Thermal and Dielectric Properties of Bismaleimide-Triazine Resins Containing Octa(maleimidophenyl)silsesquioxane

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ABSTRACT: Octa(maleimidophenyl)silsesquioxane (OMPS) was synthesized, characterized, and employed to modify the BT resin which composed of 4,4′-bismaleimidodiphenylmethane (BMI) and 2,2′-bis(4-cyanatophenyl)propane (BCE). The curing reaction between OMPS and BT resin was first investigated. It was found that OMPS accelerate the curing reaction of BCE, and the onset temperature of the cyclotrimerization was reduced up to 95.5°C (by DSC). As demonstrated by DSC and FTIR, there was no evidence that indicated the coreaction between maleimide and cyanate ester. 2,2′-diallyl bisphenol A (DBA) and diglycidyl ether of bisphenol A (E-51) (Wuxi Resin Factory, Jiangsu Province, China) were also used to enhance the toughness of BT resin, and the formulated BTA (containing DBA) and BTE (containing E-51) resins were obtained. The thermal properties of BT, BTA, and BTE resins incorporated with OMPS were then investigated. The results of DMA and TG showed that the BT, BTA, and BTE resins containing 1 wt % of OMPS exhibit enhanced thermal properties in comparison with their pristine resins respectively, while more contents of OMPS may impair the thermal properties of the polymer matrix, though the effect of OMPS was slight. Finally, the dielectric constant of these hybrid materials were detected, and their dielectric constant were distinctly reduced by the incorporation of OMPS, while overmuch contents of OMPS were disadvantageous for dielectric constant because of the aggregation of OMPS. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3114–3121, 2008

Key words: bismaleimide-triazine resin; silsesquioxane; dielectric constant; thermal properties

INTRODUCTION

Bismaleimide-triazine resins (BT resins), derived from the blend of dicyanate ester and bismaleimide resins, claim superiority over the component homopolymers in terms of physical and mechanical characteristics. Whereas, bismaleimide resins confer thermal stability, good fire resistance, low water absorption, and good retention of mechanical properties at elevated temperature, especially in hot/wet environment,[1–3] while the dicyanate esters impart processability, toughness (comparing with bismaleimide), and low dielectric constant.[4–7] BT resins were developed by Mitsubishi Gas Chemical company in 1978,[8] while were not made available until 1985 by Hi-Tek Polymers, who marketed a series of resin systems for both circuit board and advanced composite applications. So far, with so many attractive properties, a wide variety BT resins have been investigated in the applications of aircraft, reinforced plastics, injection-molding powders, circuit boards, electric motor coil windings, and semiconductor encapsulants, etc.[9,10]

The curing mechanism of BT resins system is highly controversial and sometimes conflicting, and now is still not well established. Hong et al.[11] investigated the cure reaction of 4,4′-bismaleimidodiphenylmethane and bisphenol A dicyanate by DSC and FTIR, and found coreaction between maleimide and cyanate groups occurred to form pyrimidine and/or pyridine structures, which were superior to the cyclotrimerization of cyanate group. Lin et al.[12] depicted the coreaction between dicyanate esters and maleimide by employing model compounds with the help of DSC, FTIR, and NMR, they claimed that the pyrimindine and/or pyridine structures were formed and pyrimidine structures always predominated. On the other hand, many researches believed that the BT resins are an interpenetrating network (IPN) because the resultant blends had two T_gs, which implied the microphase separation structure.[13–15] Barton et al. using model compounds and
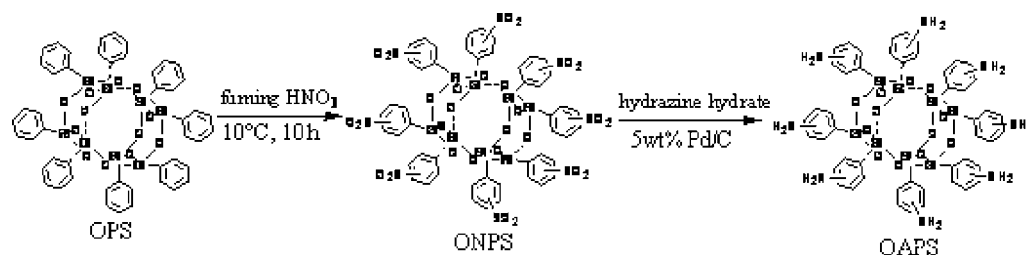
Scheme 1 Synthesis of OAPS.

with the help of heteronuclear solution,^{15}N NMR found no evidence that supported the formation of pyrimidine and/or pyridine structures.[14,15] Nair and Francis found two-stage cure reaction in the blend system by DSC and DMA.[16] However, Liu et al. reported that the dicyanate ester and bismaleimide, with dicyanate catalyst or noncatalyst, cured independently and formed two kinds of network: polycyanurate and polybismaleimide, moreover a ring-closure catalyst resulted in the coreaction between two components and formed a homogeneous network.[17] In the article, the curing mechanism of the composites system is also discussed.

Polyhedral oligomeric silsesquioxanes (POSS) are a family of nanoscale chemical structures that contain a silicon/oxygen core based on $(SiO_{1.5})_n$ and have each apex (i.e., silicon atom) connected to some organic group.[18–20] It is this combination of an inorganic core covered with an organic shell at the molecular level that has led POSS structures to being labeled as hybrid materials.[21] The most easily prepared, commercially available, and widely studied POSS structures have a core unit of eight silicon atoms: $(RSiO_{1.5})_8$ with R being a wide variety of neutral and charged organic functionalities.[22,23] POSS molecules are uniformly porous in nanometer-range size, and these nanopores contain air (dielectric constant close to 1), so pure nanoporous POSS macromolecules have been shown to have a very low dielectric constant (2.1–2.7).[24] Leu et al. synthesized several polyimides tethered with POSS, and the nanocomposites had low dielectric constants.[25] Liang et al. reported that one corner missing POSS incorporated in cyanate ester resin improved the thermal and mechanical properties of polycyanurate.[26] Wright et al. tethered POSS to dicyanate ester and obtained discrete micelle-like structures.[27] To the best of our knowledge, there is no report on POSS-BT resins. In the work, a kind of POSS (OMPS) was employed to modify BT resin, and it is anticipated that the dielectric property of the hybrid materials is promoted.

In this subject, octa(maleimidophenyl)silsesquioxane (OMPS) is synthesized and characterized by FTIR, NMR, DSC, GPC, and matrix assisted laser desorption ionization-time of flight mass spectroscopy (MALDI-TOF MS). BT resin composed of 4,4′-bisma-

leimidodiphenylmethane (BMI) and 2,2′-bis(4-cyanatophenyl)propane (BCE) is employed. Based on the BT resin, 2,2′-diallyl bisphenol A (DBA) and diglycidyl ether of bisphenol A (E-51) are incorporated to improve the toughness of BT resin. Specifically, we focus our attention on the curing behavior of BCE-OMPS (BCE and OMPS blend, 5 : 1 weight ratio), pristine BT resin, and BT/OMPS composite. Simultaneously, the thermal and dielectric properties of BT, BTA, and BTE incorporated with OMPS are also investigated by DMA, TG, and dielectric analysis (DEA).

EXPERIMENTAL

Materials

Octa(phenyl)silsesquioxane (OPS) was synthesized in our lab. Diglycidyl ether of bisphenol A (E-51) and 2,2′-diallyl bisphenol A (DBA) were purchased from Wuxi Resin Factory, Jiangsu Province, China. 4,4′-Bismaleimidodiphenylmethane (BMI) was purchased from Honghu Bismaleimide Resin Factory, Hunan Province, China. BCE was purchased from Heijang Kinglyuan Pharmaceutical Co., Ltd., Shangyu, Zhejiang Province, China. The other materials and reagents are purchased form Beijing Chemical Reagents (Beijing, China).
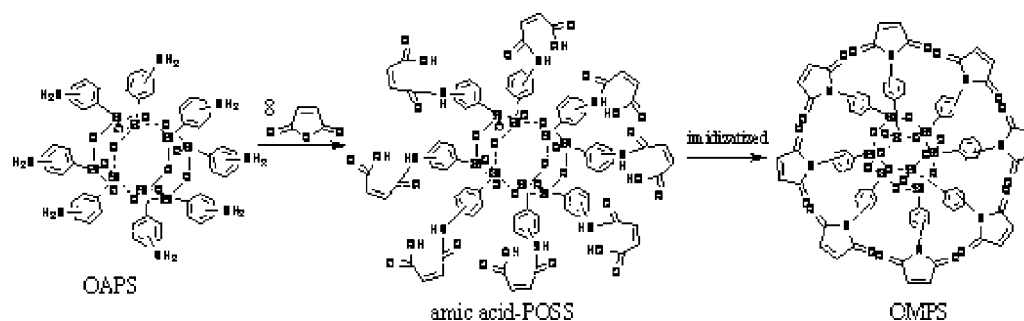
Synthesis

Octa(aminophenyl)silsesquioxane

Octa(aminophenyl)silsesquioxane (OAPS) was prepared with a procedure reported by Yu and coworkers,[28] and the route is described in Scheme 1.

FTIR (KBr powder, cm^{-1}): 3369, 3220 (N—H), 1120 (Si—O—Si). GPC: M_n = 1147, M_w = 1330, PD (polydispersity) = 1.16. ^{29}Si solid NMR (δ, ppm): −70.0, −77.5. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.8–6.0 (b, 2.0H), 5.3–3.7 (b, 1.0H).

Octa(maleimidophenyl)silsesquioxane

As shown in Scheme 2, OMPS was synthesized with a similar procedure according to Ni and Krishnan et al.[29,30] In a 100-mL three-necked flask equipped with condenser and N$_2$ inlet, OAPS (4.039 g, 3.5

Scheme 2 Synthesis of OMPS.

mmol) and 20 mL of DMF (*N*,*N*-dimethylformamide) were placed. Twenty-milliliter THF solution containing maleic anhydride (2.75 g, 28 mmol) was titrated in OAPS solution at room temperature. The mixture was stirred at room temperature for 2 h under N_2. Acetic anhydride (6.63 mL) and triethylamine (0.56 mL) were added, and then the solution was heated at 60°C for 3 h under N_2. After cooling to room temperature, ethyl acetate (50 mL) was added and the resulting solution was washed with water for two times. The separated organic layer was precipitated into petroleum ether (bp: 60–90°C). The yellowish powder was collected by filtration and dried under vacuum at 60°C. Yield 4.75 g (75.6%, 2.65 mmol). The results of MALDI-TOF MS illuminated that the product (OMPS) contain some oligomers.

FTIR (KBr powder, cm^{-1}): 1126 (Si—O—Si), 1380 (C—N), 1717 and 1777 (C=O, imide), 3103 (C—H, imide). ^{1}H NMR (DMSO-d_6, δ, ppm): 8.0–7.3 (b, 1.0H), 7.3–6.8 (b, 0.6H). GPC: M_n = 1743, M_w = 1991, PD = 1.14. MALDI-TOF MS: the signals (1935, 2006) indicating some oligomers existence.

BCE-OMPS blend preparation

BCE and OMPS (5 : 1 weight ratio) were dissolved in THF; the solvent was evaporated at room temperature, and then a homogenous blend was obtained due to their similar excellent dissolvability. The blend was degassed in vacuum oven at room temperature for 12 h. DSC and FTIR was employed to detect their cure behavior.

Prepolymers preparation

BMI and BCE with addition compounds (DBA, E-51) were mixed respectively, with stirring at 130°C for 20 min to form amber-colored transparent homogeneous mixtures, and then OMPS with different contents (1, 2, 4, and 8 wt %) were added in the mixtures, and further stirring for 5 min were needed to obtain brown transparent homogenous mixtures. The components of the prepolymers are listed in Table I.

DSC analysis of monomers, blend, and prepolymers

DSC was performed on DSC-Pyris with a heating rate of 10°C/min from room temperature to 350°C using a nitrogen purge and an empty aluminum pan as reference, the gas flow rate was 20 mL/min.

To get a clear understanding on the cure behavior of OMPS in BT resin, a series of similar DSC experiments were conducted on the monomers (BCE, BMI, and OMPS), blend (BCE-OMPS), and prepolymers (BT0, BTPS (BT0 and OMPS, 5 : 1 weight ratio)).

FTIR analysis of stepwise curing samples

FTIR spectra were recorded on a Nicolet-60SXB FTIR spectrometer at room temperature. The powder samples were mixed with the KBr and pressed into small flakes. The viscous samples were coated on the KBr plane uniformly. In all cases, 64 scans at a resolution of 2 cm^{-1} were used to record the spectra.

Using a stepwise curing procedure, BCE-OMPS, BT0, and BTPS were heated at 160°C for 30 min, 190°C for 30 min, 220°C for 30 min, and 250°C for 30 min, respectively. At every temperature, the samples were fetched out and prepared to FTIR detection.

DMA analysis of BT, BTA, and BTE composites containing OMPS

DMA was taken on a Rheometri Scientific^{TM} DMTA-V, the specimen with dimensions of ~ 25 × 6 × 1.5 mm^3 was tested in torsion fixture with a frequency of

TABLE I
Formulated Prepolymers Based on BCE and BMI

Prepolymers	Components	Ratio
BT0	BCE : BMI	1 : 1 (weight ratio)
BT1–4	BT0/OMPS	1, 2, 4, 8 wt % (OMPS)
BTPS	BT0 : OMPS	5 : 1 (weight ratio)
BTA0	BCE : BMI : DBA	5 : 3 : 2 (weight ratio)
BTA1–4	BTA0/OMPS	1, 2, 4, 8 wt % (OMPS)
BTE0	BCE : BMI : E-51	5 : 3 : 2 (weight ratio)
BTE1–4	BTE0/OMPS	1, 2, 4, 8 wt % (OMPS)

1 Hz, and the sample was heated at a rate of 5°C/min from room temperature to 350°C.

BT (0–4), BTA (0–4), and BTE (0–4) were impregnated in metallic molds (40 × 8 × 2 mm³) and degassed under vacuum at 140°C for 2 h, and then cured by programmed heating as follows: 160°C/1 h, 180°C/1 h, 200°C/1 h, 220°C/1 h, 250°C/1 h. After cooling to room temperature, the samples were ejected from the molds and cut/polished where necessary for uniform dimensions.

TG analysis of BT, BTA, and BTE composites containing OMPS

A Perkin–Elmer TGA-7 thermal gravimetric analyzer was used to investigate the thermal stability of the composites. All the tests were conducted in nitrogen atmosphere from room temperature to 700°C at the heating rate of 10°C/min.

TG curves showed the thermal stability of the cured resins: BT (0–4), BTA (0–4), and BTE (0–4) resins.

## Dielectric constant analysis of BT, BTA, and BTE composites containing OMPS

Dielectric analysis experiments were performed with a WY2851-Q apparatus at room temperature by the two parallel-plate mode at 1 MHz. Disk samples of the cured resins with a dimension {5 mm (T) × 30 mm (D)} were prepared in the dielectric experiments.

RESULTS AND DISCUSSION

DSC analysis

The curing reactions of BT resin mainly consisted of addition polymerization of maleimide, cyclotrimerization of cyanate ester, and some by-reactions induced by catalyst/impurity. The reaction between maleimide and cyanate ester is still controversial. Snow reported that pure cyanate ester did not cure at all, and such noncatalytic curing is because of adventitious impurities.[31] For this reason, catalysts are usually used to reduce the curing temperature and time of cyanate esters. It has been reported that metal complexes, organometallic salts, and hydrogen donors (e.g., phenols, acids, etc.) are suitable catalysts for the cyclotrimerization of cyanate esters.[32,33] In this study, we find that the curing temperature of BCE is quite high, while OMPS can substantially reduce its curing temperature in this resin system.

Figure 1 shows the DSC curves of three monomers (BCE, BMI, and OMPS), one blend (BCE-OMPS), and two prepolymers (BTPS and BT0). The peak temperatures at 82 and 256.2°C in BCE profile respond to the melt point and cyclotrimeriztion. The addition
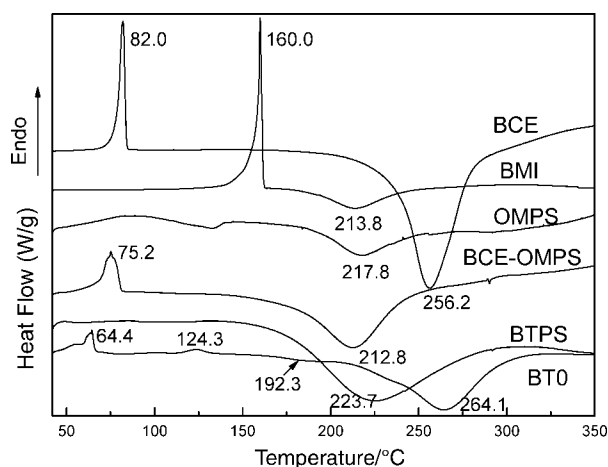

Figure 1 DSC curves of BCE, BMI, OMPS, BCE-OMPS, BTPS, and BT0.

polymerization of BMI and OMPS are closed at 213.8 and 217.8°C, respectively. BCE-OMPS curve depicts a broad peak at 75.2°C attributing to the eutectic melt of BCE and OMPS, while the onset and peak temperatures of polymerization of the blend occur at 95.5 and 212.8°C, respectively, which is much lower than that of BCE. The phenomenon indicates that OMPS may catalyze the polymerization of BCE. BT0 curve shows there are two blunt endothermic peaks at 64.4 and 124.3°C because of the eutectic melt derived from BCE (mp 82°C) and BMI (mp 160°C), there are also a weak broad exothermic peak at 192.3°C and an exothermic peak at 264.1°C corresponding to addition polymerization of BMI and cyclotrimerization of BCE. Comparing with BT0 curve, BTPS curve just has one exothermic peak at 223.7°C. There is no melting peaks in BTPS curve and the exothermic peak is higher than that of BCE-OMPS. The reason may be that the exothermic peak in DSC profile were retarded for the diffusion of cyanate ester group hindered by the network formed quickly during curing of the BTPS due to the addition of OMPS.

DSC results show that OMPS substantially reduce the curing temperature and accelerate the reaction of BCE-OMPS and BTPS. The detailed curing behaviors are investigated by FTIR spectra.

FTIR analysis

Figures 2–4 show FTIR spectra of the stepwise cured BCE-OMPS, BT0, and BTPS at different temperatures. In the three figures, it can be found that the characteristic absorption of cyanate ester appeared at 2272 and 2236 cm⁻¹ decrease and disappear finally with the cured process, and new absorption because of triazine structure emerges gradually around 1564 and 1379 cm⁻¹, which indicates the polycyclotrimeri-
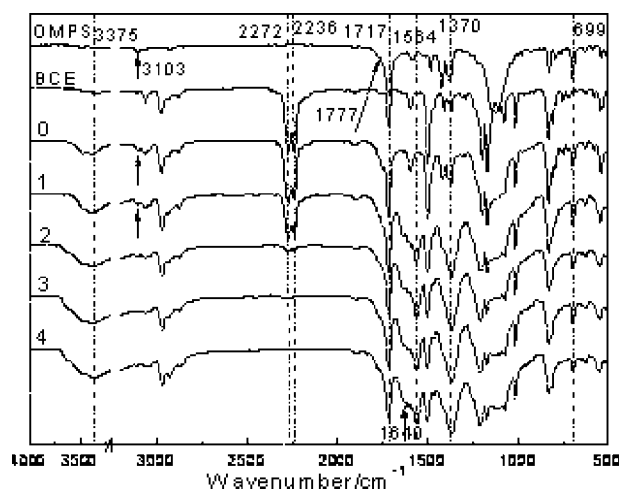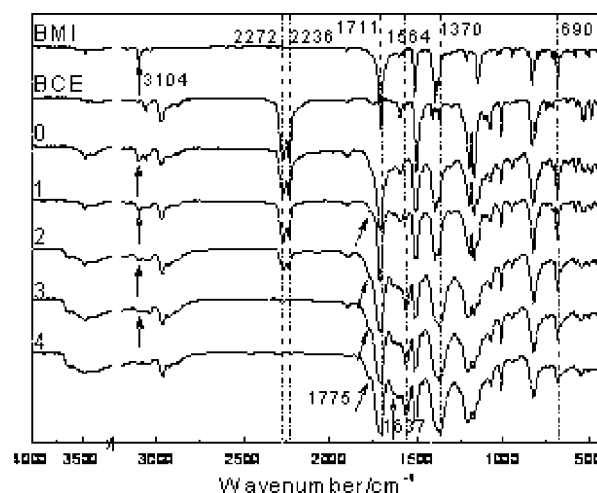
Figure 2 FTIR spectra of OMPS, BCE, and stepwise cured BCE-OMPS at different temperature (0: room temperature, 1: 160°C for 30 min, 2: 190°C for 30 min, 3: 220°C for 30 min, and 4: 250°C for 30 min).

Figure 3 FTIR spectra of BMI, BCE, and stepwise cured BT0 at different temperature (0: room temperature, 1: 160°C for 30 min, 2: 190°C for 30 min, 3: 220°C for 30 min, and 4: 250°C for 30 min).

zation of BCE. It can also be found that the characteristic absorption of maleimide around 3104 and 699 cm^{-1} (=C—H) decrease gradually during the curing process, the peak around 699 cm^{-1} does not disappear completely in the spectra of cured polymer at 250°C because of concomitant absorption due to the out-of-plane bending vibration of other C—H groups (aromatic) at the same frequency. It demonstrates the addition polymerization of maleimide. The characteristic absorption of the product (succinimide) appeared around 1717 and 1777 cm^{-1} (C=O of imide) overlap with the absorption of maleimide at the same frequency, moreover, the intensity of the peak around 1777 cm^{-1} is increased with the development of the curing process.

Figures 2–4 illuminate the polycyclotrimerization of BCE and the addition polymerization of maleimide (OMPS and BMI) respectively, while we cannot find the trace of pyrimidine and/or pyridine structures reported by Hong et al.[11] There is no evidence that confirmed the coreaction between maleimide and cyanate ester. The DSC profile of BT0 also shows two different curing temperature ranges of BMI and BCE, respectively. So we believe that, in these resin systems, maleimide and cyanate ester polymerize, respectively, by heating, and the coreaction between them does not occur.

The —OCN group of cyanate ester is strongly electrophilic and is easy susceptible for attack by nucleophilic reagents. The cyanate ester initiated by phenolic oxygen usually impart an iminocarbonate structure for the first step, and then the imidocarbonate reacts with two more —OCN groups to form the cyclotrimer. The formation of imidocarbonate is a critical step, and the imidocarbonate is the right accelerating species in the polymerization of cyanate ester.[34]

Scheme 3 depicts the possible reaction path for the polymerization of cyanate ester catalyzed by H$_2$O and hydrogen donors. When the hydrogen donor is phenolic compound, the imidocarbonate viz. cumyl imidoether is formatted for the first step in the reaction.

In Figure 3, the absorptions of —OCN are still distinct at 190°C (2-curve) and almost disappear at 220°C (3-curve), though BT0 was prepared by precured before measurement. However, the same absorptions of BCE-OMPS almost disappear at 190°C (2-curve) in Figure 2. While the precured BTPS has an obviously decreased peaks at room temperature (Fig. 4 0-curve), which indicates the polymerization of cyanate ester has been occurred quickly during
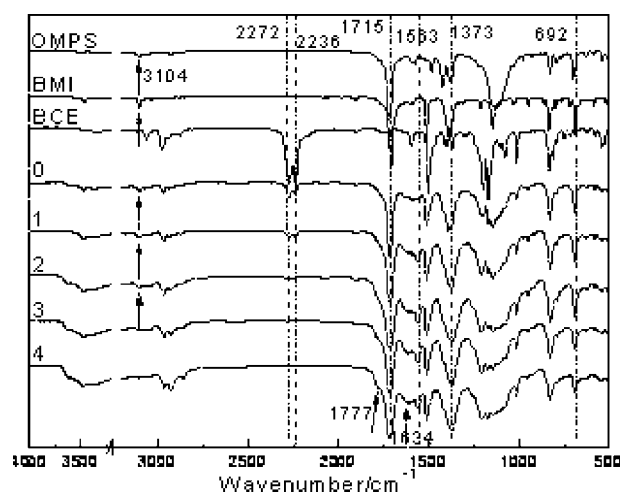
Figure 4 FTIR spectra of OMPS, BMI, BCE, and stepwise cured BTPS at different temperature (0: room temperature, 1: 160°C for 30 min, 2: 190°C for 30 min, 3: 220°C for 30 min, and 4: 250°C for 30 min).
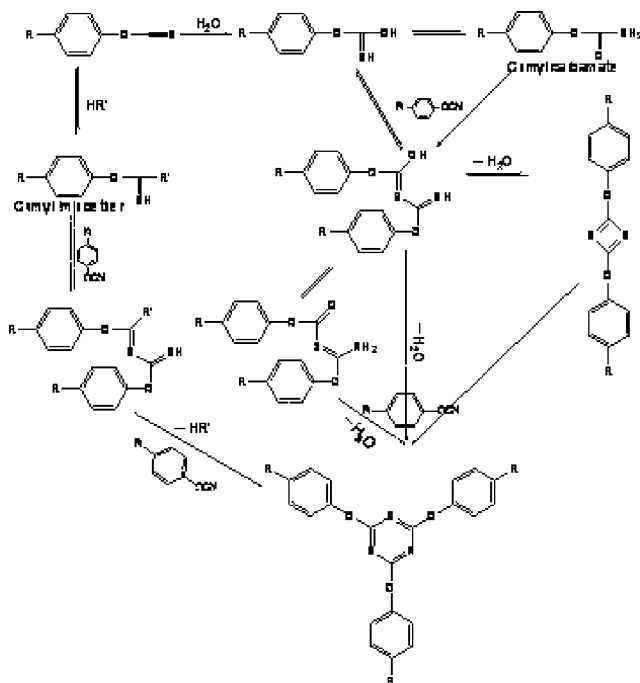
Scheme 3 Reaction mechanism for polymerization of cyanate ester catalyzed by hydrogen donors and H_2O.

precuring, and the peaks completely disappear at 190°C (2-curve). All these demonstrate that OMPS accelerate the polymerization of cyanate ester group. The broad absorption around 3375 cm^{-1} and weak peak around 1640 cm^{-1} in Figures 2–4 is due to the vibration of N—H and C=N of the imidocarbonate groups.

According to the results from DSC and FTIR, we speculate that OMPS accelerate the formation of imi-

docarbonate/cumyl imidoether, and so the temperature of cyclotrimerization is decreased and the reaction rate is accelerated, though the detailed catalysis mechanism of OMPS is not clear now.
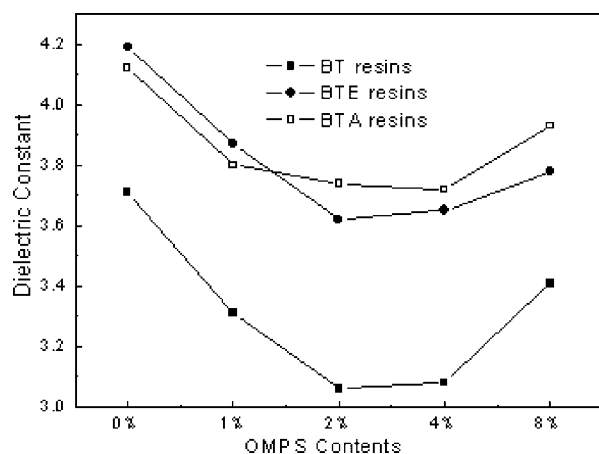
Thermal properties

Bismaleimide resins are good candidates for high-performance resin matrix due to their good thermal stability, good fire resistance, low water absorption, and so on; however, bismaleimide resins also suffer from brittleness due to high-crosslinking density after curing. Though, the crosslinking density of cyanate ester resins is lower than that of bismaleimide resins, the brittleness of BT resins is still needed to promote. 2,2'-Diallylbisphenol A (DBA) and epoxy resins are usually used to improve the toughness and processibility of BT resins while maintaining their good thermal properties.[4,35,36] In the study, DBA and E-51 are employed to modify BT resin, and we focus our attention on the effect of OMPS on the thermal properties of BT, BTA, and BTE resins.

The thermal properties of BT, BTA, and BTE resins detected by DMA and TG, and the data are listed in Table II. Converging these results, by and large, it can be found that the BT, BTA, and BTE resins containing OMPS display an enhanced storage modulus (E') (except for BT4, which may derive from the measurement error). For BT and BTE, the improvement of E' are distinct with 1 wt % content OMPS, while the content over 1 wt %, the E' of the resins are decreased instead. For BTA, the improvement of E' is almost constant. OMPS has a slight effect on the T_g, $T_{5\%}$, and $T_{10\%}$ of BT, BTA, and BTE resins,

TABLE II
DMA and TG Results of BT, BTA, and BTE Resins

Sample	DMA data			TG data		
	E_i' (GPa)	T_g (E'') (°C)	T_g (tan δ) (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Cy$_{700}$ (%)
BT0	1.29	272	285	439	453	50.3
BT1	2.03	273	282	451	462	51.2
BT2	1.90	270	281	445	456	51.5
BT3	1.37	268	280	437	448	51.8
BT4	1.18	261	277	439	450	53.4
BTA0	1.07	252	273	405	416	42.8
BTA1	1.33	257	276	406	415	43.7
BTA2	1.33	255	275	396	414	44.6
BTA3	1.30	257	279	403	414	45.4
BTA4	1.38	257	278	402	413	47.7
BTE0	1.04	268	288	386	400	39.4
BTE1	1.93	265	289	387	400	39.9
BTE2	1.70	264	285	384	398	40.7
BTE3	1.12	267	290	389	404	40.9
BTE4	1.33	271	292	386	401	43.0

E_i', initial storage modulus; T_g (E'') and T_g (tan δ), glass transition temperature from E'' and tan δ; $T_{5\%}$ and $T_{10\%}$, temperature corresponding to 5 and 10% weight loss from TG; Cy$_{700}$, char yield at 700°C from TG.

Figure 5 Dielectric constant (at room temperature, 1 MHz) of BT, BTA, and BTE resins with different OMPS contents.

and the hybrid materials maintain their thermal properties, sometimes the thermal properties are enhanced. The char yields (at 700°C) of BT, BTA, and BTE resins are uniformly increased with the increasing content of OMPS, which is because of the stable Si—O core in OMPS. It is obvious that the thermal properties of these hybrid materials are decided by their own components, curing reaction groups, crosslinking density, and so on. At the same time, it is believed that the incorporation of OMPS also lead to this outcome as follows: one is the nano-reinforcement effect of OMPS on the polymer matrix, which enhance the rigidity of the BT resins viz. enhance the E' and T_g; another is that OMPS may increase free volume by its nanoporous structure, and the Si—O core in OMPS leads to a plasticization of BT resins, which decrease the T_g of the BT resins; finally, aggregation of POSS usually occurs especially for high POSS containing in polymer matrix, which is not advantageous for the thermal properties of polymer.

Dielectric constant analysis

The signal propagating speed in an integrated circuit is inversely proportional to the square root of the dielectric constant. So a material with low dielectric constant will enhance the signal propagating speed and reduce the signal propagating loss.

Some researches reported that fluoromethylene, dimethylsiloxane, phosphorus, and POSS moieties in cyanate ester could reduce the dielectric constant of their polymers.[27,37–39] Hann et al. synthesized a series of bismaleimide and cyanate ester containing dicyclopentadiene/dipentene moieties, the modified BT resins exhibited lower dielectric constant.[40,41] In the study, OMPS are expected to reduce the dielectric constant of the BT, BTA, and BTE resins. The disk samples of the BT, BTA, and BTE resins with a

dimension {5 mm (T) × 30 mm (D)} were used, and their dielectric constant are shown in Figure 5. It can be found that these resins containing OMPS display lower dielectric constant in comparison with pristine BT0, BTA0, and BTE0 resins. BT, BTA, and BTE containing 2–4 wt % content of OMPS show the lowest dielectric constant, respectively, when OMPS content is up to 8 wt %, the dielectric constant of these resins is increased instead. The reason may exist in that the small content of OMPS dispersed in polymer matrix uniformly reduce the dielectric constant due to its nanoporous structure, while overmuch content of OMPS trend to aggregation, which may increase the dielectric constant of these hybrid materials.

CONCLUSIONS

Octa(maleimidophenyl)silsesquioxane (OMPS) was synthesized. DSC and FTIR were used to investigate the curing behavior of BCE and BT resins incorporated with OMPS. The results show that OMPS catalyze the curing reaction of BCE, which may be due to that OMPS accelerate the formation of imidocarbonate (the first step of cyclotrimerization), it can also be found that there is no evidence which demonstrated the coreaction between maleimide and cyanate ester. The thermal properties of BT, BTA, and BTE resins with different contents of OMPS were detected by DMA and TG, the results show that OMPS has a slight effect on the thermal properties of these resins, and the BT, BTA, and BTE resins containing 1 wt % of OMPS exhibit enhanced thermal properties in comparison with pristine BT0, BTA0, and BTE0 resins, while more content of OMPS may slightly impair the thermal properties of the polymer matrix. The dielectric constant of BT, BTA, and BTE resins were also measured, it can be found that OMPS distinctly decrease the dielectric constant of these hybrid materials, however, overmuch content of OMPS are disadvantageous for dielectric constant of these hybrid materials because of the aggregation of OMPS.

References

1. Wang, C. S.; Hwang, H. J. J Appl Polym Sci 1996, 60, 857.
2. Barton, J. M.; Hamerton, I.; Rose, J. B.; Warner, D. Polymer 1991, 32, 2482.
3. Hu, X.; Fan, J.; Yue, C. Y. J Appl Polym Sci 2001, 80, 2437.
4. Fan, J.; Hu, X.; Yue, C. Y. J Polym Sci Part B: Polym Phys 2003, 41, 1123.
5. Mathew, D.; Reghunadhan, N. C. P.; Ninan, K. N. J Appl Polym Sci 2000, 77, 75.
6. Wang, J. L.; Liang, G. Z.; Yang, J. Y.; Ren, P.; Zhao, W. G.; Fang, H. Q. China Plast 2004, 18, 46.
7. Lau, C.; Yong, L. M. Polymer 2002, 43, 823.
8. Gaku, M. (to Mitsubishi Gas Chem Company). U.S. Pat. 4,110,364 (1978).

9. Owusu, A. O.; Martin, G. C.; Gotro, G. T. Polym Eng Sci 1991, 31, 1604.
10. Owusu, O. A.; Martin, G. C.; Grotto, J. T. Polym Eng Sci 1992, 32, 535.
11. Hong, J. L.; Wang, C. K.; Lin, R. H. J Appl Polym Sci 1994, 53, 105.
12. Lin, R. H.; Lu, W. H.; Lin, C. W. Polymer 2004, 45, 4423.
13. Nair, C. P. R.; Francis, T.; Vijayan, T. M.; Krishnan, K. J Appl Polym Sci 1999, 74, 2737.
14. Barton, J. M.; Hamerton, I.; Jones, J. R. Polym Int 1992, 29, 145.
15. Barton, J. M.; Hamerton, I.; Jones, J. R. Polym Int 1993, 31, 95.
16. Nair, C. P. R.; Francis, T. J Appl Polym Sci 1999, 74, 3365.
17. Liu, X. Y.; Yu, Y. F.; Li, S. J. Polymer 2006, 47, 3767.
18. Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. Chem Rev 1995, 95, 1409.
19. Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. Chem Rev 1996, 96, 2205.
20. Laine, R. M. J Mater Chem 2005, 15, 3725.
21. Novak, B. M. Adv Mater 1993, 5, 422.
22. Neumann, D.; Fisher, M.; Tran, L.; Matisons, J. G. J Am Chem Soc 2002, 124, 13998.
23. Frankamp, B. L.; Fischer, N. O.; Hong, R.; Srivastava, S.; Rotello, V. M. Chem Mater 2006, 18, 956.
24. Su, R. Q.; Muller, T. E.; Prochazka, J.; Lercher, J. A. Adv Mater 2002, 14, 1369.
25. Leu, C. M.; Chang, Y. T.; Wei, K. H. Chem Mater 2003, 15, 3721.
26. Liang, K. W.; Li, G. Z.; Toghiani, H.; Koo, J. H.; Pittman, Jr., C. U. Chem Mater 2006, 18, 301.
27. Wright, M. E.; Petteys, B. J.; Guenthner, A. J.; Yandek, G. R.; Baldwin, L. C.; Jones, C.; Roberts, M. J. Macromolecules 2007, 40, 3891.
28. Zhang, J.; Xu, R. W.; Yu, D. S. J Appl Polym Sci 2006, 103, 1004.
29. Ni, Y.; Zheng, S. X. Macromol Chem Phys 2005, 206, 2075.
30. Krishnan, P. S. G.; He, C. B. J Polym Sci Part A: Polym Chem 2005, 43, 2483.
31. Snow, A. W. In Chemistry and Technology of Cyanate Ester Resins; Hamerton, I., Ed.; Blackie: London, 1994; Chapter 2, p 7.
32. Shimp, D. A. U.S. Pat. 4,604,452 (1986).
33. Shimp, D. A. U.S. Pat. 4,785,075 (1988).
34. Bauer, M.; Bauer, J. In Chemistry and Technology of Cyanate Ester Resins; Hamerton, I., Ed.; Blackie Academic and Professional: London, 1994; p 58.
35. Fan, J.; Hu, X.; Yue, C. Y. J Appl Polym Sci 2003, 88, 2000.
36. Gotro, J. T.; Appelt, B. K.; Papathomas, K. I. Polym Compos 1987, 8, 39.
37. Snow, A. W.; Buckley, L. J. Macromolecules 1997, 30, 394.
38. Maya, E. M.; Snow, A. W.; Buckley, L. J. Macromolecules 2002, 35, 460.
39. Lin, C. H. Polymer 2004, 45, 7911.
40. Hwang, H. J.; Li, C. H.; Wang, C. S. Polymer 2006, 47, 1291.
41. Hwang, H. J.; Shieh, J. Y.; Li, C. H.; Wang, C. S. J Appl Polym Sci 2007, 103, 1942.