Preparation and Properties of Maleimide-Functionalized Hyperbranched Polysiloxane and Its Hybrids Based on Cyanate Ester Resin

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ABSTRACT: A new hyperbranched polysiloxane containing maleimide (HPMA) was synthesized through the reaction between *N*-(4-hydroxyphenyl) maleimide and 3-glycidoxypropyltrimethoxysilane, which was then used to prepare cyanate ester (CE) resin-based hybrids (coded as HPMA*x*/CE, where *x* is the weight fraction of HPMA in the hybrid). The curing behavior of uncured hybrids and the typical properties (impact strength and dielectric properties) of cured hybrids were systemically investigated. Results show that the performance of hybrids is greatly related with the content of HPMA. Hybrids have obviously lower curing temperature than CE, overcoming the poor curing characteristics (higher curing temperature and longer curing time) of neat CE, for example, the curing peak temperature of HPMA20/CE is about 65°C lower than that of CE. In the case of cured resin and hybrids, the hybrids exhibit decreased dielectric constant and loss than CE resin; moreover, the former also exhibits lower water absorption than the latter. Specifically, the dielectric loss of HPMA15/CE hybrid is only about 27% of that of neat CE resin. In addition, the hybrids with suitable contents of HPMA have significantly improved impact strengths. The overall improved properties suggest that HPMA*x*/CE hybrids have great potential in applications needing harsh requirements of curing feature, dielectric properties, and toughness. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: hyperbranched polysiloxanes; cyanate ester; curing; toughness; dielectric properties

INTRODUCTION

High performance thermosetting resins with outstanding overall performance, for example, good curing characteristics (low curing temperature and suitable curing time), high service temperature, desirable toughness and strength, and good moisture resistance, have been attracting great interest of scientists and engineers worldwide because of their importance and great potential in many industries including electronic, aerospace, transportation, and insulation fields, etc.[1–3]

However, thermal resistant thermosetting resins, such as bismaleimide and cyanate ester (CE) resins, usually have poor toughness and curing characteristics. Specifically, they need to be cured at very high temperature for long time to get the best integrated performance.[4,5] It is known that high curing temperature not only causes high energy consumption, but also results in bigger internal stress and defects of the cured resin, and thereby declines the overall integrated properties of the resultant materials as well as applications, especially those with harsh requirements of outstanding overall properties.[6] Generally, adding catalysts is a common method to improve the curing characteristics,[7–13] while toughening is usually achieved by copolymerizing with other thermosetting resins, blending with engineering thermoplastics or rubbers, or introducing inorganic fillers.[14–17] Each technique has made great progress; however, it is a common phenomenon that the addition of catalyst tends to enhance the brittleness.[18] Therefore, how to simultaneously improve the curing characteristic and toughness of original resins without sacrificing the important merits of

original resins is still a difficult but interesting subject.[19,20]

The aim of this article is to develop a new way to toughen and catalyze thermosetting resins. CE resin is selected as the representative of high performance thermosetting resins for this investigation owing to its importance and great potential for many cutting-edge fields.[21–23] Compared with other high performance thermosetting resins, the biggest advantage of CE resin is the extremely low and stable dielectric constant and loss over a wide frequency and temperature range; therefore, how to significantly reduce the curing temperature, and improve the toughness without sacrificing the outstanding dielectric properties is of great interest.

Hyperbranched polymers, as a new class of three-dimensional macromolecules, have gained great attentions owing to their unique structure and properties, for example, hyperbranched polymers are known to have lower molten and solution viscosities than their linear analogs with the same molecular weight.[24,25] Another significant advantage of hyperbranched polymers is that they can be designed to have different terminal groups, supplying great potential for chemical modifications.[26]

Recently, a series of hyperbranched polysiloxanes were synthesized in our laboratory,[18,27,28] which were proved to combine the advantages of both hyperbranched polymers and polysiloxanes. However when they are used to modify high performance thermosetting resins (bismaleimide, CE, or bismaleimide-triazine resins), the molecules of hyperbranched polysiloxane, including the main chain and terminal group, should be carefully designed for obtaining the optimum overall performance. For example, hyperbranched polysiloxane terminated by epoxy groups (HPSiE) was synthesized and used to toughen bismaleimide-triazine resins[27,28]; results show that HPSiE can effectively improve the toughness and curing characteristics of bismaleimide-triazine resin, however which also increases the dielectric constant and loss.

On the basis of the aforementioned description, this article gives the first presentation of a new hyperbranched polysiloxane containing maleimide (HPMA), and its modification of CE resin. The effect of the content of HPMA on the curing behavior and the typical properties (impact strength and dielectric properties) of cured hybrids are systemically evaluated and discussed.

EXPERIMENTAL

Materials

2,2′-Bis (4-cyanatophenyl) isopropylidene (CE) was obtained from Shangyu Shengda Chemical Co., Ltd.
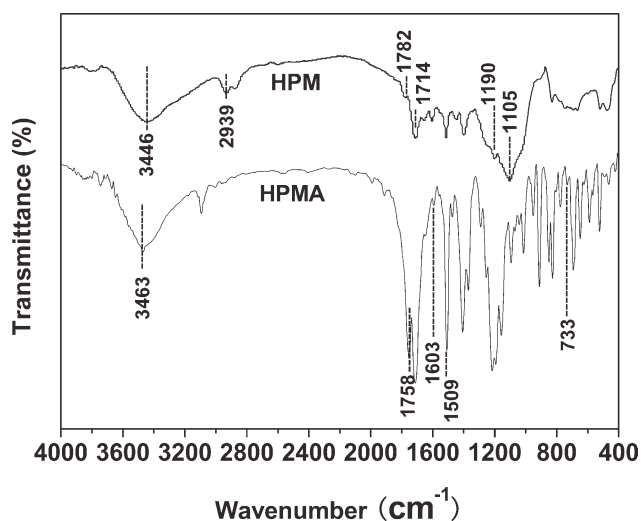

Figure 1 The FTIR spectra of HPM and HPMA.

(China); 3-glycidoxy propyltrimethoxysilane was supplied by Jingzhou Jianghan Chemical Co., Ltd. (China); 4-aminophenol was purchased from Aladdin reagent (China); maleic anhydride was supplied by Tianjin Bodi Chemical Co., Ltd. (China). Dimethylformamide (DMF), isopropanol, methanol, sulfuric acid, phosphorus pentaoxide, tetrahydrofuran (THF), NaOH, toluene, and tetramethylammonium hydroxide.5H_2O (TMAH) were commercial products of analysis grades, and purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

Synthesis of HPMA

N-(4-hydroxyphenyl) maleimide (HPM) was synthesized following the procedure in literature.[29] Typically, 4-aminophenol (21.8 g) was gradually added into a solution made up of maleic anhydride (21.6 g) and DMF (50 mL), and the mixture was stirred for 2 h at 20°C to obtain a clear amic acid solution. Then a solution consisting of phosphorus pentaoxide (11.4 g), sulfuric acid (5 g), and DMF (70 mL) was added dropwise over a period of 30 min. After stirring for 3 h at 70–80°C, the reaction mixture was cooled and poured into ice water. The obtained orange precipitate was washed several times with water, recrystallized from isopropanol, filtered, and vacuum dried to get a product coded as HPM. The Fourier transformed infrared (FTIR), ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra are shown in Figures 1–3, respectively.

FTIR (KBr, cm^{-1}): 3463 (—OH), 1758 and 733 (imide), 1603 (C=C), 1509 (phenyl).

^{1}H-NMR (CDCl$_3$ as solvent, ppm): 5.4 (—OH), 6.83 (CH=CH), 7.08 (CH—C—O—), 7.12 (CH—C—N—).

^{13}C-NMR (CDCl$_3$ as solvent, ppm): 134.5 (C=C), 170.3 (C=O), 122.5 (C—N), 128.5 (C—C—N), 156.9 (C—O), 115.4 (C—C—O).
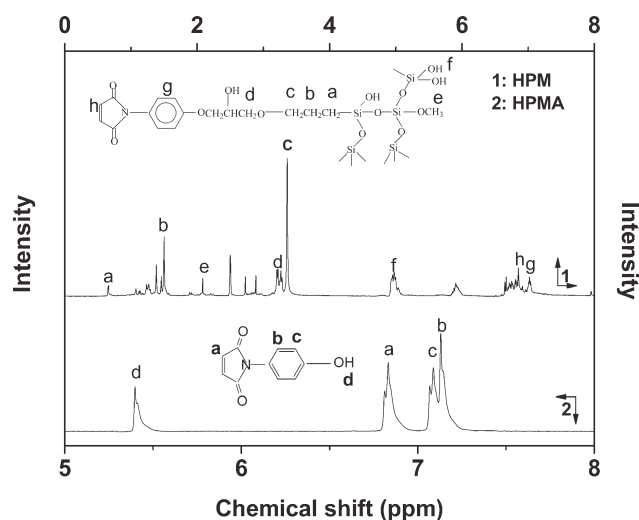
Figure 2 The ^{1}H-NMR spectra of HPM and HPMA.

Scheme 1 The synthesis of HPMA.

HPMA was synthesized by a three-step procedure as shown in Scheme 1. HPM (6.92 g, 50 mmol) and 3-glycidoxy propyltrimethoxysilane (14.16 g, 60 mmol) were dissolved in 100 mL DMF to get a solution, and then 10 mL methanol with 0.0025 mol NaOH was added into the solution to obtain a mixture. The mixture was allowed to react at 120°C for 2 h under a N$_2$ atmosphere. After cooling to room temperature, the reaction mixture was poured into excess toluene, and the precipitant was collected by filtration. The solid product was washed with toluene, and then dried at 50°C under vacuum for 24 h to give the final product, which was coded as Si-MA.

Si-MA (2 g) was dissolved in THF (20 mL) by adding distilled water (0.15 g) and tetramethylammonium hydroxide.5H$_2$O (0.01 g). The mixture was stirred at room temperature for 3.5 h, and then the solvent was removed in vacuum at 40°C. The result-
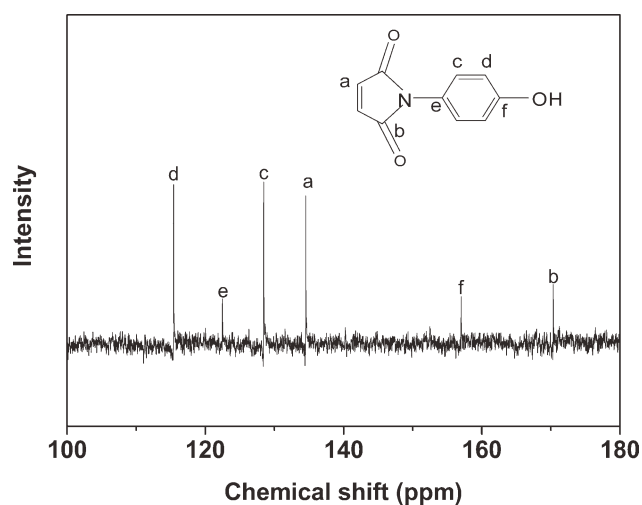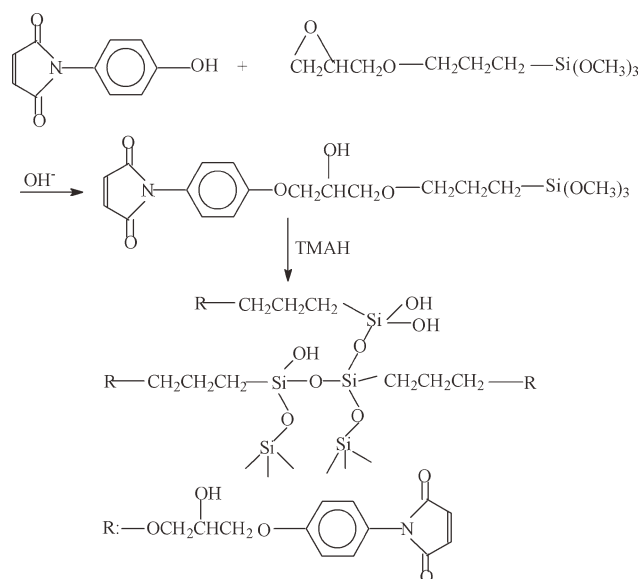
ant product was a red wine solid, and coded as HPMA, its FTIR and ^{1}H-NMR spectra are presented in Figures 1 and 2, respectively.

FTIR (KBr, cm^{-1}): 3446 (—OH), 2939 (aliphatic C—H), 1782 (C=O asymmetrical stretching), 1714 (C=O symmetrical stretching), 1165 (C—N—C in maleimide ring), 1105 (Si—O—Si).

^{1}H-NMR (N-dimethylsulfoxide as solvent, ppm): 0.66 (Si—CH$_2$—); 1.5, 3.4 (—CH$_2$—CH$_2$—CH$_2$—); 3.2 (—O—CH$_2$); 6.75(—CH=CH— of maleimide ring); 7.02 (aromatic protons).

Based on above data, it can be confirmed that the molecule of HPMA is ended with maleimide group.

Preparation of prepolymers

HPMA (2 g) was dissolved in THF (20 mL) to yield solution A. CE (40 g) was dissolved in acetone (30 mL) to form solution B. Solutions A and B were then mixed together and stirred at 85°C for 1 h. The solvent was removed in vacuum at 85°C to yield a prepolymer, which was coded as HPMA5/CE.

Forty grams of CE were dissolved in 30 mL acetone with stirring, the mixture was maintained at 85°C for 1 h. After that, acetone was removed in vacuum at 85°C to yield CE prepolymer.

Preparation of cured HPMA/CE hybrids

Each prepolymer was thoroughly degassed at 100°C and poured into a preheated (100°C) glass mold, then cured per the curing procedure of 130 °C/2 h + 150 °C/2 h + 180 °C/2 h + 200 °C/2 h. After that the cured sample was demolded and postcured in an air oven at 220°C for 4 h.

Figure 3 The ^{13}C-NMR spectrum of HPM.

Measurements

FTIR spectra were recorded between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1} on a Nicolet FTIR 5700 spectrometer (USA).

^{29}Si, ^{1}H-, and ^{13}C-NMR spectra were recorded on a Bruker WM300 (Germany), using the tetramethylsilane $(CH_3)_4Si$ as the standard substance, and N-dimethylsulfoxide as the solvent.

Dielectric properties were conducted in a frequency range from 10 to 10^6 Hz at room temperature using a Broadband Dielectric Spectrometer (Novocontrol Concept 80 Analyzer, Germany). The dimensions of each sample were $(25 \pm 0.2) \times (25 \pm 0.2) \times (3 \pm 0.1)$ mm^3.

Differential scanning calorimetry (DSC) analyses were done using DSC 200 F3 (NETZSCH, Germany) between 60 and 330°C at a heating rate of 5, 10, 15, or 20 °C/min in a nitrogen atmosphere.

Impact strength was measured according to GB2571-95 using an impact machine tester (XJJ-40, China), the dimensions of each sample were $(50 \pm 0.02) \times (6 \pm 0.02) \times (4 \pm 0.02)$ mm^3. Five samples were tested, and the average value was taken as the tested value.

Weight-average molecular weight (M_w) was performed using Multi-Angle Dynamic Laser Light Scattering Instrument made in Wyatt Company (Dawn HELEOS, Santa Barbara, CA, USA). The concentration of each sample was about 1 mg/mL.

The hot-wet resistance was measured according to GB2574-1989; three samples, each has the dimensions of $(50 \pm 0.02) \times (50 \pm 0.02) \times (4 \pm 0.02)$ mm^3, were tested for each resin to calculate the average value.

Scanning electron microscope (SEM) (Hitachi S-4700, Japan) coupled with energy disperse X-ray spectrometer (EDS) was employed to observe the morphology of samples. The resolution of the secondary electron image is 1.5 nm under 15 kV. All samples should be dried at 100°C for 6 h before tests.

Dynamic mechanical analysis (DMA) scans were performed in single-cantilever blending mode using a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA) from 50 to 350°C at a heating rate of 3 °C/min and a frequency of 1 Hz.

RESULTS AND DISCUSSION

Synthesis and structure HPMA

Liu et al. reported the synthesis of a hyperbranched polysiloxane containing maleimide group (HB-MSM) through a two-step method,[30] that is, an alkoxysilane compound containing maleimide group (MSM) was first synthesized from the reaction between HPM and 3-glycidoxy propyltrimethoxysilane, and then the resultant MSM was hydrolyzed under an acidic condition to produce HB-MSM. However, the structure of HB-MSM was not provided. Although same raw materials are used to synthesize HPMA reported herein, HPMA is believed to have different structure from that of HB-MSM owing to following reasons. First, phenolic hydroxyl is easy to be oxidized, so the reaction should be carried out under the protection of N_2 atmosphere,[31] however, HB-MSM was synthesized under an air atmosphere. Second, MSM was synthesized at 150°C for 5 h,[30] such high reaction temperature accelerates the self-polymerization rate of epoxy groups under acid conditions,[32] meaning that not full amount of HPM takes part in the reaction between HPM and 3-glycidoxy propyltrimethoxysilane, and then some amounts of HPM monomer are left in the mixture; in addition, the self-polymerization of epoxy group results in the formation of longer aliphatic chains which tend to deteriorate the thermal stability and dielectric properties of the modified resin. Third, maleimide will self-polymerize at high temperature,[33] meaning that the synthesized MSM tends to have higher molecular weight, however big molecular weight is not beneficial to the progress of hydrolysis. Fourth, shorter hydrolysis time tends to produce hyperbranched polysiloxane with a larger amount of $—OCH_3$ groups[34] which are not beneficial to remain outstanding thermal stability and dielectric properties, however, the hydrolysis time for producing HB-MSM is only 1 h.

In this article, a completely different procedure is used to synthesize HPMA. Specifically, the reaction is carried out under N_2 atmosphere at lower reaction temperature, and longer hydrolysis time is employed to form a compact branched structure.

Degree of branching (DB) and average number of branch units (ANB) are both important parameters to describe the branching structure of hyperbranched polymers. For the most common type of hyperbranched polymers, it contains three different units: dendritic unit, linear unit, and terminal unit. If D, L and T represent the chemical shifts integral of dendritic, linear, and terminal units, respectively, in ^{29}Si-NMR spectrum of the hyperbranched polymer, then DB and ANB can be calculated from eqs. (1) and (2), respectively.[35]

$$DB = \frac{2D}{2D + L} \tag{1}$$

$$ANB = \frac{D}{D + L} \tag{2}$$

Figure 4 shows the ^{29}Si-NMR spectrum of HPMA. Three major peaks at about −65.5, −56.8, and −45.4 ppm are observed, which are attributed to the
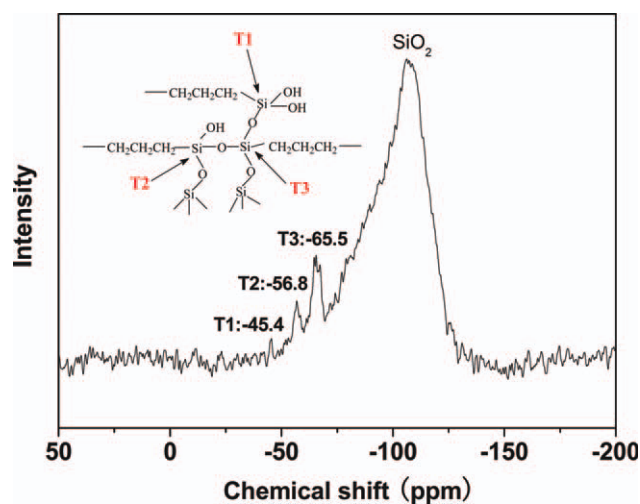
Figure 4 The ^{29}Si-NMR spectrum of HPMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
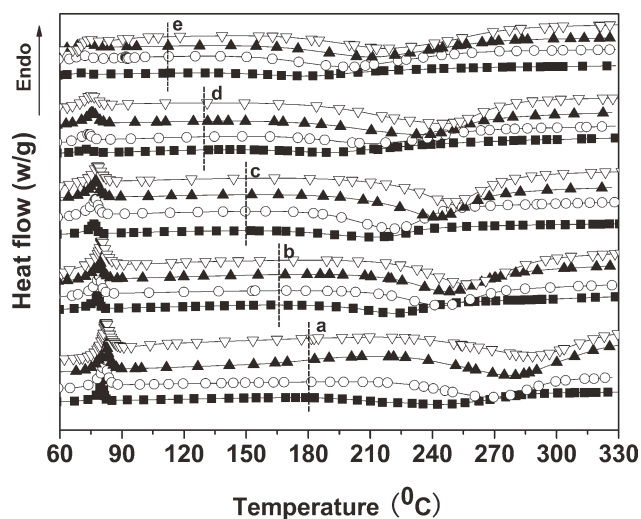

Figure 5 DSC thermograms of CE and HPMAx/CE [(a) CE; (b) HPMA5/CE; (c) HPMA10/CE; (d) HPMA15/CE; (e) HPMA20/CE; ■: 5 °C/min; ○: 10 °C/min; ▲: 15 °C/min; |: 20 °C/min].

corresponding absorption of non-hydroxy-substituted silica (T3), monohydroxy-substituted silica (T2), and dihydroxy-substituted silica (T1), respectively. The relatively small integration area of the T1 absorption peak demonstrates the high conversion of silanol groups and the formation of a silica network.[36] The values of DB and ANB calculated using eq. (1) and eq. (2) are given in Table I; moreover, M_w and the generation number (n^*) for HPMA are also shown in Table I. The above results further confirm the hyperbranched structure of HPMA.

From the above analyses, it can be stated that HPMA is a new maleimide contained hyperbranched polysiloxane, which has the structure as shown in Scheme 1.

Curing behavior and kinetics of HPMAx/CE hybrids

Typical DSC thermograms of neat CE and HPMAx/CE prepolymers under different heating rates are shown in Figure 5, and the total heats of reaction at different heating rates were calculated and summarized in Table II. Each sample shows one exothermic peak; however, compared with the peak of CE, each HPMAx/CE shifts toward lower temperature. The larger is the content of HPMA, the lower is the curing peak temperature, suggesting that the addition of HPMA to CE decreases the curing temperature,

and accelerates the whole curing process. Specifically, the curing peak temperature of HPMA20/CE is about 65°C lower than that of CE. The catalytic role of HPMA on the curing reaction of CE can be endowed to the existence of a plentiful amount of silanol and carbinol groups in HPMA, because these groups have been proved to have significant catalytic effect on the curing of CE.[6,37,38] From Table II, it can be seen that total heats of reactions are not similar, so in order to further study the effect of HPMA on the curing reaction of CE, the values of activation energy (E_a) at different curing degree for the whole curing reaction induced by the addition of HPMA to CE are calculated by employing the Friedman method [eq. (3)],[39,40] of which the main advantage is that the reaction activation energy can be directly derived without the assumption of the kinetic model of the curing reaction.

$$\ln(\beta \frac{d\alpha}{dT}) = \ln A + \ln f(\alpha) - \frac{E_a}{RT} \qquad (3)$$

where T is the temperature, β is the heating rate, E_a is the activation energy, A is the pre-exponential factor, R is the gas constant and α is the curing degree.

TABLE I
Structural Parameters of HPMA

| M_w (g/mol) | Integral in ^{29}Si-NMR spectra | | | DB | ANB | n^* |
	T	L	D			
3800–4200	1.00	8.41	18.66	0.69	0.82	11–13

TABLE II
The Total Heats of Reaction at Different Heating Rate

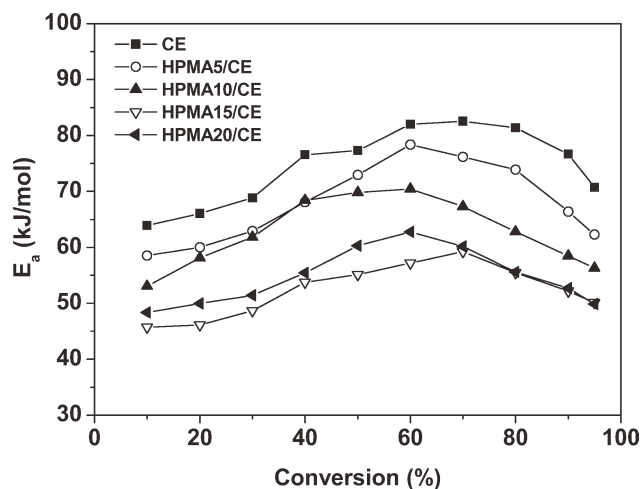| Sample | E (w/g) | | | |
	5°C/min	10°C/min	15°C/min	20°C/min
CE	55.17	79.46	115.92	146.69
HPMA5/CE	40.29	75.01	105.81	131.61
HPMA10/CE	38.75	78.02	118.93	121.68
HPMA15/CE	29.28	70.97	110.06	146.21
HPMA20/CE	26.20	75.81	96.98	111.74

Figure 6 Activation energies at different curing degree calculated by the Friedman method for CE and HPMAx/CE hybrids.

According to eq. (3), the calculated values of E_a are summarized in Figure 6. It can be observed that E_a decreases with increasing the content of HPMA, and then reaches its minimum value when the content of HPMA is 15 wt %, suggesting that the curing reaction of the hybrids is much easier to occur than that of CE. When the content of HPMA exceeds 15 wt %, the value of E_a almost levels off.

Whether there is a co-reaction between —OCN and maleimide is still a controversial topic. Up-to-data, only several literatures reported the existence of the co-reaction. Honc et al. carried out the representative work, they observed the appearance of the absorption peak at 1507 cm^{-1} in the IR spectrum, so they proposed that the reaction between the maleimide and —OCN groups produces a pyrimidine-type structure.[41] However, from the FTIR spectra of CE and HPMA10/CE after being cured via different procedures (Fig. 7), it can be seen that the characteristic absorption peak assigning to the pyrimidine-type structure was seriously overlapped with other characteristic bands, so it is not reasonable to confirm the formation of pyrimidine-type structure. Hamerton and coworkers studied the reactivity of model compounds using ^{15}N-NMR spectroscopy over a temperature range at which the reaction was thought to have occurred (180–230°C).[42,43] No evidence of pyrimidine-type product was found, but rather a product predominantly made up of unreacted maleimide ($\delta_N = -213.99$ ppm relative to nitromethane), CE monomers ($\delta_N = -217.27$ ppm), and the cyanurate tris-(4-cumylphenoxy)-1,3,5-triazine ($\delta_N = -179.30$ ppm), reflecting that BMI and CE do not truly react. Many other scholars also accept that there is no reaction between maleimide and —OCN groups, and the curing mechanism of maleimide/CE system is believed that maleimide

and CE crosslink to form two discrete networks which interpenetrated with each other in the cured resin[44]; briefly, the crosslinked network is an Interpenetrating Polymer Network (IPN) structure. In the case of HPMAx/CE hybrids, it is worth noting that besides the reactions taking place in maleimide/CE system, there are additional reactions including the reaction between Si—OH and CE, and that among maleimide groups. Moreover, the curing reaction of CE is catalyzed owing to the presence of a plentiful amount of silanol and carbinol groups in HPMA as described above. Many literatures reported the reaction between Si—OH and —OCN,[18,45–47] Liang et al. prepared CE/POSS nanocomposites,[45] and confirmed that there is a reaction between the silanol hydroxyl and —OCN groups during curing. As for the self-polymerization of maleimide groups, many literatures have proved that maleimide groups can crosslink through a fast homopolymerization in the absence of initiators,[33,48] because two carbonyl groups endow the double bonds with more activities than common double bonds. Therefore, compared with CE, HPMAx/CE has different reaction mechanism as shown in Scheme 2.

Figure 7 shows the FTIR spectra of HPMA10/CE hybrid after curing via different procedures. It can be seen that with the progress of curing, the intensities of the peak (1600 cm^{-1}) attributing to C=C groups of maleimide disappear gradually owing to the polymerization of double bonds. On the other hand, the complete consumption of —OCN groups (2270 and 2236 cm^{-1}) is accompanied by the formation of sym-triazine rings (1568 cm^{-1}).[49] These results confirm that under the curing and postcuring conditions developed herein, the curing of all hybrids is complete.
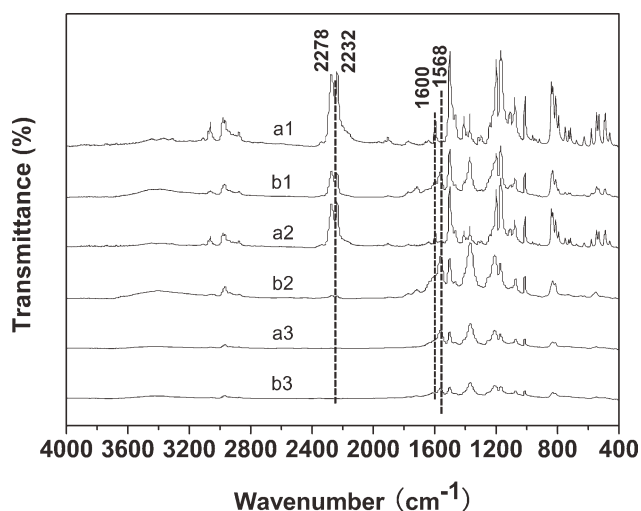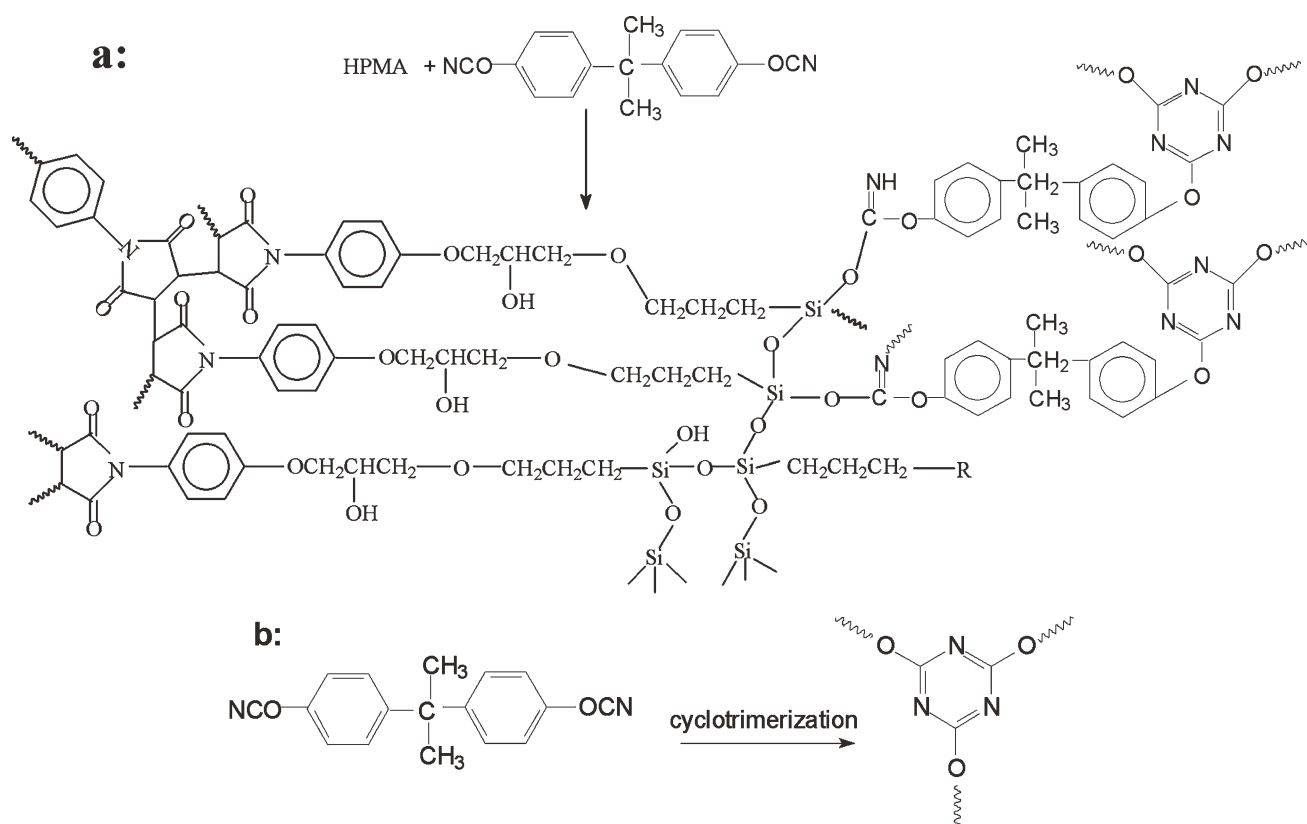

Figure 7 FTIR spectra of CE (a) and HPMA10/CE (b) after being cured via different procedures (1: without curing; 2: 150 °C/2 h; 3: full procedure).

Scheme 2 The reaction between HPMA and CE (a) and the cyclotrimerization of CE (b).

The crosslinking density (v_e), generally including chemical and physical aspects,[50] is one of the most important parameter for a thermosetting resin, and can be calculated from the theory of rubber elasticity as shown in eq. (4).[51]

$$E_r = 3RT_r v_e \qquad (4)$$

where E_r is the storage modulus (Fig. 8) of the cured sample in the rubbery plateau region; T_r is the abso-lute temperature at which the sample is in rubbery state, herein T_r is selected as the temperature which is 40°C higher than the glass transition temperature (T_g); R is the gas constant; and the corresponding v_e values of cured CE resin and hybrids are depicted in Figure 9. It can be seen that HPMA5/CE hybrid has a slightly larger crosslinking density than CE resin, but other hybrids have smaller crosslinking density than CE resin, and the crosslinking density reaches the minimum when the content of HPMA is 15 wt
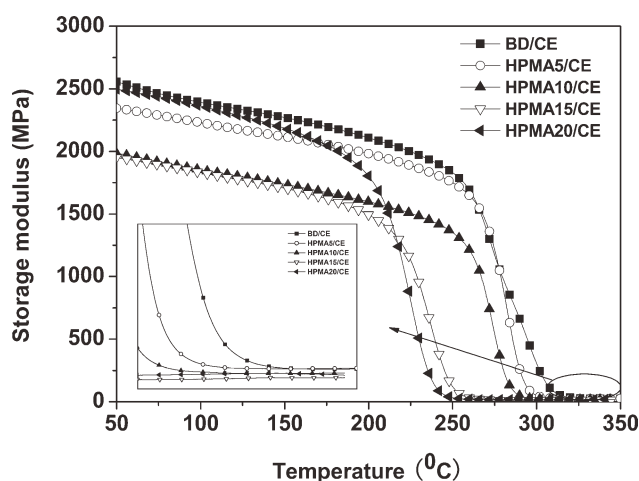

Figure 8 Overlay plots of storage modulus vs. tempera-ture of cured CE resin and HPMAx/CE hybrids.
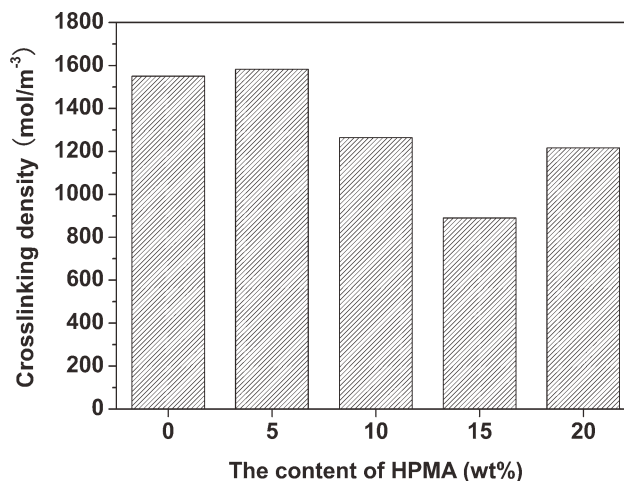

Figure 9 The crosslinking densities of cured CE resin and HPMAx/CE hybrids.
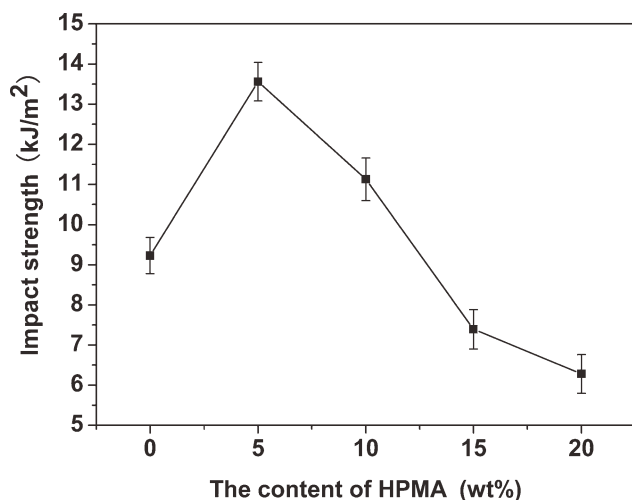
Figure 10 Impact strengths of cured CE resin and HPMAx/CE hybrids.

%. This phenomenon can be attributed to the additional chemical bonds induced by the co-reactions between HPMA and CE resin as described above. When a small amount of HPMA is added to CE resin, HPMA mainly acts as a catalyst for curing CE, and thus leading to an increased crosslinking density. While with increasing the content of HPMA, additional effects also play roles. Specifically, the reaction between Si—OH and —OCN decreases the amount of rigid homopolymer of —OCN groups, leading to decreased crosslinking density. However, when the content of HPMA is very large, the hydrogen bonds among molecular chains increase, and thus resulting in increased crosslinking density.

Impact strength of HPMAx/CE hybrids

The impact resistance of a polymer reflects its ability to absorb the energy of a rapidly applied load. The ability of a polymer to withstand this sudden impact is related to the toughness of the material.[52]

The impact strengths of CE resin and HPMAx/CE hybrids with different contents of HPMA are presented in Figure 10. The impact strength of the hybrids is closely related with the content of HPMA in hybrids. The hybrid with a small content of HPMA (no larger than 10 wt %) has higher impact strength than CE resin, for example, HPMA5/CE has about 1.5 times higher impact strength than CE resin. This is mainly attributed to the flexibility of Si—O—Si bonds in HPMA,[53] and the existence of a fewer amount of rigid triazine rings owing to the reaction between —OCN and silanol groups. However, a larger content of HPMA is not beneficial to get high impact strength because of the change of the network. Specifically, when the content of HPMA is large enough (for example, >10 wt %), the network belonging to HPMA becomes more compact

via the self-polymerization of maleimide groups (Scheme 2) and Si—OH groups, and thus entangling with that network from the cyclotrimerization of CE groups in the cured resin; moreover, the stereo-hindrance effect would also become prominent.[54] This resultant structure should restrict the flexibility and molecular movement, and therefore, there exists an optimum content of HPMA to get the maximum impact strength. Similar results are also reported by other hyperbranched polymer modified thermosetting resins.[55–57]

The dependence of impact strength on the content of HPMA in the hybrid can be also observed from the SEM micrographs of CE resin and HPMAx/CE hybrids as shown in Figure 11. The fractured surface of neat CE resin, HPMA15/CE, and HPMA20/CE
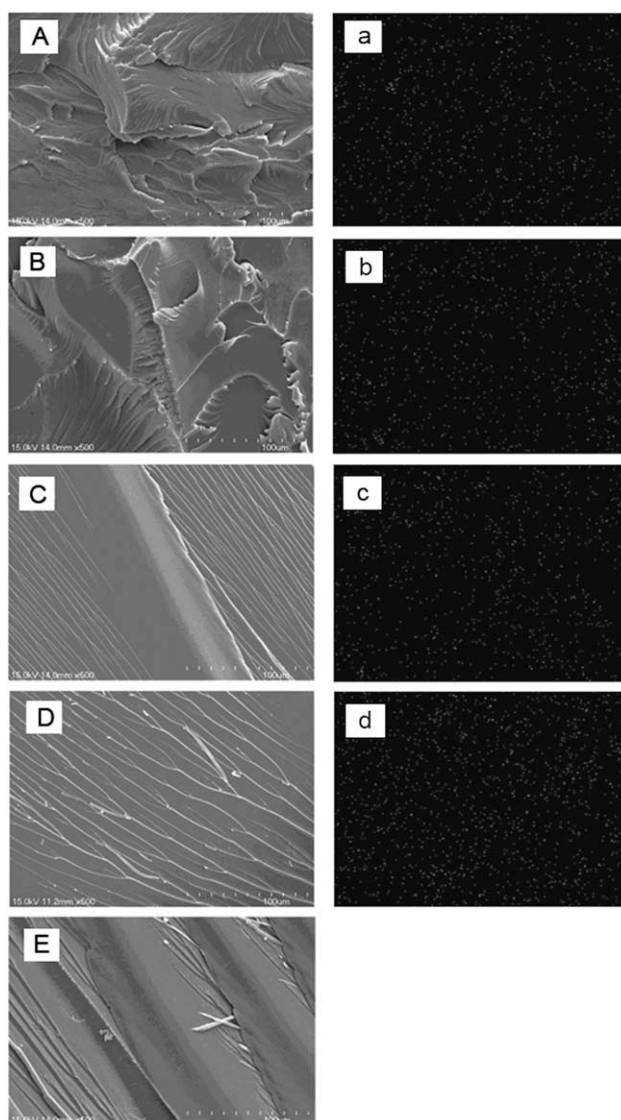

Figure 11 SEM and EDS-Si mapping micrographs of cross-section surfaces of HPMAx/CE hybrids [(a) HPMA5/CE; (b) HPMA10/CE; (c) HPMA15/CE; (d) HPMA20/CE; (e) CE).
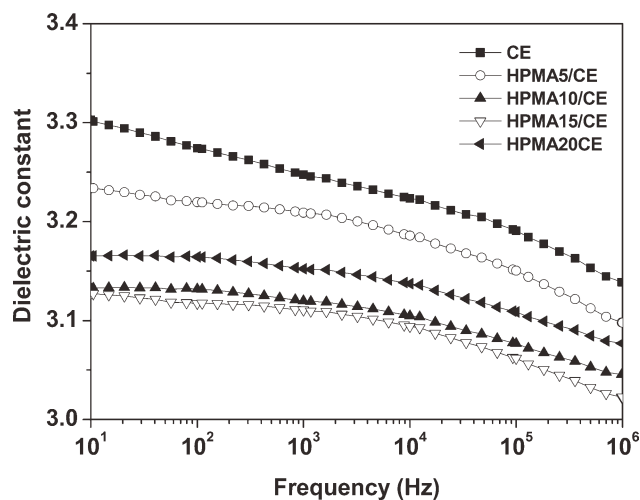
Figure 12 Dependence of dielectric constant on frequency of cured CE resin and HPMAx/CE hybrids.

Figure 14 Water absorptions of cured CE resin and HPMAx/CE hybrids.

hybrids display smooth and glassy surfaces, indicating brittle features; while HPMA5/CE and HPMA10/CE hybrids have many dimples, showing a typical tough feature.

Many researchers used SEM-EDS silicon mapping to observe the distribution of fillers containing silicone,[30,58] so this technique is also employed to observe the distribution of HPMA in the cured CE resin, and corresponding pictures are also shown in Figure 11. It can be seen that silicon atoms (shown as the bright dots), assigned to the silsesquioxane structure, are homogeneously distributed in CE resin.

Dielectric properties

Figures 12 and 13 show the dielectric constant and loss of cured CE resin and HPMAx/CE hybrids over a wide frequency range. All hybrids have similar de-
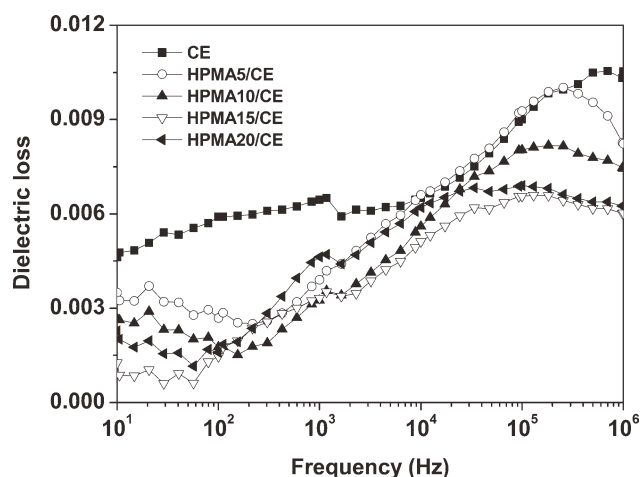

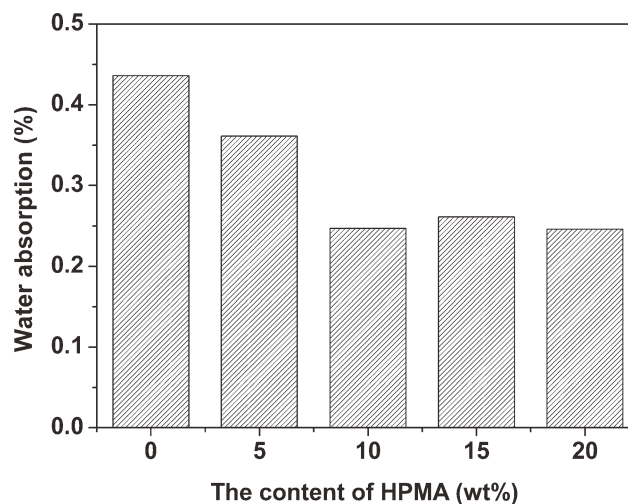**Figure 13** Dependence of dielectric loss on frequency of cured CE resin and HPMAx/CE hybrids.

pendence of dielectric constant and loss on frequency as CE resin does; more interesting, all hybrids exhibit lower dielectric constant and loss than CE resin over the whole frequency range. Specifically, the dielectric loss of HPMA15/CE at 10 Hz is 0.00122, and only about 0.27 times of that of neat CE resin. These results are very attractive for cutting edge applications.

It is believed that HPMA has two effects on the dielectric properties of HPMAx/CE hybrids. First, being a silicone resin, HPMA has low dielectric constant and loss; hence the addition of HPMA and a larger content of HPMA tend to decrease the dielectric constant and loss. Second, HPMA has significant influence on the structure of HPMAx/CE hybrids as stated above, which is related with the content of HPMA in the hybrid. In detail, the domain role of a small amount of HPMA on the structure of resultant resin is to catalyze the curing of CE resin, leading to increased crosslinking density, and thus decreased dielectric constant and loss; with increasing the content of HPMA, besides the catalyzing effect, the amount of NH=C—O resulting from the reaction between silanol groups in HPMA and —OCN groups increases, and that of the homopolymer of CE decreases, resulting in higher dielectric constant and loss. These effects combine together, and thus bring the data shown in Figures 12 and 13.

Hot-wet resistance

Outstanding moisture resistance is a very important property of a material, especially those requiring stable and high performance, because, in general, absorbed water will decline almost all properties of the original material including thermal, mechanical, and dielectric properties, etc, so moisture resistance
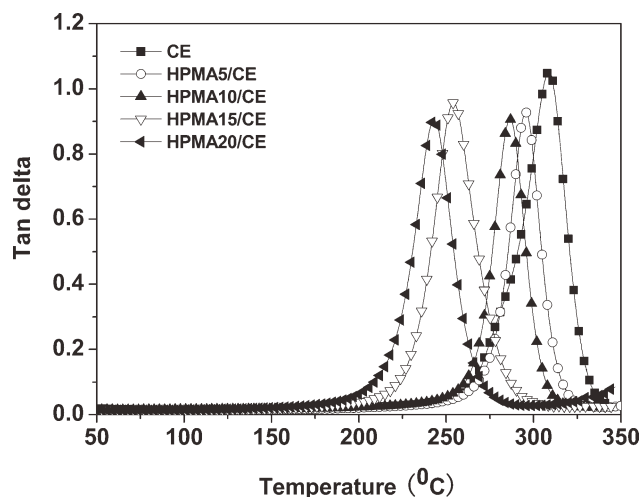
Figure 15 Overlay plots of tan δ vs. temperature of cured CE resin and HPMA*x*/CE hybrids.

should be investigated to evaluate the integrated property of any new developed resins.[59]

The dependence of the water absorption on the immersing length of time for the cured resin and hybrids is shown in Figure 14. It can be seen that the water absorption decreases with the addition of HPMA, and all HPMA*x*/CE hybrids have significantly lower water absorption than CE resin. In the case of HPMA20/CE, its water absorption is 0.246%, only about 56.4% of the water absorption of CE resin, suggesting that HPMA*x*/CE hybrids have improved water resistance compared with CE resin.

HPMA has two opposite influences on the water absorption of CE resin. First, Si—O—Si chains in HPMA have excellent hydrophobic properties,[18] indicating a positive role on reducing the water absorption of cured CE resin. Second, the decrement of the crosslinking density and the introduction of silanol and carbinol groups in HPMA play a negative role on reducing the water absorption of cured CE resin.

T_g

Several methods can be used to detect the T_g value of a thermosetting resin, of which DMA technique is an effective one.[60] The peak temperature of loss modulus–temperature plot is defined as T_g herein. Figure 15 shows the overlay plots of tan δ vs. temperature for cured CE resin and HPMA*x*/CE hybrids. It is noted that with increasing the content of HPMA, T_g value decreases, this can be contributed to the changes in network induced by the presence of HPMA and the decreased crosslinking density as described above. When the content is not large (<10 wt %), the T_g values of these hybrids are higher than 285°C, meeting the requirement of high performance resins. On the other hand, all hybrids have a single peak as that of CE resin, reflecting that

no phase separation appears at least up to the scale of DMA tests.

CONCLUSIONS

A new HPMA was successfully synthesized through the reaction between HPM and 3-glycidoxypropyl trimethoxysilane. HPMA can significantly reduce the curing temperature of CE owing to the significant catalytic effect of a plentiful amount of silanol and carbinol groups in HPMA on the curing of CE. In addition, the addition of HPMA to CE can decrease the apparent activation energy of the curing reaction.

The performance of hybrids is greatly related with the content of HPMA. HPMA*x*/CE hybrids exhibit decreased dielectric constant and loss than CE resin; moreover the hybrids also exhibit lower water absorption than CE resin. HPMA*x*/CE hybrids with suitable contents of HPMA have improved impact strengths compared with CE resin. For example, the impact strength of HPMA5/CE hybrid is about 1.5 times of that of CE resin, while the dielectric loss at 10 Hz of the hybrid is only about 70.1% of that of CE resin.

The overall improved properties suggest that HPMA*x*/CE hybrids have great potential in applications which have harsh requirements of curing feature, dielectric properties, toughness, hot-wet, and thermal resistance.

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