

Methyl Silsesquioxane/Cyanate Ester Resin Organic–Inorganic Hybrids with Low Dielectric Constant

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ABSTRACT: A kind of nonfunctional oligomeric silsesquioxane (SSQ), methyl silsesquioxane (Me-SSQ), was used to modify cyanate ester (CE) resin in this article. First, Me-SSQ was synthesized by the hydrolysis and condensation of methyltriethoxysilane. Then, a series of Me-SSQ/CE hybrids containing 0, 1, 5, 10, and 20 wt % of Me-SSQ were prepared. The effect of Me-SSQ content on the reactivity, mechanical, dielectric, thermal, and hot/wet properties of materials was investigated. Fourier transform infrared spectroscopy was used to study the reactivity of hybrid CE resin systems, indicating that the addition of Me-SSQ does not show significant effect on the conversion of CE. Mechanical and dielectric properties of the Me-SSQ/CE hybrid materials were also studied. Impact

strength of the Me-SSQ/CE hybrids reaches its maximum value when Me-SSQ content is 5 wt %. However, the flexural strength reaches the maximum value when Me-SSQ content is 1 wt %. The Me-SSQ/CE hybrid containing 20 wt % of Me-SSQ shows a dielectric constant of 2.78, that is, much lower than the pure CE resin. At the same time, the dielectric loss of the Me-SSQ/CE hybrids was slightly increased ($\tan \delta < 0.006$). Therefore, Me-SSQ/CE hybrid is a promising candidate for high-performance printed circuit board matrix materials. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1004–1012, 2011

Key words: silsesquioxane; inorganic–organic hybrid materials; modification

INTRODUCTION

Owing to the excellent dielectric properties, mechanical properties, hot/wet resistance, and processability, cyanate ester (CE) resins have found wide application in high-frequency numeric printed circuit board (PCB), high-performance wave-transparent structural materials, and the structural materials in aero and space fields.^{1–5} After curing, CE monomers will form stiff network consisting of highly crosslinking triazine groups (see Fig. 1). The structure of pure cured CE cannot be used directly because of its brittleness. Usually, CE must be modified and toughened. The main modifiers for CE include thermoplastics,^{6,7} thermosetting polymers,^{8–10} and elastomers.^{3,11}

Silsesquioxane (SSQ) is a compound with the empirical chemical formula $\text{RSiO}_{1.5}$, where R is either

hydrogen or an alkyl, alkene, aryl, arylene group.¹² It can be random structure, ladder structure, cage structure, and partial cage structure.¹³ Polyhedral oligomeric silsesquioxane (POSS) is one of the most important nanostructured materials attracting much attention of materials scientists. It refers to the particular organosilicon compounds with the molecular formula of $(\text{RSiO}_{3/2})_n$.¹⁴ The octahedral or cube SSQ, usually called T_8 , with $n = 8$ is one of the most important SSQ compounds (see Fig. 2).^{15,16} SSQ is of great interest because of its excellent properties including mechanical properties, thermal stability, and especially for its low dielectric constant.^{17,18} For example, dielectric constant of methyl silsesquioxane (Me-SSQ) is ~ 2.7 . The dielectric constant in the 2.0–2.2 range can be achieved at porosity levels of $< 20\%$.¹⁹

With the miniaturization and the development of high speed of electronic components, a number of technologies such as digital simulation, high-speed digital data processing, and wide-frequency high-speed communication require high-performance polymer circuit board matrix materials with low dielectric constant and low dielectric loss.²⁰ At the same time, the dimension of integrated circuit devices continues to shrink; interconnection delay becomes a limiting factor to increase device speed.²¹ Therefore, it is necessary to use low dielectric constant (low- k) materials to reduce the capacitance between the metal interconnection.²²

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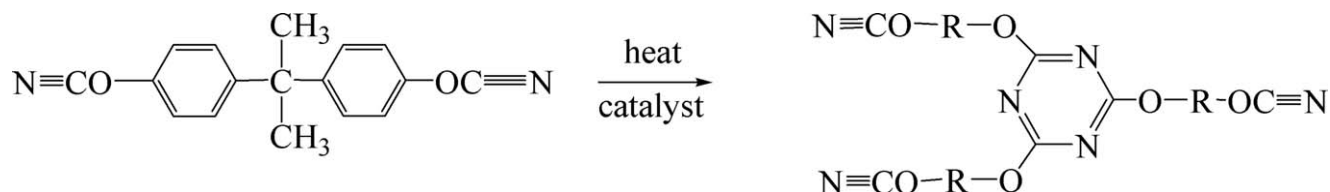


Figure 1 Curing of cyanate ester resin.

With the consideration of the low dielectric constant of SSQ, it is expected to obtain SSQ/CE hybrid materials with excellent dielectric properties by using SSQ to modify CE. Our group reported the synthesis and characterizations of two POSS compounds, octa(cyclohexyl)silsesquioxane and octa(aminopropyl)silsesquioxane in our previous studies,^{23,24} which were incorporated into epoxy and CE resins to prepare organic-inorganic hybrids showing excellent mechanical and thermal properties.²⁵⁻²⁸ Recently, many new POSS derivatives containing various functional groups such as multi-*N*-methylol groups²⁹ and epoxy rings³⁰ have been synthesized. A number of metal-containing POSS (Zr, Fe, Zn, and Al) were also reported.³¹⁻³³ They have been introduced into several polymer matrixes to form organic-inorganic hybrids.³⁴⁻³⁶ However, to date, Me-SSQ has not been incorporated into thermosetting resins including CE resins. CE resin monomers form highly crosslinking triazine groups with symmetric structure under heating.³⁷ The modifiers for CE resin may affect the curing reaction to some extent, i.e., the reactivity of CE resin.^{38,39} The reactivity is a vital factor to determine the curing techniques, even the final properties of materials.⁴⁰ Therefore, it is necessary to investigate the effect of Me-SSQ on the reactivity of CE resin. Furthermore, the dielectric properties of the CE resin/SSQ hybrids were not clear. In this research, the nonfunctional silsesquioxane Me-SSQ was used to form hybrids with CE, aiming to obtain Me-SSQ/CE hybrids with excellent dielectric properties. Me-SSQ/CE hybrid systems were studied in terms of curing reactivity, mechanical properties, and dielectric properties. The morphology, thermal stability, and wet/hot resistance were also investigated.

EXPERIMENTAL

Materials

Bisphenol A dicyanate (2,2'-bis(4-cyanatophenyl)isopropylidene) with purity >99.5 wt %, white particular crystal, was purchased from Shanghai Huifeng Kemao (Shanghai, China). Methyltriethoxysilane, colorless clear liquid, with purity >97 wt %, was produced by Jingzhou Jiangnan Fine Chemical, China. Methyl silsesquioxane was synthesized by the hydrolysis and condensation of methyltriethoxy-

silane. Typically, 9.7 mL of anhydrous alcohol and 7.2 mL of deionized water were added to 10 mL of methyltriethoxysilane in sequence under stirring. NaOH solution (1M) was used to adjust pH value to 8-9. The mixture was stirred for 48 h at 50°C to get white crystalline precipitate. The product was filtrated, washed with deionized water, and dried under vacuum at 100°C for 24 h to obtain a white powder.

Preparation of specimens

Bisphenol A dicyanate (BADCy) was melted at 100°C in oil bath, to which different amount of Me-SSQ was added under mechanical stirring. The blend was stirred to be clear and transferred to a stainless steel mold, which was coated with release agent on the inner walls and preheated to 120°C. The mold containing the resin blend was degassed at 90-100°C for 20 min in a digital vacuum oven. This was followed by cure procedures (120°C for 1 h, 150°C for 1 h, 180°C for 2 h, and 200°C for 4 h). Then, it was cooled to room temperature. At last, the cured resin plates were cut with a water coolant to required sizes: 15 mm × 10 mm × 4 mm (Type I), 27 mm × 27 mm × 4 mm (Type II), or 30 mm × 30 mm × 4 mm (Type III). Different hybrid resin systems containing 0, 1, 5, 10, and 20 wt % of Me-SSQ were prepared. They are designated as CE, MC1, MC2, MC3, and MC4, respectively. The compositions for various resin systems are listed in Table I.

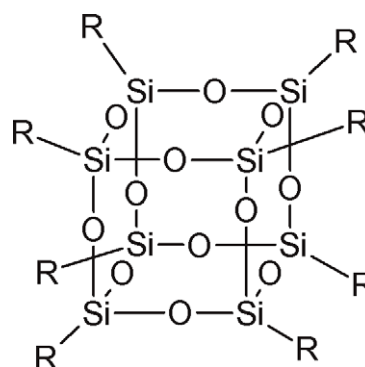


Figure 2 Structure of polyhedral oligomeric silsesquioxane (POSS).

TABLE I
Compositions of Different Cyanate Ester Resin Systems

Samples	CE (wt %)	Me-SSQ (wt %)
CE	100	0
MC1	99	1
MC2	95	5
MC3	90	10
MC4	80	20

Instrument and performance testing

Fourier transform infrared spectroscopy and determination of conversion of $-\text{OCN}$ group

The polymer solution was coated on the KBr pellet and subsequently dried in desiccators for 3 h at room temperature. An IBM instruments WQF-300IR spectrometer was used to study the cure reaction. Spectra were obtained in an optical range of $400\text{--}4000\text{ cm}^{-1}$ by averaging six scans at a resolution of 8 cm^{-1} to minimize the effects of dynamic scanning.

The height of the peak of benzene ring at 1500 cm^{-1} was adopted as the internal standard to investigate the conversion of $-\text{OCN}$ group, because the content of benzene ring in all curing systems studied in this research does not change. The conversion of CE group (α) was calculated according to eq. (1)⁴¹:

$$\alpha(t) = 1 - [H(t)_{2272}/H(t)_{1500}]/[H(0)_{1500}/H(0)_{2272}], \quad (1)$$

where $H(t)$ and $H(0)$ are the height of absorption peak at time t and time 0, respectively.

Mechanical, dielectric properties testing, and scanning electron microscopy

Ten specimens of Type I without obvious flaws were tested according to ASTM D 790 to obtain the flexural strength, and another 10 specimens of Type I were tested according to ASTM D 4812 to obtain the impact strength. At 1 MHz and 298 K, three specimens of Type II were used to determine the dielectric constant and dielectric loss. They were measured on S914 dielectric loss instrument with QBG-3B high-frequency apparatus manufactured by Shanghai Aishi Electronical Instrument Corporation according to GB1409-78 of China.

The micromorphologies of the cured resin were investigated by scanning electron microscopy (SEM) on a HITACHI S-570 SEM instrument. Fracture surfaces of the failure specimens were coated with gold by vapor deposition using a Polaron SC502 vacuum sputter coater for SEM observation.

DSC and TG

DSC measurement was performed with a Perkin Elmer DSC-7 supported by a Perkin Elmer computer

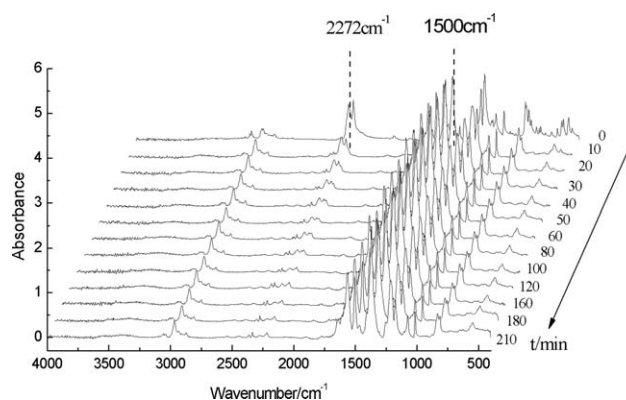


Figure 3 FTIR spectra of CE cured isothermally at 210°C .

for data acquisition: the DSC was calibrated with high-purity indium. Sample (8–10 mg) was weighed into small DSC aluminum pans, sealed with holed aluminum lids, and experiments were conducted under a nitrogen flow of $20\text{ cm}^3/\text{min}$. All the samples were subjected to a dynamic DSC scan from $50\text{ to }300^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$. Thermogravimetric analysis was performed using a Perkin Elmer TGA-7 microbalance coupled with a 1022 Perkin Elmer microprocessor. The microbalance was calibrated making use of the Curie points of perkalloy and nickel. The cured samples, about 7 mg, milled beforehand were placed in a Pt cell and heated at a rate of $10^\circ\text{C}/\text{min}$ from $30\text{ to }800^\circ\text{C}$ in air.

Water absorption

Three specimens of Type III were used for water absorption testing. Before testing, the specimens were placed at 100°C until their weights reached an asymptotic value (W_0). Then, the specimens were placed in boiling water. The weight gain (W_t) of each specimen because of moisture absorption was measured on a chemical balance after the removal of the moisture from the specimen surface by soft paper tissue. The moisture content was calculated as follows:

$$\text{Moisture content (\%)} = (W_t - W_0)/W_0 \times 100\%.$$

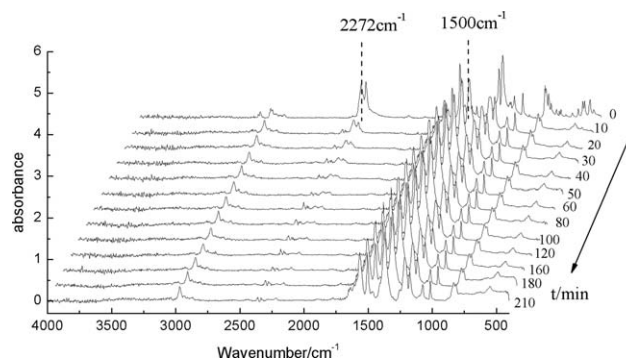


Figure 4 FTIR spectra of MC1 cured isothermally at 210°C .

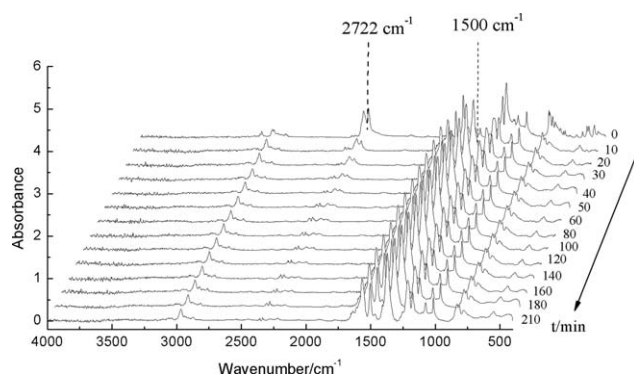


Figure 5 FTIR spectra of MC2 cured isothermally at 210°C.

RESULTS AND DISCUSSION

Reactivity of Me-SSQ/CE hybrid systems

Various Me-SSQ/CE systems were cured isothermally at 210°C and were monitored by Fourier transform infrared (FTIR) spectroscopy. Figures 3–7 are the FTIR spectra of CE, MC1, MC2, MC3, and MC4, respectively. The peaks at 830/3062 and 2872/2962 cm^{-1} are ascribed to the νCH in benzene ring and CH_3 , respectively. The peak at 1500/1600 cm^{-1} is the skeleton vibration of benzene ring. The absorption at 1012 cm^{-1} is due to $\nu\text{C}-\text{O}$. The absorption at 1369/1560 cm^{-1} is caused by the vibration of triazine ring. The peaks of 1073 and 780 cm^{-1} are attributed to $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{C}$, respectively.⁴² The characteristic absorption of $-\text{OCN}$ group is at 2272 cm^{-1} , with the intensity of which reduced during the curing reaction.⁴² Therefore, this absorption is used to calculate the conversion and monitor the curing reaction.

It can be seen that $-\text{OCN}$ group decreases during the curing reaction of CE. Figure 8 shows the conversion of $-\text{OCN}$ group as a function of time for various curing systems, showing that the conversion of $-\text{OCN}$ group increases with reaction time for all systems. All systems show a rapid increase of conversion at the initial stage (~ 25 min at the begin-

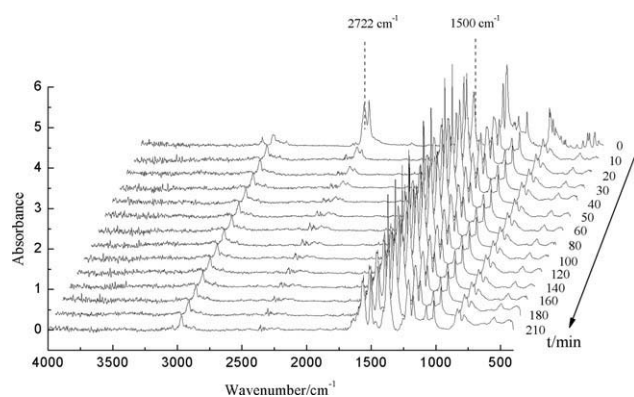


Figure 6 FTIR spectra of MC3 cured isothermally at 210°C.

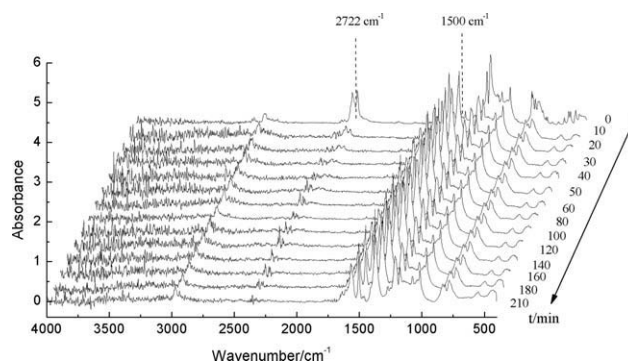


Figure 7 FTIR spectra of MC4 cured isothermally at 210°C.

ning). After that conversions increase slowly and go to a certain stable value. Comparison of the conversion curves for different systems indicates that the addition of Me-SSQ does not show significant effect on the conversion of CE. Besides, DSC was performed to further confirm the curing reactivity of the hybrid resin systems (Fig. 9). The reason is that lower peak temperature (T_p) indicates faster curing reaction.³⁹ The T_p of CE, MC1, MC2, MC3, and MC4 is 259.7, 257.7, 256.6, 253.6, and 250.5°C, respectively. The decrease of T_p on the DSC curves is not so significant with the increase of Me-SSQ content. A total of 20 wt % of Me-SSQ decreases the T_p of CE only by 9.2°C. On the whole, Me-SSQ does not influence the reactivity of CE significantly, that is, favorable for the determination of curing technique. It can be explained by the completely condensed structure and very stable chemical properties of Me-SSQ. It only possesses methyl groups showing no catalytic effect on the curing of CE. As a result, all the hybrid resin systems can be cured using the same curing procedures.

SSQ is a nanostructured material with organic-inorganic hybrid structure. Organic groups in SSQ

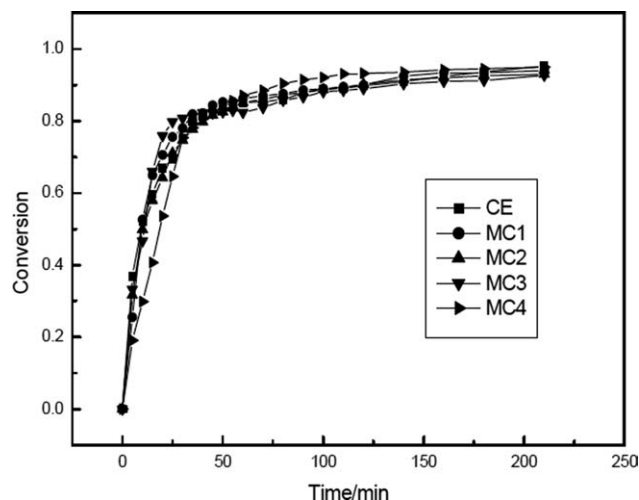


Figure 8 Conversion of $-\text{OCN}$ for various systems cured isothermally as a function of time.

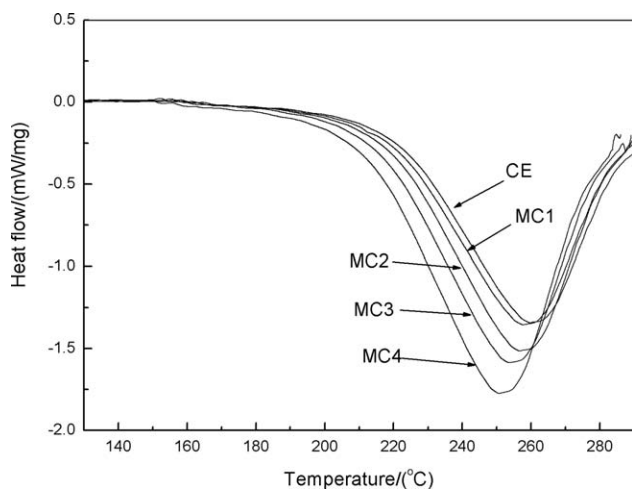


Figure 9 DSC curves of various Me-SSQ/CE hybrid resin systems.

molecules can reinforce its compatibility with matrix and help them to disperse in the resin matrix.⁴³ Figure 10 shows the formation of organic-inorganic network structure consisting of CE and Me-SSQ.

Mechanical properties of Me-SSQ/CE hybrid materials and SEM analysis

The relationship between mechanical properties of Me-SSQ/CE hybrid materials and Me-SSQ content is shown in Figure 11. It can be seen that both impact and flexural strengths increase first and decrease later with the increase of Me-SSQ content. Both mechanical strengths get to their maximum values at certain Me-SSQ content. Impact strength reaches the maximum value when Me-SSQ content is 5 wt %. On contrast, flexural strength reaches

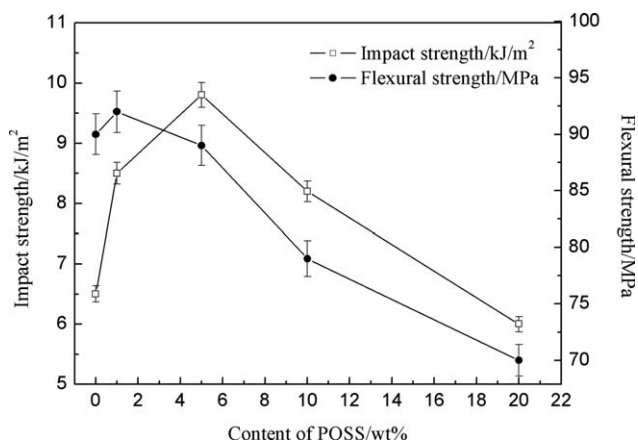


Figure 11 Mechanical properties of Me-SSQ/CE hybrid materials.

the maximum value when Me-SSQ content is 1 wt %. The increase of impact strength of materials is mainly due to two reasons. On the one hand, the uniformly dispersed Me-SSQ nanoparticles can attract energy when the materials break.²⁵ On the other hand, the addition of Me-SSQ can decrease the crosslinking density of triazine groups to some extent, so as to increase the impact strength. The improvement of flexural strength is mainly attributed to the peculiar properties of Me-SSQ, which are hybrid particles and can hinder the movement of molecular chains, increasing the stiffness of molecular chains.^{25,43} However, too high content of SSQ will inevitable cause serious agglomeration of nanoparticles, leading to the deterioration of mechanical properties, as shown later in the micro-morphology of materials. Figure 10 shows that when Me-SSQ content is 5 wt %, impact strength

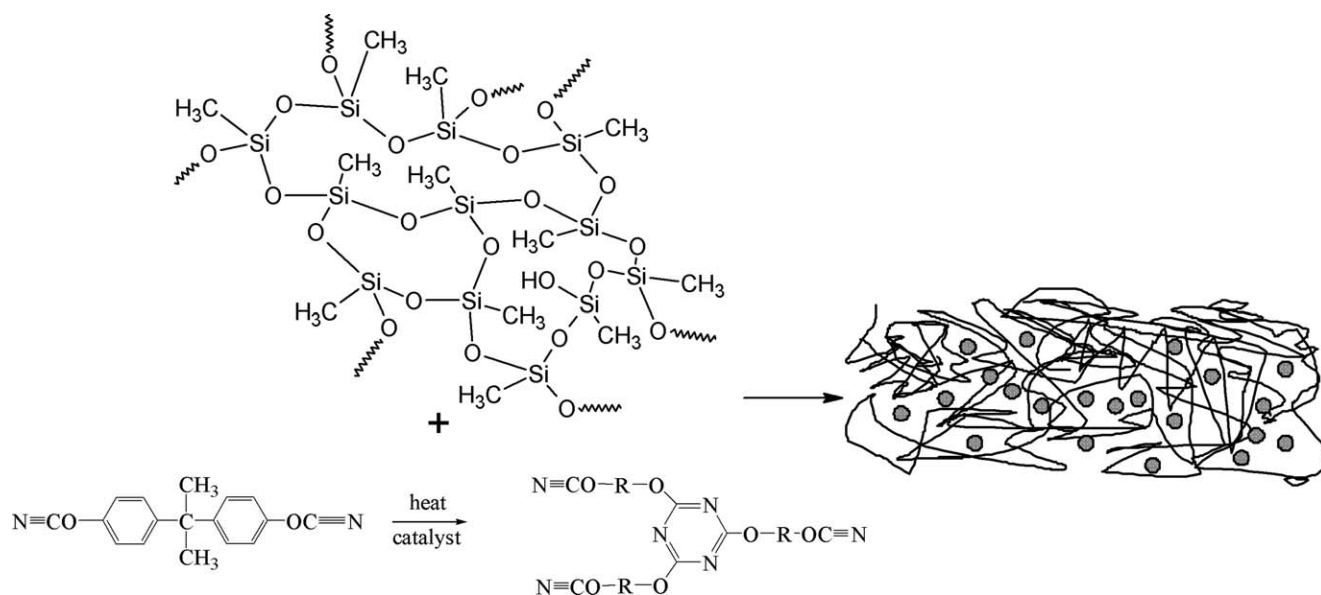


Figure 10 Formation of the organic-inorganic hybrid structure of the Me-SSQ/CE materials.

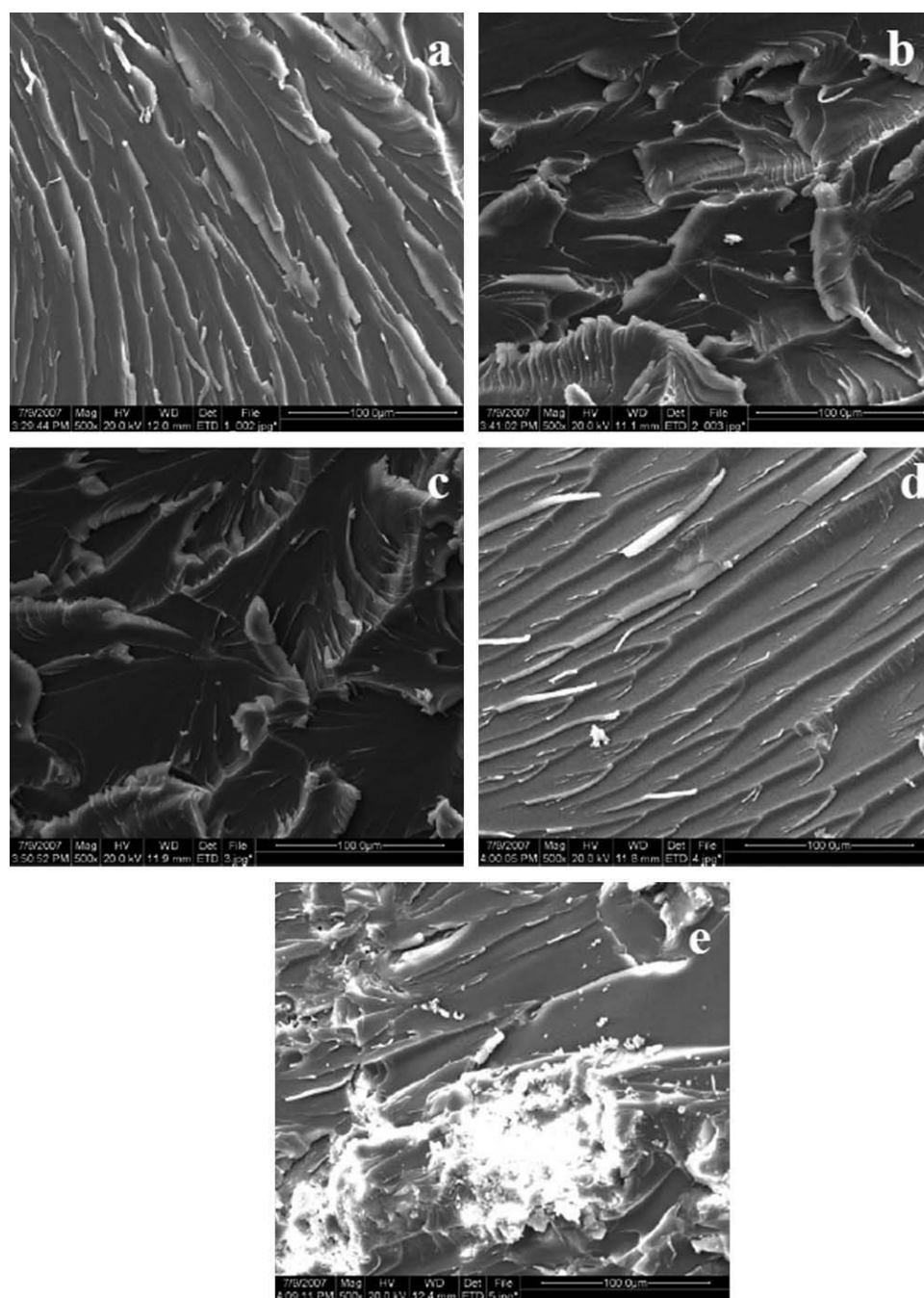


Figure 12 SEM images of the fracture surfaces of various Me-SSQ/CE hybrids. (a) CE, (b) MC1, (c) MC2, (d) MC3, and (e) MC4. The scale bar for all systems is 100 μm .

reaches the maximum value and flexural strength is also relatively high, i.e., system MC2 shows the optimum overall mechanical properties. Therefore, appropriate amount of Me-SSQ can improve impact and flexural strengths of CE at the same time.

The micromorphology of the fracture surfaces of various hybrid systems after impact break is studied by SEM to analyze the effect of Me-SSQ on the mechanical properties of CE, as shown in Figure 12. It can be seen that the fracture surface of pure CE is very smooth [Fig. 12(a)], showing the typical brittle

break.^{25,39} When Me-SSQ content is ≤ 5 wt %, a number of tough whirls that can absorb large amount of energy of break are observed. It indicates that MC1 and MC2 should possess higher mechanical strength [Fig. 12(b,c)]. When POSS content is 10 wt %, the fracture surface shows fiber pull-out characteristics locally [Fig. 12(d)], revealing that MC3 also possesses relatively high strength. However, serious agglomeration of Me-SSQ occurs when Me-SSQ is too high, leading to the remarkable decrease of mechanical properties [Fig. 12(e)].

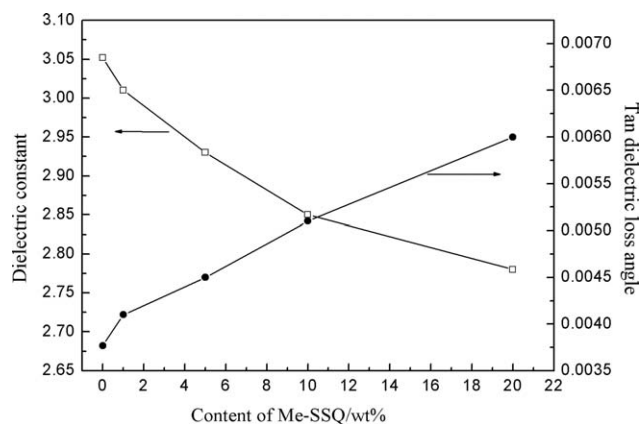


Figure 13 The relationship between the dielectric properties of Me-SSQ/CE hybrids and the content of Me-SSQ.

Dielectric properties of Me-SSQ/CE hybrids

The dielectric constant and dielectric loss are the two main indexes to characterize the dielectric properties of materials, especially for the polymeric PCB matrix.⁴⁴ Therefore, the effect of Me-SSQ content on dielectric constant (ϵ) and tangent dielectric loss angle ($\tan \delta$) of CE was studied. Figure 13 shows the ϵ and $\tan \delta$ vs. Me-SSQ content under testing frequency of 1 MHz. ϵ is a physical quantity that evaluates the polarization extent of mediums. It is dependent on the polarities of mediums.⁴⁵ It can be seen from Figure 13 that ϵ of materials decreases significantly with the increase of Me-SSQ content. This can be explained by the low dielectric constant of Me-SSQ. SSQs have lower ϵ (~ 2.7) than that of CE resin (3.0). The addition of Me-SSQ will inevitably decrease the ϵ of CE resin. In addition, ϵ decreases more significantly with the increase of Me-SSQ content at lower Me-SSQ content. For example, when only 5 wt % of Me-SSQ was added, ϵ decreased from 3.05 to 2.93, showing a decrease of 3.9%. While ϵ decreased from 2.85 to 2.78 when Me-SSQ content increased from 10 to 20 wt %, showing a decrease of 2.3%. The reason may be that higher content of Me-SSQ will destroy the orderly and symmetric structure of cured resin, resulting in the increase of ϵ .

Dielectric loss is dependent on the polarity of polymeric molecules and the density of polar groups. The higher the polarity of molecules and the density of polar groups, the higher the dielectric loss.⁴⁵ Figure 13 also shows that $\tan \delta$ increases linearly with the increase of Me-SSQ content. Me-SSQ would destroy the regularity of cured CE resin, loosening the molecular chains and making the movement of molecules easier. As a result, the relaxation polarization loss of dipole chains was raised and $\tan \delta$ was increased. However, $\tan \delta$ is still less than 0.006 when Me-SSQ content reaches as high as 20 wt %. There-

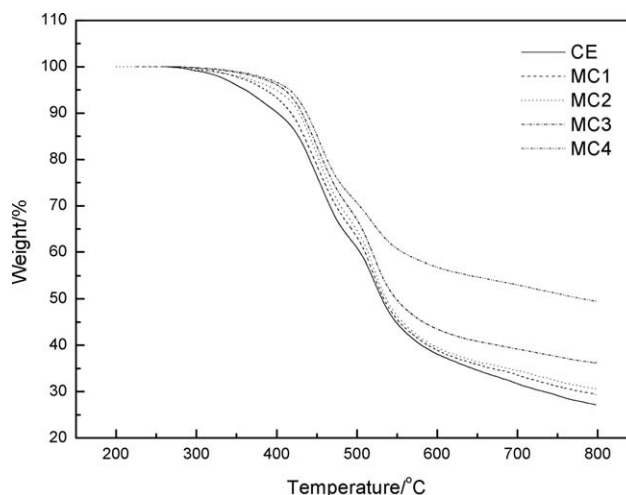


Figure 14 TG curves of Me-SSQ/CE hybrids.

fore, Me-SSQ/CE hybrid materials are expected to be used as the matrix for PCB materials.

Thermal stability of the Me-SSQ/CE hybrids

Figure 14 is the TG curves of Me-SSQ/CE hybrids. The initial decomposition temperature T_{di} and the char yield are listed in Table II. As shown in Figure 14 and Table II, T_{di} is increased with the increase of Me-SSQ content. A total of 10 wt % of Me-SSQ can increase T_{di} by 50°C. The char yield is also enhanced significantly. The char yield of MC3 is 7.5% higher than that of the pure CE. The increase of T_{di} can be explained by the following two reasons. On the one hand, Me-SSQ is a hybrid material, which possesses superior thermal resistance to that of CE resin. On the other hand, an inert silica-like layer will form on the surface of hybrid materials during the thermal decomposition process.^{15,25,26,46} It can preclude the diffusion of substances and energy, so as to hold back the thermal decomposition of materials, leading to the increase of T_{di} . As far as the char yield is concerned, the higher the content of Me-SSQ, the higher the content of inorganic component in the system, the higher the char yield.

Hot/wet resistance of Me-SSQ/CE hybrids

Water absorption is a very important factor to influence the performance of CE resin and its composites,

TABLE II
TG Data of Me-SSQ/CE Hybrids

System	CE	MC1	MC2	MC3	MC4
T_{di} (°C)	360	386	398	410	416
Char yield at 800°C	31.7	33.5	34.5	39.2	53.0

T_{di} is the temperature at which the weight loss is 5%.

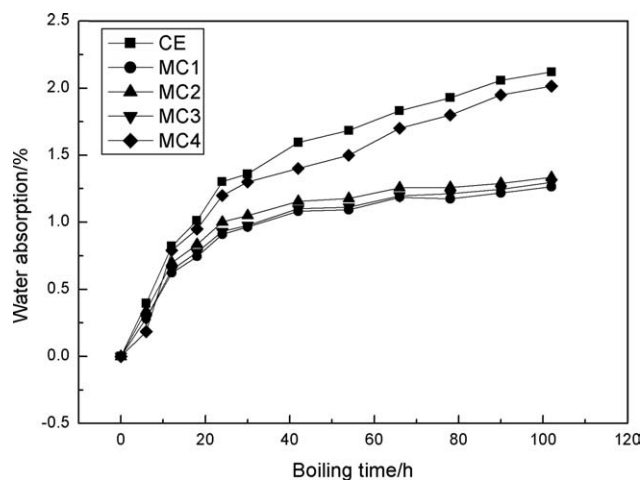


Figure 15 Water absorption curves of Me-SSQ/CE hybrids.

such as modulus, strength, and dielectric properties.⁴⁷ Therefore, it is of great importance to study the water absorption of Me-SSQ/CE hybrids. Figure 15 is the water absorption curves of Me-SSQ/CE hybrids. It can be seen that water absorption of Me-SSQ/CE hybrids is significantly decreased than that of CE. In addition, the increasing rate of water absorption vs. boiling time is lower than that of CE. In general, water exists in polymers as two types of conditions. Some water combined with the polar groups. The other exists as free water molecules in the free volume of polymer.³⁹ Therefore, water absorption is dependent on the free volume of resin matrix and the types and content of polar groups. Me-SSQ possessing symmetry nonpolar structure causes little effect on the polarity of materials. Therefore, the lower water absorptions of Me-SSQ/CE hybrids are mainly due to the decrease of free volume of materials. Me-SSQ is a nanostructured material and compatible with the resin matrix. It can fill the microcavities formed from the curing process and decrease the free volume of materials. Besides, MC1 shows the lowest water absorption. Water absorption increases with the increase of Me-SSQ content. When Me-SSQ content is as high as 20 wt %, water absorption is still lower than CE.

CONCLUSIONS

A series of Me-SSQ/CE hybrids containing various content of Me-SSQ (Me-SSQ/CE, 100/0, 99/1, 95/5, 90/10, and 80/20 wt/wt) were prepared by melt casting and then curing. Me-SSQ does not show significant influence on the curing reaction of CE, which is favorable to the determination of curing techniques. Appropriate content of Me-SSQ could toughen and reinforce CE resin simultaneously, increasing the impact strength by 50% at most. Me-

SSQ could effectively decrease the dielectric constant and slightly increase the dielectric loss of CE resin. TG results indicated that thermal stability of Me-SSQ/CE hybrids is greatly enhanced with the increase of Me-SSQ content. Water boiling test reveals that Me-SSQ can lower the water absorption of CE significantly. Owing to their low dielectric constant and excellent overall properties, Me-SSQ/CE hybrids may be used as the matrix for high-performance PCB materials.

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