Novel Modification of Cyanate Ester by Epoxidized Polysiloxane

Chunzhuang Yang, Aijuan Gu, Hongwei Song, Zhongbin Xu'Zhengping Fang, Lifang Tong

Institute of Polymer Composites, Zhejiang University, Hangzhou, Zhejiang 310027, China

ABSTRACT: A novel modification of cyanate ester (CE) resin by epoxidized polysiloxane (E-Si) has been developed, and the modified system is coded as CE/E-Si. E-Si was prepared by the reactions among octamethylcyclotetrasiloxane, hexamethyldisiloxane, (3-aminopropyl)-methyldiethoxysilane, and diglycidyl ether of bisphenol-A resin. Six formulations were designed to evaluate the effect of the weight ratio between CE and E-Si on performance parameters. Results reveal that the addition of E-Si in CE resin cannot only significantly decrease the curing temperature of the CE resin but also improve the water resistance and toughness of original CE resin. Moreover, these positive effects increase with the increase of E-Si concentration in CE/E-Si systems. Thermal property investigation shows that the glass-transition temperature and initial degradation temperature of CE/E-Si systems are lower than that of original CE resin. For the flexural properties of the CE/E-Si systems, the E-Si concentration in the system exists a threshold, that is, when the E-Si concentration is smaller than the threshold, original CE and CE/E-Si systems have similar flexural properties, whereas when the E-Si concentration is higher than the threshold, CE/E-Si systems have lower flexural properties than original CE resin. All these changes of properties are closely correlated to the structure alteration from neat CE to CE/E-Si networks. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2020–2026, 2007

Key words: cyanate ester; polysiloxane; epoxy resin; toughness; water absorption

INTRODUCTION

The fast development of our modern industry has been increasingly requiring the information-related electrical equipments to deliver information at even greater speeds. Therefore, only reliable high-performance composites with light-weight, low dielectric constant (D_k), and dissipation factor (D_f) as well as excellent mechanical properties can be used for fabricating high-speed printed circuit boards (HSPCBs).[1] Cyanate esters (CEs) have attracted worldwide attentions because of their desirable properties such as low toxicity, good processing characteristics, excellent dielectric properties, and high service temperature, so they have been considered as the candidate matrices with great potential to produce HSPCBs. However, the cured CEs are generally brittle and have very high curing temperature,[2,3] which are the major disadvantages to restrict further prosperity of CEs into the advanced industrial applications.

Up to now, many methods have been developed to improve the toughness of CEs by using elastomers, thermoplastics, or thermosetting resins. Among them, the modification of CEs by high-performance thermosetting resins, such as bismaleimides (BMIs), epoxy (EP) resins, has been proved to be an effective route,

which may be the optimum method from the view of engineers due to its good processing characteristics, but this method still has some disadvantages. For example, comparing with pristine CEs, CE/EP systems have somewhat lower curing temperature, but their curing temperatures are still so high that it is difficult to be accepted by industries. Moreover, CE/EP systems have higher water absorption owing to the strong polarity of epoxy groups.[4] On the other hand, BT resin is a famous modified CE system by BMI, which is an important matrix used to product high-performance PCBs, but BT resin is so sensitive to the curing condition that it is difficult to guarantee the good quality of the resulting products. Therefore, there is a great deal of interest to develop new modified CE systems.

Polysiloxanes are remarkable for their low dielectric loss, low water absorption, high electrical resistance, and thermal stability as well as chemical inertness, so polysiloxanes may act as the desirable tougheners of CEs, especially when developing a new modified CE resin that is intended for the environments requiring outstanding water-resistance and dielectric properties. But polysiloxanes are immiscible with CEs, a simple blend can only lead to an obvious phase separation. Generally, functional polysiloxanes with reactive groups (—OH, —NH$_2$...) at the chain ends were employed to increase the compatibility by reactive blending.[5] However, it is worthy to note that the reaction between —NH$_2$ and —OCN groups is
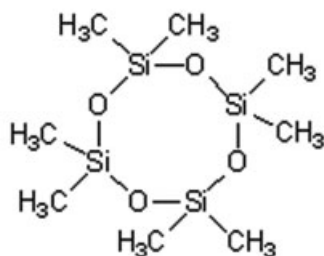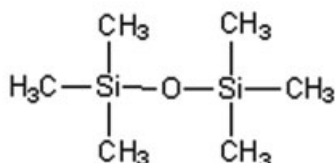
Correspondence to: A. Gu (ajgu@suda.edu.cn).
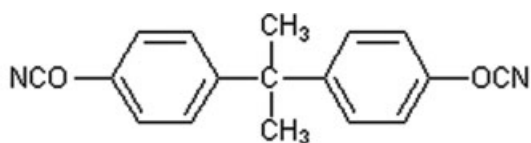
4-4'-dicyanate-2-2'-diphenylpropane (SD-1)
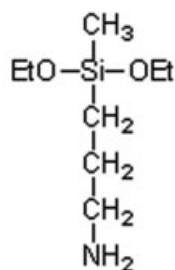
(3-aminopropyl)-methyldiethoxysilane (AMDES)

octamethylcyclotetrasiloxane (D$_4$)

hexamethyldisiloxane (MM)

Scheme 1 Chemical structures of main raw materials.

too drastic to be controlled and the property of the resultant product is very poor.[6]

To overcome aforementioned difficulties, in this work an epoxidized polysiloxane (E-Si) was designed and prepared via the reaction between polysiloxane and epoxy resin at the reflux temperature of Z-Butanone, and a modified CE system, coded as CE/E-Si, has been developed. E-Si can not only improve the compatibility between polysiloxanes and CEs but also avoid the reaction between —NH$_2$ and —OCN to form the unstable isourea structure $\overset{NH}{\underset{\parallel}{—O—C—NH—}}$.[7]

The focus of this work is put on investigating the effect of E-Si concentration on the properties of the CE/E-Si system, and discussing the reason resulting from the effect from the view of the structure–property relationship.

EXPERIMENTAL

Materials

CE was 4-4'-dicyanate-2-2'-diphenylpropane, commercially named SD-1, which was available from Zhejiang Newgen Pharmaceutical, China. The diglycidyl ether of bisphenol-A resin with an epoxy equivalent of about 185–195 was purchased from Jiangsu Wujiang Heli Resin, China. (3-Aminopropyl)-methyldiethoxysilane (AMDES) with 97.0% purity was obtained from Zhangjiagang Guotai-Harong New Chemical Materials, China. Hexamethyldisiloxane (MM) and octamethylcyclotetrasiloxane (D$_4$) were supplied by Zhejiang Xinan Chemical Industrial Group, China. Other reagents were commercial products and used as received. The chemical structures of main raw materials used are presented in Scheme 1.

Preparation of amino-silicone oil

Amino-silicone oil was prepared according to the reported procedure[8] with slight modification. A three-necked flask equipped with a magnetron, a reflux condenser, and a nitrogen inlet was charged with 10 g (0.052 mol) of AMDES, 4 g (0.014 mol) of D$_4$, 1 g (0.0062 mol) of MM, and 0.01 g of potassium hydroxide. The reaction mixture was stirred at 125°C for 5 h in a nitrogen atmosphere (Scheme 2). Then, the product was degassed under reduced pressure to remove the side products (such as ethanol, ether, etc.). The resultant product was amino-silicone oil, which was a viscous and transparent liquid, and could be dissolved in polarity solvents such as toluene, Z-Butanone, THF, and so on.

Preparation of E-Si

The calculated amount of epoxy resin (50 g) was dissolved in Z-butanone (50 mL) at the reflux temperature to form epoxy resin/Z-butanone solution. After complete dissolution, a solution of 10 g amino-silicone oil prepared earlier in 10 mL Z-Butanone was added dropwise to the epoxy resin/Z-butanone solution mentioned earlier. The mixture was maintained at the reflux temperature for 1 h to guarantee the full conversion of primary amine to tertiary amine (Scheme 3). After that, the Z-Butanone was removed under
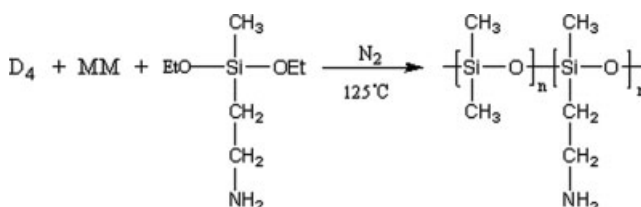
Scheme 2 Synthesis of amino-silicone oil.
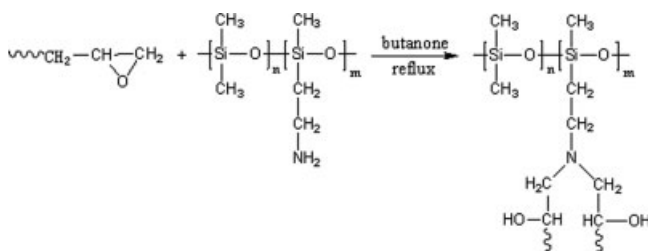
Scheme 3   Synthesis of E-Si.

reduced pressure at 70°C for 1 h. The resultant product was epoxidized polysiloxane and coded as E-Si.

Preparation of cured CE/E-Si systems

Appreciated amounts (according to each formulation as shown in Table I) of cyanate resin and E-Si were thoroughly blended at 100°C for 15 min with vigorous stirring. Then the mixture was degassed to remove entrapped air at 90°C in the vacuum, followed by casting into a mold for curing via the procedure of 140°C/1 h + 160°C/1 h + 180°C/1 h + 200°C/2 h + 220°C/2 h and postcuring at 240°C for 4 h. Finally the cured modified CE resin was demolded and coded as CE/E-Si system.

Measurements

DSC analyses were done by using a DSC Q100 (TA Instruments, New Castle, DE) in the temperature range between 50 and 300°C at a heating rate of 5 K/min in a nitrogen atmosphere.

Thermogravimetric analysis (TGA) was carried out using PerkinElmer Pyris 1 at a heating rate 10 K/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 %.

Dynamic mechanical analysis (DMA) was performed in a dual-cantilever blending mode by using TA DMA Q800 apparatus at a heating rate of 3 K/min and a frequency of 1 Hz. The glass-transition temperature (T_g) is defined as the peak (maximum) temperature in the tan δ-temperature plot.

The flexural strength was measured according to GB/T2570-1995 by using Electronic universal testing

TABLE I
Formulations

Sample	Weight ratio of CE/E-Si
Neat CE	100/00
CE/E-Si-1	100/06
CE/E-Si-2	100/12
CE/E-Si-3	100/18
CE/E-Si-4	100/24
CE/E-Si-5	100/36

machines (RIGER-20; China) at a crosshead speed of 2 mm/min.

The unnotched impact strength of a sample was tested according to GB/T2571-1995 using Charpy impact machine tester (XCJ-L; China).

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

A scanning electron microscope (Hitachi *S*-570′; Japan) was employed to observe the morphology of the fractured surfaces of samples.

RESULTS AND DISCUSSION

Influence of the E-Si concentration on the curing behavior of CE/E-Si systems

The DSC traces of neat CE and CE/E-Si systems are presented in Figure 1. The curve of neat CE resin shows a single exothermic peak, of which the initial reaction temperature (T_i), the peak reaction temperature (T_p), and the end reaction temperature (T_e) are
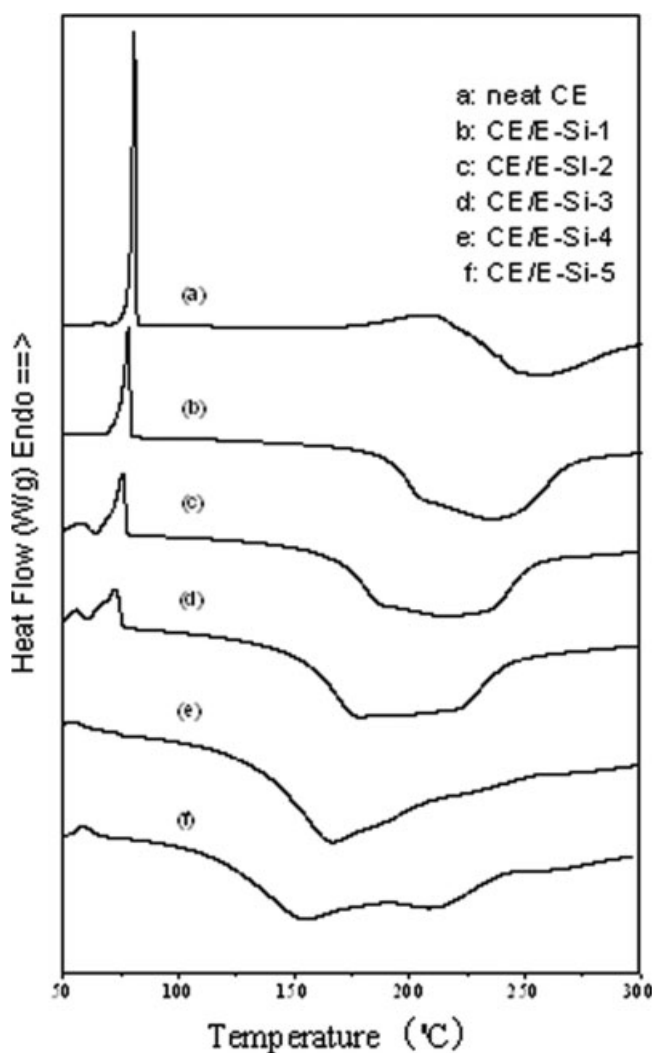

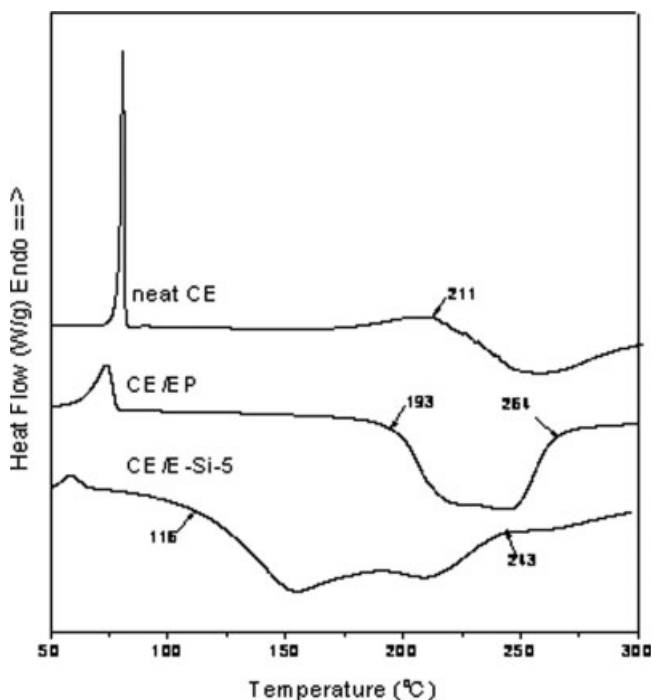**Figure 1**   DSC traces of various samples at a heating rate of 5 K/min.

Figure 2 DSC traces at a heating rate of 5 K/min.

211, 255, 300°C, respectively. While, with the addition of E-Si into CE system, the peak is obviously shifted to lower temperature. In case of CE/E-Si-5 system, it has a broader exothermic peak, and its T_i and T_e are 116 and 243°C, respectively, suggesting that CE/E-Si systems have faster reaction rate and lower curing temperature than original CE resin. Because it is well known that high curing and postcuring temperature is one of the key disadvantages of CEs, so the decreased curing and postcuring temperature of CE/E-Si system is beneficial to manufacture CE-based composites for industries. To evaluate the curing temperatures of CE/EP and CE/E-Si systems, DSC analy-
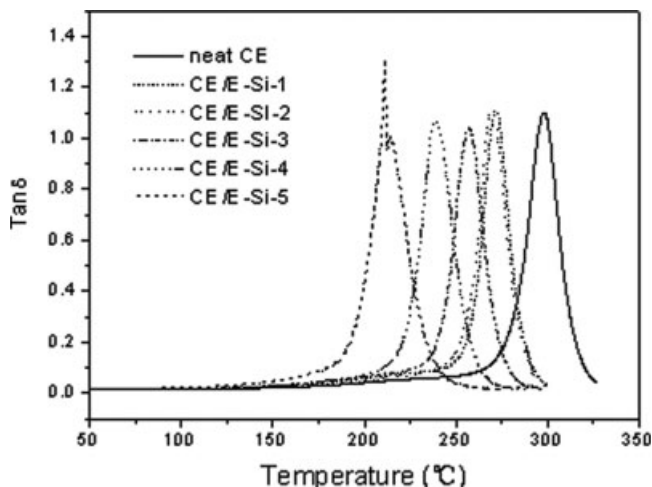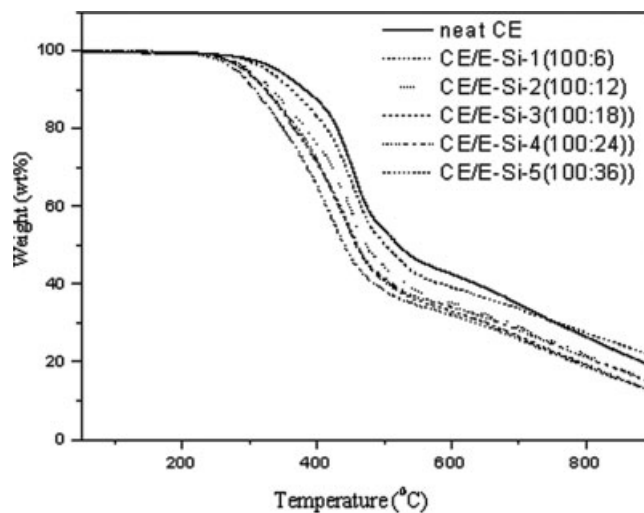

Figure 4 TGA curves of neat CE and CE/E-Si systems.

ses of CE/EP and CE/E-Si systems with the same weight ratio of CE and EP were done, and the corresponding DSC curves were shown in Figure 2. As for comparison, above information of neat CE resin is also included. It can be seen from Figure 2 that comparing with the exothermic peak of neat CE, the reaction peaks of CE/EP and CE/E-Si systems appear in lower temperature range, especially for CE/E-Si-5 system. The shift of the reaction temperature for CE/E-Si-5 system results from plentiful hydroxyl groups in E-Si, which has been proved to have effective catalytic effect on the curing of CE.[9]

Thermal and thermal stability of CE/E-Si systems

For a thermosetting resin, its T_g is very important because it is the maximum employing temperature of the resin. Generally, for a thermosetting network, its T_g is easier to be measured by DMA method than by
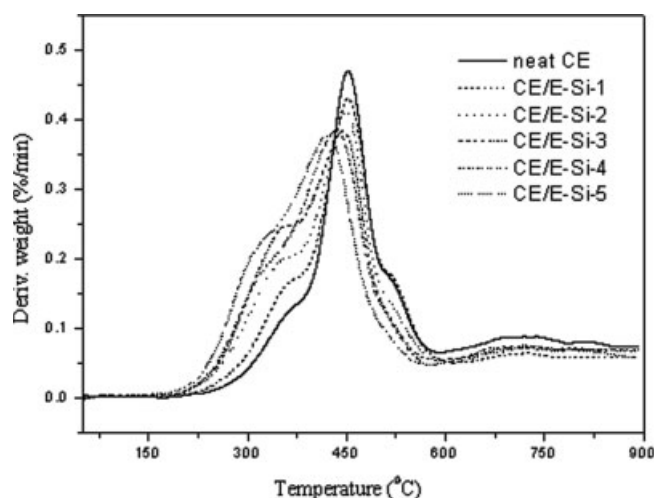

Figure 3 Tan δ-temperature curves from DMA tests of neat CE and CE/E-Si systems.

Figure 5 DTG curves of neat CE and CE/E-Si systems.

Sample	T_{di} (°C)	T_{max} (°C)
Neat CE	294	455
CE/E-Si-1	280	455
CE/E-Si-2	264	454
CE/E-Si-3	259	447
CE/E-Si-4	255	439
CE/E-Si-5	249	424

DSC method. So in this article, the T_g values of pristine CE and CE/E-Si resins were tested by DMA method. Figure 3 shows the dependence of tan δ on temperature, and it can be seen that the incorporation of E-Si into CE has the significant influence on T_g. For example, the T_g values of CE/E-Si systems containing 6, 12, 18, 24, and 36 wt % of E-Si, respectively, decrease from 298 to 272, 270, 257, 239, and 213°C, respectively. This may be contributed to two reasons. Firstly, CE/E-Si systems have flexible linkages of —Si—O—Si— and —C—C—. Secondly, CE/E-Si systems have lower crosslink density than neat CE resin because the molecular length of E-Si is longer than that of CE, in addition, the number of triazine rings in CE network is more than that in CE/E-Si network due to the reactions between CE and E-Si.

TGA was used to study the influence of E-Si concentration on the thermal stability of CE/E-Si systems. Figures 4 and 5 show the TGA and DTG curves of CE and CE/E-Si systems, respectively, and the typical data obtained from these curves such as T_{di} and the temperature of maximum degradation rate (T_{max}) were listed in Table II. It can be seen from Table II that the addition of E-Si into CE decreases all typical degradation data (T_{di}, T_{max}), and the more the E-Si content in the CE/E-Si system, the worse the thermal stability of the system, but the katabatic tendency of T_{di} is different from that of T_{max}. In detail, with the increase of E-Si content, T_{di} decreases gradually from
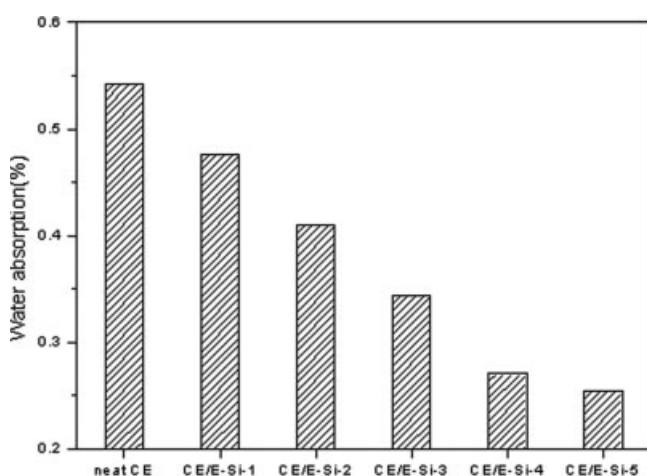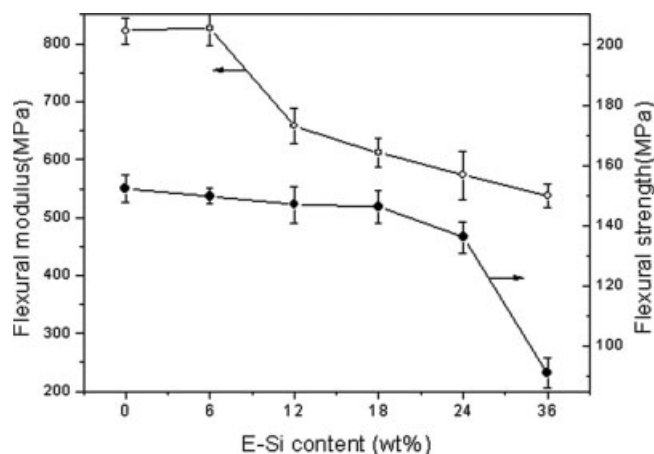

Figure 7 The dependence of E-Si concentration on the flexural properties of cured resins.

294 to 249°C, while T_{max} almost does not changed until the E-Si content excesses 12 wt %, and after that, with continually increasing of the E-Si content, T_{max} begins to decrease sharply. It is believed that two factors lead to this outcome, one is the lower crosslink density as discussed earlier, the other is the existence of oxazolidinone rings resulting from the coreactions between the triazine rings and epoxy groups in E-Si molecular; previous research has proved that oxazolidinone rings are relatively unstable at high temperature.[10]

Water absorption behaviors of CE/E-Si systems

One of the advantages of the cured CE is its low water absorption, but even if small content of absorbed water existed in the network can still depress the electrical property acutely due to the high dielectric constant of water (ε ≈ 23).[11,12] Therefore much less water absorption is one important target for developing new resin systems to be used in electric

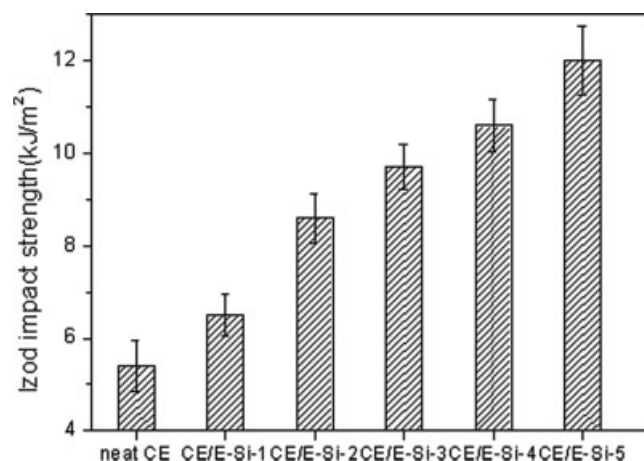**Figure 6** Water absorption of CE and CE/E-Si systems.

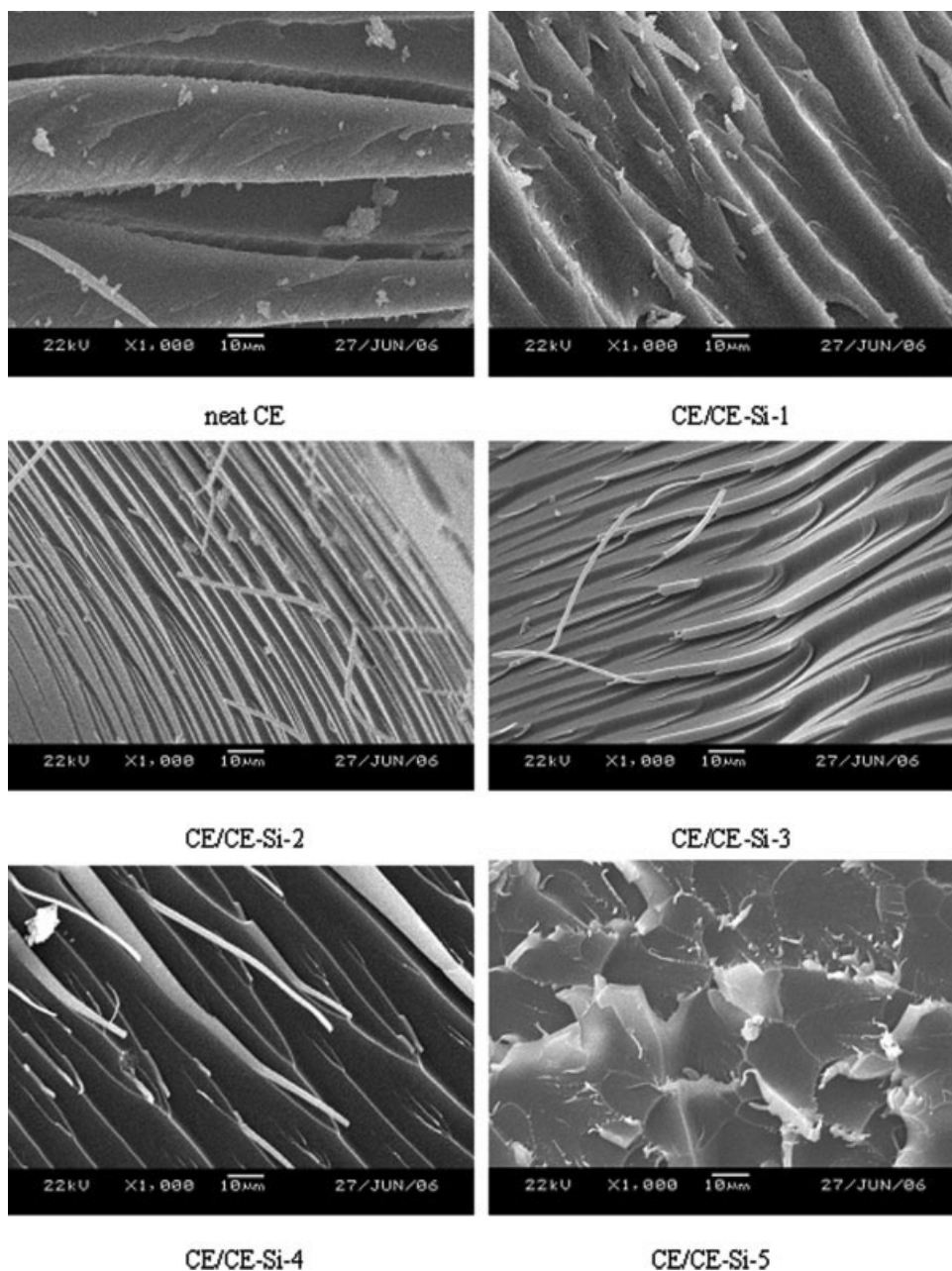**Figure 8** The impact strength of CE and CE/E-Si systems.

Figure 9 SEM micrographs of neat CE and CE/E-Si systems.

industry. Figure 6 gives the water absorption of five CE/E-Si systems and that of neat CE resin for comparison. It can be seen that the water absorption decreases sharply from 0.54 to 0.4 wt % with the small addition (10 wt %) of E-Si into CE, and which continually decreases with the continuous increase of E-Si content in CE/E-Si systems. In case of CE/E-Si-5 system, its water absorption is 0.25 wt %, which is about half value of neat CE resin. The improvement of water-resistant property of CE/E-Si systems results from two facts. Firstly, it is the increasing of the conversion of the —OCN groups in the same cured condition due to the greatly decreased curing temperature as discussed earlier. Secondly, outstanding

hydrophobic property of the methyl siloxane chains plays the major role in improving the water-resistant property of cured CE/E-Si resins.

Mechanical properties

The influence of the E-Si content on the flexural properties of CE systems is presented in Figure 7. It is easily noticed that the desirable addition of E-Si into CE does not change the flexural properties, but when the E-Si content is higher than a ''threshold,'' CE/E-Si systems have poorer flexural properties than original CE. The noteworthy ''threshold'' value of the E-Si content for flexural strength or flexural modulus is 20

or 5 wt %, respectively. The different effect of the E-Si content on flexural strength and modulus may be interpreted from the effect of the E-Si content on the internal stress of cured CE/E-Si networks.

It is known that the failure of the cured CE resins can be mainly contributed to the internal residual stress resulting from the shrinkage during the curing process. Equation (1) shows that the thermal stress (σ) is dependent on T_g and the flexural modulus (E_m) of the systems,[13,14] the reductions of T_g and E_m lead to the decrease of the thermal stress. From Figures 3 and 7, it is observed that both T_g and E_m of the CE resin decrease with the incorporation of E-Si in CE resin, so the thermal stress (σ) decreases with the addition of E-Si.

$$\sigma = k \int_{25}^{T_g} E_m(\alpha_m - \alpha_x)\, dt \tag{1}$$

where k is the constant, T_g is the glass-transition temperature, E_m is the flexural modulus, α_m and α_x are thermal expansion coefficients of different components in the system.

Mechanics of materials proves that the flexural strength is more sensitive to the internal residual stress (or defects) in the materials than flexural modulus. The addition of E-Si into CE tends to reduce the flexural modulus mainly owing to the flexibility of —Si—O—Si— linkages, whereas in case of flexural strength, the reduced thermal stress counteracts the negative role of oxazoline and oxazolidinone rings, which are produced from the reactions between CE and epoxy groups and have been proved to have lower strength than trazines.[15]

Figure 8 shows the izod impact property of neat CE and CE/E-Si systems. It is observed that the toughness of CE increases with the incorporation of E-Si in CE. For example, the izod impact strengths for CE/E-Si systems containing 6, 12 18, 24, and 36 wt % of E-Si, respectively, increase from 5.4 to 6.5, 8.6, 9.7, 10.6, and 12.0 kJ/m^2, respectively. The increase of toughness for the CE/E-Si systems can be also observed by the SEM micrographs of the fractured surfaces of the systems (Fig. 9). These photographs show that the fractured surface of the neat CE exhibits typical brittle feature, but with the increase of the E-Si content in CE, the fractured surfaces appear stream-like and fiber patterns. When the E-Si content is up to 30 wt %, the fractured surface exhibits the typical tough feature, which has higher efficiency to absorb the impact energy. The improvement of toughness by the E-Si incorporation may be explained as

the presence of flexible siloxane linkages due to the free rotation and high-energy absorption of —Si—O—Si—O— bonds.[16]

CONCLUSIONS

E-Si was synthesized by the reaction between epoxy resin and amido-siloxane. The modification of CE by E-Si overcomes the problem of phase separation, which generally occurs when a polysiloxane is used as the modifier of CEs. The addition of E-Si into CE resin leads to significantly different curing behavior, thermal, mechanical, and water-absorbing properties due to the change of the network structure.

Firstly, CE/E-Si systems have the better processing property such as much lower curing temperature than neat CE and CE/EP systems. Secondly, CE/E-Si systems have drastically improved toughness and water resistance. Thirdly, T_g and the initial degradation temperature of CE/E-Si systems are lower than those of original CEs. Lastly, there is an optimum E-Si concentration in CE/E-Si systems to retain desirable flexural property.

References

1. Daisuke, F.; Yasuyuki, M.; Nozomu, T.; Shigeo, S.; Harumi, N.; Takeshi, S. In Proceedings of IEEE Polytronic 2002 Conference, Zalaegerszeg, Hungary, 2002; p 114.
2. Treliant, F.; David, A. S. Prog Polym Sci 1995, 20, 61.
3. Ieana, B. R.; Dagmar, R.; Rosa, G. L.; Clara, M. G. Eur Polym J 2005, 41, 2635.
4. Liang, G. Z.; Zhang, M. X. J Appl Polym Sci 2002, 85, 2377.
5. Cabanelas, J. C.; Serrano, B.; Gonzalez, M. G.; Baselga, J. Polymer 2005, 46, 6633.
6. Bauer, J.; Bauer, M. Macromol Chem Phys 2001, 202, 2213.
7. Lin, R. H.; Hsu, J. H. Polym Int 2001, 50, 1073.
8. Wang, X. R. Silicone Mater 2001, 4, 6.
9. Clara, M. G.; Ileana, B. R.; Inaki, M. Eur Polym J 2005, 41, 2734.
10. Cheng, X. B. High-Performance Base Body Resin; Chemical Industry Press: Beijing, 1999; p 102.
11. Takao, T.; Satoru, K.; Wakichi, F.; Masao, T. J Appl Polym Sci 2000, 76, 208.
12. Gu, Z. J.; Wang, S. T. The Electronic and Magnetic Properties of Polymer; Shanghai Jiaotong University Press: Shanghai, 1990.
13. Wang, D. Z. Production and Application of Epoxy Resin; Chemical Industry Press: Beijing, 2001; p 486.
14. Kang, S.; Hong, S.; Choe, C. R.; Park, M.; Rim, S.; Kim, J. Polymer 2001, 42, 879.
15. Yang, J. Y.; Liang, G. Z.; Ren, P. G.; Wang, J. L.; Fang, H. Q.; Gong Z. H. J Aeronautical Mater 2004, 24, 21.
16. Ashok, K. A.; Alagar, M.; Rao, R. J Appl Polym Sci 2001, 18, 2330.