si–O–Si) gives PSQ excellent performances, such as great thermal properties, mechanical behavior, and weatherability, and the organic group makes them more miscible with polymer matrices.^{2,3} Because of the organic/inorganic molecular architecture, PSQ can be incorporated into polymer matrices through copolymerization or blending. PSQ molecules functionalized with reactive groups, such as epoxy, amine, isocyanate or vinyl have been used to

incorporate into polymethacrylate,^{4,5} epoxy,^{6,7} polyurethane, and other systems.⁸

Polystyrene (PS) is ranked as the third general plastics next to polyethylene (PE) and polypropylene (PP). But in some circumstances the applications of conventional PS are limited, especially due to their unsatisfied thermal properties.⁹ There have been many researches involving PS and PSQ. PSQ is usually acted as a surfactant to improve compatibility between PS and inorganic reinforcing fillers, which facilitated the well dispersion of clay, silica, or carbon nanotubes in the polymer and leading to the better thermal and mechanical properties.^{10–12} For PSQ bulk modification researches, previous reports were primarily focused on introducing different functional polyhedral oligomeric silsesquioxane (POSS) into PS, including octavinyl-POSS, phenethyl-POSS, magnetic-POSS, and etc. The thermal performance, dielectric properties, rheological behavior, and vertex group effects of PS and various substituted POSS hybrid composites were investigated.^{13–21} The studies indicated that POSS usually acted as nanoparticle or joint point to enhance the properties of polymer matrices. Li GZ studied the properties of ladderlike polyphenylsilsesquioxanes (PPSQ) and PS blends, including miscibility, crystallization, and rheological properties, and the mechanical properties of PS could be improved by addition of this rigid ladderlike PPSQ.^{22–25} Kim

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proved that aromatic (π - π) interactions between phenyl groups of PS and ladderlike PPSQ played a critical role for forming the homogeneous hybrid composites.²⁶ However, PS modified by a random structured PSQ has rarely been reported. Furthermore, the synthesis of PSQ is usually in a simple hydrolytic polycondensation process, which results in a random structured oligomer and contains incomplete condensation molecules. In contrast, the synthesis of POSS or ladderlike PSQ with a well-defined structure is complicated and costly. So we investigated the properties and the hybrid mechanism of PS and a vinyl functional PSQ, which synthesized by a facile method.

In this article, we first synthesized a random structured polyvinylsilsesquioxane (PVSQ) oligomer by hydrolytic polycondensation of vinyltriethoxysilane (VTES). The PVSQ oligomer then performed an *in situ* bulk polymerization with styrene. SEM, XPS, and the static contact angle measurement were employed to study the morphology and the surface properties of the hybrid composites. DSC, TGA, and DMA were used to investigate the thermal properties of the hybrids.

EXPERIMENTAL

Materials

Styrene was purchased from Beijing Chemical Reagents Co., China and distilled under reduced pressure. Azobis(isobutyronitrile) (AIBN) was obtained from Beijing Chemical Reagents Co., China and recrystallized from ethanol. Vinyl triethoxysilane (VTES) was received from Wuhan University Silicone New Material Co., (Hubei, China) and used as received. Other chemicals obtained from Beijing Chemical Reagents Co., China were used without further purification.

Preparation of the organic-inorganic hybrid composites

PVSQ oligomer was synthesized by a hydrochloric acid-catalyzed hydrolytic polycondensation of VTES according to our patent.²⁷ PS/PVSQ hybrid composites were prepared by an *in situ* bulk free radical polymerization. The proportion of PVSQ in the hybrids was controlled to be 2, 6, 11, 23, and 55 wt %, respectively. Typically, for 2 wt % PS/PVSQ hybrid, PVSQ oligomer (0.5 g) was dissolved in styrene monomer (27 mL) containing AIBN (0.0245 g, 0.1 wt % based on styrene). The styrene/PVSQ mixture was stirred for 1.5 hour at 80 °C, and then the mixture was sealed and heated in an oven for 80 °C/10 h, 100 °C/2 h, 120 °C/2 h, 140 °C/1 h, and 160 °C/1 h to obtain the hybrid. For comparison, the PS homopolymer was also synthesized by the same procedure.

Characterization

¹H-NMR was carried out on a Bruker 400 M instrument using deuterated chloroform as solvent. ²⁹Si-NMR was measured on a Bruker 300 M spectrometer with tetrahydrofuran as solvent and tetramethylsilane as external reference, and chromium (III) acetylacetonate (1 wt %) was used as paramagnetic relaxation agent.

Fourier transform infrared (FTIR) spectrum was recorded on a Bruker Equinox 55 spectrometer and the range is 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. The hybrid was ground and pressed with KBr for measurement.

Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) was performed on a BIFLEX III (Bruker Daltonics) instrument. Positive ion spectrum was acquired using delayed ion extraction and reflection modes with a nitrogen laser at the wavelength of 337 nm. α -Cyano-4-hydroxycinnamic acid (CHCA) was used as the matrix and THF as the solvent. Adventitious sodium and potassium were found to be the cationizing agents of the peak positions.

Differential scanning calorimetry (DSC) was performed on a PerkinElmer Diamond DSC with a constant nitrogen flow of 20 mL/min. The sample was preheated from 50 to 200 °C and then cooled quickly to 50 °C to eliminate heat history, and the next procedure was from 50 to 200 °C at 20 °C/min to measure the T_g .

Thermogravimetric analysis (TGA) was carried out on a PerkinElmer Pyris1 at a heating rate of 15 °C/min from 25 to 750 °C under a 20 mL/min nitrogen flow.

Dynamic mechanical analysis (DMA) was recorded on a Netzsch DMA 242C at a heating rate of 5 °C/min. The specimen was loaded in a three point bending mode with a frequency of 1 Hz. The experiments were carried out from 25 °C until the samples became too soft to be tested.

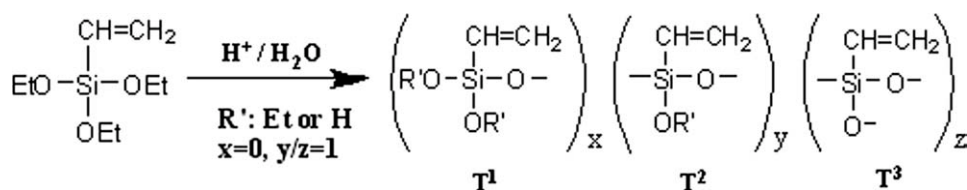
Angle-dependent X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALab 220I-XL electron spectrometer. Al K α radiation was used as the X-ray source and the takeoff angle was 15, 30, 45, and 90°, respectively.

Scanning electron microscopy (SEM) was performed on a Hitachi S4800 at an activation voltage of 15 kV. The ground samples were observed after being calcined at 450 °C for 10 min, and the surfaces were coated with a thin layer of platinum.

RESULTS AND DISCUSSION

Characterization of PVSQ oligomer

PVSQ oligomer was prepared by an acid-catalyzed hydrolytic polycondensation, as shown in Scheme 1.



Scheme 1 Preparation of PVSQ oligomer from VTES monomer.

Chemical shifts of silicon atoms in oligomer are referred to using the traditional terminology T^n , where n corresponds to the number of oxygen bridges to other silicon atoms. The reaction is demonstrated by two steps: first, the alkoxy groups hydrolyze to form silanol; second, silanol, and other alkoxy groups condense to form siloxane. The structure of PVSQ oligomer was characterized by means of FTIR (Fig. 1) and $^1\text{H-NMR}$ (Fig. 2). FTIR (KBr, cm^{-1}): 3360 and 890 (Si—OH), 2950–3070, 1607 and 1405 ($-\text{CH}=\text{CH}_2$), 1110 (Si—O—Si), 967 (Si—OEt). The FTIR spectrum illustrates the formation of siloxane and silanol, and the molecules also contain the Si—OEt. $^1\text{H-NMR}$ (CDCl_3 , ppm): 5.9–6.1 (Si—CH=CH₂), 4.0 (Si—OH), 3.6–3.7 ($-\text{CH}_2-\text{CH}_3$), 1.2–1.3 ($-\text{CH}_2-\text{CH}_3$). From the $^1\text{H-NMR}$ spectrum, we can calculate that the ratio of the remained Si—OEt to vinyl is 8%, and the ratio of silanol to vinyl is 40%, according to D₂O replacement of active hydrogen of silanol in PVSQ oligomer. Figure 3 shows the $^{29}\text{Si-NMR}$ spectrum of PVSQ oligomer. The peaks at -71.4 and -79.6 ppm were ascribed to T^2 and T^3 structures.³ The ratio of $T^2 : T^3$ content determined from their peak area is 1 : 1. Both the FTIR and the NMR results indicate the incomplete condensation of PVSQ oligomer containing a large amount of reactive Si—OH and Si—OEt groups.

The molecular weight and the detailed structures of PVSQ oligomer were studied by MALDI-TOF-MS

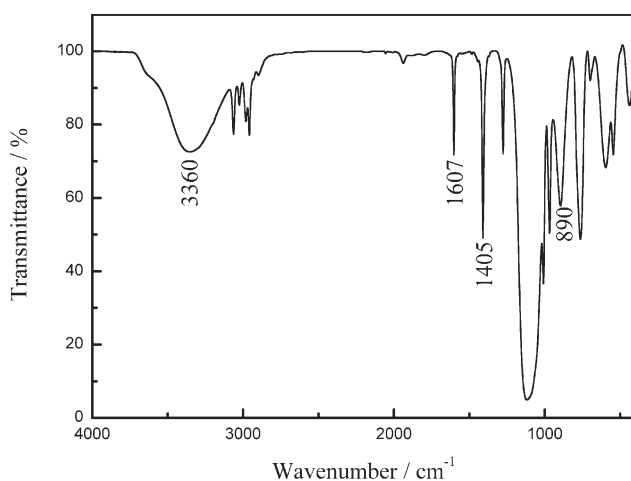
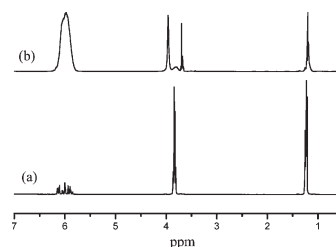


Figure 1 FTIR spectrum of PVSQ oligomer.

(Fig. 4). The interpretation of mass spectra is made by comparing the value of molar mass for an expected PVSQ formula with the experimentally obtained ones. Most of the peaks could be accounted by successive additions of a 88 g/mol unit from condensation of a vinylsilanetriol or of a 158 g/mol ($\text{CH}_2=\text{CHSi}(\text{O})_{3/2}$)₂ unit. Some molecules still have residual ethoxy groups and a difference of 28 g/mol is from hydrolysis of an ethoxy group. The fully condensed PSQ with the formula $(\text{RSiO}_{3/2})_n$ will form a finite three-dimensional molecular skeleton and build a polyhedral or cage-like structure. Partially hydrolyzed PSQ represent on a formula $T_n(\text{OH})_x(\text{OR}')_y$, where $T = \text{RSiO}_{1.5-(m/2n)}$ and $m = x + y$, x , and y are hydroxyl or alkoxy groups.^{28,29} The attributions of the main peaks of MALDI-TOF mass spectrum are shown in Table I. The peaks are the sodium or potassium adducts and the data have been subtracted Na^+ or K^+ mass from the ionized samples. The n is in the range from 7 to more than 11 and the number of silanol is from 2 to 6, and some molecules have 1 or 2 ethoxy groups. Based on the aforementioned investigation, it is clear that the prepared PVSQ oligomer is highly branched and contains several hydroxyl groups, which is crucial for the formation of crosslinking structure by intermolecular or intramolecular condensations.³⁰

Structure of PS/PVSQ hybrid composites

Figure 5 shows the FTIR curves of pure PS and PS/PVSQ hybrid composites. The spectra of PS/PVSQ hybrids are similar to that of PS except a strong Si—O—Si stretching vibration peak at 1100 cm^{-1} . The peak at 1600 cm^{-1} assigned to the benzene skeleton vibration, and the hydrogen absorption of phenyl

Figure 2 $^1\text{H-NMR}$ spectrum of VTES monomer (a) and PVSQ oligomer (b).

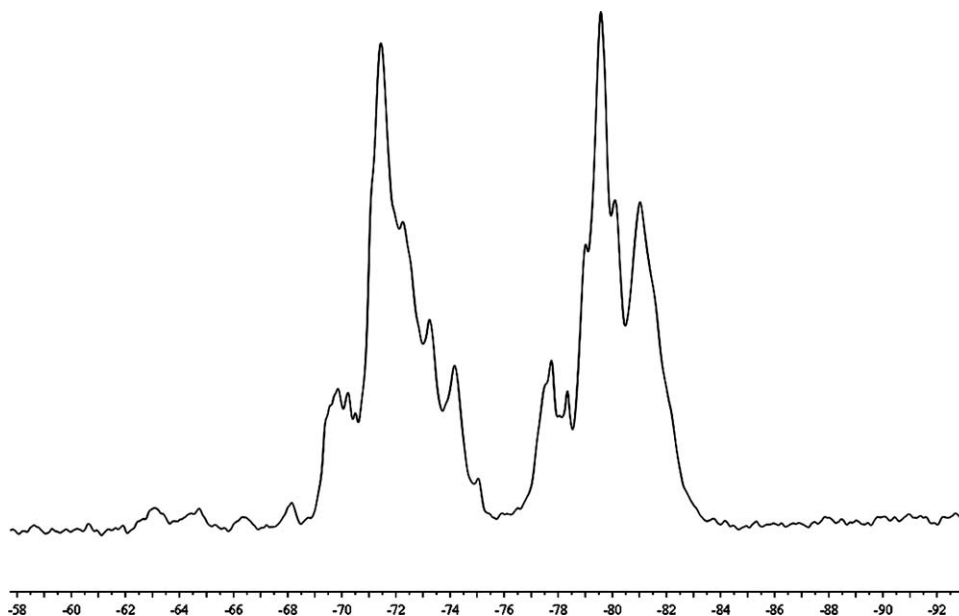


Figure 3 ^{29}Si -NMR spectrum of PVSQ oligomer.

group at 700 cm^{-1} was used as the internal standard. The band at 1630 cm^{-1} , which assigned to the conjugated structure of benzene disappeared, indicating the complete reaction of styrene. The band at 1410 cm^{-1} ascribed to the unreacted vinyl of PVSQ and the peak intensity increased with the PVSQ contents, suggesting the vinyl in PVSQ did not react completely. It is also noted that the characteristic absorptions of Si—OH at 3360 and 890 cm^{-1} occurred in Figure 1 disappear, implying the Si—OH condensed with each other in the hybrids during the thermal curing process. Furthermore, the results of 96 h Soxhlet extraction experiment in tetrahydrofuran (THF) showed that the residues of hybrids containing 6, 11, and 23 wt % PVSQ were 76, 87, and 95%, respectively, while the PS homopolymer dissolved completely. The FTIR and the Soxhlet extrac-

tion results confirmed that the hybrids we obtained were not a simple blend of PS and PVSQ. Chemical reaction occurred between the styrene and the PVSQ oligomer, and as expected, with increasing PVSQ content, the percentage of insoluble copolymer also increased. The process of the reaction may be as follows: at the beginning the styrene would be first initiated and began to form PS radicals because of the higher radical reactivity of styrene monomer than PVSQ oligomer.³¹ Then the vinyl in PVSQ oligomer began to copolymerize with PS. The conformational difficulty and steric hindrance of PVSQ oligomer lead to the incomplete reaction of vinyl. On the other hand, the reactive silanol groups condensed mutually as the temperature increased. Consequently, the PS was copolymerized with PVSQ by the vinyl addition reaction and meanwhile the

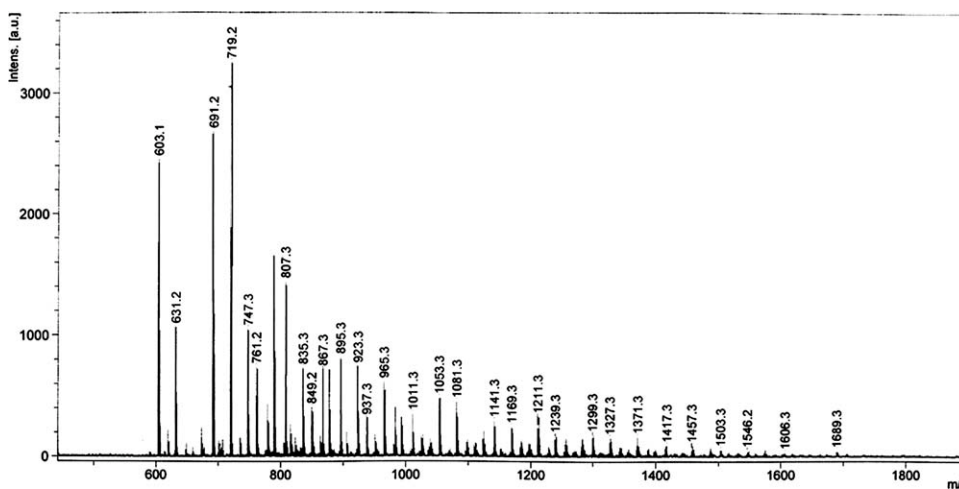


Figure 4 MALDI-TOF-MS of PVSQ oligomer.

TABLE I
The Main Peaks of MALDI-TOF-MS Attributions of PVSQ Oligomer

m/z	$T_n(\text{OH})_x(\text{OEt})_y$	m/z	$T_n(\text{OH})_x(\text{OEt})_y$	m/z	$T_n(\text{OH})_x(\text{OEt})_y$
580.1	$n = 7, x = 3$	784.3	$n = 9, x = 4, y = 1$	942.3	$n = 11, x = 4, y = 1$
608.2	$n = 7, x = 2, y = 1$	812.3	$n = 9, x = 3, y = 2$	988.3	$n = 11, x = 5, y = 2$
668.2	$n = 8, x = 4$	826.2	$n = 10, x = 4$	1030.3	$n = 12, x = 5, y = 1$
696.2	$n = 8, x = 3, y = 1$	844.3	$n = 10, x = 6$	1058.3	$n = 12, x = 4, y = 2$
724.3	$n = 8, x = 2, y = 2$	872.3	$n = 10, x = 5, y = 1$	1118.3	$n = 13, x = 6, y = 1$
738.2	$n = 9, x = 3$	900.3	$n = 10, x = 4, y = 2$	1146.3	$n = 13, x = 5, y = 2$
756.3	$n = 9, x = 5$	914.3	$n = 11, x = 5$	1188.3	$n = 14, x = 5, y = 1$

hybrid composite was crosslinked by the condensation of silanol.

Thermal properties of PS/PVSQ hybrid composites

The T_g of the PS/PVSQ measured by DSC is shown in Figure 6. The T_g of PS we prepared is 90.8°C, and the T_g of the hybrids increases gradually with the PVSQ content. The thermal data are summarized in Table II. In the hybrids, PVSQ acts as a crosslinking agent. Therefore, the more PVSQ in the system, the higher crosslinking density of the hybrids, and the less chain motility were resulted. But the T_g declined slightly when the PVSQ content increased from 23 to 55 wt %. This may be due to the greater steric hindrance of the aggregated PVSQ oligomer tending to inhibit the activity of styrene monomer, leading to the formation of a large fraction of low molecular weight components and thereby resulted in T_g decrease. This tendency also occurred in PMMA/OV-POSS and phenolic/OP-POSS systems.^{31,32} Therefore, the final T_g of the hybrids is determined by two competitive factors: the crosslinking effect of

the reactive silanol and the inhibition to styrene reactivity caused by PVSQ.

The thermal stability of the hybrids was investigated by TGA as shown in Figure 7, and the data were also listed in Table II. The T_d of PS homopolymer was 360°C, and the T_d of the hybrids was higher than that of PS and increased with the PVSQ concentration. This can be explained in terms of the crosslinking effect of PVSQ. This three-dimensional network structure will retard the thermal motion because the chain breakage mainly occurs at intermolecular at the beginning of decomposition.

Comparing to the pure PS which almost had no remnant at 500°C, the char yield of hybrids increased according to the addition of PVSQ. The increase of char yield corresponds firstly to the increase concentration of PVSQ, which are more thermal resistance, and secondly to the increased crosslinking density of this three-dimensional network.³³ Char formation is one of the important factors that relate to the flammability of materials. Increased char formation limits the production of combustible gases, decreases the exothermicity of the pyrolysis reaction and the thermal conductivity from the surface of the burning

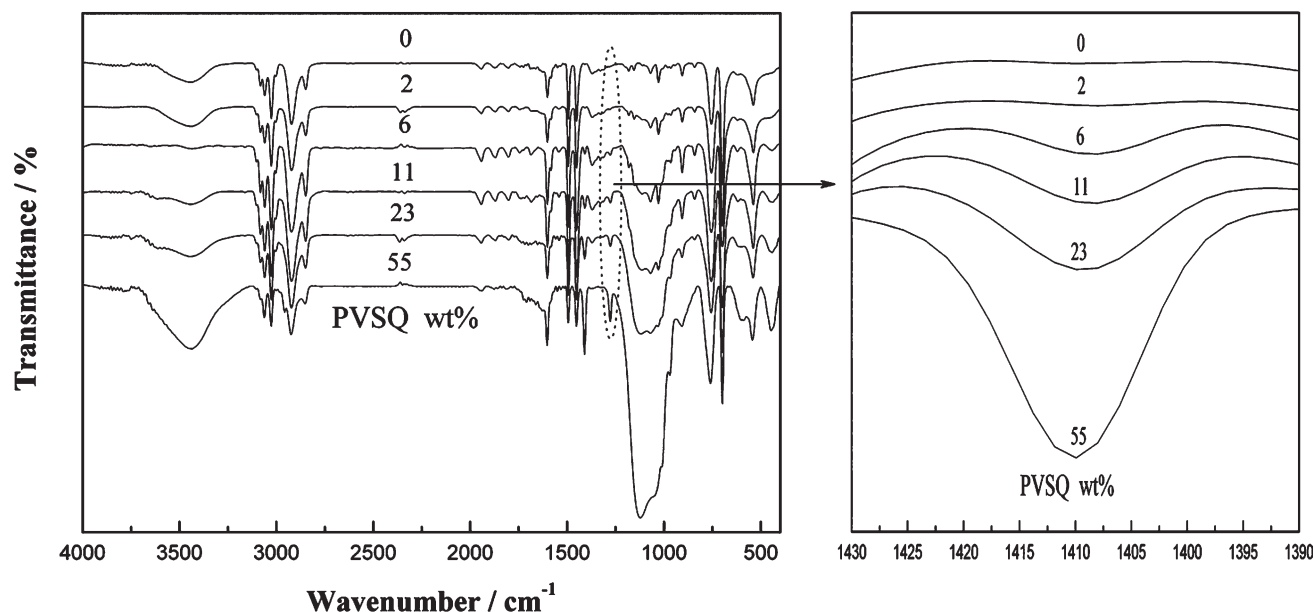


Figure 5 FTIR curves of pure PS and PS/PVSQ hybrid composites.

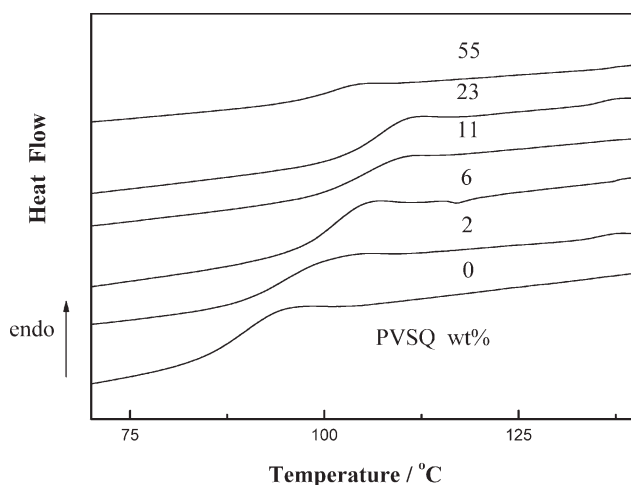


Figure 6 DSC thermograms of pure PS and PS/PVSQ hybrid composites.

materials. A linear relationship between the oxygen index and the char residue on pyrolysis for halogen-free polymer has been proposed.³⁴

In addition, Turri and Levi reported that POSS units prefer to be oriented toward the air-side.^{35,36} We suspected that the as-prepared PVSQ in hybrid composites also oriented toward the air-side to form an inorganic protection layer due to the lower surface tension. The static contact angle was measured and listed in Table II. The static contact angles increased with the PVSQ content, indicating the gradually reduced surface energy of the hybrids. The calculated atomic ratio of silicon of 11 wt % PS/PVSQ hybrid in bulk material is 1.8% but the atomic ratio of silicon (based on the total amount of detected elements of C, O, Si) measured by the angle-dependent XPS spectrum are 17.1, 16.6, 15.2 and 14.7% at a takeoff angle of 15, 30, 45, and 90°, respectively. The amount of silicon element decreased slightly with the detection depth and the silicon ratio on the surface was much larger than

TABLE II
Thermal Properties and Static Contact Angle of PS and PS/PVSQ Hybrid Composites

PVSQ wt %	T_g^a (°C)	T_d^b (°C)	Char yield (%)	Static contact angle ^c (°)
0	90.8	360.7	0	83.0 ± 1.6
2	96.1	377.2	1.9	92.4 ± 0.8
6	101.4	385.2	4.9	95.2 ± 0.7
11	105.4	392.1	8.5	97.8 ± 0.8
23	107.8	400.3	24.6	101.2 ± 0.7
55	105.7	466.4	60.3	104.3 ± 0.8

^a The T_g were taken as the midpoint of the heat capacity transition.

^b The T_d were taken to the temperature at 5% weight loss.

^c Data were obtained based on the average of 5 measurements using a 3 μ L water as the probe liquid.

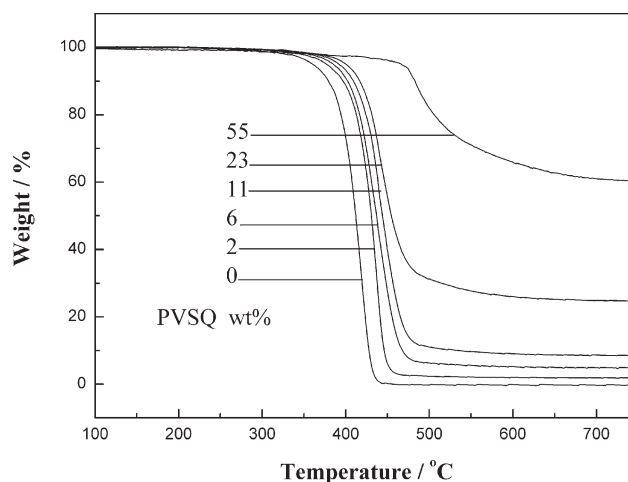


Figure 7 TGA curves of pure PS and PS/PVSQ hybrid composites.

that in bulk, indicating the surface enrichment of PVSQ occurred. The XPS results combined with the static contact angle investigation confirm that PVSQ can provide a barrier against the direct exposure of PS to the air, which contributes to the improvement of the thermal properties of the hybrids. Moreover, the improvement is more obvious than the previously reported PS/vinyl-POSS hybrid composites.¹³

Dynamic mechanical analysis of PS/PVSQ hybrid composites

Figure 8 shows the results of the dynamic mechanical analysis of the hybrid composites and PS. The storage moduli (E') of all the hybrids are higher than that of PS. The increased E' could be attributed to the reinforcement of this three-dimensionally structured PS/PVSQ. The PVSQ copolymerized with PS and acted as the chemical crosslinking agent to make the hybrids stiffer. When the samples were

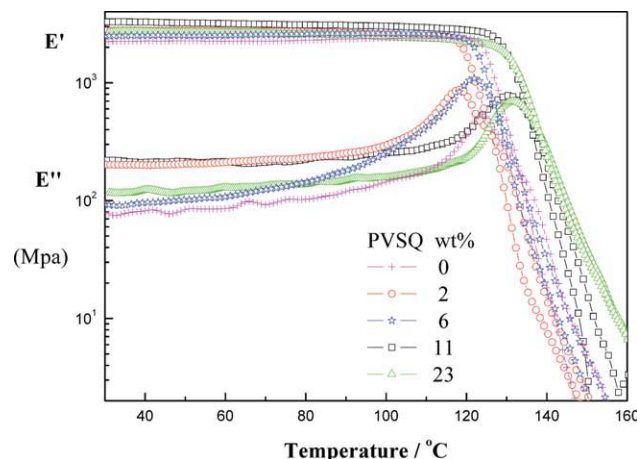


Figure 8 DMA curves of pure PS and PS/PVSQ hybrid composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

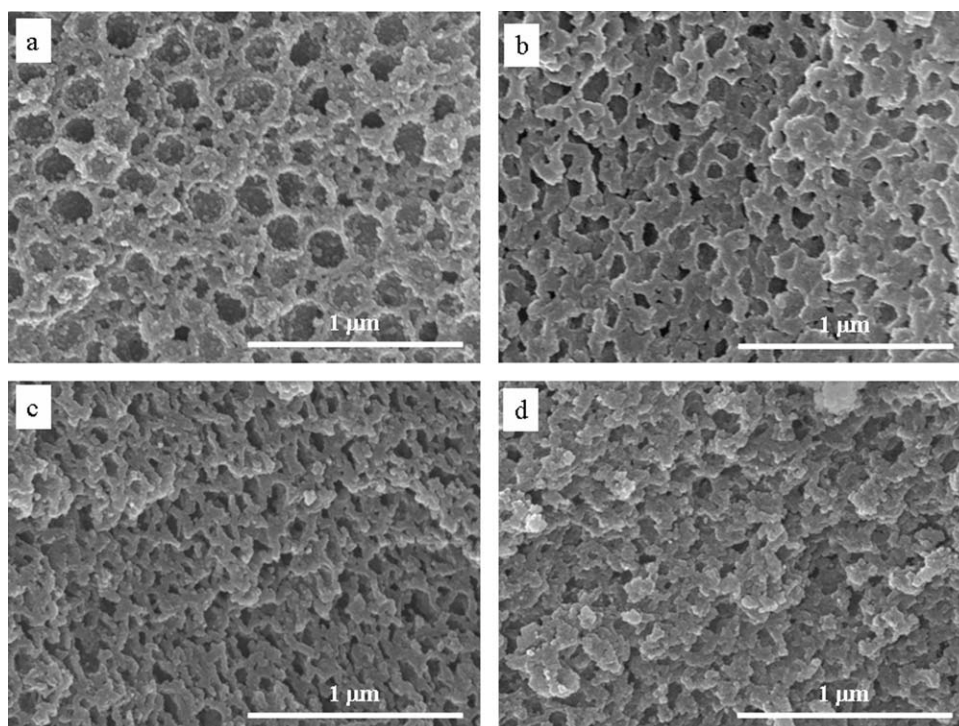


Figure 9 The SEM images of the calcination residue of PS/PVSQ hybrid composites containing (a) 2, (b) 6, (c) 11, and (d) 23 wt % PVSQ.

heated to elevated temperature, the glassy state transformed to viscous flow state quickly and caused sudden drop of E' . There seems no regularity between E' and the amount of PVSQ present in the

hybrids. But all the hybrids show better E' values than that of PS homopolymer, indicating the thermal properties of PS can be improved by the PVSQ without mechanical loss.

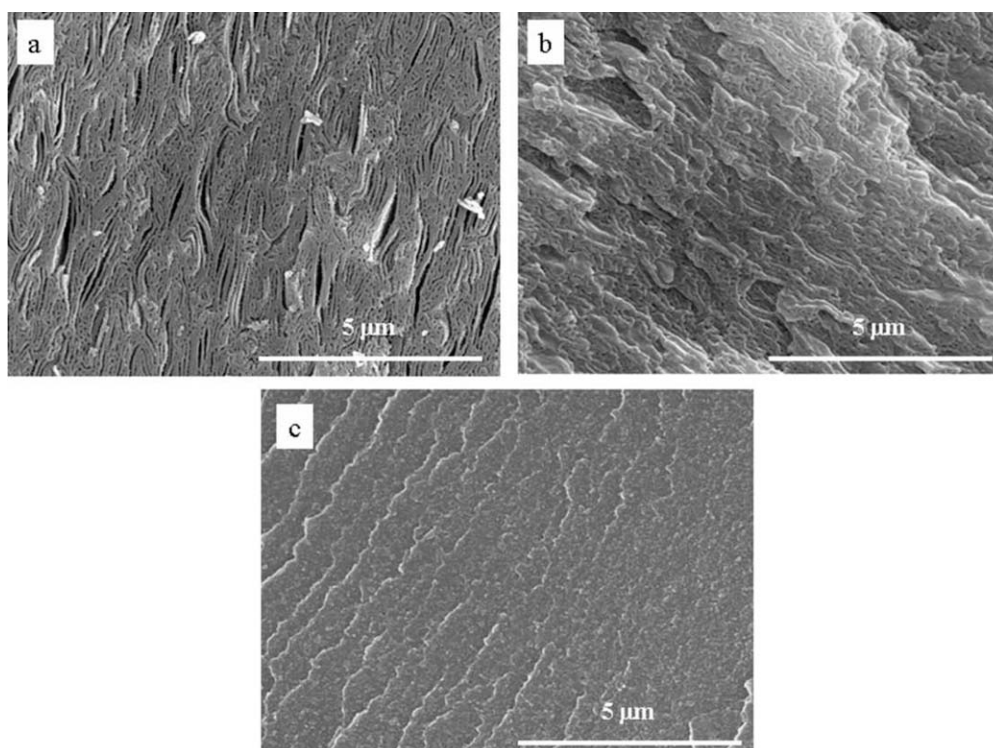


Figure 10 The SEM images of 55 wt % PS/PVSQ hybrid composites (a) the residue of calcination, (b) the residue of Soxhlet extraction, (c) the fracture section of hybrid.

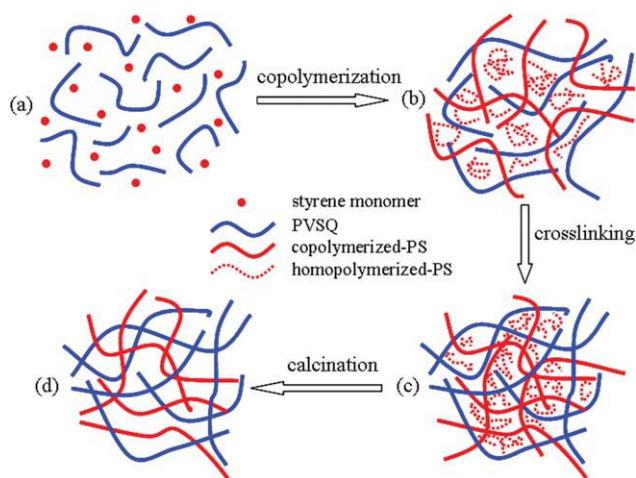


Figure 11 Schematic illustration of formation of PS/PVSQ hybrid composites morphology. (a) PVSQ oligomer dispersed in styrene monomer. (b) Styrene began to homopolymerize and then some PS radicals copolymerized with PVSQ by vinyl reaction (the red lines cross with blue lines). (c) A three-dimensional network of PS/PVSQ formed by condensation of silanol (the blue lines cross with each other). (d) Porous structure formed after removing homo-PS by calcination. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Morphology of PS/PVSQ hybrid composites

A homogeneous and transparent mixture formed when PVSQ oligomer was mixed with styrene at the beginning of the reaction. But the transparent solution gradually became cloudy with the reaction proceeding, implying the occurrence of phase separation. The fracture morphology of the hybrid at room temperature presented a featureless structure. When the hybrids were heated at 450 °C for 10 min, lots of small pores formed, as shown in Figure 9. The formation of the dispersed pores is attributed to the removing of PS homopolymer phase by the calcination. The dimension of these irregular pores becomes smaller with the increase of PVSQ concentration since the crosslinking density is increased, but the sizes are more than 100 nm which cause materials opaque. It is interesting to note that the 55 wt % PS/PVSQ hybrid displayed multiple layer architecture, as shown in Figure 10. The fracture morphology of hybrid before treatment was a uniform appearance, while both the residues of calcination [Fig. 10(a)] and Soxhlet extraction [Fig. 10(b)] showed analogous appearance. Soxhlet extraction experiment can only dissolve homo-PS and reserve the copolymer, which indicates that the PS/PVSQ copolymer (PS-*co*-PVSQ) formed the continuous phase and the homo-PS were removed.

The driving force of phase separation is the decreased contribution of mixing entropy to mixing free energy. Along with the polymerization, the

increased molecular weight of the system would decrease the entropic contribution to miscibility, and thus phase separation took place. The illustration of formation of PS/PVSQ hybrid morphology is shown in Figure 11. The styrene monomer was first initiated and formed homo-PS in the reaction system due to the higher reactivity of styrene. Then the PVSQ oligomer began to copolymerize with PS until the reaction activity of PVSQ oligomer was comparable to that of PS radical. Furthermore, the reactive silanol groups condensed intermolecular or intramolecular with the reaction proceeding. As a result, PS chain was partly copolymerized with vinyl of PVSQ and meanwhile crosslinked by the condensation of Si—OH. After being calcinated in 450 °C, the homo-PS was removed and the PS-*co*-PVSQ mostly retained, so the hybrid composite displayed the heterogeneous morphology.

CONCLUSION

An incompletely condensed PVSQ oligomer was synthesized by acid-catalyzed hydrolytic polycondensation of VTES. The as-prepared PVSQ oligomer with a random structure contains plenty of reactive silanol groups. PVSQ oligomer was incorporated into PS in different ratio by an *in situ* bulk polymerization. The phase separation induced by polymerization was observed and the PS-*co*-PVSQ formed the continuous phase with the increase of PVSQ. Moreover, PVSQ formed a surface barrier to prevent the degradation of PS and made the hybrids more hydrophobic. Considerable improvements in the thermal properties with higher T_g , T_d , and the char yield are resulted for the hybrid composites without obvious mechanical loss when compared with PS homopolymer. Therefore, the three-dimensional network hybrids with better thermal properties were obtained by adding this incompletely condensed PVSQ oligomer.

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