

Preparation and Properties of Cyanate Ester Modified by Epoxy Resin and Phenolic Resin

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ABSTRACT: Stiff and brittle cyanate ester (CE) resin was modified by copolymerizing it with epoxy resin (ER) and phenolic resin (PR) to improve its toughness and flexibility. The cure process of the modified CE resin was characterized by gel time curves and differential scanning calorimetry curves. The Fourier transform infrared spectra of the modified CE resin showed its chemical structure during the curing process. The mechanical properties, thermal behavior, dielectric properties, and morphology of the modified CE resins were investigated. The results showed that an increase in epoxy and phenolic resins resulted in

improved flexibility while maintaining thermal stability. When the mass ratio of CE/ER/PR was 70 : 15 : 15 (w/w), flexural strength and impact strength of the modified CE resin increased from 113.6 MPa and 5.2 kJ/m² to 134.5 MPa and 16.7 kJ/m², respectively. Little of the thermal stability and dielectric properties was sacrificed in the modification of the CE. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3150–3156, 2007

Key words: modification; resins; stiffness; toughness; differential scanning calorimetry (DSC)

INTRODUCTION

Cyanate ester (CE) is a type of high-performance thermosetting resin with outstanding mechanical, electrical, and thermal properties. It has high glass-transition temperatures (250°C–300°C), good mechanical properties, high fracture toughness, and very low moisture absorption. Its electric properties (dielectric constant, $\epsilon = 2.6$ –3.1; tangent of dielectric loss angle, $\tan \delta = 0.002$ –0.005) are superior to all other existing thermosetting resins. These attractive features make CE suitable for use in high-performance composites such as printed circuit boards and structural composites for the aerospace and microelectronic industries.^{1–5} Therefore, CE resin has become an increasingly important class of matrix resins since its development in the early 1970s. However, the application of CE has been limited by its poor flexibility, high melting or softening temperature, and high brittleness. The improvement of the flexibility of CE while retaining its high thermal stabil-

ity and dielectric properties has been an important issue in the past few decades. Current and prior attempts to improve flexibility have been done through transforming the basic rigid-triazine structures into flexible structures by copolymerization with thermoplastic hybrids or flexible rubbers. There are three types of popular modification methods^{6–8}: (1) copolymerizing CE with linear resins such as epoxy resin (EP); (2) blending CE with thermoplastic resins such as polycarbonate (PC), polysulfone, and polyamide (PI); and (3) using rubber to improve the toughness of CE. These modification methods can improve the flexibility of the CE resins, but simultaneously lead to decreases in the thermal stability and electrical properties, which in turn limit the applications for which CE can be used.^{9,10} Our aim in this work was to modify CE resin by copolymerizing it with epoxy resin (ER) and phenolic resin (PR) in order to obtain desirable flexibility without appreciable sacrifice in the dielectric properties and heat resistance. The preparation, curing parameters, heat stability, and factors that influence modified CE resin were investigated. The modification method greatly extended the utility of CE resins.

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EXPERIMENTAL

Materials

Bisphenol A CE (an industrial product with a molecular weight of 426) was supplied by No. 637 Insti-

tute of the China Aeronautical Group of Science and Technology (Jinan/Shandong Province, China). Linear phenolic resin (an industrial product with a molecular weight of 5000) was purchased from Factory 704 (Xianyang/Shaanxi Province, China). The epoxy resin (ER), E-51, was purchased from the Wuxi Resin Factory (Wuxi/Jiangsu Province, China). E-glass fiber cloths were supplied by the Xingping Glass Fiber Factory (Xianping/Shaanxi Province, China). The other chemicals were used as received.

Preparation of modified CE

The CE, ER, and PR were weighed to make up predetermined proportions and placed in 200-mL dry, clear glassware. The resins mixture was heated to 90°C while stirring until a transparent yellow viscous solution was obtained. The viscous solution was poured into a heating mold to get modified CE sheet, and the thickness of the sheet was controlled at 2.0 mm. Then the mold sheet was put into a vacuum oven and heated at 90°C for 0.5 h in a vacuum in order to remove the air bubbles dissolved in the viscous solution. The viscous solution was further cured by successively heating at 150°C for 1 h, 170°C for 1 h, 190°C for 2 h, and finally 220°C for 3 h under atmospheric pressure. Then it was slowly cooled to room temperature. The cured resin was the modified CE resin.

Preparation of composites

The mixed CE, ER, and PR resins were dissolved in acetone at room temperature according to predetermined proportions. Then the acetone solution of mixed resins was daubed on a glass fiber cloth to form a resin coating. The resin coating had been dried at room temperature for 24 h and heated at 50°C for 1 h in order to remove the acetone solvent, at which point the glass fiber cloths were laid on the

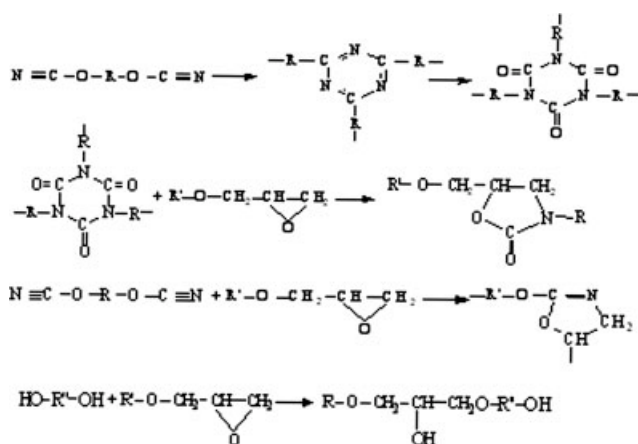


Figure 1 Principle and mechanism of modified CE with ER and PR.

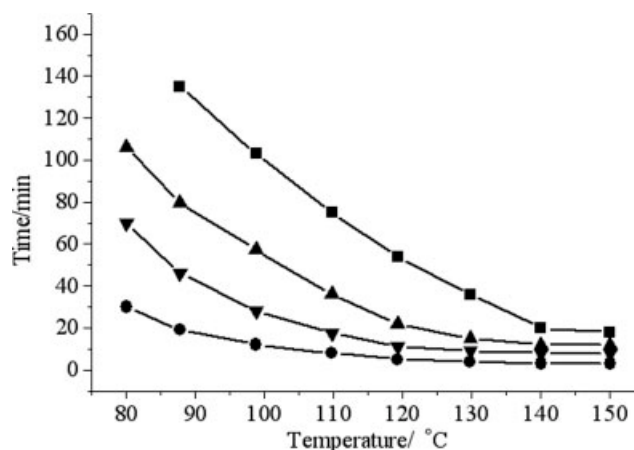


Figure 2 Effect of temperature on gel time curve of CE/ER/PR: (■) CE/ER/PR = 100 : 0 : 0, (▲) CE/ER/PR = 70 : 30 : 0, (▼) CE/ER/PR = 70 : 20 : 10, (●) CE/ER/PR = 70 : 15 : 15.

mold in order to obtain the composite sheet. The thickness of the composite sheets was controlled at 2.00 mm. The molding conditions were: 100 for 20 min under 10 MPa and then heated at 150°C for 1 h, at 170°C for 1 h, at 190°C for 2 h, and at 220°C for 3 h under 20 MPa. After unloading, the sheets were put into a heated oven and heated at 250°C for 6 h under atmospheric pressure.

Tests and measurements

The gel time of the resins was measured by the plate small knife method. The cured temperature of the mixed resin and the glass-transition temperature of the cured resin were characterized by differential scanning calorimetry (DSC) at a heating rate of 2°C/min (or 5°C/min, 10°C/min, 15°C/min, or 20°C/min) on a NETZSCH Instruments model 200PC differential

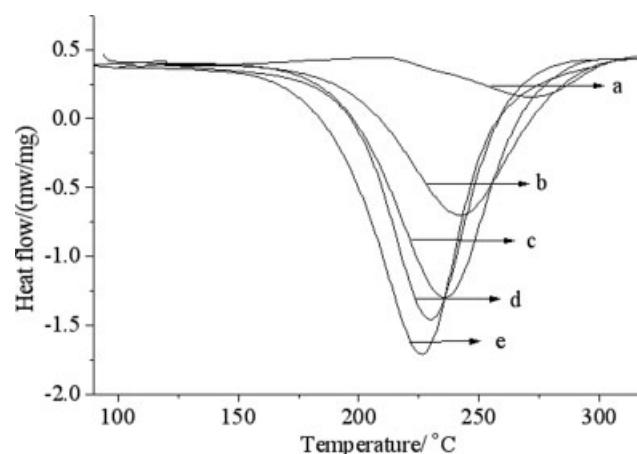


Figure 3 DSC curve of modified CE resins of CE/ER/PR (10°C/min): (a) CE/ER/PR = 100 : 0 : 0, (b) CE/ER/PR = 70 : 30 : 0, (c) CE/ER/PR = 70 : 25 : 5, (d) CE/ER/PR = 70 : 20 : 10, (e) CE/ER/PR = 70 : 15 : 15.

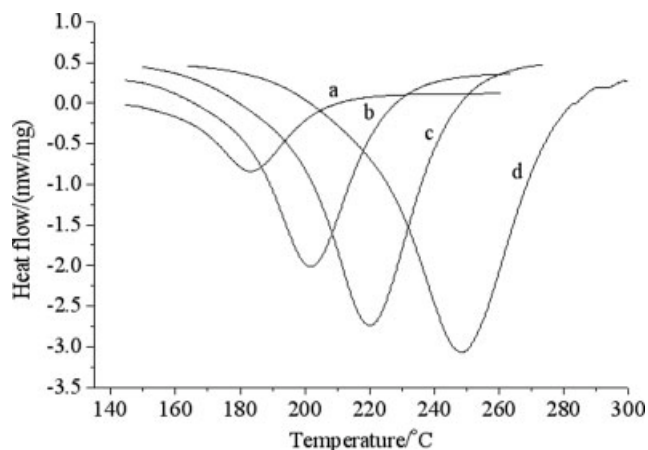


Figure 4 Effect of heating rate on DSC curve of CE/ER/PR: (a) 2°C/min, (b) 5°C/min, (c) 10°C/min, (d) 20°C/min.

scanning calorimeter in a dry nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried on a TA Instruments model 2960 thermogravimetric analyzer at a heating rate of 10°C/min under a dry nitrogen atmosphere. Thermal decomposition temperatures were taken when the cured resins had lost 10%, 30%, and 50% of their initial mass. Bending strength and interlaminar shear strength (ILSS) were measured according to GB3357-1982 (the People's Republic of China National Standard Methods) on a Guangzhou Instruments model ZMG1 material tester. Impact strength was measured according to GB/T2571-1995 on a Guangzhou Instruments model X CJ material tester. The cross sections of the composites were observed by a HITACH S-570 scanning electron microscope. Fourier transform infrared (FTIR) spectra were obtained on KBr pellets of the resins using a Bruker Vector22 FTIR spectrometer.

RESULTS AND DISCUSSION

Principle of modification of CE reaction

CE resin and the modified CE resin are both thermosetting resins with high mechanical performances. The cured CE resin was heated to form triazine networks with a high degree of crosslinking and high crystallinity. Therefore, cured CE resin had a brittle nature with poor resistance to crack growth. The

TABLE I
Reaction Temperatures at Various Heating Rates

	T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)
2°C/min	161.2	185.2	210.4
5°C/min	175.8	198.2	227.8
10°C/min	195.9	225.9	250.1
20°C/min	217.6	258.4	278.7
Y axis	148	177	198

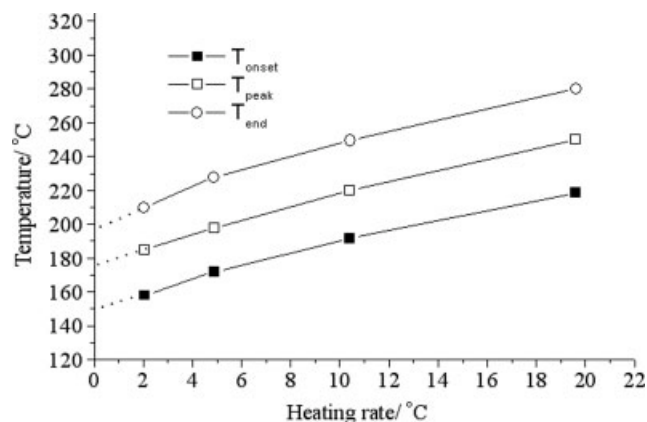


Figure 5 Reaction temperatures at various heating rates: (○) T_{end} , (□) T_{peak} , (■) T_{onset} .

modified CE was prepared by adding ER and PR in suitable quantities with heating to improve its flexibility. The reaction of ER with CE and CE was able to transform triazine into isocyanate, which reacted with ER to form oxazolinone. ER could react with PR to form a flexible structure. The modification results show that crosslink density and yield of triazine decreased and the flexibility of the cured modified resin improved as the contents of ER and PR increased in the resin systems. The modification reaction equation is shown in Figure 1.

Properties of cured reactions

The gel-time curves of the CE/ER/PR resin system are shown in Figure 2, which reflects the effect of temperature on the gel time of the resin system. The

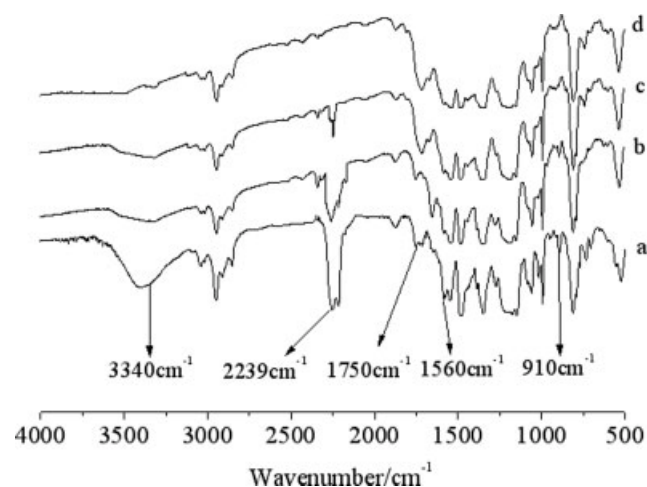


Figure 6 FTIR spectra of curing CE/ER/PR resins after heating at different temperatures: (a) CE/ER/PR = 100 : 0 : 0 at 150°C for 1 h, (b) CE/ER/PR = 70 : 30 : 0 at 180°C for 1 h, (c) CE/ER/PR = 70 : 25 : 5 at 200°C for 2 h, (d) CE/ER/PR = 70 : 15 : 15 at 220°C for 3 h.

results indicate that gel time decreased remarkably with increasing contents of PR and ER in the resin system. It can also be seen from Figure 2 that there was a minimum gel time, when the mass ratio of CE, ER, and PR was 70 : 15 : 15. This means the addition of ER and PR can greatly enhance the cured reaction.

The DSC curves of the resin system in nitrogen are shown in Figure 3, which reflects reacted peaks of various resin systems at various heating temperatures. The results show that the reacted peaks of the resin system shifted toward lower temperatures. This means the activity of the resin system increased because the OH— in the PR could react with CE and ER.

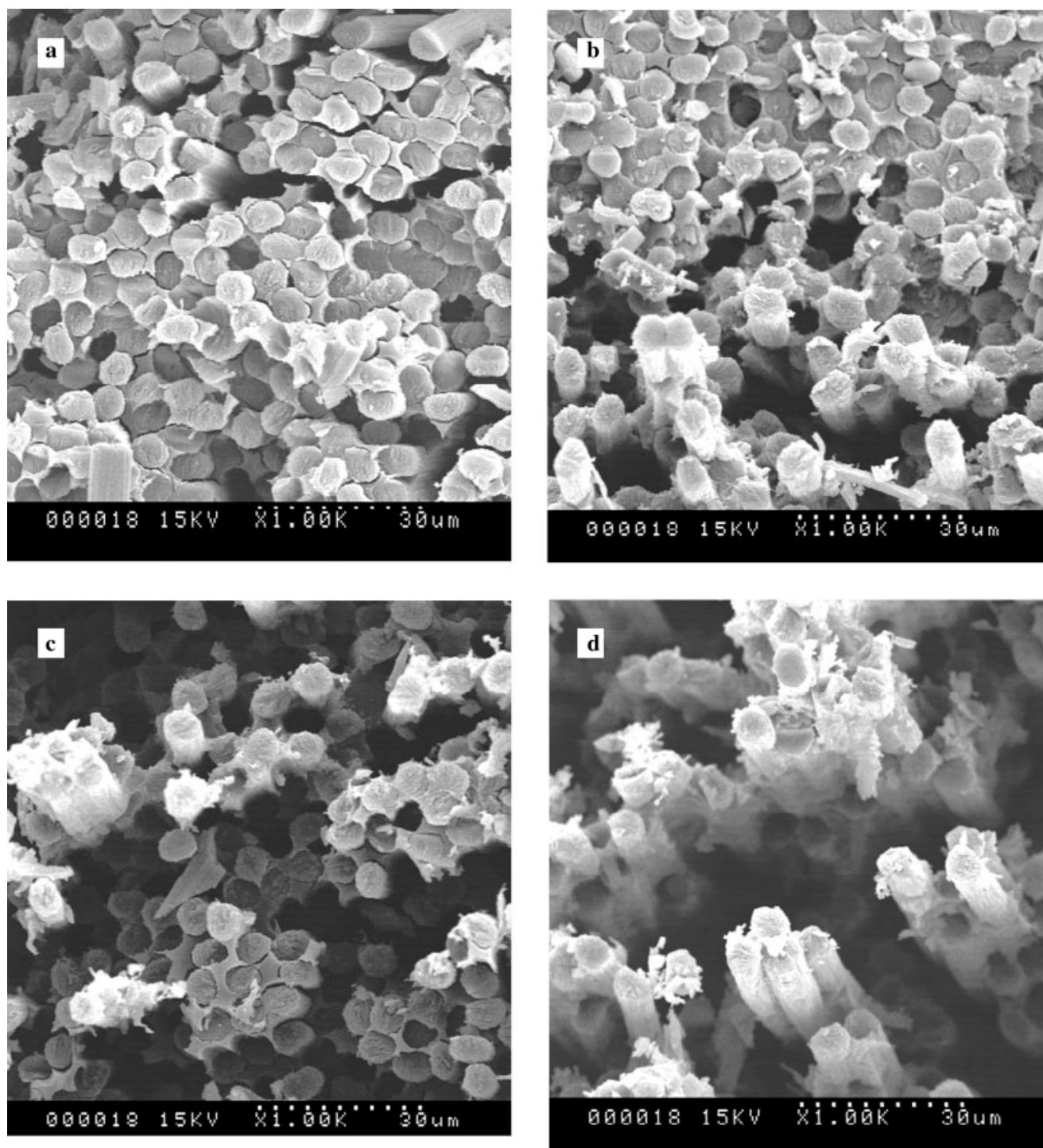


Figure 7 SEMs of fracture section of modified CE composite sheets: (a) CE/ER/PR = 100 : 0 : 0, (b) CE/ER/PR = 70 : 30 : 0, (c) CE/ER/PR = 70 : 25 : 5, (d) CE/ER/PR = 70 : 15 : 15.

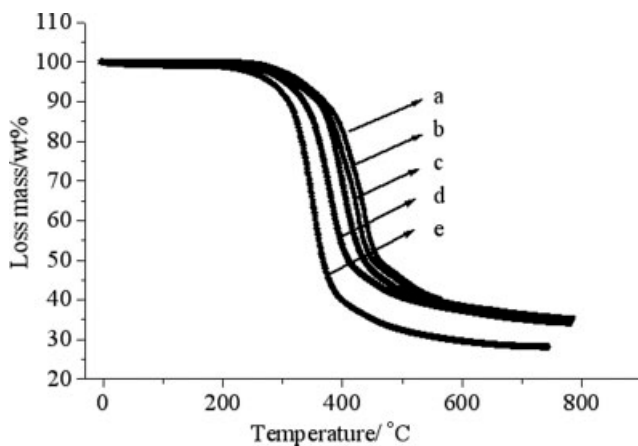


Figure 8 Thermal gravimetric analysis (TGA) curves of CE/ER/PR: (a) CE/ER/PR = 100 : 0 : 0, (b) CE/ER/PR = 70 : 15 : 15, (c) CE/ER/PR = 70 : 20 : 10, (d) CE/ER/PR = 70 : 25 : 5, (e) CE/ER/PR = 70 : 30 : 0.

The effects of heating rate on the DSC curves of CE/ER/PR are shown in Figure 4. The mass ratio of CE, ER, and PR was 70 : 15 : 15. The results show that the reaction peaks of the resin system shifted toward higher temperatures and were beneficial in determining the gel time of the resins. The onset temperature (T_{onset}), peak temperature (T_{peak}), and end temperature (T_{end}) of the composite resin at various heating rates are shown in Table I. The effects of heating rate on T_{onset} , T_{peak} , and T_{end} are shown in Table I according to Figure 4. The T_{onset} , T_{peak} , and T_{end} of the resins, shown in Figure 5, are indicated by the three straight lines extended to the y axis. Therefore, the cured conditions were: 150°C for 1 h, followed by 170°C for 1 h, then 190°C for 1 h, and finally 220°C for 3 h by successive.

FTIR spectra analysis

The FTIR spectra of the resins cured at different temperatures for different times are shown in Figure 6, from which it can be seen that the peaks at 3340 and 2239 cm^{-1} of the $-\text{OCN}$ of CE and $-\text{OH}$ of ER decreased with increasing curing temperature and increasing curing time of each cure cycle, disappearing after 2 h at 210°C. At the same time, after the cure cycle a new absorption peak appeared at 1750 cm^{-1}

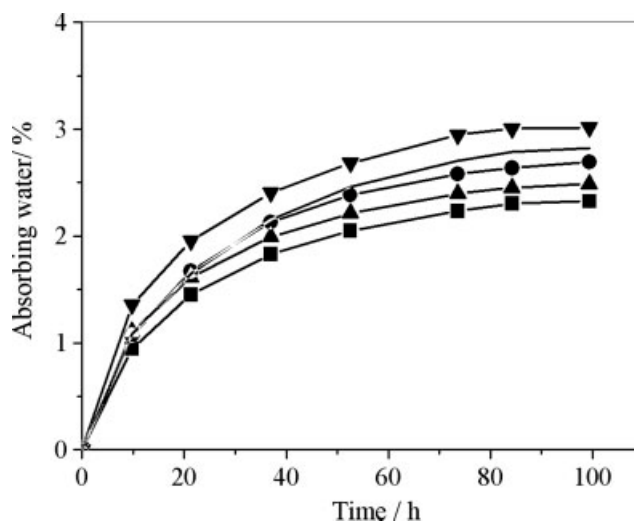


Figure 9 Water uptake curve of cured, modified CE resin: (—) CE/ER/PR = 100 : 0 : 0, (■) CE/ER/PR = 100 : 15 : 15; (●) CE/ER/PR = 70 : 20 : 10, (▲) CE/ER/PR = 70 : 25 : 5; (▼) CE/ER/PR = 70 : 30 : 0.

which was characteristic of the oxazole ring. The FTIR results show that the CE could react with ER and PR, which in turn could produce oxazole rings.

Mechanical properties

The mechanical properties of the cured CE/ER/PR resins are shown in Table II. The results indicate that bending strength, bending modulus, and impact strength increased with an increasing ER content in the modified resins. The tensile strength and tensile modulus of CE decreased with the addition of ER and PR. The mechanical properties of CE/ER/PR composite sheets are shown in Table III. It was found that bending strength, bending modulus, inter-laminar shear strength (ILSS) and impact strength of the composite sheets increased rapidly with an increasing ER and PR content in modified CE resins. This means the addition of ER and PR were able to greatly enhance the flexibility of the modified CE. The results imply that CE can react with ER and ER and decrease the content of triazine in the cured CE resin. The fracture sections of composites of modified resins and fiberglass are shown in Figure 7. Figure 7(a) shows the sur-

TABLE II
Mechanical Properties of Curing Resin of CE/ER/PR

Mechanical properties	CE/ER/PR (wt %)				
	100 : 0 : 0	70 : 15 : 15	70 : 20 : 10	70 : 25 : 5	70 : 30 : 0
Bending strength (MPa)	123.6	134.5	137.8	139.3	143.32
Bending modulus (GPa)	3.6	9.3	10.8	11.1	13.2
Tensile strength (MPa)	77.1	76.2	74.6	73.6	72.1
Tensile modulus (GPa)	3.71	3.23	2.84	2.75	2.61
Impact strength (KJ/m^2)	5.2	16.7	17.4	17.1	16.4

TABLE III
Mechanical Properties of CE/ER/PR Composite Sheets

Mechanical properties	CE/ER/PR (wt %)				
	100 : 0 : 0	70 : 15 : 15	70 : 20 : 10	70 : 25 : 5	70 : 30 : 0
Bending strength (MPa)	742.1	744.0	776.1	721.6	673.2
Bending modulus (GPa)	23.5	25.7	26.2	25.4	24.3
ILSS (KPa)	50.7	63.9	66.8	61.3	59.6
Impact strength (KJ/m ²)	126.2	146.5	149.1	142.5	140.8

faces of fracture sections of composites of fiberglass and CE resins. It can be seen that the surfaces were neat and clear because the matrix resin CE and fiberglass were brittle and stiff, which also shows that there was a strong adhesive force between the fibers and CE matrix. From Figure 7(b–d), which shows the fracture sections of composites of the modified CE resins and fiberglass, it can be seen that the fracture surface was not uniform and clear because the modified CE resins improved their toughness and flexibility, which exhibited better adhesion between the fiberglass and the modified resin.

Thermal properties

The thermal weight loss curves of the resin systems are shown in Figure 8. The results show that the thermal stability of the resin system decreased with an increase in the content of ER and improved with the addition of PR. The temperatures of 10%, 30%, and 50% weight loss were obtained according to the weight loss curves and are shown in the Table IV. The thermal decomposition temperature of modified CE resin decreased significantly with increasing ER content and improved with increasing PR content, according to a comparison of the thermal stability of the CE resins. The high-activity hydroxyl group in the phenolic resin could react with the cyanate group (—OCN) in CE and the hydroxyl group in epoxy resin to form crosslinked networks, which decreased the loss of heat resistance of the modified CE. The modified resins had good thermal stability.

Water uptake

Water uptake of the modified CE resin increased with increased ER content. When the mass ratio of CE to ER was 70 : 30 (w/w), the water uptake of the

modified resin was larger than that of the CE resin. The results are shown in Figure 9, which indicates that the larger the mass fraction of ER, the larger was the water uptake of the modified resins. This is because there were many hydrophilic hydroxyl groups in ER. From Figure 9 it can be seen that the water uptake of the modified resin decreased successively with an increasing PR content. Therefore, water uptake of the modified resin was improved by the addition of PR resin.

Dielectric properties

The dielectric properties of epoxy resin are weak, but the dielectric properties of phenolic resin are excellent. Modifying CE with the simultaneous addition of ER and PF can meet the need of applications without appreciable sacrifice of the dielectric properties. The dielectric data of the modified resin are compiled in Table V. The dielectric constant, ϵ , and dielectric loss angle, $\tan \delta$, of CE were 2.9 and 0.007, respectively. The ϵ and $\tan \delta$ at 1 MHz decreased slightly, exceedingly, and monotonically with increases in ER and PR content in the modified CE resin system. When the mass ratio of CE, ER, and PR was 70 : 15 : 15, the ϵ and $\tan \delta$ at 1 MHz were 3.0 and 0.008, respectively. The results indicated that the introduction of ER and PR improved the flexibility of modified CE resin without too much sacrifice of the dielectric properties.¹⁰

CONCLUSIONS

Stiff and brittle CE was modified by adding ER and PR to improve its toughness and flexibility. The curing parameters of the modified CE resins were determined by the gel time curves and DSC curves of the modified CE resins. The FTIR analysis showed that

TABLE IV
Heat Stability of Cured CE/ER/PR Resin

	CE/ER/PR (wt %)				
	100 : 0 : 0	70 : 15 : 15	70 : 20 : 10	70 : 25 : 5	70 : 30 : 0
Loss mass 10%	395.2	372.3	364.5	360.2	362.2
Loss mass 30%	431.5	420.3	406.7	381.8	354.7
Loss mass 50%	472.3	451.8	426.5	412.6	386.1

TABLE V
Dielectric Properties of the Cured Modified Resin

Modified CE resin (wt %)	Dielectric constant	Dielectric loss (tan δ)
CE/ER/PR = 100 : 0 : 0	2.9	0.007
CE/ER/PR = 70 : 15 : 15	3.0	0.008
CE/ER/PR = 70 : 20 : 10	3.1	0.009
CE/ER/PR = 70 : 25 : 5	3.1	0.009
CE/ER/PR = 70 : 30 : 0	3.3	0.011

the modified CE resins formed flexible structures during the curing process. The mechanical properties, thermal behavior, dielectric properties, and morphology of modified CE were investigated. The results showed that the modified CE resins attained excellent mechanical properties without sacrificing too much thermal stability. When the mass ratio of CE, ER, and PR was 70 : 15 : 15, the flexural strength and impact strength of the modified CE resins increased from 113.6 MPa and 5.2 kJ/m², to 134.5 MPa and 16.7 kJ/m², respectively. At the same time, there

was a small sacrifice in the dielectric properties of the modified CE resins, but they were still able to meet the needs of high-performance composites such as printed circuit boards and structural composites.

References

1. Hamerton, I. *Chemistry and Technology of Cyanate Ester Resins*; Glasgow, Scotland: Chapman and Hall, 1994.
2. Mathew, D.; Reghunadhan Nair, C. P.; Ninan, K. N. *J Appl Polym Sci* 2000, 77, 75.
3. Wang, J. L.; Liang, G. Z.; Zhao, W. *China Plast* 2004, 18(1), 46.
4. Lau, C.; Yongli, M. *Polymer* 2002, 43, 823.
5. Ghosh, P.; Siddhanta, S. K.; Chakrabarti, A. *Eur Polym J* 1999, 35, 699.
6. Kiatkamjornwong, S.; Suwanmala, P. *Radiat Phys Chem* 1998, 52, 1.
7. Kou, S.-W.; Chan, S.-C.; Chang, F.-C. *Polymer* 2002, 43, 3653.
8. Iijima, T.; Katsurayama, S.; Fukuda, W.; Tomoi, M. *J Appl Polym Sci* 2000, 76, 208.
9. Guo, B. C.; Fu, W. W.; Jia, D. M.; Wang, L.; Qui, Q. H. *Acta Materiae Composite Sinica* 2002, 19(3), 1.
10. Chen, P.; Cheng, Z. X.; Zhu, X. S.; Lei, Q. Q. *Acta Materiae Composite Sinica* 2001, 18(3), 10.