

Synthesis of Epoxy-Functionalized Hyperbranched Poly(phenylene oxide) and Its Modification of Cyanate Ester Resin

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Received 28 January 2011; accepted 24 April 2011

DOI 10.1002/app.34791

Published online 24 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: High curing temperature is the key drawback of present heat resistant thermosetting resins. A novel epoxy-functionalized hyperbranched poly(phenylene oxide), coded as eHBPPPO, was synthesized, and used to modify 2,2'-bis (4-cyanatophenyl) isopropylidene (CE). Compared with CE, CE/eHBPPPO system has significantly decreased curing temperature owing to the different curing mechanism. Based on this results, cured CE/eHBPPPO resins without postcuring process, and cured CE resin postcured at 230°C were prepared, their dynamic mechanical and dielectric properties were systematically investigated. Results show that cured CE/eHBPPPO resins not

only have excellent stability in dielectric properties over a wide frequency range (1–10⁹Hz), but also show attractively lower dielectric constant and loss than CE resin. In addition, cured CE/eHBPPPO resins also have high glass transition temperature and storage moduli in glassy state. These attractive integrated performance of CE/eHBPPPO suggest a new method to develop high performance resins. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2351–2359, 2012

Key words: hyperbranched; dielectric properties; thermosets; poly(phenylene oxide); curing

INTRODUCTION

Heat resistant thermosetting resins have been attracting great attentions of scientists and engineers worldwide owing to their great potential in many cutting-edge fields including aerospace, electric, and electronic industries.^{1,2} Note that they have a common disadvantage, that is, they should be cured and postcured via the procedure including high curing temperature for a long length of time.^{3,4} Obviously, through this procedure, this is generally easy to produce cured resins with big internal residual stress, and thus resulting in poor stability of materials in service performance.⁵ Therefore, how to overcome the curing disadvantage of heat resistant resin has been a key issue of high performance resins.

Cyanate ester (CE) resin has been regarded as the candidate with the greatest competition to fabricate advanced functional/structural materials for many cutting edge fields (including electronic and electric, aerospace, etc.) in this century.^{6,7} However, CE also has poor curing characteristics, which needs to be cured at high temperature for a relatively long time to get desirable integrated properties. It is worth noting that the biggest advantage of CE resin is its extremely low and stable dielectric constant and loss over a wide frequency range. Therefore, reducing the curing temperature of CE should not sacrifice the dielectric properties of original CE resin.

Many researches have proved that CE is very sensitive to the material around,⁸ so many materials can be used to catalyze the curing reaction of CE, which can be classified into three types, they are active hydrogen catalysts (phenol, amine, imidazole, etc),^{9,10} UV activated catalysts (organotin catalyst),¹¹ and transition metal catalysts.¹² Of them, dibutyl tin dilaurate is the most effective and commonly used catalyst for CE, but which has metal atoms, and thus the catalyzed CE resin does not have desirable dielectric properties. Similar problem also exists for transition metal catalysts. With regard to active hydrogen catalysts, epoxy resin is the most often used one. In fact, epoxy resin acts as not only a catalyst, but also a modifier of CE; however the dielectric constant and loss of epoxy/CE resins are

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Contract grant sponsor: Scientific Innovation Research of College Graduate in Jiangsu Province; contract grant number: CX09B_023Z.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20974076.

Contract grant sponsor: Priority Academic Program Development of Jiangsu Higher Education Institutions, Jiangsu Province.

significantly bigger than those of neat CE resin.¹³ The reason in deteriorated dielectric properties induced by the addition of epoxy resin may be due to the large amount of epoxy groups in each molecule of epoxy resin. Therefore, it is of great interest to develop new catalysts for curing CE without sacrificing the excellent dielectric properties of CE resin.

Poly(phenyl oxide) (PPO) is an engineering plastic, its dielectric property is also the major advantage besides outstanding thermal and mechanical properties. However, PPO is impossible to modify CE resin owing to its high molten viscosity and poor solubility in common solvents.

It is known that hyperbranched polymers possess considerably lower viscosities owing to the unique structure; moreover, the existence of many terminal functional groups provides great possibilities to chemical modifications.^{14–16} It should be noted that many hyperbranched polymers, including hyperbranched polyethersulfone, hyperbranched poly(ether-ketone), etc., have been synthesized, but the synthesis of hyperbranched poly(phenyl oxide) (HBPPO) is seldom reported because the monomers for synthesizing HBPPO usually do not contain functionalized groups, and thus leading to big difficulty for polymerization.

This article gives the first presentation on synthesizing a new HBPPO, epoxy-functionalized hyperbranched poly(phenylene oxide) (coded as eHBPPO), and the systematical investigation on the effect of eHBPPO on the curing mechanism and kinetics of CE, and that on the dynamic mechanical, and dielectric properties of cured resin.

EXPERIMENTAL

Materials

The 2,2'-bis (4-cyanatophenyl) isopropylidene (CE) was purchased from Shangyu Chemical of Zhejiang in China. The 3-chloro-1,2-epoxypropane, hexamethylene, methyl alcohol (MeOH), ethanol, tetrahydrofuran (THF), and kalium hydroxide (KOH) were obtained from China Medicine (Group) Shanghai Chemical Reagent Corp.

Synthesis of eHBPPO

eHBPPO was synthesized according to the method outlined in Figure 1. Briefly, it includes two steps: the first one is the synthesis of HBPPO, and the second one is the epoxy-functionalization of HBPPO. HBPPO was prepared by the procedure described in literature,¹⁷ its weight-molecular weight (M_w) is about 2200–2300.

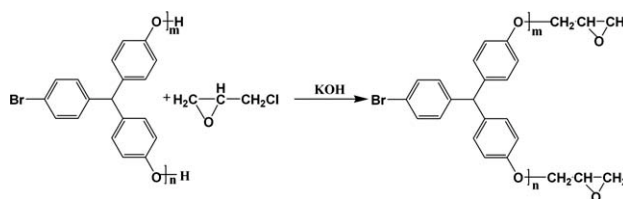


Figure 1 Synthesis of eHBPPO.

Following is the typical procedure for the second step: 0.5 g HBPPO, 40 g THF, 10 g ethanol, and 0.1 g KOH were added into a 250-mL three-necked flask with a thermometer and a condenser at 50°C for 0.5 h with stirring, and then 3.0 g 3-chloro-1,2-epoxypropane was added dropwise into the three-necked flask, followed by heating at 50°C for 24 h. After that the solvent was removed by vacuum distillation, and the resultant mixture was dissolved in THF, followed by filtering to eliminate the indiscernible materials. The obtained filtrate was precipitated into hexamethylene to get a crude product. After purifying, a brown yellow solid with a yield of 95% was obtained, which was eHBPPO.

Preparation of cured CE resin

Two kinds of cured CE resins were prepared, one was postcured, and the other was not postcured.

CE was placed in a flask equipped with a mechanical stirrer and thermometer at 120°C with stirring for 0.5 h to get a clear liquid, which is CE prepolymer.

The resultant CE prepolymer was put into a preheated mold followed by degassing at 120°C for 0.5 h in a vacuum oven, then the mold was moved into an oven for curing via the procedure of 130°C/2 h + 150°C/2 h + 180°C/2 h + 220°C/2 h. The resultant resin was cooled and demolded, the resultant product is cured CE resin.

The cured CE resin was postcured at 230°C for 4 h, followed by cooling to room temperature naturally to get a postcured CE resin, coded as *p*-CE resin.

Preparation of cured CE/eHBPPO resins

CE was placed in a flask equipped with a mechanical stirrer and thermometer at 120°C with stirring till a clear liquid was obtained. Then preweighted HBPPO was added into the flask with stirring. The mixture was maintained at 120°C for 0.5 h to obtain a brown-red transparent liquid, which is CE/eHBPPO prepolymer.

The prepolymer was put into a preheated mold followed by degassing at 120°C for 0.5 h in a vacuum oven, then the mold was moved into an oven for curing via the procedure of 130°C/2 h + 150°C/

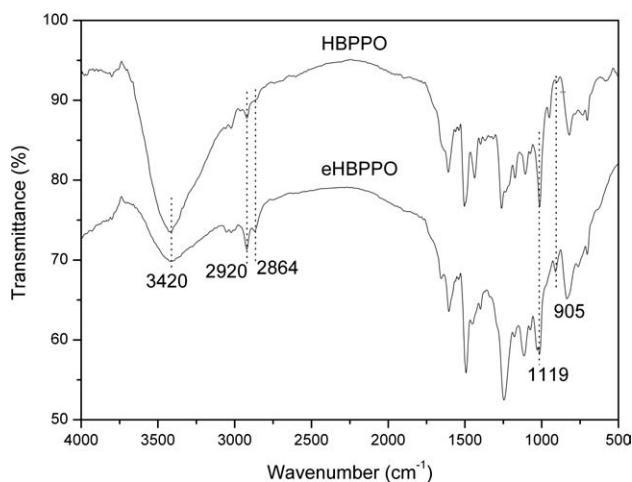


Figure 2 FTIR spectra of HBPPO and eHBPPO.

2 h + 180°C/2 h + 220°C/2 h. The resultant resin was cooled and demolded, and the resultant resin was coded as CE/neHBPPO, where n represents the weight loading of eHBPPO per 100 g CE.

Measurements

Fourier Transform Infrared (FTIR) spectra were measured using a Nicolet (USA) FTIR spectrometer. The specimen was prepared by coating the sample on a potassium bromide disk, and subsequently heated in the oven.

Nuclear magnetic resonance (NMR) spectra were recorded on a Unity Inova 400 NMR spectrometry system (USA), DMSO- d_6 was used as the solvent.

Gel permeation chromatography (GPC) was carried out on a Waters GPC 515-2410 system equipped with a RI detector and packing column (Waters Styragel HT3-5-6E, USA). THF was used as the elution solvent.

Differential scanning calorimeter (DSC) curves were recorded using a TA calorimetry (2910 MDSC, TA) from room temperature to 300°C at different heating rate of 5, 10, 15, or 20°C min^{-1} under a N_2 atmosphere.

Dynamic mechanical analyses (DMA) scans were measured 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 350°C with a heating rate of 3°C min^{-1} at 1 Hz. The dimensions of each sample were 35 × 12 × 2 mm^3 .

The dielectric constant and loss were measured by a Broad Band Dielectric Spectrometer (Novocontrol Concept 80, Germany) at the frequency between 1 and 10⁹ Hz. The sample with a dimension of (20 ± 0.1) × (20 ± 0.1) × (2 ± 0.1) mm^3 for testing in the low frequency range (1–10⁶ Hz), and that with a dimension of (10 ± 0.1) × (10 ± 0.1) × (2 ± 0.1)

mm^3 for testing in the high frequency range (10⁶–10⁹ Hz).

RESULTS AND DISCUSSION

Characteristics of eHBPPO

Figure 2 shows the FTIR spectra of eHBPPO and HBPPO. Compared with the spectrum of HBPPO, the spectrum of eHBPPO shows different features. First the broad peak around 3420 cm^{-1} assigning to —OH groups is very weak; second, several new absorption peaks attributing to epoxy (905 cm^{-1}), Ph—O—CH₂ (1119 cm^{-1}), and —CH₂— (2920 and 2864 cm^{-1}) groups appear, reflecting that epoxy groups were successfully introduced on the molecules of HBPPO.

This statement is further confirmed by the ¹H NMR spectrum as shown in Figure 3. The chemical shifts of hydrogen atom assigning to the epoxy group (2.80, 3.16, and 3.70–4.30 ppm), methine (4.96–5.55 ppm), and phenyl ring (6.44–7.76 ppm) can be observed. Note that no peak attributing to the terminal phenolic groups appears at 9.00–10.00 ppm, indicating that all terminal hydroxy groups in HBPPO molecules have been modified. However, a very slight peak belonging to hydroxyl groups appears at 2.00 ppm, reflecting the hydrolysis of epoxy group. The ratio of hydrolysis is about 3.5%, which is calculated from the ¹H NMR spectrum.

The epoxy-functionalization of HBPPO can be reflected by the difference in solubility between HBPPO and eHBPPO. eHBPPO exhibits not only relatively good solubility in polar solvents such as chloroform, 1,2-dichloroethane, and acetic ester, but also partially solubility in weak polar solvents such as toluene or benzene. However, HBPPO can not be soluble in above solvents. This difference reflects

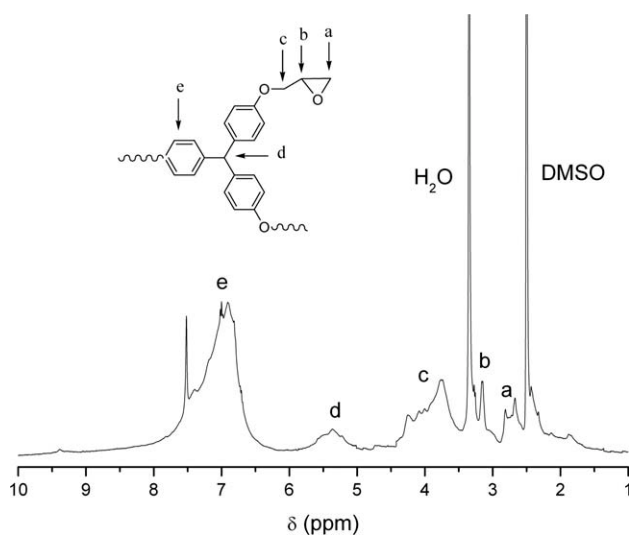


Figure 3 The ¹H NMR spectrum of eHBPPO.

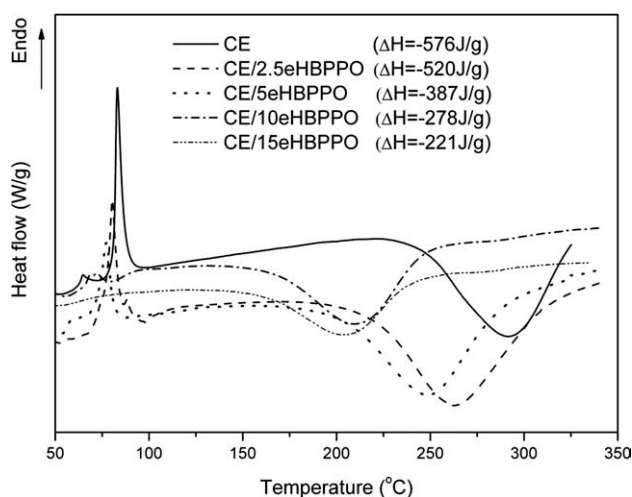


Figure 4 DSC thermograms for CE and CE/eHBPPO prepolymers at a heating rate of $20^{\circ}\text{C min}^{-1}$.

that the introduction of epoxy groups significantly improves the solubility.

Curing behavior and kinetics of CE/eHBPPO resins

To discuss the reasons contributing to the different performances between CE/eHBPPO and CE resin, the curing behavior and kinetics as well as the cross-linked structure should be discussed at first.

Figure 4 shows the DSC thermograms for CE and CE/eHBPPO prepolymers at a heating rate of $20^{\circ}\text{C min}^{-1}$. Each prepolymer has one exothermic peak; however, interestingly, all peaks of CE/eHBPPO prepolymers appear at significantly lower temperature compared with that of CE prepolymer, demonstrating that there is additional reaction in the CE/eHBPPO system.

Based on Figure 4, the dependence of curing conversion (α) on the curing time for either CE or CE/eHBPPO prepolymer can be calculated according to eq. (1),¹⁸ and the corresponding plot is shown in Figure 5. It can be seen that CE/eHBPPO prepolymer needs shorter length of time to get the same conversion (including the full conversion), this phenomenon enhances with the increase of the content of eHBPPO. For example, to get a monomer conversion of 50%, CE and CE/10eHBPPO need 23.8 and 16.3 min, respectively. These results suggest that the addition of eHBPPO is indeed beneficial to catalyze the whole curing process.

$$\alpha = \frac{(H_{\text{noniso}})_T}{H_{\text{noniso}}}, \quad (1)$$

where $(H_{\text{noniso}})_T$ is the enthalpy released up to a temperature T calculated from the nonisothermal mode, and H_{noniso} is the total enthalpy from the nonisothermal mode.

Above results are attributed to the fact that CE and CE/eHBPPO systems have different curing mechanisms as shown in Figure 6. The curing mechanism of CE is the cyclotrimerization of cyanate ester, while that of CE/eHBPPO includes the cyclotrimerization of cyanate ester under the catalysis of $-\text{OH}$ groups in eHBPPO,⁹ the copolymerization between epoxy and $-\text{OCN}$ groups as well as triazine rings,^{19,20} and the self-polymerization of eHBPPO. Therefore, CE/eHBPPO system will cure at lower temperature than CE does.

On the other hand, the total curing exothermal heat of each CE/eHBPPO prepolymer is remarkably smaller than that of CE prepolymer; moreover, the former decreases with increasing the content of eHBPPO, suggesting that CE/eHBPPO has better curing feature. It is known that CE is very sensitive to the curing temperature and the material surroundings; if these parameters are not carefully designed and controlled, thermal explosion tends to appear owing to the big curing heat produced. Therefore, the decreased curing heat of CE/eHBPPO prepolymer is beneficial to avoid the heat accumulation and thermal explosion; hence the curing of CE/eHBPPO is controllable. Obviously it is a very attractive feature for fabricating materials, especially those with big thickness.

To further study the effect of eHBPPO on the curing reaction of CE prepolymer, the nonisothermal method is carried out to evaluate the curing kinetic parameters such as the reaction order (n), kinetic constant (A), and activation energy (E) for the whole reaction of CE and CE/eHBPPO system by employing Kissinger method [eq. (2)] and Crane equation [eq. (3)].^{15,21}

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_p}, \quad (2)$$

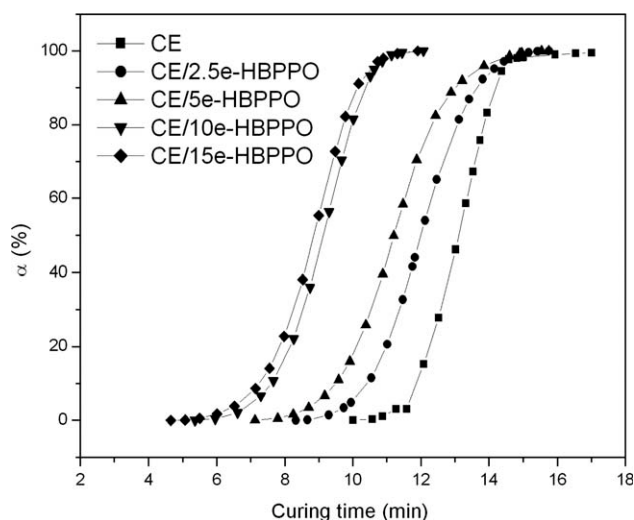


Figure 5 Dependence of curing conversion on time for CE and CE/eHBPPO systems at $20^{\circ}\text{C min}^{-1}$.

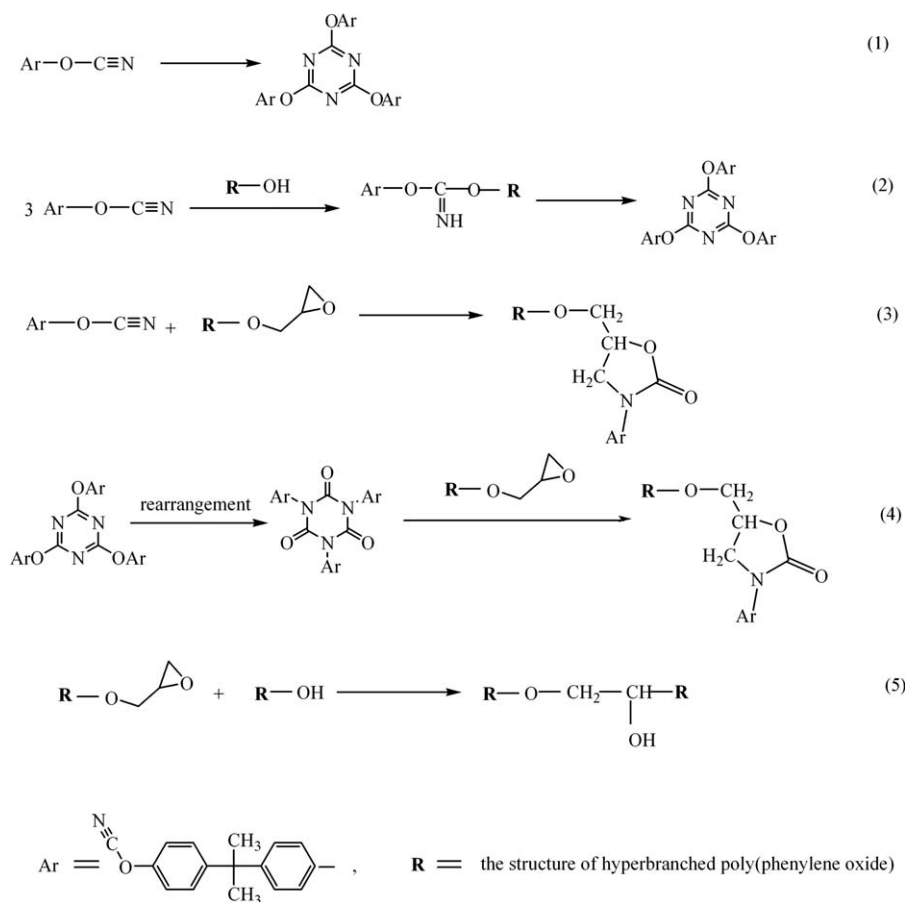


Figure 6 The curing mechanism of CE/eHBPPO systems.

where T_p is the peak temperature, β is the heating rate, E is the activation energy, A is the pre-exponential factor, and R is the gas constant.

$$\frac{d(\ln \beta)}{d(1/T_p)} \approx -E/nR, \quad (3)$$

Typical DSC thermograms for the curing reactions of CE and CE/eHBPPO system under different heating rates are shown in Figure 7, the plots of $\ln(\beta/T_p^2)$ versus reciprocal peak temperature ($1/T_p$), and that of $\ln(\beta)$ versus $1/T_p$ are given in Figures 8 and 9, respectively. The calculated results of E , A , and n

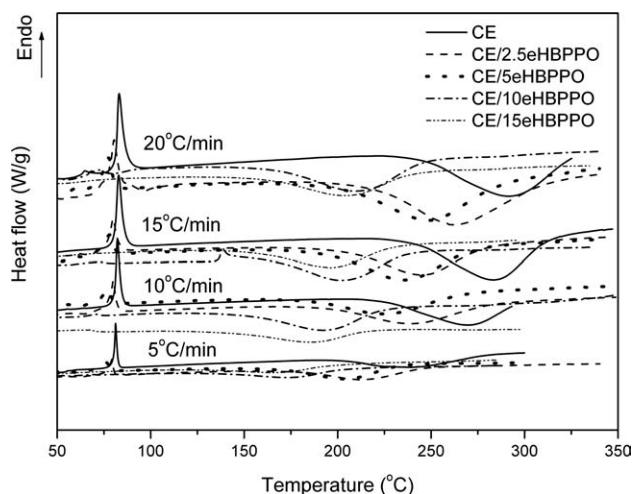


Figure 7 Overlay DSC thermograms of CE and CE/eHBPPO systems at different heating rates.

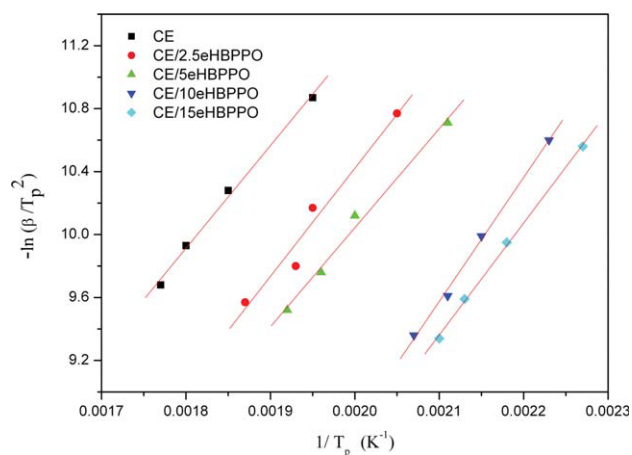


Figure 8 Overlay plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for CE and CE/eHBPPO prepolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

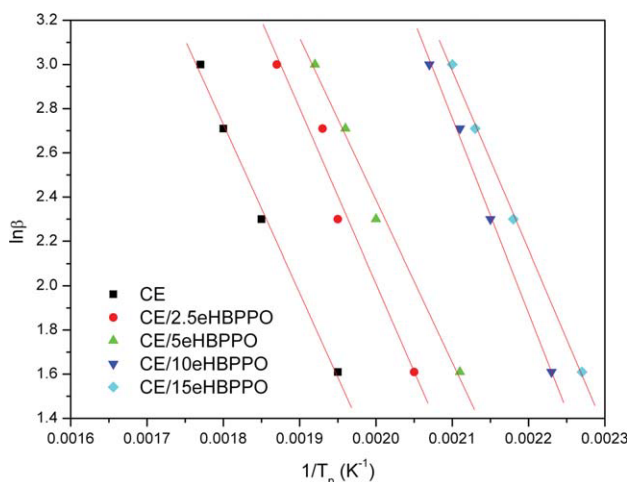


Figure 9 Overlay plots of $\ln(\beta)$ versus $1/T_p$ for CE and CE/eHBPPO prepolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are summarized in Table I. All curing kinetic parameters of CE/eHBPPO system are lower than those of CE. In detail, the curing of CE/eHBPPO system has slightly decreased reaction order than that of CE, indicating that the former is little dependent on the reactant than the latter, this result may be attributed to the catalytic effect on the cyclotrimerization of cyanate ester under the catalysis of $-\text{OH}$ groups in eHBPPO. While CE/eHBPPO has slightly smaller apparent activation energy ($55\text{--}57\text{ kJ mol}^{-1}$) than CE (58 kJ mol^{-1}), indicating that the curing reaction of CE/eHBPPO becomes easier to occur with the addition of eHBPPO to CE. On the other hand, CE/eHBPPO has smaller pre-exponential factor than CE, meaning that the molecules in CE/eHBPPO system have less possibility to collide each other for curing than those in CE do. It is known that hybranched polymers have a large amount of terminal active groups grafted on the shell, however, which usually exhibit spheroidal configuration, and thus their branched molecular chains are too short to entangle, so hybranched polymers usually show high reactivity only at high temperature.^{22,23}

Based on above DSC analyses, it is concluded that compared with CE, CE/eHBPPO system has different curing kinetics owing to the different curing

TABLE I
Curing Kinetics Parameters of CE and CE/eHBPPO

System	E (kJ mol^{-1})	A (s^{-1})	n
CE	58.19	5.74×10^7	0.926
CE/2.5eHBPPO	57.16	1.25×10^7	0.905
CE/5eHBPPO	55.93	1.10×10^7	0.838
CE/10eHBPPO	53.21	1.00×10^7	0.761
CE/15eHBPPO	55.00	0.54×10^7	0.817

mechanism, and thus leading to the improvement in activity of the curing reaction.

Dynamic mechanical analyses

The influence of eHBPPO on the curing mechanism and behavior of CE will be undoubtedly reflected in the macro-performance of crosslinked network. DMA measures the modulus (stiffness) and damping (energy dissipation) properties of materials as they are deformed under periodic stress, in addition, it detects essentially all changes in the state of molecular motion as temperature is scanned. Hence DMA technique is used to further investigate the effect of the addition of eHBPPO on the curing structure of CE.

Figure 10 shows the dependence of $\tan \delta$ on temperature for cured CE and CE/eHBPPO resins. Generally, the glass transition temperature (T_g) is defined as the peak (maximum) temperature in the $\tan \delta$ -temperature plot. It can be seen that cured CE resin has three overlapped $\tan \delta$ peaks, appearing at 243 , 282 , and 321°C , suggesting that the morphology of the cured CE resin is complex because of the resin does not get enough high conversion, so the glass transition of CE resin will occur over a wide temperature range. This statement is confirmed by observing the $\tan \delta$ -temperature plot of cured *p*-CE resin. Specifically, cured *p*-CE resin only has one $\tan \delta$ peak at 314°C . This phenomenon is attributed to the curing process of a thermosetting resin. It is known that the curing rate of a thermosetting resin is initially controlled by chemical factor, and then by diffusion in the later stage of curing,^{24–26} meaning that the morphology of a network without high conversion is usually not homogeneous, that is, including the regions with different conversions; while the

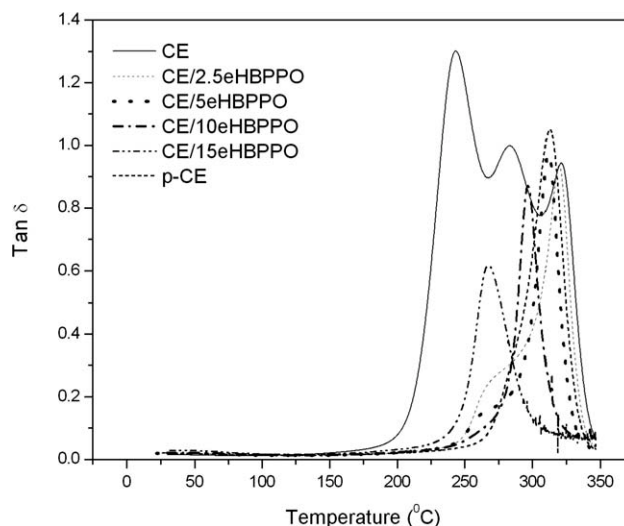


Figure 10 Overlay plots of $\tan \delta$ versus temperature for cured CE, *p*-CE and CE/eHBPPO resins.

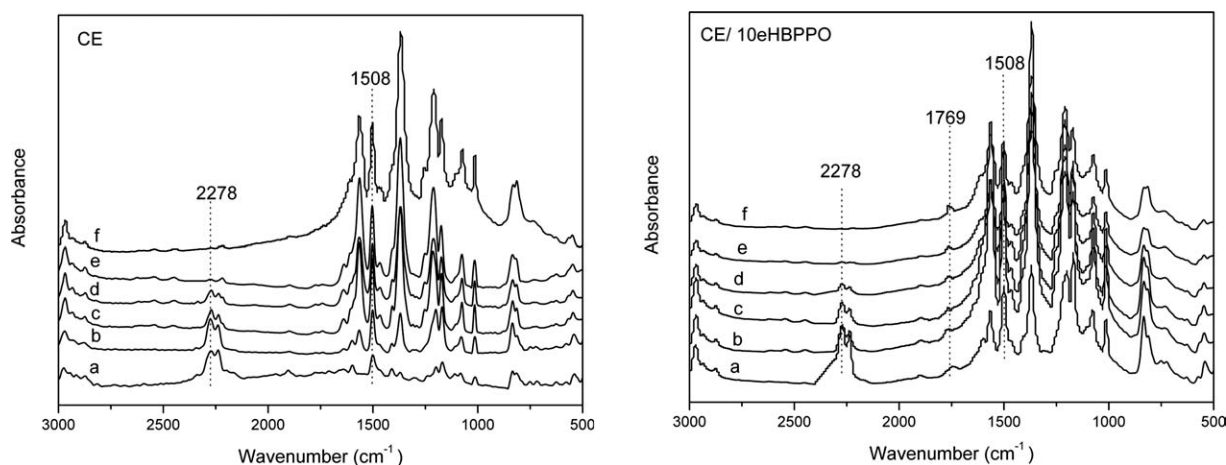


Figure 11 FTIR spectra of CE and CE/10eHBPPO systems after cured per various procedures: (a) room temperature, (b) 130°C/2 h, (c) 130°C/2 h + 150°C/2 h, (d) 130°C/2 h + 150°C/2 h + 180°C/2 h, (e) 130°C/2 h + 150°C/2 h + 180°C/2 h + 220°C/2 h, and (f) 130°C/2 h + 150°C/2 h + 180°C/2 h + 220°C/2 h + 230°C/4 h.

morphology will become more and more uniform with the increases of conversion. Hence the existence of three $\tan \delta$ peaks for cured CE resin reflects that the structure of cured CE resin is not complete, while the single peak for *p*-CE resin suggests that the structure of cured *p*-CE resin has high conversion.

With the addition of eHBPPO to CE resin, the plot of $\tan \delta$ versus temperature changes because of the change in the curing mechanism as discussed above. In detail, CE/2.5eHBPPO resin exhibits a sharp $\tan \delta$ peak with a smaller shoulder at the side of low temperature, which can be divided into two overlapped peaks, one main peak at about 320°C, and a small one at about 280°C. Compared with CE resin, CE/2.5eHBPPO only remains the two peaks at higher temperature without the appearance of the peak at the lowest temperature (about 240°C), reflecting that the main curing mechanism of CE/2.5eHBPPO is the homopolymerization of CE under the catalytic role of $-\text{OH}$ groups in eHBPPO molecules.

CE/5eHBPPO resin exhibits similar $\tan \delta$ shape as CE/2.5eHBPPO, however, the peak at high temperature shifts toward low temperature, suggesting that the amount of the copolymer resulting from the reaction between CE and epoxy increases. With the increase of the content of eHBPPO, the influence of eHBPPO on the curing mechanism and kinetics enhances, so either CE/10eHBPPO or CE/15eHBPPO resin shows a single $\tan \delta$ peak, this also reflects that the two resins have homogeneous morphology. These observations are in good agreement with the results of the curing behavior and kinetic as discussed above. Note that cured CE/10eHBPPO or CE/15eHBPPO resin still has very high value of T_g (296 or 266°C), so the positive role of eHBPPO on reducing the curing temperature is very attractive.

To further explain above results, FTIR is used to follow-up the change of characteristic absorption peaks for CE and CE/10eHBPPO systems during the progress of curing, the corresponding spectra are shown in Figure 11. The dependence of the conversion of $-\text{C}\equiv\text{N}$ groups in CE at each curing stages was calculated and plotted in Figure 12. It can be seen that CE/10eHBPPO system has higher conversion of $-\text{C}\equiv\text{N}$ group than CE after cured per the same procedure; moreover the former can get the maximal conversion after cured via the procedure with lower temperature. For example, after curing at 150°C for 2 h, the conversion of $-\text{C}\equiv\text{N}$ group in CE and that of CE/10eHBPPO are 47 or 77%, respectively; in addition, cured CE/10eHBPPO resin has the maximal conversion, but CE must be postcured at 230°C for 4 h to get its maximal conversion.

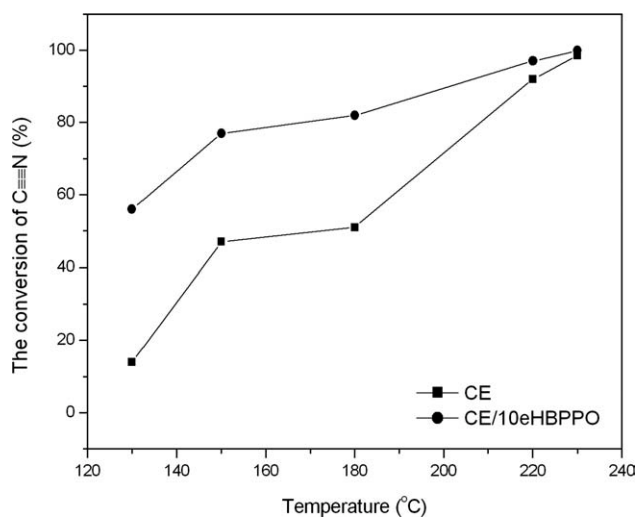


Figure 12 The dependence of the conversion of $-\text{C}\equiv\text{N}$ group in CE at different curing stages.

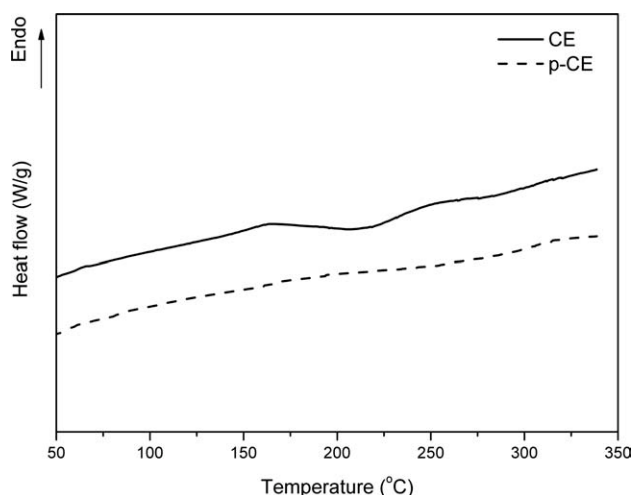


Figure 13 DSC curves of cured CE and *p*-CE resins at $10^{\circ}\text{C min}^{-1}$.

Above statement can be further confirmed by the DSC curves of cured CE resin and *p*-CE resin as shown in Figure 13. It can be seen that there is still an exothermic peak for cured CE resin, while no peak can be observed in the DSC curve of *p*-CE resin, reflecting that CE needs to be postcured to get a high conversion.

From Figure 14, it can be seen that cured CE/*e*HBPPO resins have bigger storage moduli in glassy state than cured CE resin, especially CE/10*e*HBPPO. This observation can be interpreted by the influence of *e*HBPPO on the crosslinked structure. Specifically, the large amount of rigid phenyl structure of *e*HBPPO is responsible for the increased rigidness of the crosslinked network of CE/*e*HBPPO resins; on the other hand, the larger amount of *e*HBPPO will also reduce the amount of formation of triazine network resulting from the homo-polymerization of CE,

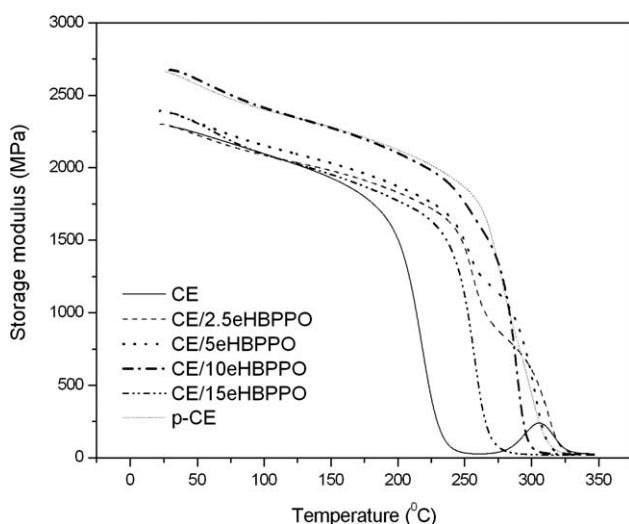


Figure 14 Overlay plots of storage modulus versus temperature for cured CE, *p*-CE, and CE/*e*HBPPO resins.

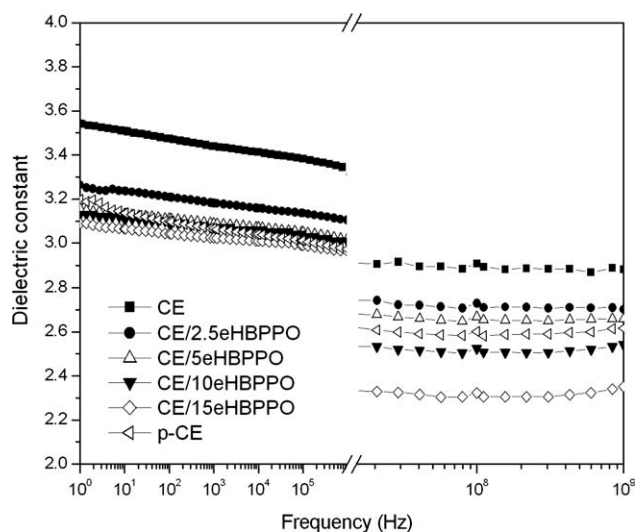


Figure 15 Dependence of dielectric constant on frequency for cured CE, *p*-CE, and CE/*e*HBPPO resins.

hence there is an optimum content of *e*HBPPO to get the biggest rigidness reflected by the biggest storage modulus.

Dielectric properties

It is known that the biggest advantage of CE resin is its extremely low and stable dielectric constant and loss over a wide frequency range. Therefore, reducing the curing temperature of CE should not sacrifice the dielectric properties of original CE resin. In addition, the dielectric properties are also sensitive macro-performance to the structure of the network. Therefore, it is necessary to evaluate the dielectric properties of cured CE and CE/*e*HBPPO resins.

Figures 15 and 16 show the overlay plots of dielectric constant-frequency, and those of dielectric loss-frequency for cured resins, respectively. All CE/

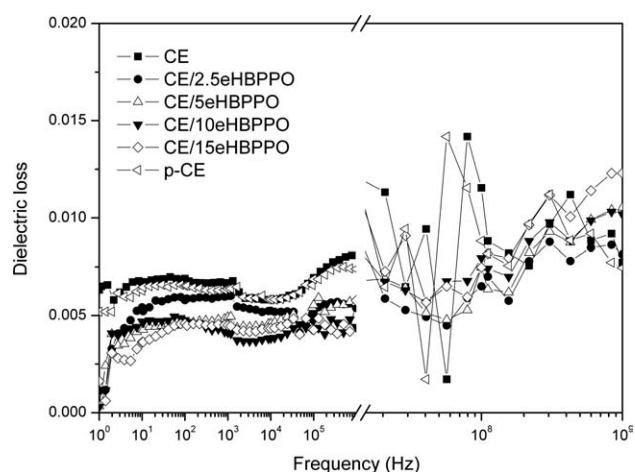


Figure 16 Dependence of dielectric loss on frequency for cured CE, *p*-CE, and CE/*e*HBPPO resins.

eHBPPO resins exhibit not only excellent stability in both dielectric constant and loss as CE resin over the whole frequency range, but also attractively decreased dielectric constant and loss than CE resin, demonstrating that the CE/eHBPPO system has much better dielectric properties than CE resin.

As described above that cured CE resin prepared herein was not postcured, so it is necessary to compare the dielectric properties of *p*-CE resin (which was postcured), and CE/eHBPPO resins. It is expected to find from Figures 15 and 16 that *p*-CE resin has lower dielectric constant and loss than CE resin; interestingly, the difference in dielectric constant between *p*-CE and CE/eHBPPO resins is in the range of $\pm 3\%$, so it is reasonable to state that CE/eHBPPO resins has similar dielectric constants as *p*-CE resin.

With regard to dielectric loss, CE/eHBPPO resins have lower dielectric loss than *p*-CE resin, especially in the low frequency range. For example, the dielectric loss at 10^3 Hz of CE/10HBPPO resin is only about 62% of that of *p*-CE resin.

Based on above analyses, it can be concluded that although CE/eHBPPO resins are prepared without postcuring procedure, they have better dielectric properties than *p*-CE resin. This attractive result can be attributed to the outstanding dielectric properties of poly(phenylene oxide).

CONCLUSIONS

New modified CE resins by epoxy-functionalized hyperbranched poly(phenylene oxide), eHBPPO, were developed. The addition of eHBPPO to CE can simultaneously decrease the curing temperature without sacrificing the excellent integrated of cured CE resin. Specifically, to get desirable performance, CE should be postcured at high temperature, while CE/eHBPPO system does not need. Attractively, cured CE/eHBPPO resins not only have high glass transition temperature and storage moduli in glassy state, but also possess lower and stable dielectric

constant and loss, showing great potential in fabricating high performance adhesives, advanced composites, etc.

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