# Preparation and Characterization of Organic–Inorganic Hybrid Composites Based on Multiepoxy Silsesquioxane and Cyanate Resin

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**ABSTRACT:** A multiepoxy cubic silsesquioxane was prepared by the hydrolysis and polycondensation of trifunctional monomer ($\gamma$-glycidoxypropyl)trimethoxysilane in a solvent mixture of methyl isobutyl ketone and anhydrous ethanol with a tetraethyl ammonium hydroxide aqueous solution acting as the catalyst, and it was successfully introduced into a cyanate resin and formed highly crosslinked organic–inorganic hybrid composites on a molecular level via a mutual cure reaction. The properties of the multiepoxy cubic silsesquioxane/bisphenol A dicyanate ester resin composites were investigated, and the results showed that introducing the cubic silsesquioxane unit into the cyanate resin successfully modified the local structure of the molecule, made the chain more rigid, restricted the chain mobility, and eventually improved the thermal stability and flame retardancy of the resin. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3652–3658, 2006

**Key words:** composites; resins; calorimetry

## INTRODUCTION

Silicon-based organic–inorganic composite materials have been studied to develop new materials with the properties of both organic and inorganic materials.[1] Polyhedral oligomeric silsesquioxanes (POSSs) are interesting organosilicon compounds, with the formula $[RSiO_{1.5}]_n$ ($n$ is an even integer),[2] that combine unique hybrid inorganic–organic chemical compositions with nanosized cage structures and offer a unique opportunity in this area for preparing truly molecularly dispersed composites.[3,4] POSS reagents can be incorporated into polymer chains to modify the local structure and chain mobility in polymeric materials[5–8] and eventually enhance the mechanical, thermal, and other physical properties of conventional polymer systems.[9,10] These enhancements have been shown to apply to a wide range of thermoplastics[11–15] and a few thermoset systems.[16–18] However, unlike silica, silicones, or fillers, each POSS molecule may contain a nonreactive organic substituent[19–22] and one or more covalently bonded reactive functionalities[23–26] suitable for grafting, polymerization, or blending[27–29] with a common organic polymer. Furthermore, through the proper choice of polymerizable R groups, the organic component can be varied to control the crosslinking density about the cube, the segment distances between the crosslinks, the packing of individual cubes with respect to one another, and the stability of the cube–organic bond.[30,31]

3-Glycidyloxypropyltrimethoxysilane (GTMS) is an organofunctional alkoxysilane monomer that can undergo both the sol–gel polymerization of the alkoxy groups and further form a hybrid network through the reaction between the functional epoxy groups with other functional groups and form covalent bonds between organic and inorganic phases.[32, 33] The polysilsesquioxane cluster formed from GTMS is intended as a precursor of crosslinking to form an organic–inorganic hybrid network through a reaction of the epoxy functionalities.[34] This article describes the polymerization of GTMS by the sol–gel process and formation of multiepoxy cubic silsesquioxane (SSQE) structures with pendant epoxy functionalities that are prone to a later reaction.

Cyanate ester resins have attracted much interest in recent years because of their excellent properties.[35,36] Cyanate/epoxy composites provide superior performance through the coreaction of cyanate esters with epoxies, modify the crosslinking density

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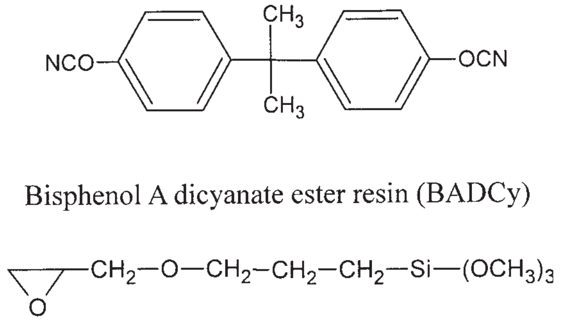


**Scheme 1** Chemical structure of the cyanate ester and silane.

of the network, and increase the extent of reaction of the individual functional groups; as a result, fine properties for a cyanate/epoxy composite can be obtained.[37] In this study, composites based on SSQE and cyanate ester resin were prepared through the coreaction of cyanate with epoxy groups attached to the Si atoms in the corner of cubic silsesquioxane. The characteristics of the composites, such as the thermal and flammability properties, were investigated.

## EXPERIMENTAL

### Materials

Bisphenol A dicyanate ester resin (BADCy), a white, particulate crystal, was obtained from Jinan Special Functional Material Co. with a molecular weight of 278.13 g/mol. ($\gamma$-Glycidoxypropyl)trimethoxysilane (GPMS), a colorless-clarity liquid, was supplied by Jingzhou Fine Chemical Corp. with a purity of 98%. Methyl isobutyl ketone [MIBK; $(CH_3)_2CH_2CH_2COCH_3$] was supplied by Tianjin BoDi Chemical Corp. Tetraethyl ammonium hydroxide ($Et_4NOH$; 25% aqueous solution) was obtained from the Shanghai Reagent Plant. Anhydrous ethanol was obtained from the Tianjin Baishi Chemical Plant. Hexane was supplied by the Tianjin New Fine Chemical Center. Dichloromethane was obtained from the Tianjin Fine Chemical Reagent Plant. All these reagents were analytically pure and were used without further treatment. The chemical structures of the cyanate resin and silane are given in Scheme 1.

### Preparation of SSQE

A solvent mixture of MIBK and anhydrous ethanol (200 mL) with a volume ratio of 50/50 was added to the flask. Then, GPMS (0.2 mol) and 3 equiv of deionized water were added to the solution. An aqueous 25% solution of $Et_4NOH$ (11.28 mL) was used as a catalyst. The reaction solution was stirred and heated to the boiling temperature and kept there for almost 3–7 days under reflux. The crude product was obtained after the removal of the solvents and was washed with methanol several times. The crude, white product was recrystallized by hexane/dichloromethane, and the pure compound was obtained.

Fourier transform infrared [FTIR (WQF-310 FTIR spectrometer); KBr, $cm^{-1}$]: $\upsilon$ C—H, 2930, 2856; $\delta$ C—H, 1415, 1270; $\upsilon$ C—O of the epoxy, 1233, 915; $\upsilon$ Si—O, 1122; $\upsilon$ Si—C, 1265, 760; $\upsilon$ C—O of the aliphatic chain, 1150.

The FTIR spectra showed that a relatively low number of Si—OH groups still persisted, as revealed by the presence of a small band at 3475 $cm^{-1}$.

NMR spectra were taken with an Inova 400 NWU400 spectrometer at about 20°C. The chemical shift ($\delta$) in the spectra used tetramethylsilane [$(CH_3)_4Si$] as the standard substance.

$^1$H-NMR (399.8 MHz, $CDCl_3$, 20°C, $\delta$, ppm): 2.67, 2.82 [oxirane ring, —$CH_2$—$CH$(O)$CH_2$], 3.42 [oxirane ring, —$CH_2$—CH(O)$CH_2$], 0.85 ($\alpha$-$CH_2$). $^{29}$Si-NMR (49.7 MHz, $CDCl_3$, 20°C, ppm): $-64$ to $-70$.

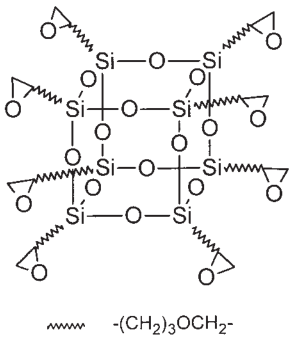
The four peaks and the maxima at $-65.4$ were assigned to Si atoms joined to three other Si atoms through Si—O—Si bonds.[32,34] A small peak at $-58.5$ was assigned to the presence of a small portion of incompletely condensed product.

Anal. Calcd (model 1106, Carlo Erba): C, 43.11%; H, 6.59%. Found: C, 42.93%; H, 6.68%. High thermal stability in an $N_2$ atmosphere: temperature at 95% weight loss = 357.89°C; char residue ($\Delta W_i$) = 43.38% (850°C).

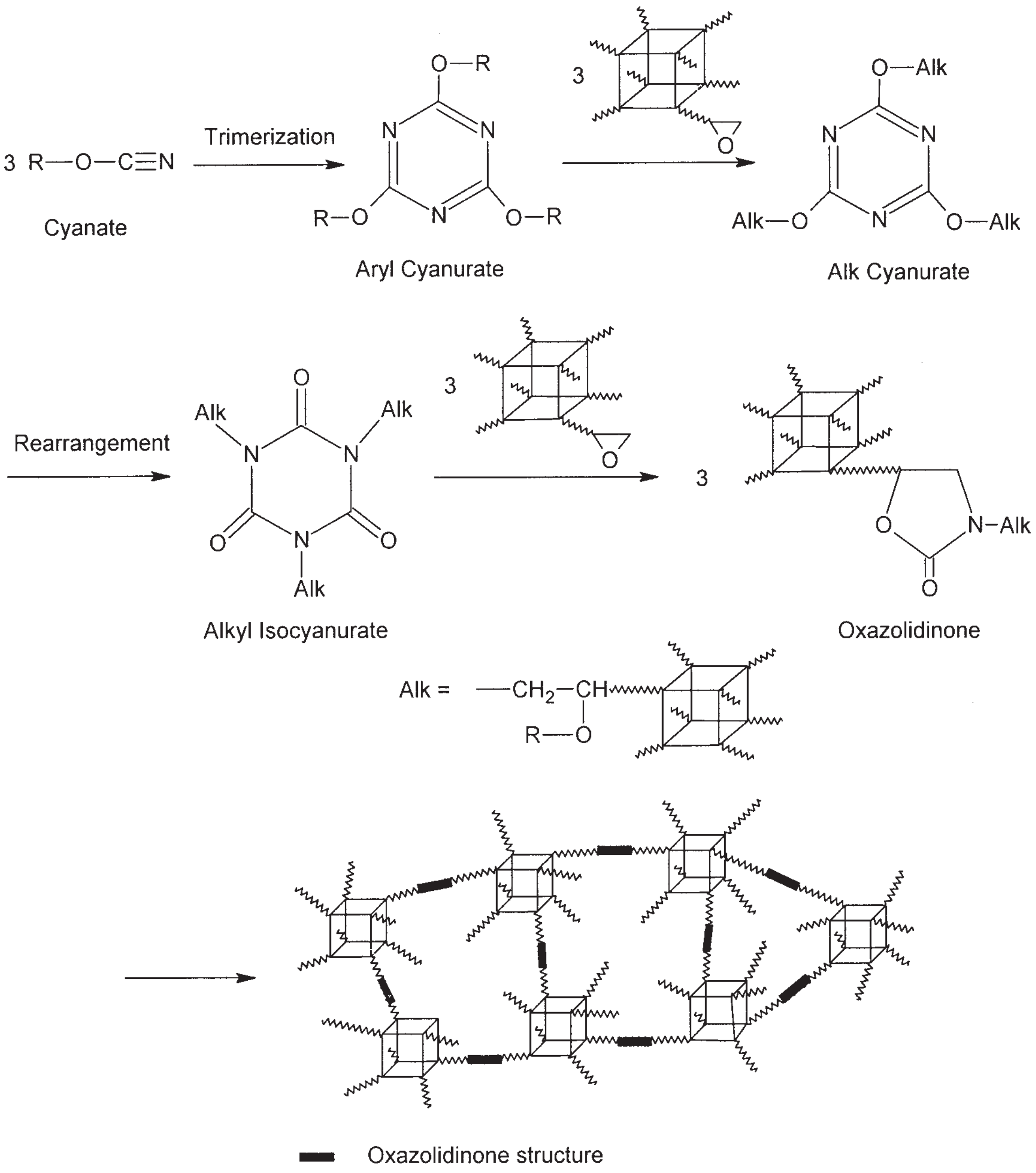
The ideal chemical structure of a multifunction silsesquioxane (SSQE) with eight epoxy groups is shown in Scheme 2.

### Preparation of the composite

Composites of BADCy and SSQE were prepared by a coreaction between —OCN groups in BADCy with the oxirane rings in SSQE under heating (Scheme 3). Various composites with different SSQE contents are shown in Table I. The composites with an SSQE/BADCy molar ratio higher than 1/1 are not listed in



**Scheme 2** Ideal chemical structure of SSQE.



**Scheme 3** Formation of the SSQE/BADCy hybrid composites.

**TABLE I**
**Hybrid Composites with Different SSQE Contents**

| Composite | SSQE content (phr) | BADCy content (phr) | SSQE/BADCy (molar ratio) | SSQE (mol %) |
|---|---|---|---|---|
| SSQE/BADCy-1 | 20 | 80 | 1/20 | 4.8 |
| SSQE/BADCy-2 | 40 | 60 | 1/7 | 12.5 |
| SSQE/BADCy-3 | 50 | 50 | 1/5 | 16.7 |
| SSQE/BADCy-4 | 60 | 40 | 1/3 | 25 |
| SSQE/BADCy-5 | 80 | 20 | 1/1 | 50 |

Table I for the higher epoxy content resulted in unreacted epoxy as litter molecules in the final composites and eventually the poor properties of these composites.

The curing schedule of each sample was determined by differential scanning calorimetry (DSC). The composite with a lower SSQE content (4.8 mol %) was cured at a lower temperature (200°C) in a short time, whereas a higher SSQE content (50 mol %) needed a higher temperature and a longer time to obtain the cured materials. Curing processing (150°C for 120 min, 180°C for 120 min, and 200°C for 180 min) was employed and modified properly according to the SSQE molar content.

### Measurements

The heat distortion temperature (HDT) was determined to study the thermomechanical behavior of the matrix systems. The heat deflection temperature of the samples was tested per ASTM D 648-72, which defines HDT of a test specimen as the temperature at which it has a 0.25-mm deflection under a given load.

Samples for the measurement of the glass-transition temperature ($T_g$) were prepared from the cured SSQE/BADCy composite, and this was followed by milling to obtain a fine powder. This powder (5–10 mg) was placed in the DSC cell, and the normal scanning procedures were carried out with a 2910 MDSC V4.4E thermal analyzer. The dynamic DSC scanning was carried out up to 450°C at a heating rate of 10°C/min in a nitrogen atmosphere (flow rate = 60 mL/min).

The thermal stabilities of the composites under nitrogen were tested with a TGA Q50 instrument (TA Instruments, Inc., United States). Samples (15–25 mg) were loaded into platinum pans and ramped to 1000°C (10°C/min/$N_2$). The $N_2$ flow rate was 60 mL/min.

Limited oxygen index (LOI) values were measured on a Stanton Redcraft flame meter according to the standard oxygen index test (ASTM D 2863/77) with sample dimensions of 100 × 6.5 ×3 mm. The percentage in the $O_2$–$N_2$ mixture at a flow rate of 16 L/min was deemed sufficient to sustain the flame and was taken as LOI.

## RESULTS AND DISCUSSION

### Reaction of SSQE with BADCy

The reaction between SSQE and BADCy was monitored by FTIR, and the spectra are shown in Figure 1. The absorption spectra of both the initial reactive mixture (before the reaction) and the reactive mixture heated at 150°C for 120 min are shown. A comparison of these two spectra shows that the curing at 150°C led to a drastic decrease in the optical density of the —OCN group band at 2270 $\mathrm{cm}^{-1}$ and to some decrease in the stretching vibration band of the epoxy ring at 915 $\mathrm{cm}^{-1}$. At the same time, the absorption peak of the band at 1370 $\mathrm{cm}^{-1}$ strongly increased, and the intensity of the band at 1680 $\mathrm{cm}^{-1}$ also grew. The band at 1370 $\mathrm{cm}^{-1}$ is related to a triazine ring vibration, which indicates cyanurate formation through the trimerization of BADCy at this temperature. The band at 1680 $\mathrm{cm}^{-1}$ may correspond to $\nu(\mathrm{C{=}N})$.[38] Further heat treatment of the sample at 180°C led to drastic drops in the intensity of the stretching vibration band of both the cyanate group and epoxy ring at 2270 and 915 $\mathrm{cm}^{-1}$, respectively. These two bands were disappeared completely after 300 min at 180°C. A new band at 1750 $\mathrm{cm}^{-1}$ was related to oxazolidinone that was formed through the reaction of epoxy and cyanate ester. According to the FTIR spectra, the Si—O—Si band at 1120 $\mathrm{cm}^{-1}$ showed no or little change,[39] and this indicated that the cubic silsesquioxane structure had been successfully introduced into the cyanate chain and formed the organic–inorganic hybrid composites on a molecular level.

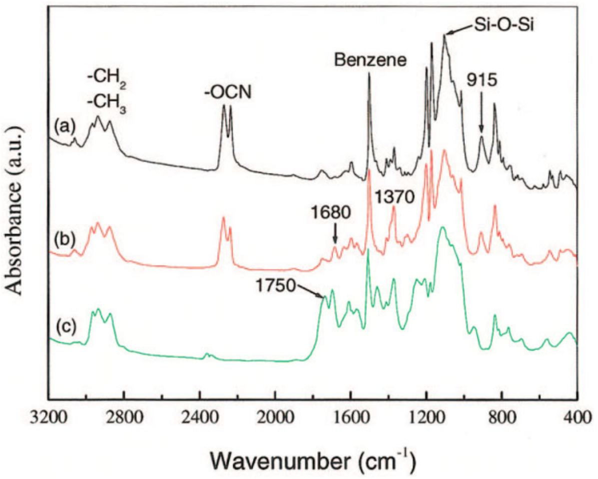


**Figure 1** FTIR spectra of the BADCy coreaction with 50 phr SSQE at different temperatures: (a) initial reaction blend at room temperature, (b) 150°C for 120 min, and (c) 180°C for 120 min and 200°C for 300 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Therefore, the reactions between SSQE and BADCy involved cyanurate formation through the trimerization of cyanate ester and oxazolidinone formation through the reaction of epoxy and cyanate ester. At a lower temperature, cyanurate formation dominated the curing reaction and the epoxy groups consumed little, whereas at the higher temperature, oxazolidinone formation was the main reaction. All the epoxy groups in the SSQE molecular structures were equally reactive, and the oxazolidinone ring structure in the composites acted as the crosslinker. SSQE and BADCy coreacted, and the resulting organic/inorganic hybrid composite formed with a structure of inevitably crosslinked networks, just as the following scheme shows.

### HDT

HDT of a material represents the upper stability limit of the material in service without significant physical deformation under load and thermal effects.[40,41] HDT values for SSQE/BADCy composites are presented in Figure 2. The curve shows that the HDT values depended on the SSQE content. At the lower SSQE content, the HDT values of the composites were lower than that of the polycyanate and decreased as the SSQE concentration increased to 12.5 mol %. The HDT

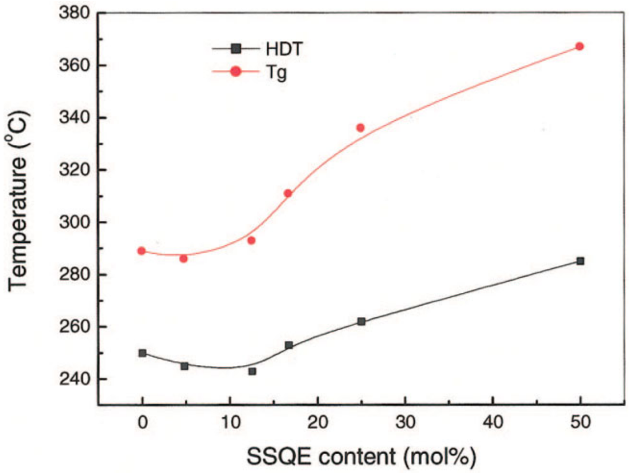


**Figure 2** HDT and $T_g$ values with different SSQE contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

values increased with increasing SSQE concentration and were higher than that of polycyanate with an SSQE concentration higher than 25 mol %. This result was different with the system of diglycidyl ether of bisphenol A (DGEBA)/BADCy composites, which had a lower HDT value than polycyanate, and HDT decreased with increasing DGEBA content.[36]

Introducing SSQE into BADCy had two effects on the final hybrid composites. One was the consumption of the rigid triazine ring for the reaction between the epoxy group and triazine ring, which reduced the stiffness of the molecular chain and lowered the HDT value. The other was bringing a large inorganic Si—O—Si cage structure into the molecular chain, which was rigid in nature and brought large steric hindrance to the molecular movement; therefore, a higher temperature was required to induce the chain motions, and as a result, the HDT value was higher. These two effects, caused by the incorporation of SSQE, dominated the stiffness and movement of the composite molecular chain and eventually decided the HDT values.

### $T_g$

A curing reaction may form a crosslinked structure, and $T_g$ of a cured network is related directly to the network crosslink density and the stiffness of the crosslinked chains.[42] $T_g$ of the composite was determined by DSC, and the results are shown in Figure 2. $T_g$ had a tendency similar to that of HDT. $T_g$ was lower than that of polycyanate at the lower SSQE concentration (4.8 mol %), whereas it was higher than that of polycyanate and increased with SSQE increasing when the SSQE concentration was higher than 12.5 mol %.

The decrease in $T_g$ with the composite containing 4.8 mol % SSQE might be due to the lower crosslinking density of the composite with the lower epoxy group content. Further increasing the SSQE content resulted in a stiffer molecular chain and a higher crosslinking density network. Moreover, the silsesquioxane cores were bulk in size and mass in nature; this restricted the segmental motion of the molecular chain and, as a result, the higher transition temperature ($T_g$) of the cured network.

### Thermal stability

Thermogravimetric analysis (TGA) curves of SSQE/BADCy composites with different SSQE contents are shown in Figure 3. The initial decomposition temperature ($T_i$; i.e., the temperature at which the weight loss was ca. 5%) and $\Delta W_i$ (taken as the weight percentage of the sample remaining after the TGA test) obtained from the TGA curves reflected the thermal stability of the final composites.[11] Table II summarizes the results of the TGA tests.

The $T_i$ values for polycyanate and the composite with 4.8 mol % SSQE were 411 and 388.32°C, respectively. $T_i$ decreased almost 23°C when the composite contained 4.8 mol % SSQE. This result was similar to that for a system of epoxy-modified cyanate;[36] the introduction of the epoxy group into cyanate made $T_i$ of the composite lower than that of polycyanate because of the consumption of the high-thermal-stability triazine ring through the reaction with the epoxy group. With increasing SSQE content, $T_i$'s of the composites were all higher than that of polycyanate and increased as far as 510.66°C with 50 mol % SSQE, in contrast to the common epoxy-modified cyanate system.

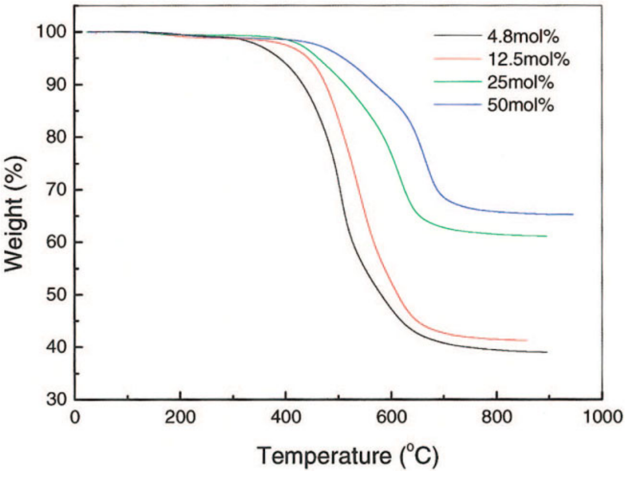


**Figure 3** TGA of SSQE/BADCy composites with different SSQE molar contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**TABLE II**
**Thermal Stability Data from the TGA Tests**

| | SSQE (mol %) | | | | |
|---|---|---|---|---|---|
| | 0 | 4.8 | 12.5 | 25 | 50 |
| $T_i$ (°C) | 411[a] | 388.32 | 443.88 | 462.67 | 510.66 |
| $\Delta W_1$ (%) at 800°C | 38[a] | 39.44 | 41.51 | 61.5 | 65.80 |
| $\Delta W_2$ (%) at 900°C | — | 39.02 | 41.26 | 61.12 | 65.27 |
| $\Delta W_1 - \Delta W_2$ (%) | | 0.40 | 0.25 | 0.38 | 0.53 |

[a] The data were obtained from http://www.polymerintermediates.com.

It is well known that the $T_i$ magnitude of a material is mainly determined by its chemical structure, such as the bond energy, defects inside the molecule, and reactivity of the bonds. The higher the bond energy is, the higher the thermal stability is. The higher energy bond of Si—O (422.5 kJ/mol) gave the composite higher thermal stability than the polycyanate system because there was no Si—O bond. Furthermore, the addition of the inorganic cubic structure of SSQE to the molecule also increased the ability of the composite to endure heating. As a result, $T_i$ of the composite with an SSQE concentration higher than 12.5 mol % was higher than that of polycyanate and increased with increasing SSQE concentration. This indicated that the incorporation of this special multiepoxy silsesquioxane into the cyanate resin increased the thermal stability of the cyanate resin.

$\Delta W_i$ ($N_2$) at 800°C for a composite containing 4.8 mol % SSQE (39.44%) was also higher than that of polycyanate (38%), as expected because of the inorganic silicon incorporation. It increased from 39.44 to 65.80% as the SSQE content increased from 4.8 to 50 mol %. $\Delta W_i$ of a material is determined by the contents of organic elements and inorganic elements in the molecules. The larger the mass is of the inorganic groups in the material, the higher its char residue yield is. There was about 34 wt % inorganic Si—O—Si in the SSQE molecule, and the formation of the composites introduced an inorganic cage structure into the molecular chain, so they had higher values of $\Delta W_i$ than the polycyanate network. The increase in $\Delta W_i$ with the SSQE concentration increasing was due to the higher inorganic content in the composites.

When the temperature increased from 800 to 900°C, $\Delta W_i$ for all the composites decreased little and remained almost unchanged. This suggested the high thermal stability of $\Delta W_i$. The conclusion was that the SSQE/BADCy composites not only had higher $\Delta W_i$ values but also had higher thermal stability of $\Delta W_i$ at higher temperatures. That is, these hybrid composites had high thermal stability.

### Flame retardancy

Silicon enhances flame retardation by the formation of stable char and through a solid-phase mechanism.[43,44] Research has shown that the addition of a relatively small amount of a silicon compound to various polymeric materials can significantly improve their flame retardance.[45,46]

The flame retardancy of the SSQE/BADCy hybrid composites was investigated by the measurement of their LOI values, and the results are listed in Table III. With the SSQE concentration increasing from 0 to 50 mol %, the LOI values of the composites were raised from 32 to 61 and demonstrated a significant improvement in the flame retardancy of the composites. The incorporation of SSQE into the cyanate resins was beneficial for improving their flame retardancy.

This performance was based on the concept that silsesquioxane produces a lot of silica ($SiO_2$) char and interferes with the combustion process during heating, pyrolysis, ignition, or flame spreading. Thick char is a better thermal insulating layer; it undergoes slow oxidative degradation, prevents heat from reaching the remaining polymer, and eventually leads to remarkable improvements in the overall flame retardancy of SSQE/BADCy composites. Furthermore, both the amount of the char formed and the thermal stability of the char play important roles in flame retardancy. A TGA curve showed that the SSQE/BADCy composites had a higher char formation tendency with higher SSQE contents; in particular, a weight loss was almost not observed for the char from 800 to 900°C. This result indicated that silsesquioxanes not only favorably provide the formation of char but also provide thermal stability of char. Both of these factors gave the hybrid composites good flame retardancy.

## CONCLUSIONS

Organic–inorganic hybrid composites were prepared via the cocured reaction of SSQE and cyanate resin

**TABLE III**
**Flame Retardance of the SSQE/BADCy Composites**

| | SSQE content (mol %) | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 4.8 | 12.5 | 16.7 | 25 | 50 |
| LOI | 32 | 35 | 41 | 48 | 53 | 61 |

BADCy. The coreaction of SSQE and BADCy was monitored with FTIR spectra, and the results showed that the coreaction was similar to that of the common epoxy-modified cyanate resin and that the cubic silsesquioxane structure experienced no or little change during the whole reaction process. The structure and properties of the composites were characterized and largely depended on the SSQE concentration. A lower SSQE concentration (4.8 mol %) resulted in lower stiffness of the molecular chain, lower crosslinking density, an inorganic group contained in the hybrid composites, and eventually lower HDTs, $T_g$'s, and thermal stability. Higher values were obtained with SSQE concentrations higher than 12.5 mol %. A high SSQE concentration led to hybrid composites with a higher crosslinked hybrid network, bulk size, and mass cubic silsesquioxane structure and, as a result, excellent flame-retardant properties and good thermal stability.

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