

# Preparation and Properties of APPSSQ-like/Polyimide Hybrid Composites

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**ABSTRACT:** Hydrolysis and condensation proceeded to generate 3-aminopropyl polysilsesquioxane-like (APPSSQ-like) particles from 3-aminopropyl triethoxysilane. An APPSSQ-like particle includes two domains: crosslinking Si—O—Si networks inside and 3-aminopropyl groups outside the particle. The APPSSQ-like/polyimide (APPSSQ-like/PI) hybrid composites were prepared from a solution of poly(amic acid) (PAA, polyimide precursor) and APPSSQ-like particles using *N,N*-dimethylacetamide as a solvent. Scanning electron microscopy (SEM) showed that the APPSSQ particle sizes were about 100 nm, and there was no obvious phase separation between the APPSSQ-like particles and the PI matrix in the fracture surfaces of the hybrid films. Owing to the highly crosslinked Si—O—Si networks inside the APPSSQ-like particles, the APPSSQ-like/PI hybrid composites possessed desired properties such as improved thermal resistance and reduced coefficients of thermal expansion (CTE). The presence of covalent bonds be-

tween the APPSSQ-like particles and the PI molecules improved the compatibility between these two components. Thus, the tensile strength increased with the APPSSQ-like content, and the elongation at break also slightly increased with the APPSSQ-like content. The initial tensile and storage moduli of the APPSSQ-like/PI hybrid composites increased with the APPSSQ-like content, which indicates that the mechanical properties of these hybrid composites were enhanced by the incorporation of the APPSSQ-like content in the PI matrix. Furthermore, the glass transition temperatures of these composites increased with the APPSSQ-like content because the adhesion between the APPSSQ-like particles and the PI molecules restricts the PI chains' mobility. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2865–2874, 2003

**Key words:** polyimides; compatibility; crosslinking; mechanical properties; thermal properties

## INTRODUCTION

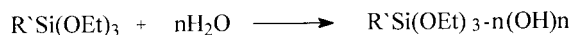
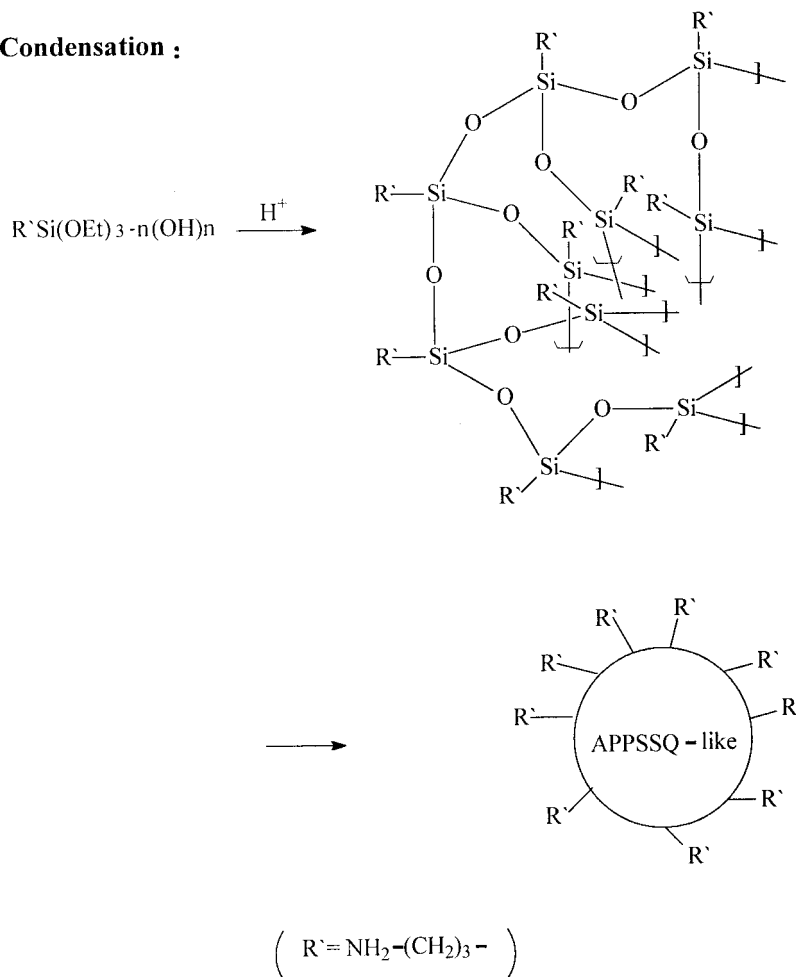
Aromatic polyimides (PIs), being widely applicable engineering plastics, exhibit numerous excellent properties such as chemical, physical, and thermal properties.<sup>1,2</sup> In recent years, they have been adopted increasingly in such industrial fields as aerospace and electronics. Generally, aromatic PIs are prepared through a two-step procedure of the ring-opening polyaddition of aromatic diamine to aromatic dianhydride in an NMP [or *N,N*-dimethylacetamide (DMAc)] solution. This yields soluble poly(amic acid) (PAA) and is followed by thermal imidization to obtain PIs. PIs have numerous applications in the electronic industry, which includes interlayer, insulation films, alpha-ray shielding films, buffer coating films, and alignment films for liquid crystal displays. Thus, their improvement is vital to such applications.<sup>3</sup>

In recent years, incorporating silica components in PIs in the form of hybrid composites has enhanced their thermal properties and reduced their coefficients of thermal expansion.<sup>4–7</sup> However, due to the lack of

interfacial interactions between an organic polymer and an inorganic silica particles, these hybrid composites reduce the mechanical strength. Therefore, the covalent bonds between an organic polymer and inorganic silica particles are the result of the hybrid composites' compatibility.<sup>8–13</sup> In previous research, as small silica particles have a greater interfacial area between an organic polymer and inorganic silica fillers, a silane coupling agent was used to form covalent bonds in the hybrid composites. Adhesion between an organic polymer and inorganic silica components was improved using a silane coupling agent by the following two methods: (1) After the surface of the silica particles was modified via a silane coupling agent that had reacted with the silica particles, the surface-modified silica particles were introduced into the polymer matrix to form hybrid composites.<sup>9,14–16</sup> (2) The hybrid composites were prepared via a sol-gel process.<sup>5,17–19</sup> The mixtures of the alkoxysilane solution and silane coupling agents were well mixed with the polymer. Subsequently, hydrolysis and condensation were performed to produce the hybrid composites.

Herein, 3-aminopropyl triethoxysilane (3-APS) was used, via a sol-gel process, to produce 3-aminopropyl polysilsesquioxane-like (APPSSQ-like) particles which have a structure similar to that of polysilsesquioxane.

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**Hydrolysis :****Condensation :****Scheme 1**

Then, these particles were mixed thoroughly with PAA. After imidization was completed via a thermal treatment, APPSSQ-like/PI hybrid composites were formed.

FTIR and <sup>29</sup>Si-NMR were employed to characterize the structure of the ultrafine APPSSQ-like particles. Scanning electronic microscopy (SEM), tensile testing, dynamic mechanical analysis (DMA), thermal mechanical analysis (TMA), and thermogravimetric analysis (TGA) were employed to investigate the microstructure, tensile properties, viscoelastic properties, thermal expansion properties, and thermal stability, respectively, of the APPSSQ-like/PI hybrid composites.

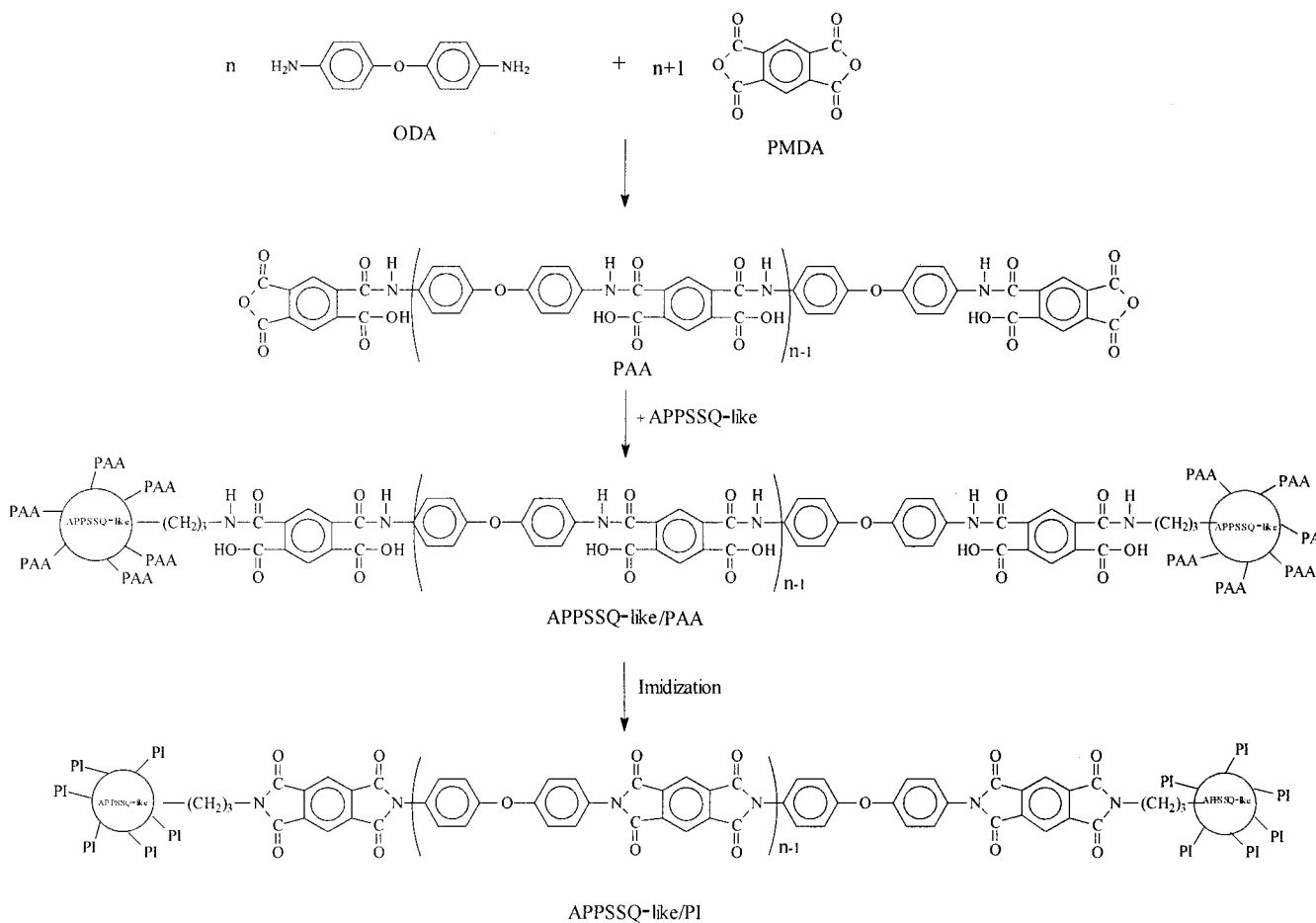
**EXPERIMENTAL****Materials**

Pyromellitic anhydride (PMDA) was purchased from the Criskev Co. (USA) and purified from acetic anhy-

dride. 4,4'-Oxydianiline (ODA) was purchased from the Criskev Co. and used without any purification. DMAc was dried by distillation under reduced pressure over sodium hydride. The 3-APS coupling agent was purchased from Acros (USA) and used without any purification. Toluene and tetrahydrofuran (THF) from Tedia (USA) were dried and stored over molecular sieves before use.

**Preparation of APPSSQ-like particles**

APPSSQ-like particles were prepared as follows: In a 250-mL three-neck flask, which was under a nitrogen condition, 8.84 g (0.04 mol) of the 3-APS coupling agent and 2.16 g (0.12 mol) of H<sub>2</sub>O were introduced and stirred at room temperature for 3 h for hydrolysis to occur. Thereafter, HCl<sub>(aq)</sub> was added and stirred at 100°C for 24 h to facilitate condensation. The reaction



Scheme 2

mixture was cooled to room temperature. After the mixture was filtered, white powders were obtained. The white powders were washed three times with toluene and THF, respectively, to remove the unreacted 3-APS coupling agent and vacuum-dried at 100°C overnight.

### Preparation of APPSSQ-like/PI hybrid films

Prior to preparing the hybrid composites, various amounts of APPSSQ-like particles were mixed with 25 mL toluene and well dispersed therein via ultrasonification for 1 h. PAA from PMDA and ODA was prepared as follows: ODA, 5.94 g (0.0297 mol), and DMAc, 50 g, were put into a 500-mL four-neck flask with a nitrogen inlet and a mechanical stirrer. After ODA was completely dissolved in DMAc, 6.54 g (0.03 mol) of PMDA was added in three batches with a time interval of 10 min between each batch. The residual PMDA was washed to the flask with 40 g of DMAc. The reaction mixture was stirred at 15–20°C for 1 h. Subsequently, various concentrations of APPSSQ-like particle/toluene mixtures were added into the flask and mixed with PAA. The mixtures of APPSSQ-like

powders and PAA were stirred for 5 h to achieve complete mixing. The APPSSQ-like/PAA mixtures were cast onto glass plates and dried in an air-convection oven at 60°C for 10 h. The APPSSQ-like/PAA hybrid films were cured to complete imidization based on the following thermal schedule: 100°C/1 h, 150°C/1 h, 200°C/1 h, 250°C/1 h, and 300°C/3 h. Following the thermal treatments, APPSSQ-like/PI hybrid films with various APPSSQ-like contents (0, 0.5, 1, 3, and 5 wt %) were obtained.

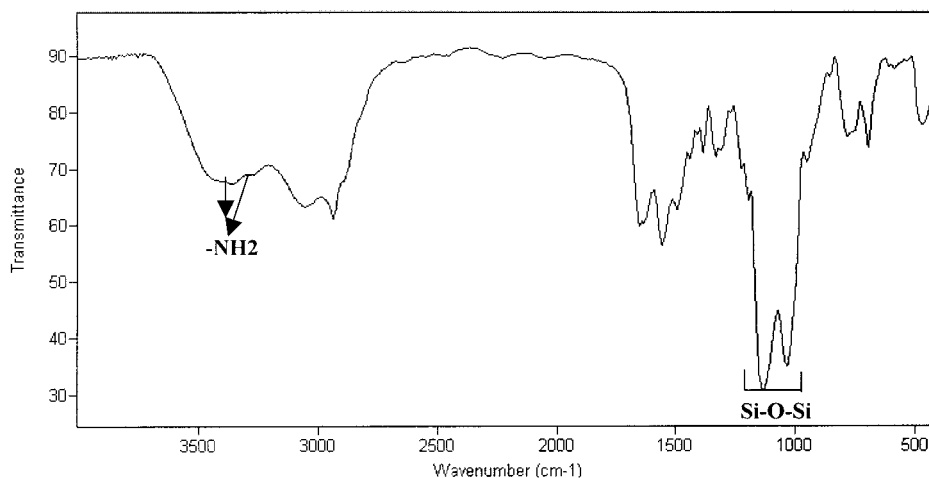
### Characterization and measurements

#### Infrared analysis

The structure of the APPSSQ-like particles synthesized from a 3-APS coupling agent was followed by analysis of the infrared spectrum. The sample for Bio-Rad FTS-404 FTIR analysis was mixed with KBr powder and pressed into a pellet.

#### <sup>29</sup>Si-NMR

A solid-state <sup>29</sup>Si-NMR spectrum was obtained on a Bruker AVANCE 400 spectrometer. Zirconia rotors, 7



**Figure 1** FTIR spectrum of APPSSQ-like content.

mm in diameter, were spun in air at 5 kHz. A  $^{29}\text{Si}$  spectrum was acquired at 79.49 MHz, using a pulse angle of 30 s and recycling delay of 60 s. The spectrum was referenced to an external TMS standard.

#### Morphology of the hybrid composites

The morphology of the fracture surface via a tensile test of the hybrid films was observed and mapping photographs by an HITACH S-4100 field-emission SEM.

#### Tensile properties

The results of the tensile strength, elongation at break, and initial tensile modulus of the hybrid films were recorded on an Instron-4464 universal tester at a drawing rate of 5 mm/min. All samples were prepared in pieces of  $150 \times 25$ -mm size, and the thickness of the pieces was in the range of 50–60  $\mu\text{m}$ .

#### Viscoelastic properties

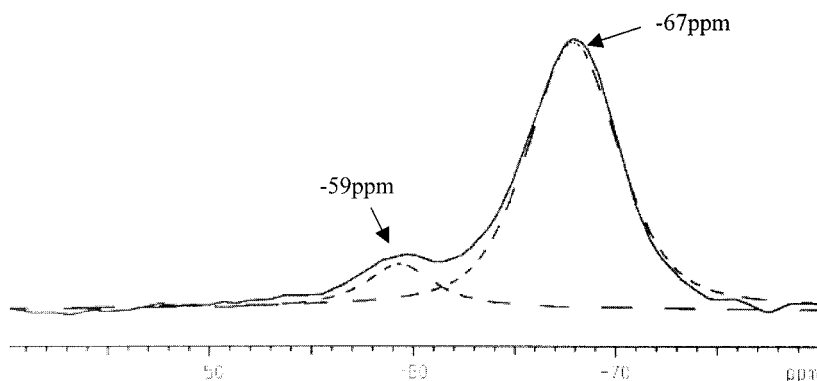
The storage modulus ( $E'$ ) and loss factor ( $\tan \delta$ ) were obtained with a DuPont 2980 dynamic mechanical analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$ .

#### Thermal expansion properties

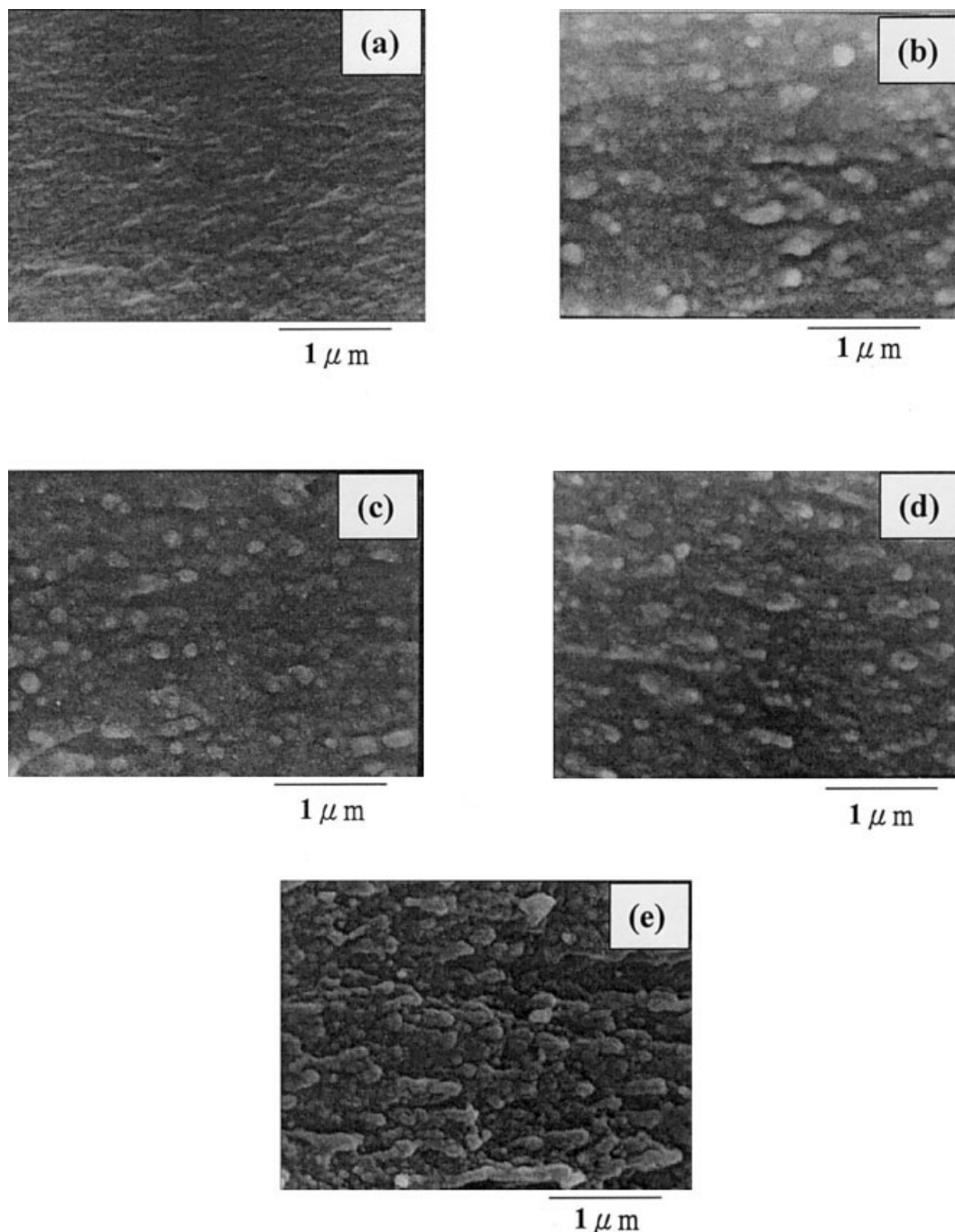
The coefficients of linear thermal expansion of the APPSSQ-like/PI hybrid films were measured on a DuPont 2940 thermal mechanical analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen flow.

#### Thermogravimetric analysis

TGA was performed with a Perkin-Elmer TAC 7/DX under a nitrogen flow. Samples of 5–10 mg were loaded onto a platinum plate and preheated at  $100^\circ\text{C}$  for 10 min to remove any water absorbed from the atmosphere. The temperature range for the TGA measurements was from 100 to  $800^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$ . Isothermal



**Figure 2** Deconvolution of  $^{29}\text{Si}$ -NMR of APPSSQ-like content.



**Figure 3** SEM photographs of the fracture surfaces of APPSSQ-like/PI hybrid films with various APPSSQ-like contents: (a) 0 wt %; (b) 0.5 wt %; (c) 1 wt %; (d) 3 wt %; (e) 5 wt %.

TGA was carried out with a Perkin–Elmer TAC 7/DX, heating the sample (ca. 5–10 mg) from 30 to 550°C at a heating rate of 40°C/min and then maintaining the temperature at 550°C for 120 min.

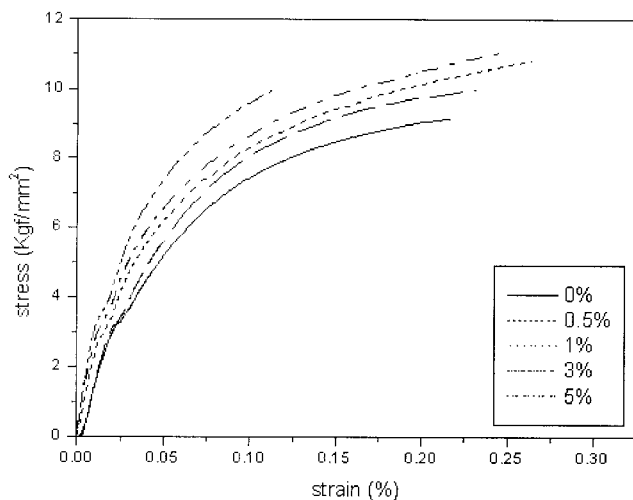
## RESULTS AND DISCUSSION

### Sample preparation

Schemes 1 and 2 show the preparation of APPSSQ-like particles and APPSSQ-like/PI hybrid composites, re-

spectively. An APPSSQ-like particle was generated from 3-APS via hydrolysis and condensation and includes two domains in its structure: the crosslinking Si—O—Si networks inside and the 3-aminopropyl groups outside the particle. The structure of an APPSSQ-like particle is similar to that of polysilsesquioxane.

PAA was synthesized from PMDA and ODA with a molar ratio of 1:0.99 in DMAc, and the anhydride groups from PMDA were produced at the ends of its



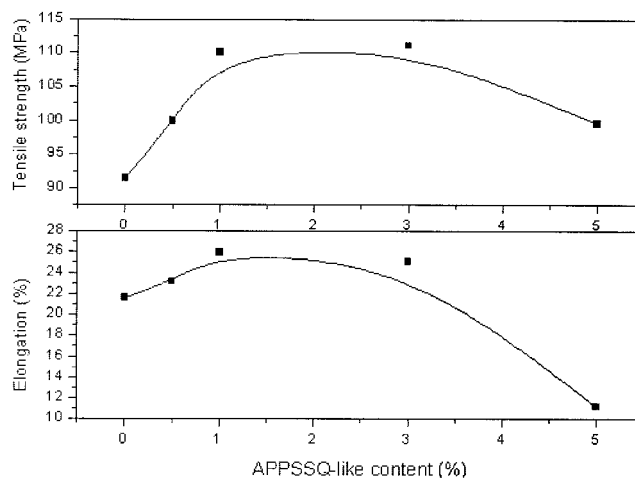
**Figure 4** Stress-strain curves of APPSSQ-like/PI hybrid films with various APPSSQ-like contents.

polymer chains as the terminated groups. When the APPSSQ-like particles were mixed thoroughly with PAA, the amino groups from the APPSSQ-like particles reacted with the terminated anhydride groups from PAA to form covalent bonds between the APPSSQ-like particles and the PAA molecules. A series of thermal treatments on the APPSSQ-like particles/PAA produced the APPSSQ-like/PI hybrid composites.

#### Characterization of APPSSQ-like particles

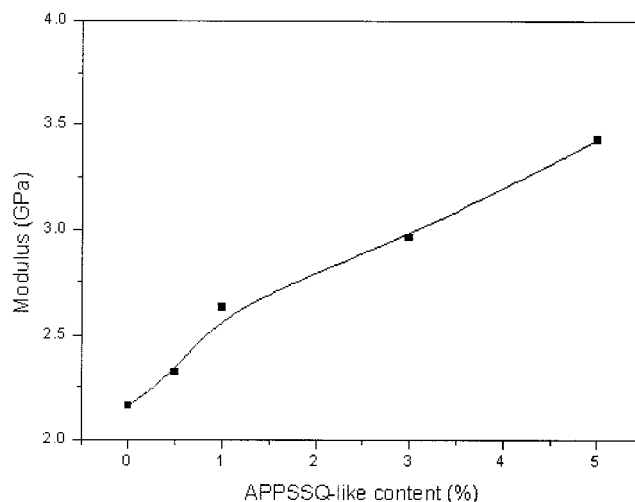
Figure 1 shows the FTIR spectrum of the APPSSQ-like particles. The strong absorbance at 1036 and 1135  $\text{cm}^{-1}$ , due to Si—O—Si asymmetric and symmetric stretching, characterizes the spectrum of the APPSSQ-like powders. The —OH and Si—O stretching of Si—OH as well as of the Si—OH deformation produced the other characteristic peaks at 3400, 953, and 785  $\text{cm}^{-1}$ . Another characteristic peak of Si—O—Si symmetric stretching occurs at 473  $\text{cm}^{-1}$ . The absorption bands at 3357 and 3271  $\text{cm}^{-1}$  are characteristic of —NH<sub>2</sub> asymmetric and symmetric stretching, respectively, and the peak of N—H bending is at 1653  $\text{cm}^{-1}$ .

Figure 2 shows the <sup>29</sup>Si-NMR spectrum of the APPSSQ-like particles. Following a hydrolysis reaction, a silanol group (Si—OH) of a coupling agent molecule reacts with the Si—OH of another one to form the Si—O—Si structure. Thus, three types of reaction within a coupling agent molecule could occur: monoreacted, directed, and trireacted of silanol groups to form R'Si(—O—)(OH)<sub>2</sub>, R'Si(—O—)<sub>2</sub>(OH), and R'Si(—O—)<sub>3</sub> [R' = NH<sub>2</sub>—(CH<sub>2</sub>)<sub>3</sub>], respectively. From the result of <sup>29</sup>Si-NMR, it is shown that two kinds of structures in an APPSSQ-like particle can be formed: R'Si(—O—)<sub>2</sub>(OH) from the direaction at -59 ppm and R'Si(—O—)<sub>3</sub> from trireaction at -67 ppm.

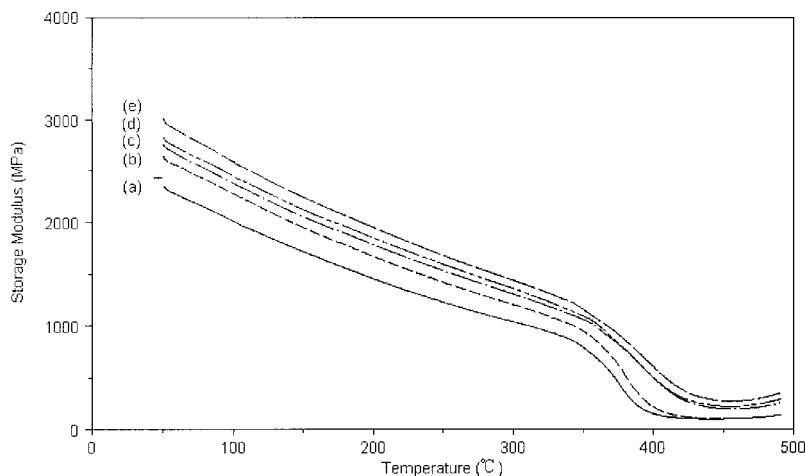


**Figure 5** Effect of APPSSQ-like content on tensile strength and elongation of APPSSQ-like/PI hybrid films.

Figure 2 also shows the results of deconvolution of the <sup>29</sup>Si-NMR spectrum for APPSSQ-like particles. The integral areas of the peaks indicate the molar ratio of the structures of R'Si(—O—)<sub>2</sub>(OH) and R'Si(—O—)<sub>3</sub> and displays that the molar ratio of R'Si(—O—)<sub>2</sub>(OH)/R'Si(—O—)<sub>3</sub> is 13.15/86.85. The R'Si(—O—)<sub>2</sub>(OH) has 1 molar equivalent of Si—PH and 2 molar equivalents of Si—O—Si. Thus, the 13.15% molar percentage is divided into two parts: where the molar percentages of Si—PH and Si—O—Si are 4.38 and 8.77%, respectively. Additionally, the R'Si(—O—)<sub>3</sub> has 3 molar equivalents of Si—O—Si with the molar percentage of 86.85%. Thus, the total molar percentage of the Si—O—Si structure from R'Si(—O—)<sub>2</sub>(OH) and R'Si(—O—)<sub>3</sub> inside the APPSSQ-like particles is 95.62%, indicating that a high degree of condensation of silanol groups is achieved to obtain Si—O—Si net-



**Figure 6** Effect of APPSSQ-like content on initial tensile modulus of APPSSQ-like/PI hybrid films.



**Figure 7** Temperature dependence of storage modulus of APPSSQ-like/PI hybrid composites with various APPSSQ-like contents: (a) 0 wt %; (b) 0.5 wt %; (c) 1 wt %; (d) 3 wt %; (e) 5 wt %.

works with a high crosslinked density inside the APPSSQ-like particles.

### Morphology of the hybrid films

Figure 3 presents the SEM of the fracture surfaces of APPSSQ-like/PI hybrid films. It is observed that the sizes of most APPSSQ-like particles are about 100 nm. From these micrographs, because the covalent bonds enhance the compatibility between the APPSSQ-like particles and the PI molecules, the APPSSQ-like particles are embedded into the PI matrix without any obvious phase separation. When the APPSSQ-like content increases within the APPSSQ-like/PI hybrid composites, cracks appear and increase, which is caused by the aggregation of the APPSSQ-like particles. This is because these APPSSQ-like particles do not bond to each other; thus, the aggregations of APPSSQ-like particles form a defect within the composites, which results in cracks after the hybrid films are lengthened to break.

### Tensile test

The stress–strain curves of the APPSSQ-like/PI hybrid films are shown in Figure 4. Figure 5 shows the APPSSQ-like content on the tensile strength and elongation at break of the APPSSQ-like/PI hybrid films. It is observed that the tensile strength of the hybrid films increases to a maximum value of 111.1 MPa at a 3 wt % APPSSQ-like content. Owing to the adhesion between the APPSSQ-like particles and the PI molecules, the compatibility between these two components is enhanced. Thus, the tensile strength increases with the APPSSQ-like content. When the APPSSQ-like content exceeds 3 wt %, the tensile strength decreases. This can be explained by that the reduced tensile strength results from the aggregations of fewer APPSSQ-like

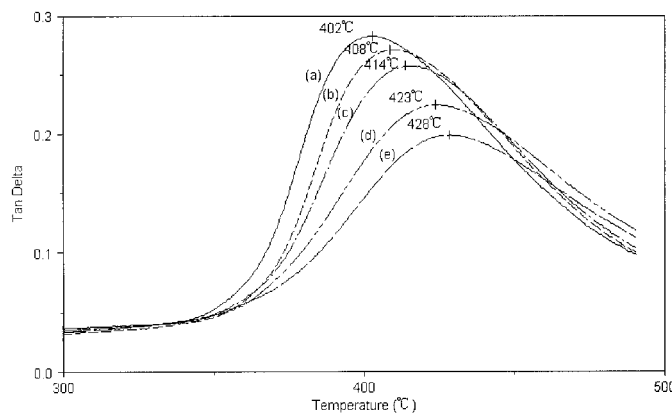
particles, which is a defect in the hybrid composites. The elongation at break slightly increases with the APPSSQ-like content, which is also attributed to the adhesion between the APPSSQ-like particles and the PI molecules. When the APPSSQ-like content exceeds 3%, the elongation of the hybrid films decreases dramatically, which is also assumedly caused by the defect of the aggregated APPSSQ-like particles in the hybrid films.

Figure 6 shows the effect of the APPSSQ-like content on the initial tensile modulus of the APPSSQ-like/PI hybrid films. Because the crosslinked Si—O—Si networks are more rigid than are the PI molecules, the initial tensile modulus of these hybrid composites is enhanced by the APPSSQ-like loading. The increase in the initial tensile modulus of the hybrid films reveals that the mechanical property of the APPSSQ-like/PI hybrid composites is enhanced by the addition of APPSSQ-like particles.

### Dynamic mechanical properties

The temperature dependence of the storage modulus ( $E'$ ) and loss factor ( $\tan \delta$ ) for the APPSSQ-like/PI hybrid composites and the pure PI are shown in Figures 7 and 8. The storage modulus is indicative of the elastic modulus, which is relative to the rigidity of a material. The APPSSQ-like particles in the hybrid composites possess Si—O—Si networks with a high crosslinked density, which enhances the stiffness of the APPSSQ-like/PI hybrid composites. Thus, the storage modulus of the hybrid composites increases as the APPSSQ-like content increases.

The glass transition temperatures ( $T_g$ ) from the  $\tan \delta$  peaks of these composites increase with increase of the APPSSQ-like content. Because the PI chains are tethered to the surface of the APPSSQ-like particles by covalent bonds, the motion of the PI chains is re-



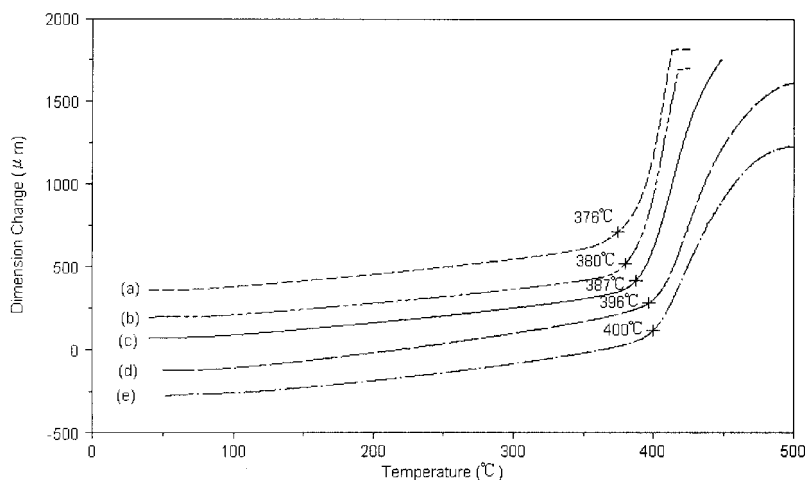
**Figure 8** Temperature dependence of  $\tan \delta$  and the glass transition temperatures (maximum values of  $\tan \delta$  peaks) of APPSSQ-like/PI hybrid composites with various APPSSQ-like contents: (a) 0 wt %; (b) 0.5 wt %; (c) 1 wt %; (d) 3 wt %; (e) 5 wt %.

stricted more severely. Therefore, the  $T_g$  increases as the APPSSQ-like content increases. Concurrently, the  $\tan \delta$  peak also becomes broader and its height becomes lower by the incorporation of APPSSQ-like particles in the PI matrix. The height of the  $\tan \delta$  peak at  $T_g$  is a measure of the energy-damping characteristic of a material, and the breadth of the  $\tan \delta$  peak is indicative of the relaxation process of the polymer chains. Owing to the good compatibility between the APPSSQ-like particles and the PI molecules, the highly crosslinked Si—O—Si networks directly enhance the stiffness of the hybrid composites, which results in the reduced height of the  $\tan \delta$  peaks of the APPSSQ-like/PI hybrid composites. Conceptually, the polymer chains of pure PI move in concert through the glass transition temperature, resulting in a sharp  $\tan \delta$  peak. Because of the adhesion between the APPSSQ-like particles and the PI molecules, the APPSSQ-like/PI hybrid composites have polymer chains that

resist the concerted motion that is characteristic of broader  $\tan \delta$  peaks.

#### Thermal expansion properties

Typical dimensional change versus temperature curves are shown in Figure 9. The effect of the APPSSQ-like content on the coefficients of thermal expansion (CTE, below and above the  $T_g$ ) and the reduced extent of the CTE of the hybrid composites is shown in Figure 10. It is observed that the CTE below and above the  $T_g$  decreases as the APPSSQ-like content increases, and the reduced extent of the CTE above the  $T_g$  is much higher than that below the  $T_g$ . This can be explained by that the highly crosslinked Si—O—Si networks inside the APPSSQ-like particles are more rigid than are the pure PI molecules and neither deform nor relax like PI molecules. Therefore, given the excellent compatibility between the



**Figure 9** Dimensional change versus temperature curves and the onset glass transition temperatures of APPSSQ-like/PI hybrid composites with various APPSSQ-like contents: (a) 0 wt %; (b) 0.5 wt %; (c) 1 wt %; (d) 3 wt %; (e) 5 wt %.



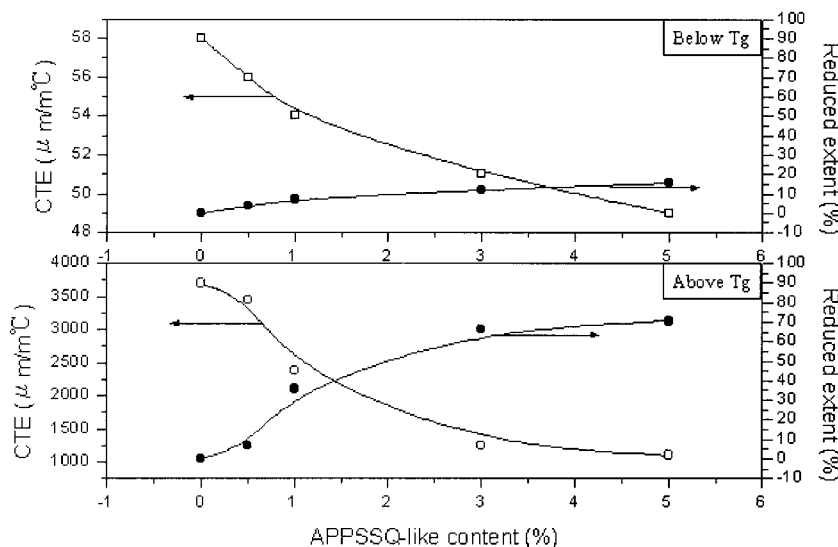


Figure 10 Effect of APPSSQ-like content on CTE and reduced extent of CTE of APPSSQ-like/PI hybrid composites.

APPSSQ-like particles and the PI molecules, the thermal expansion of the PI molecules is effectively retarded by the APPSSQ-like particles upon heating.

Figure 9 also shows the onset glass transition temperatures of these hybrid composites. It can be found that the  $T_g$  increases with increase of the APPSSQ-like content, which can be explained by that the covalent bonds between the APPSSQ-like particles and the PI molecules restrict the PI chains' mobility upon heating. Thus, the  $T_g$  of the hybrid composites is higher than that of pure PI. The tendency of the  $T_g$  from TMA is consistent with that from DMA.

**Thermal stability**

Figure 11 shows TGA curves of APPSSQ-like/PI hybrid composites. Figure 12 shows the effect of the

APPSSQ-like content on the decomposition temperature at a 5% weight loss. Notably, the hybrid composites possess higher decomposition temperatures than those of pure PI. This result can be explained by that the highly crosslinked Si—O—Si networks inside the APPSSQ-like particles possess higher thermal resistance than that of the PI molecules; therefore, the thermal resistance of the hybrid composites is improved.

**CONCLUSIONS**

APPSSQ-like, including the structures of crosslinking Si—O—Si networks inside and 3-aminopropyl groups outside the particle, was successfully generated from 3-APS via hydrolysis and condensation. With the incorporation of APPSSQ-like particles in the PI matrix,

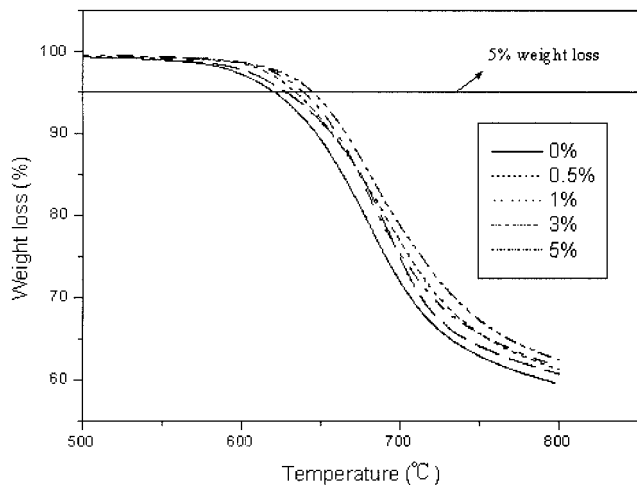


Figure 11 TGA curves (weight loss percent versus temperature) of APPSSQ-like/PI hybrid composites with various APPSSQ-like contents.

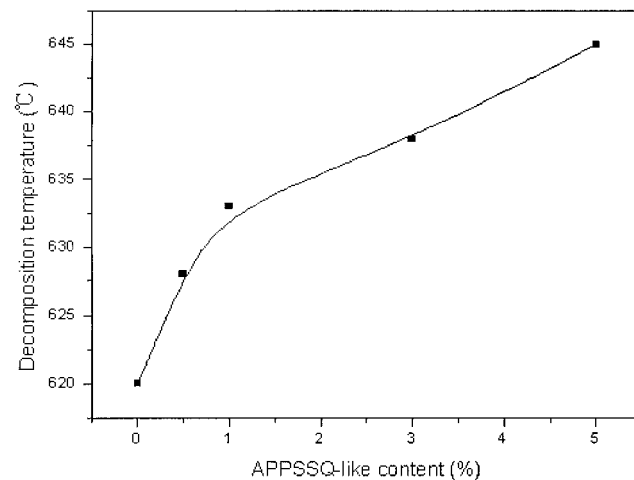


Figure 12 Effect of APPSSQ-like content on decomposition temperature (decomposition temperature versus content) at 5 wt % weight loss of APPSSQ-like/PI hybrid composites.

the highly crosslinked Si—O—Si networks and the presence of covalent bonds enhance the thermal and mechanical properties of APPSSQ-like/PI hybrid composites. Furthermore, the  $T_g$  of these hybrid composites also increases with the APPSSQ-like content, because the adhesion between the APPSSQ-like particles and the PI molecules restricts the PI chains' mobility upon heating.

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