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Novel modification of bismaleimide–triazine resin by reactive hyperbranched polysiloxane

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Abstract A novel kind of modified bismaleimide–triazine (CE/BD) resins by copolymerizing with reactive hyperbranched polysiloxane (HPSiE) was first reported, and the effect of HPSiE content on key properties was systemically investigated. Results show that the addition of HPSiE into CE/BD resin effectively improves the toughness and water resistance, moreover, the positive effect enhances with the increase of HPSiE loading. CE/BD/HPSiE resin with desirable HPSiE content also remains the good thermal and dielectric properties of CE/BD resin, suggesting that the toughening route by copolymerizing a thermosetting resin with reactive hyperbranched polymers provides a promising approach for developing high performance resins. These changes of properties are explained by an inherent feature of HPSiE, and the alteration of chemistry in network.

Introduction

High performance thermosetting resins have gained much attention over the last 70 years because of their wide applications, for example, they are usually used as matrices for advanced composites, adhesive, coatings, etc. [1–4]. Up-to-date, they are playing more and more important role in many cut-edged industries including aerospace, microelectrics, transportation, and biomedicine, etc. [5–8].

BT resin is a kind of high performance resins based on bismaleimides (BMI) and cyanate esters (CE), which has many attractive properties such as very good thermal stability, moisture resistance, low dielectric constant, and low dielectric loss, so BT resin has been preferred to be used in rigorous environments requiring excellent dielectric properties, thermal, and mechanical properties [9, 10]. However, BT resin is so sensitive to the curing condition that it is difficult to guarantee the good performance of the resulting products, and its toughness needs to be improved [11].

In fact, since the invention of BT system in 1970', a lot of researches have been carried out to develop modified BT resins for adapting various applications, however, more work still needs to be done for developing new BT resins with significantly improved toughness without sacrificing the good dielectric property of original BT resin, how to address the issue has been a challenging assignment in the development of high performance resins.

Silicone resin is one kind of high performance resins, which possesses high heat resistance, good dielectric properties, and low water absorption due to the prominent contribution of Si–O chains [12, 13], so it has great potentiality to be a good tougher for thermosetting resins. However, the viscosity of silicone resin is relatively large and thus causing poor processing characteristics; in addition, silicone resin usually has poor compatibility with other resins, so it is difficult to prepare high performance resins.

Recently, 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 [14, 15]. Another significant advantage of hyperbranched polymers is that they can be designed to have a lot of functional termination groups, supplying a great potentiality for chemical modifications [16].

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In recent years, hyperbranched polymers have been successfully applied to toughen epoxy resins [17, 18], these researches focused on investigating the influence of hyperbranched polymers on the toughness of epoxy resin, however, the influence of hyperbranched polymers on other properties (especially dielectric property) is seldom addressed. In case of BT resins, no similar work has been done, more importantly, as described above excellent dielectric property is one of the most attractive features of BT resins, so toughening BT resin must be carried out without sacrificing the good dielectric property of original BT resin, indicating that toughening of BT resin is not as easy as that of epoxy resins.

In this paper, a reactive hyperbranched polysiloxane (HPSiE) terminated by epoxy groups was designed and synthesized to develop a novel high performance modified BT resin, which is expected to have the combined advantages of both hyperbranched polymers and BT resins, and thus the resultant new resin system has excellent dielectric properties, good toughness, high temperature resistance, and low water absorption.

Experiments

Materials

2,2′-Bis(4-cyanatophenyl)isopropylidene (CE), was purchased from Shengda Chemical Industrial Group, Zhejiang Province, China. 4,4-bismaleimidodiphenylmethane (BDM) was obtained from Northwestern Institute of Chemical Engineering. O,O-diallylbisphenol A (DBA) was purchased from Laiyu Chemical Co. Ltd, China. γ-glycidoxypropyltrimethoxysilane (KH-560) was obtained from Xiangfei Chemistry, Jiangsu Province, China. All materials were used without further purification.

Hyperbranched polysiloxane (HPSiE) was synthesized via the hydrolyzation of KH-560 by us [19]. The molecular weight and viscosity of HPSiE were 9,320 and 295 mPa s, respectively.

Preparation of BD prepolymer

2 mol BDM and 1 mol DBA were mixed with stirring at 130–150 °C for 30 min to form a transparent, amber-colored liquid, which was coded as BD prepolymer, and cooled to room temperature for use.

Preparation of cured CE/BD/HPSiE resins

Table 1 Formulations of CE/BD and CE/BD/HPSiE resins

Resin code	Mass ratio (CE/BD/HPSiE)
CE/BD	70/30/0
CE/BD/HPSiE5	70/25/5
CE/BD/HPSiE10	70/20/10
CE/BD/HPSiE15	70/15/15
CE/BD/HPSiE20	70/10/20
CE/BD/HPSiE25	70/5/25

Appropriate amounts (according to each formulation as shown in Table 1) of CE, BD prepolymer, and HPSiE were thoroughly blended at 150 °C for 1 h with vigorous stirring to form CE/BD/HPSiE prepolymer, then the prepolymer was poured into a mold and degassed at 150 °C for 2 h in a vacuum oven. After that the mold was put in a furnace for curing via the procedure of 180 °C/2 h + 200 °C/2 h + 220 °C/2 h, and postcuring at 240 °C for 4 h. Finally, the mold was cooled to room temperature and demolded, the resultant resin was coded as CE/BD/HPSiE resin.

Preparation of cured CE/BD resin

Appropriate amounts (according to the formulation in Table 1) of CE and BD prepolymer were thoroughly blended at 150 °C for 1 h with vigorous stirring, then the mixture was poured into a mold and degassed at 150 °C for 2 h in a vacuum oven. After that the mold was put into a furnace for curing via the procedure of 180 °C/2 h + 200 °C/2 h + 220 °C/2 h, and postcuring at 240 °C for 4 h. Finally, the mold was cooled to room temperature and demolded.

Characterizations

The unnotched impact strength was tested according to GB/T2571-1995 using Charpy Impact Machine Tester (XCJ-L, China).

Scanning Electron Microscope (SEM, Hitachi S-4700, Japan) was employed to observe the fractured surfaces of samples.

Dynamic mechanical analysis (DMA) was performed using TA DMA Q800 apparatus from TA Instruments (USA). A single cantilever clamping geometry was used. DMA tests were carried out from room temperature to 320 °C with a heating rate of 3 °C/min at 1 Hz.

Thermogravimetric analysis (TGA) was carried out using PerkinElmer Pyris 1 (USA) at a heating rate of 20 °C/min in a nitrogen atmosphere. The initial degradation temperature (T_{di}) is the temperature at which the weight loss of the sample reaches 5 wt%.

The water absorption of a sample was tested according to GB/1034-86*.

The dielectric property of a sample was tested by using Novocontrol Concept 80 (Germany) apparatus between 1 Hz and 1 MHz at room temperature.

Results and discussion

Curing mechanisms

In order to discuss the reasons contributing to the different performances between CE/BD/HPSiE resins and CE/BD resin, the chemistry of the two cross-linking networks should be discussed at first.

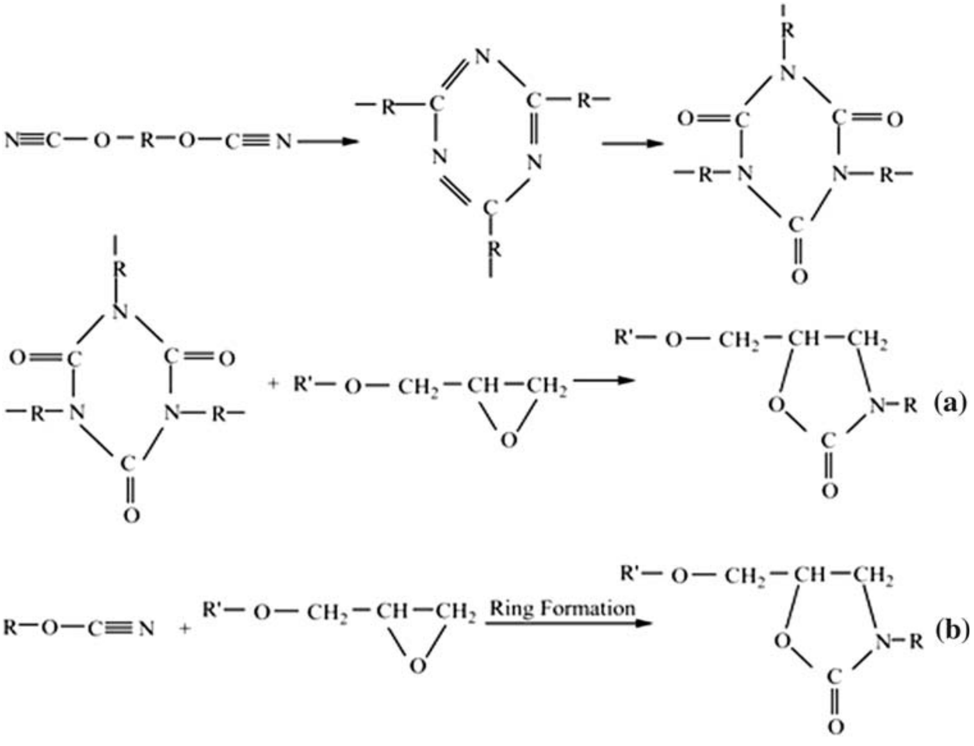
CE/BD resin is made up of BD prepolymer and CE, several reactions such as the cyclotrimerization of cyanate ester under the catalysis of –OH groups in DBA, "Ene" and "Diels–Alder" reactions between BMI and DBA, and the homopolymerization of BMI are responsible for the formation of network structures. BD and CE are believed to crosslink through the above mentioned reactions to form two discrete networks which interpenetrated with each other in the cured resin [20].

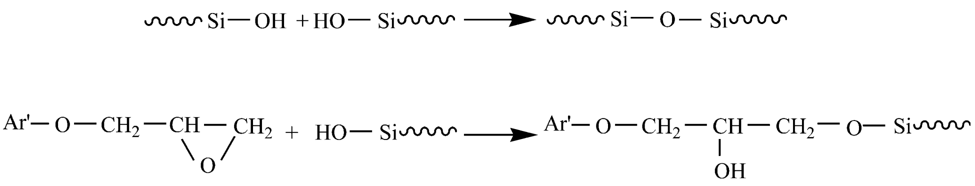
In case of CE/BD/HPSiE resins, besides the complex reactions in the CE/BD resin, the incorporation of HPSiE into CE/BD resin brings additional reactions, such as the copolymerization between epoxy and –OCN groups as well as triazine rings (Scheme 1) [21], and the self-polymerization of HPSiE (Scheme 2). Because the products resulting from the additional reactions are tough oxazolidinone rings and polyether structures, in addition, HPSiE has many unoccupied spaces and flexible Si–O bonds, so the network of CE/BD/HPSiE resins is expected to be flexible and tougher than that of CE/BD resin.

It is worthy to note that there maybe some other reactions, such as the copolymerizations between epoxy groups and imide rings or hydroxyl groups, but suitable catalysts (for example tertiary amine) should be used for insuring the progress of these reactions, so in case of CE/BD/HPSiE resins, these reactions are thought to be not the main reactions.

Impact strength

The impact strength of CE/BD and CE/BD/HPSiE resins are presented in Fig. 1, it can be seen that each CE/BD/


Scheme 1 Main reactions between HPSiE and CE


Scheme 2 Self-polymerizations of HPSiE

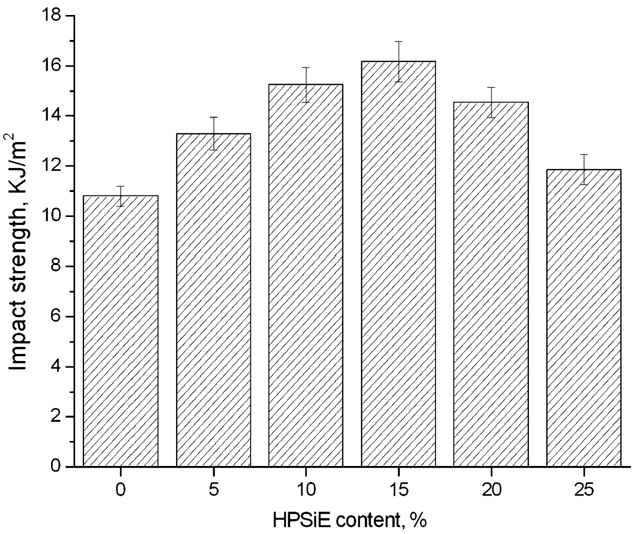


Fig. 1 Impact strengths of CE/BD resin and CE/BD/HPSiE resins

HPSiE resin developed in this paper has higher impact strength than CE/BD resin, and the stoichiometry between BD and HPSiE has obvious effect on the impact strength. In detail, there is an optimum stoichiometry between BD and HPSiE for obtaining the maximum impact strength (which is about 150% times of that of original CE/BD resin).

The improvement of toughness by the incorporation of HPSiE may be explained by the chemistry change of the cross-linking network. First, compared to CE/BD resin, CE/BD/HPSiE resins have tough oxazolidinones by the reaction between epoxy groups in HPSiE and –OCN groups besides of triazine rings. Second, the presence of unique unoccupied structure and flexible siloxane linkages of HPSiE also plays a significant role in obtaining good toughness for CE/BD/HPSiE resins. However, when the HPSiE content is big enough, the self-polymerization of HPSiE increases the cross-linking degree, and thus reducing the impact strength, as a result, there is an optimum stoichiometry between BD and HPSiE for obtaining the maximum impact strength, similar results are obtained by He et al. [22].

The improved toughness for CE/BD/HPSiE systems can be also confirmed by SEM micrographs of the fractured surfaces as shown in Fig. 2. All SEM micrographs are homogeneous and monophase structure. The fractured surface of CE/BD resin exhibits brittle feature, but with the incorporation of HPSiE into CE/BD resin and the increase of HPSiE content, stream-like and fibrous patterns begin to appear followed by typical tough feature in the fractured surface of CE/BD/HPSiE15.

In order to further discuss the toughening effect of HPSiE on CE/BD resin, DMA were also carried out. Figure 3 shows the overlay storage moduli (E') as a function of temperature for CE/BD resin and CE/BD/HPSiE resins, CE/BD/HPSiE resins have lower values of E' over the temperature range before T_g than CE/BD resin. Moreover, when the HPSiE content is less than 20 wt%, E' decreases with an increase in HPSiE content. Continuously, increase in the HPSiE content, the E' begins to decrease slightly. These phenomena clearly confirm the toughening effect of HPSiE on CE/BD resin.

On the other hand, it is known that the modulus in the rubber plateau for a polymer network is generally related to the cross-linking density of the material [23, 24], the decreased storage moduli of the CE/BD/HPSiE systems imply that CE/BD/HPSiE systems have lower cross-linking density than CE/BD resin, which is consistent with the change of structure as discussed above. This is another reason to explain the toughening effect of HPSiE on CE/BD resin.

Thermal properties

Thermal property of a resin can be characterized by glass transition temperature (T_g) and typical thermodegradation data. For a thermosetting resin, its T_g is an important property because it is the maximum application temperature of the resin. Generally, DMA is an effective method for measuring the T_g value of a thermosetting network. In this paper, T_g is defined as the peak (maximum) temperature in the tanδ-temperature plot from DMA tests [25].

Figure 4 shows the dependence of tanδ on temperature for CE/BD resin and CE/BD/HPSiE resins. Each CE/BD/HPSiE resin shows its tanδ peak at lower temperature than CE/BD resin does, and the more HPSiE content, the lower T_g is. The phenomenon can be mainly interpreted by two facts. First, as discussed above, the chemistry of CE/BD/HPSiE resins is different from that of CE/BD resin, the former has additional flexible and tough structure due to the presence of HPSiE, while the latter has rigid one. Second, the cross-linking density of CE/BD/HPSiE resins is lower than that of CE/BD resin.

The thermal stability of the cured HPSiE, CE/BD, and CE/BD/HPSiE resins was characterized by TGA, corresponding curves are shown in Fig. 5, and the typical data obtained from these curves such as the initial degradation temperatures (T_{di}) and the temperature of maximum degradation rate (T_{max}) are listed in Table 2. It can be observed that the addition of HPSiE into CE/BD resin decreases the T_{di}, and the more the HPSiE content in the CE/BD/HPSiE resin, the lower the T_{di} value is, this is mainly attributed to the low thermodegradation temperatures of HPSiE and oxazolidinones.

DTG curves show that CE/BD and CE/BD/HPSiE resins have two peaks reflecting the maximum degradation rate,

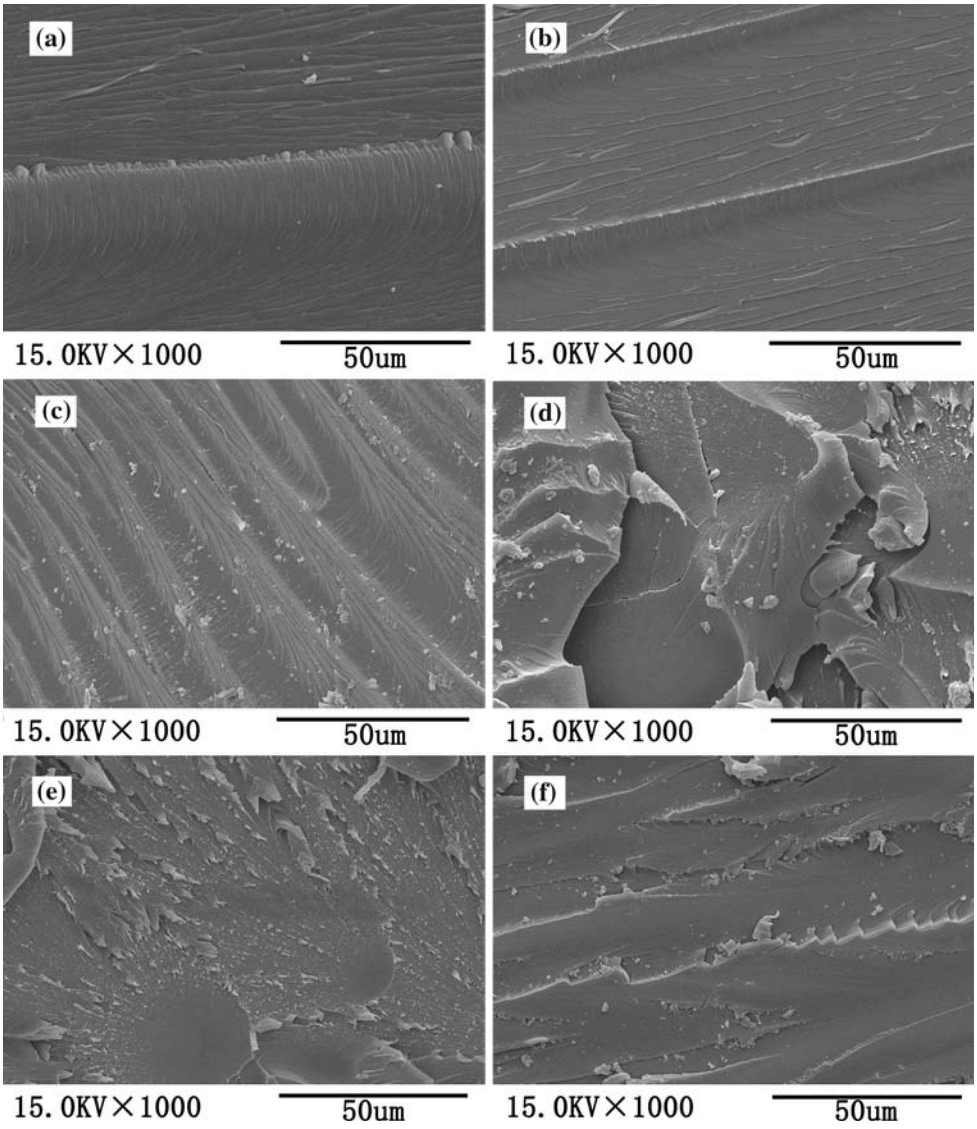


Fig. 2 SEM micrographs of the fractured surfaces of CE/BD resin and CE/BD/HPSiE resins (**a** CE/BD, **b** CE/BD/HPSiE5, **c** CE/BD/HPSiE10, **d**: CE/BD/HPSiE15, **e** CE/BD/HPSiE20, **f** CE/BD/HPSiE25)

and all of them have a peak with small intensity ($T_{\max2}$) at about 520 °C, however, the main peak with a big intensity ($T_{\max1}$) appears at different temperature, CE/BD/HPSiE resin with more HPSiE content tends to have lower $T_{\max1}$. Previous investigations have proved that triazine rings will break at about 450 °C, and oxazolidinone rings will break at a lower temperature [26], while HPSiE resin has the maximum degradation rate at about 420 °C, so with the addition of HPSiE into CE/BD resin, $T_{\max1}$ shifts to lower temperature.

Dielectric property

Figures 6 and 7 show the overlay curves of dielectric constant and dielectric loss of CE/BD and CE/BD/HPSiE resins over a frequency of 1 Hz–1 MHz, respectively. It can be seen that all CE/BD/HPSiE resins have very good dielectric stability over the frequency range as CE/BD resin does.

For dielectric constant, the concrete value of each CE/BD/HPSiE resin is dependent on the stoichiometry between BD and HPSiE, but the changing degree is lower than 3%, so it can be considered that CE/BD/HPSiE resins and CE/BD resin have equal values of dielectric constant.

Figure 7 shows that CE/BD/HPSiE resins with small HPSiE content exhibit very slightly lower dielectric loss than CE/BD resin, and with the further increased HPSiE content, the dielectric loss tends to increase, however, the increased degree is also small, which does not excess 10%. The dielectric loss factor of a material is mainly determined by the polarity of the material, HPSiE has both strong polar bonds (epoxy groups, hydroxyl groups) and weak polar bonds (Si–O bonds), so the effect of HPSiE on the dielectric loss is not significant.

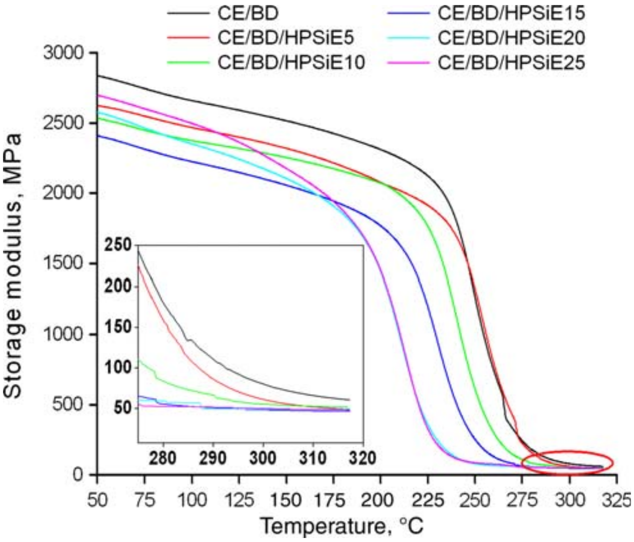


Fig. 3 Overlay storage moduli versus temperature for CE/BD and CE/BD/HPSiE resins

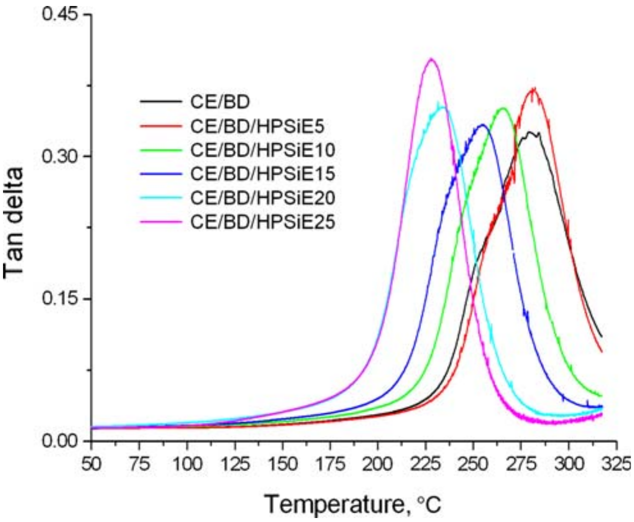


Fig. 4 Dependence of tanδ on temperature for CE/BD and CE/BD/HPSiE resins

Based on overall dielectric property over a wide frequency range, it can be concluded that CE/BD/HPSiE resins retain the excellent dielectric property of original CE/BD resin, which is very attractive.

Water absorption

Water absorption is an important property for the material used in microelectric industry, because a small amount of absorbed water existed in the network can still depress the electrical property acutely due to the high dielectric constant of water ($\varepsilon = 23$) [27]. Therefore, much less water absorption is one important target for developing new resin systems for microelectric industry.

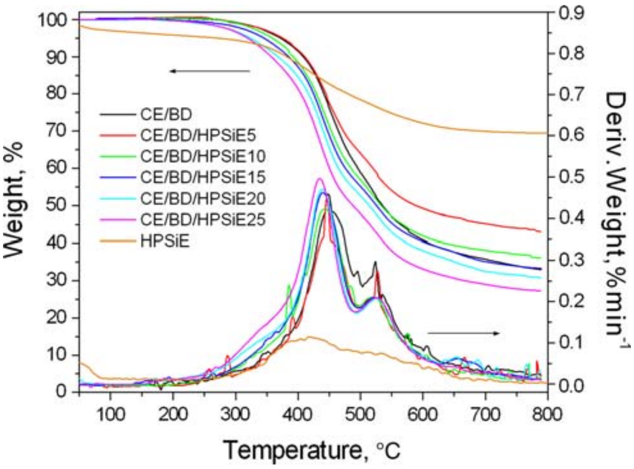


Fig. 5 TGA and DTG curves of cured HPSiE, CE/BD, and CE/BD/HPSiE resins

Table 2 Typical thermodegradation data of HPSiE, CE/BD resin, and CE/BD/HPSiE resins

Resin	T_{di} (°C)	T_{max1} (°C)	T_{max2} (°C)
CE/BD	372.3	448.1	524.3
CE/BD/HPSiE5	375.3	446.3	527.6
CE/BD/HPSiE10	358.9	442.1	523.9
CE/BD/HPSiE15	345.8	439.9	523.3
CE/BD/HPSiE20	324.1	439.6	525.8
CE/BD/HPSiE25	319.4	434.9	525.9
HPSiE	272.5	420.3	/

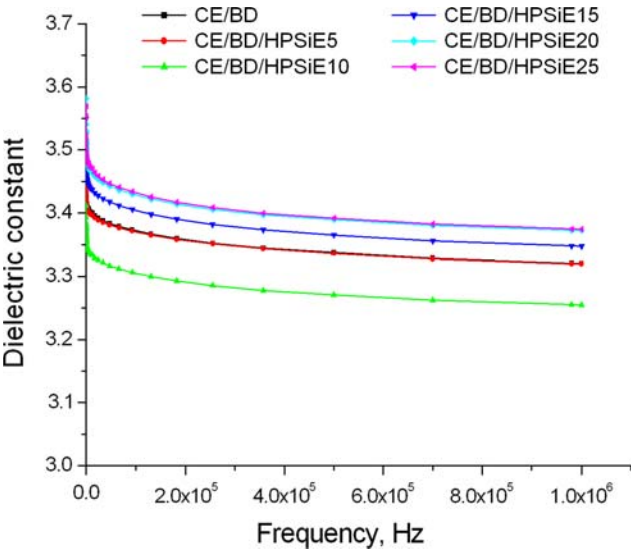


Fig. 6 Dependence of dielectric constant on frequency of CE/BD and CE/BD/HPSiE resins with various HPSiE contents

The water behaviors of the cured resins are shown in Fig. 8. It can be seen that the water absorption decreases with the addition of HPSiE, and all CE/BD/HPSiE resins

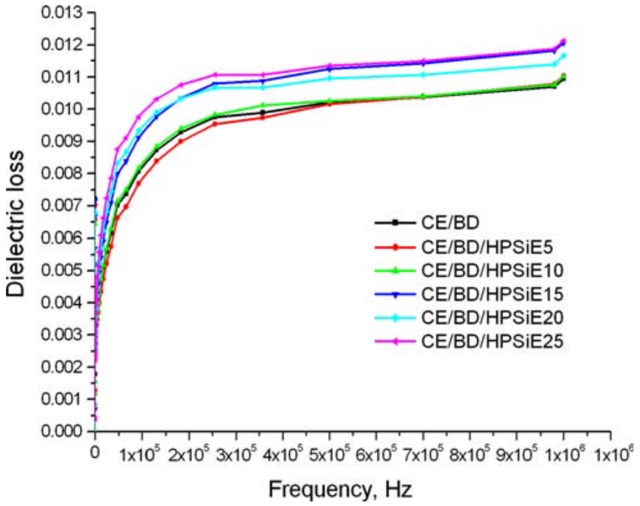


Fig. 7 Dependence of dielectric loss on frequency of CE/BD and CE/BD/HPSiE resins with various HPSiE contents

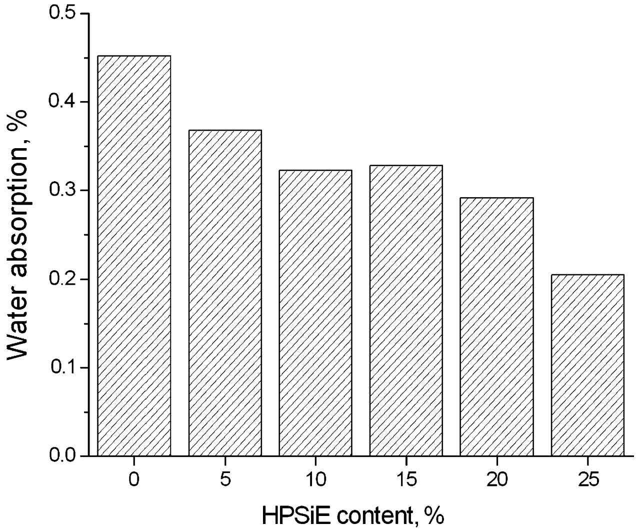


Fig. 8 Dependence of water absorptions of CE/BD/HPSiE on the HPSiE content

have significantly lower water absorption than CE/BD resin. In case of CE/BD/HPSiE25, its water absorption is 0.205%, only about 45.4% of the water absorption of CE/BD resin, suggesting that CE/BD/HPSiE resins have much better water resistance than CE/BD resin. Obviously, the improvement is also mainly contributed to the outstanding hydrophobic property of methyl siloxane chains [11].

Conclusions

The addition of HPSiE into CE/BD resin alternates the chemistry of the cross-linking network, and thus leading to significant influence on the properties including toughness, thermal, and dielectric properties as well as water resistance. The modified CE/BD/HPSiE resins with desirable HPSiE contents have much better integrate properties than original CE/BD resin, suggesting that the modification by reactive hyperbranched polymers provides a promising approach for developing high performance resins.

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