

Cure Kinetics and Thermal Properties of Tetramethylbiphenyl Epoxy Resin/Phthalazinone-Containing Diamine/Hexa(phenoxy)cyclotriphosphazene System

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ABSTRACT: Inherently flame retardant epoxy resin is a kind of halogen-free material for making high-performance electronic materials. This work describes an inherently flame retardant epoxy system composed of 4,4'-diglycidyl (3,3',5,5'-tetramethylbiphenyl) epoxy resin (TMBP), 1,2-dihydro-2-(4-aminophenyl)-4-(4-(4-aminophenoxy) phenyl) (2H) phthalazin-1-one (DAP), and hexa(phenoxy) cyclotriphosphazene (HPCTP). The cure kinetics of TMBP/DAP in the presence or absence of HPCTP were investigated using isoconversional method by means of nonisothermal differential scanning calorimeter (DSC). Kinetic analysis results indicated that the effective activation energy (E_a) decreased with increasing the extent of conversion (α) for TMBP/DAP system because diffusion-controlled reaction dominated the curing reaction gradually in the later cure stage. TMBP/DAP/HPCTP(10 wt %) system

had higher E_a values than those of TMBP/DAP system in the early cure stage ($\alpha < 0.35$), and an increase phenomenon of $E_a \sim \alpha$ dependence in the later cure stage ($\alpha \geq 0.60$) due to kinetic-controlled reaction in the later cure stage. Such complex $E_a \sim \alpha$ dependence of TMBP/DAP/HPCTP(10 wt %) system might be associated with the change of the physical state (mainly viscosity) of the curing system due to the introduction of HPCTP. These cured epoxy resins had very high glass transition temperatures (202–235°C), excellent thermal stability with high 5 wt % decomposition temperatures (>340°C) and high char yields (>25.6 wt %). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1397–1404, 2009

Key words: curing of polymers; epoxy resins; thermal properties; cure kinetic

INTRODUCTION

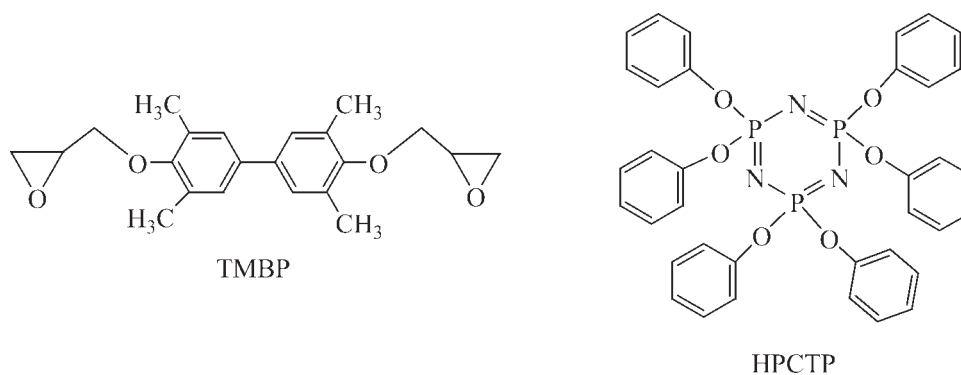
Epoxy resins are widely used in industrial applications because of their great versatility, low shrinkage, good chemical resistance, outstanding adhesion, and high-grade electrical insulation. However, epoxy resins cannot meet the requirement of the electronic/electrical industry unless their disadvantages such as flammability and brittleness are minimized. Moreover, halogen-free flame retardant epoxy materials^{1–35} has to be developed for environmental consistency. Generally, there are two ways to improve the properties of epoxy materials: chemical synthesis of new epoxy resins/hardeners or modification of the formulation, and improvement of cure techniques, which have great influences on the properties of the cured epoxy.

The second way demands the knowledge of cure kinetics.

Related to the development of halogen-free epoxy materials with excellent properties, phosphorus-containing flame retardants for epoxy resins such as 9, 10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide derivatives^{2–19} and nitrogen-containing flame-retardants^{11–13,19–29} such as melamine-phenol formaldehyde novolac resins^{11,18,26} isocyanurate-containing resins,^{21–24,27} oxazene-containing resins,³⁶ aromatic azomethine-containing, and phthalazinone-containing bisphenols^{25,27,28} have been attracted a lot of attention because, they are environmentally friendly with less toxicity, no dioxin and low evolution of smoke during combustion. Due to P – N positive synergistic effect on the improvement of the flame resistance, introducing P and N elements instantaneously into the epoxy matrix^{11–13,19} was proved to be a very effective route for improving the flame retardancy. Furthermore, inherently flame retardant epoxy polymers,^{2,3} which contain highly aromatic structures,^{2,25,34,35} demonstrate excellent heat stability and good flame resistance, because these

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Scheme 1 The structures of TMBP and hexa(phenoxy) cyclotriphosphazene (HPCTP).³⁷

structures are favorable for the formation of the char residue during combustion. For example, 4,4'-diglycidyl (3,3',5,5'-tetramethylbiphenyl) epoxy resin [(TMBP), Scheme 1], which is an epoxy monomer with rigid biphenyl structure, hydrophobic tetramethyl structure, and low melting viscosity, had been used for making high-performance electronic materials.^{37–42}

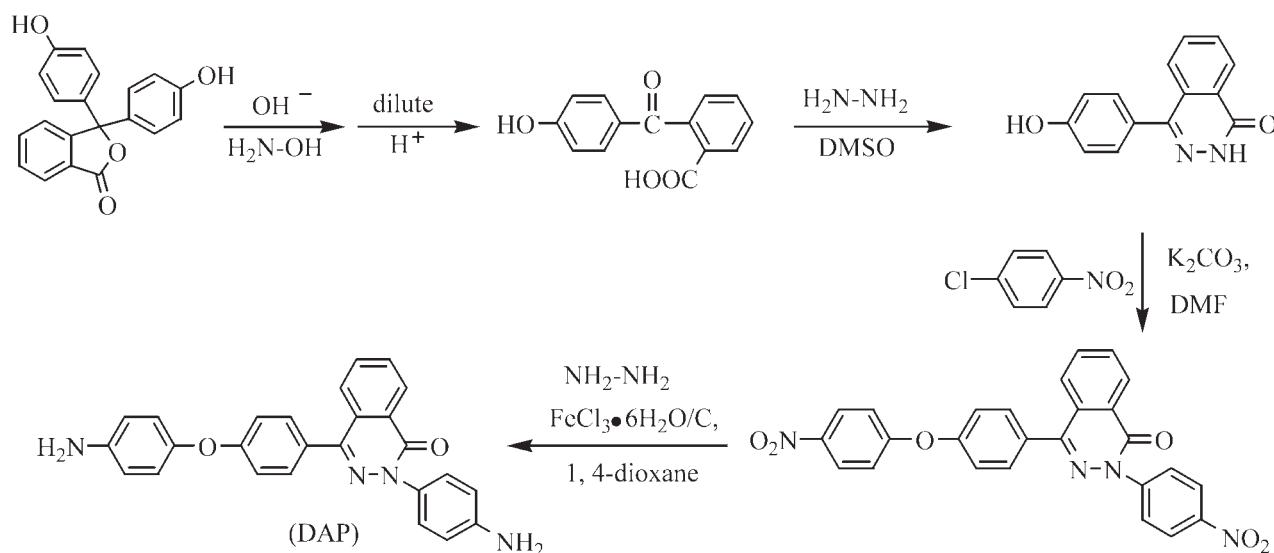
This work, aimed at preparation of novel inherently flame retardant epoxy system with high thermal stability, TMBP was used as an epoxy monomer, and a diamine named 1,2-dihydro-2-(4-aminophenyl)-4-(4-(4-aminophenoxy) phenyl) (2H) phthalazin-1-one²⁵ (DAP, see Scheme 2) that contain highly aromatic structures was synthesized and used as a hardener. Hexa(phenoxy)cyclotriphosphazene⁴³ [(HPCTP), see Scheme 1], which has a low melting point but is a heat-stable organic flame retardant with effective flame resistance due to its high P and N content, was introduced into TMBP/DAP system for the sake of improving the flame retardancy and toughness of the resultant materials.

It is known that physical properties of cured epoxy resins are also depended on their network structures which are decided by the extent of cure, cure time, and temperatures and kinetic parameters relating to network formation. The cure kinetics can provide substantial information on the final network structures, properties, and processibility of the epoxy resins. The objective of this study was to investigate the cure kinetics of TMBP/DAP system in the presence and absence of HPCTP via isoconversional method. The thermal properties (T_g , $T_{d,5 \text{ wt } \%}$) of the resultant epoxy thermosets were also evaluated in detail.

EXPERIMENTAL

Materials

All reagents and solvents were reagent-grade. Phenolphthalein, *p*-chloronitrobenzene, hydroxylamine, hydrazine hydrate (85 wt % water solution), and phenol were purchased from Sinopharm Chemical Reagent, (Shanghai, China) and used without further



Scheme 2 The synthetic route of DAP.

purification, 4, 4'-diglycidyl TMBP (white powder, EEW = 178–185 g/mol, melting point is 104–110°C) was kindly granted from Gansu Research Institute of Chemical Industry (Lanzhou, China). 1,4-dioxane, dimethylformamide, dimethylsulphoxide (DMSO) were purchased from Hangzhou Shuanglin Chemical Reagent, (Hangzhou, China) and purified by standard methods before use. Hexachlorocyclotriphosphazene (Aldrich) was purified by recrystallization from petroleum ether.

Synthesis of DAP

The synthesis of DAP was described in detail elsewhere.²⁵ The synthetic route is shown in Scheme 2. m.p.: 261–262°C. IR (KBr, cm⁻¹): 3460, 3406, 3367, 3338, 3229 (–NH₂), 1655 (C=O), 1622 (–NH₂), 1100–1300 (Ar–O–Ar). ¹H-NMR (500 MHz, DMSO-*d*₆, ppm): 8.407–8.390 (m, 1H), 7.910–7.924 (t, 2H), 7.752, 7.770 (d, 1H), 7.567, 7.583 (d, 2H), 7.242, 7.259 (d, 2H), 6.995, 7.012 (d, 2H), 6.838, 6.637 (d, 2H), 6.620, 6.637 (d, 4H), 5.293, 5.026 (s, 4H, NH₂). Elemental analysis: C₂₆H₂₀O₂N₄ (420.472): Cal: C, 74.27%; H, 4.79%, N, 13.33%; Found: C, 74.35%; H, 4.81%, N, 13.37%.

Instrumentation and sample preparations

Infrared spectrum was recorded by Vector 22 FT-IR spectrophotometer (KBr pellet). ¹H-NMR was obtained with an Avance DMX 500 NMR spectrometer at 35°C using DMSO-*d*₆ as solvent and tetramethylsilane as an internal standard. Elemental analysis was performed on a Flash EA1112 CHN–O–Rapid elemental analyzer using acetanilide as a standard. The curing exotherm and *T*_g were determined using a differential scanning calorimeter (DSC) Q200 (TA) thermal analyzer. Thermogravimetric analyzes (TGA) were carried out for the cured resins on a Perkin-Elmer Pyris 1 under N₂ atmosphere with a heating rate of 10°C/min from 50 to 850°C.

Stoichiometric TMBP and DAP (with 0, 5, 10, and 20 wt % HPCTP) were mixed under vigorous stirring at ~ 120°C in a few minutes. The obtained samples were preserved in the refrigerator (–10°C) for DSC test. Samples consisting of 3.00–3.50 mg mixtures were placed in aluminum DSC pans. Dynamic scans were conducted at heating rates of 2.5, 5, and 7.5°C/min, and were used to determine the heat relating to the cure process. The carrier gas was nitrogen at a flow of 50 mL/min. The second heat scanning at a heating rate of 10°C/min was carried out for determination of the residual cure heat.

All cured samples were prepared as following: the curing temperature was raised from 100 to 180°C with a heating rate of 5°C/min, kept at 180°C for 1 h, then heated to 240°C with a heating rate of

5°C/min, then kept at this temperature for 2 h. The resulting polymers were used as samples for thermal properties analyzes (*T*_g and *T*_{*d*,5 wt %}).

Kinetic analysis method

The DSC curves were analyzed on the basis of the following assumptions: the area under the curves is proportional to the extent of conversion α , whereas the extent of reaction during the mixing of epoxy resin and diamine is neglected. The extent of the conversion α at any time is defined as:

$$\alpha = \frac{\Delta H_t}{\Delta H_0} \quad (1)$$

where ΔH_t is the heat of reaction determined from the partial area under DSC curve up to the point of interest, ΔH_0 is the ultimate heat of cure. All kinetic analysis can start with the basic equation that relates to the rate of conversion to the function of the concentration of reactants. For a thermosetting resin, $d\alpha/dt$ can be usually expressed as:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha) \quad (2)$$

where A is the frequency factor, E_α is the effective activation energy, $f(\alpha)$ is a function of the fractional extent of conversion α and is associated with a certain reaction mechanism, R is the gas constant (8.314 J mol K), and T is the absolute temperature at time t . eq. (2) can be described as:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A - \frac{E_\alpha}{RT} + \ln f(\alpha) \quad (3)$$

From eq. (3), a plot of $\ln(d\alpha/dt)$ versus $1/T$ at the same α from a series of nonisothermal DSC curves with various heating rates would result in a straight line with a slope of $-E_\alpha/R$ and an intercept of $\ln A f(\alpha)$. Repeating this procedure, the relationship between E_α and α can be obtained, i.e. $E_\alpha \sim \alpha$ dependence.^{44,45} This is the so-called Friedman's method.⁴⁴

RESULTS AND DISCUSSION

Structure of diamine DAP

The synthesis of DAP was reported early by Cheng et al.⁴⁶ Now, DAP was synthesized by a modified procedure (Scheme 2) reported previously.²⁵ Because of its unique molecular structure, DAP seems to be an ideal hardener for epoxy resins used as advanced electronic/electrical materials. DAP has unsymmetrical and kink noncoplanar heterocyclic phthalazinone structure which favors to improve the heat-resistance,^{25,46} compatibility with the epoxy resins. The

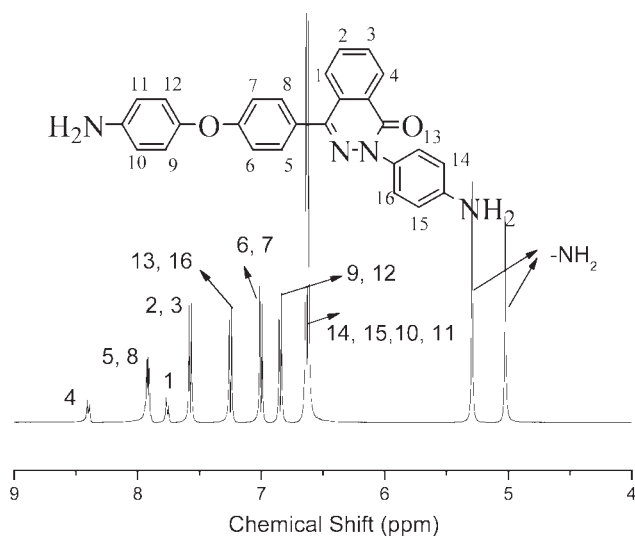


Figure 1 $^1\text{H-NMR}$ spectrum of diamine DAP.

flexible aromatic ether linkage of DAP favors to decrease the rigidity of the chain segment of the resultant epoxy thermoset. Furthermore, compared with other aromatic diamines such as 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenyl sulfone, DAP presents a very big molecular π conjugated structure and has a carbonyl ($\text{C}=\text{O}$) group. Such molecular structure can effectively absorb short light waves under UV irradiation. Thus DAP can also be used as a UV-blocking agent for making high-performance epoxy-based copper clad laminates. It is interesting that $^1\text{H-NMR}$ spectrum of DAP (Fig. 1) shows that $-\text{NH}_2$ linked to phenoxy structure and phthalazinone structure are 5.02 and 5.29 ppm, respectively. This means that two $-\text{NH}_2$ groups in DAP have different reactivity to epoxy resins. DAP may be regarded as mixed diamines when it cured with epoxy resin.⁴⁷ Herein, isoconversional method, which is a phenomenological method (no need of hypothesis for cure mechanism), was used to evaluate cure kinetics of TMBP/DAP system in the presence and absence of HPCTP.

Kinetic analysis with isoconversional method

Practically, a slow heating rate for epoxy-amine curing system is often used in industry for avoiding the heat aggregation, which may result in low T_g due to the decomposition of part of polymer chains, and heat stress in the resultant materials, because polymer chains can not be relaxed timely. Thus, slow heating rates of 2.5, 5, and 7.5°C/min were used for evaluating the curing kinetics of TMBP/DAP and TMBP/DAP/HPCTP(10 wt %) systems.

Figures 2 and 3 show the nonisothermal DSC curves of the stoichiometric TMBP/DAP systems in the presence and absence of HPCTP (10 wt %) with

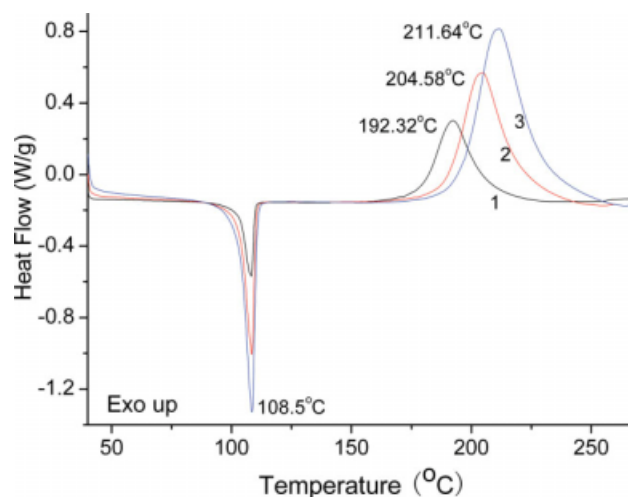


Figure 2 The nonisothermal curves of TMBP/DAP in heating rates of: Line-1: 2.5°C/min, Line-2: 5°C/min, and Line-3: 7.5°C/min at a N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the heating rates of 2.5, 5, and 7.5°C/min, respectively. Endothermic peaks at 108.5°C were found in all DSC curves, which were the melting peaks of the epoxy monomer TMBP. For TMBP/DAP/HPCTP (10 wt %) system, another endothermic peak at 79.3°C was found from each DSC curve, which was the melting peak of HPCTP. Due to low melting point and good compatibility with TMBP/DAP system, HPCTP can be distributed in the system very well. It can be seen from Figures 2 and 3 that all the cure exotherms shifted to higher temperatures with increasing the heating rate. The temperatures at which the maximum conversion rate occurred in the DSC curve (T_p s) at 2.5, 5, and 7.5°C/min are 192.32,

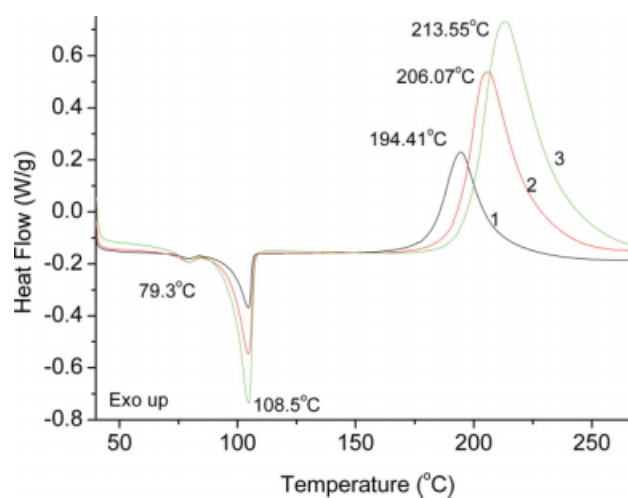


Figure 3 The nonisothermal curves of TMBP-DAP/HPCTP (10 wt %) in heating rates of: Line-1: 2.5°C/min, Line-2: 5°C/min, and Line-3: 7.5°C/min at a N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

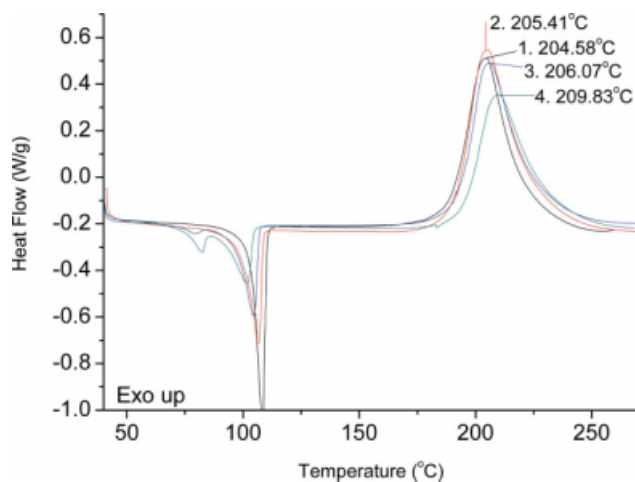


Figure 4 The nonisothermal curves of TMBP/DAP system with various HPCTP contents in a heating rate of 5°C/min at a N₂ atmosphere. Line-1: 0 wt %, Line-2: 5 wt %, Line-3: 10 wt %, and Line-4: 20 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

204.58, and 211.64°C, respectively, for TMBP/DAP system, and 194.41, 206.07, and 213.55°C for TMBP/DAP/HPCTP (10 wt %) system. Furthermore, T_p s of the TMBP/DAP/HPCTP system increase with increasing the content of HPCTP in the epoxy systems (Fig. 4). It seems that the curing reaction of TMBP/DAP was inhibited in the presence of HPCTP, and the addition of more HPCTP was disadvantaged for the curing reaction of TMBP/DAP. Note that the second heating scanning of all cured samples did not show any residual heat release so that the cure reactions were assumed to be completed.

Figure 5 presents the plots of the extent of conversion (α) versus the temperature of TMBP/DAP system at different heating rates and reveals a typical S-shape curves, which might be related to an autocatalytic reaction mechanism in the early cure stage.^{48,49} Figure 6 shows the plots of $\ln(d\alpha/dt)$ versus $1000/T$ for various appointed α (α is 0.05, 0.10, ..., 0.90, and 0.95). By fitting linear regression lines, a set of E_α values were obtained for each α . The plot of E_α versus α of TMBP/DAP curing system is shown in Figure 7 (curve 1). Using the same method, the plot of E_α versus α of TMBP/DAP/HPCTP (10 wt %) system was also obtained (see curve 2 in Fig. 7).

For the curing reaction of TMBP/DAP system, it is found from Figure 7 that E_α decreases with increasing the extent of conversion α . The decrease in E_α is an indication that the rate determining step of curing changes to a process having smaller activation energy.⁵⁰ Some reported epoxy-amine system^{50–52} had the same E_α versus α relationship. For such $E_\alpha \sim \alpha$ dependence of TMBP/DAP system, two reasons may be mainly responsible. Firstly, DAP has a nitro-

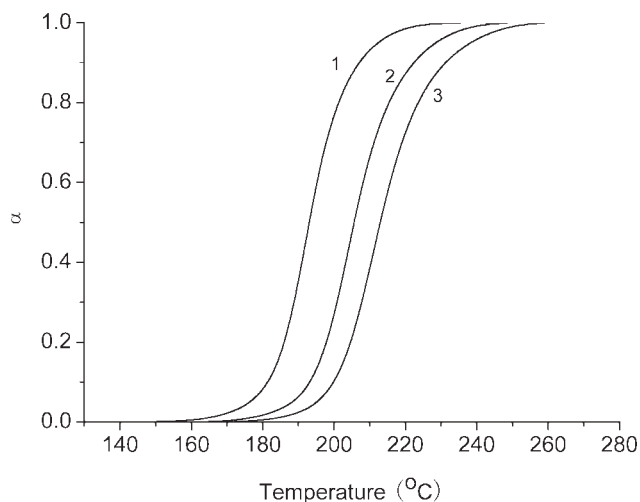


Figure 5 The conversion (α)-temperature relationship of TMBP/DAP nonisothermal curing reaction with heating rates of Line-1: 2.5°C/min, Line-2: 5°C/min, and Line-3: 7.5°C/min.

gen in phthalazinone ring which has a pair of electron. Speculatedly, it might also act as a curing accelerant when it reacted with TMBP, and result in an autocatalytic effect, which can decrease E_α effectively. Secondly, for epoxy-amine curing reaction, kinetic-controlled and diffusion-controlled reactions can dominate the cure in all temperature ranges in dynamic curing process and both are competitive during cure.^{24,52} Generally, kinetic-controlled reaction dominates the polymerization in the early cure stage, while diffusion-controlled reaction, which is indicative of low activation energy,⁵² dominates the chain propagation due to the occurrence of verifications and increase of the viscosity. For this curing system, the molecular motion is hindered by the growing polymer

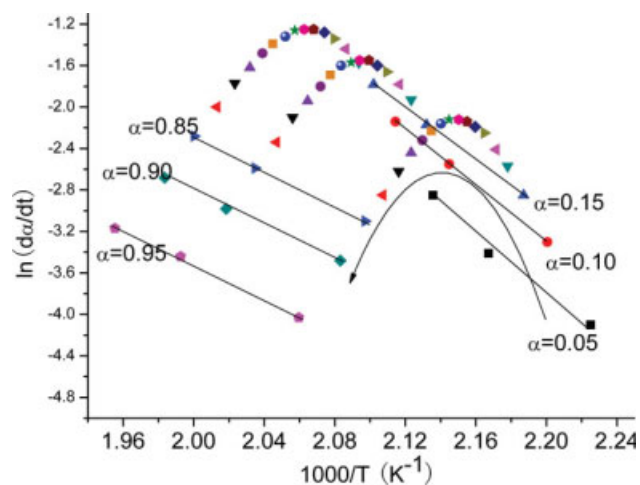


Figure 6 Plots of $\ln d\alpha/dt$ versus $1000/T$ of TMBP/DAP system during nonisothermal curing reaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

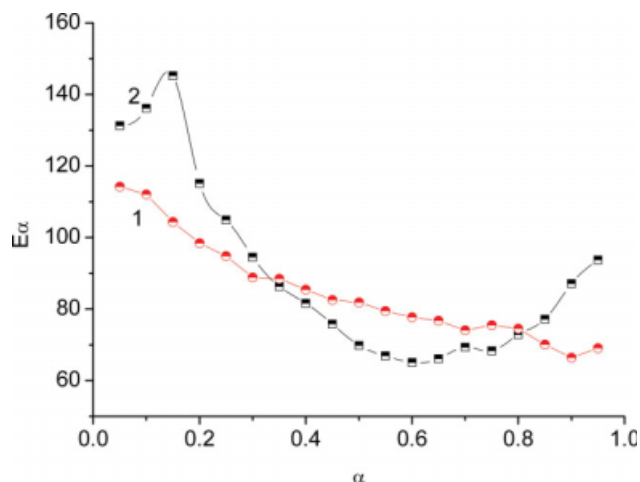


Figure 7 Plots of E_α versus α of TMBP/DAP system during nonisothermal curing reaction. Line-1: without HPCTP, Line-2: with 10 wt % HPCTP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

chains in the later cure stage, and the diffusion of chain segments and unreacted monomers becomes a rate determining factor. That is, the decrease of E_α could be explained by shifting the rate determining step from a kinetic to a diffusion regime. Note that the transition of kinetic-controlled reaction into diffusion-controlled reaction is gradual during cure, there are no clear limitations in two reaction mechanisms. The combined effects of kinetic-controlled and diffusion-controlled reactions result in the relationship of $E_\alpha \sim \alpha$ dependence. Furthermore, the average E_α of TMBP/DAP system is 85.0 kJ/mol and higher than that of DGEBA/DAP system (73.8–77.4 kJ/mol)²⁵ due to the bulky tetramethyl structure of TMBP.

When introducing 10 wt % HPCTP into the TMBP/DAP system, the $E_\alpha \sim \alpha$ dependence became much more complex as indication of curve 2 in Figure 7. At the very early stage ($\alpha < 0.15$), E_α increases from 131 to 145 kJ/mol that are higher than those of the TMBP/DAP system at the same α (the trend ends at $\alpha = 0.35$). It is clear that HPCTP in the system inhibits the cure reaction of TMBP/DAP system in the beginning of the cure. That is, the propagation reaction rate of TMBP/DAP became slow in the presence of HPCTP. This may be associated with the dramatically change of the reaction medium due to the introduction of HPCTP. Further cure progress was accompanied by a dramatic decrease from 145 kJ/mol to 66.1 kJ/mol in E_α and followed by an increase from 66.1 to 93.7 kJ/mol. A significant increase in E_α from 68.3 to 93.7 kJ/mol was observed in the later stage (esp. after $\alpha > 0.75$). Totally, this may result from the competition effect of kinetic-controlled and diffusion-controlled reactions on the curing rate. The kinetic-controlled reaction may

dominate the curing reaction in the later cure stage when HPCTP was introduced. Presumably, the existence of HPCTP put the verification off, decrease the viscosity of the curing system, as well as creates freer volume⁵² accommodated for the cooperative motion of chain segment in the later cure stage. So an increase in E_α can be mainly associated with chemical process. Similar results of epoxy-amine curing systems have been reported.^{53–57} Moreover, the fact that the average E_α of TMBP/DAP/HPCTP (10 wt %) is 89.9 kJ/mol and higher than that of TMBP/DAP system (85.0 kJ/mol), which confirmed the inhibition effect of HPCTP on the cure of TMBP/DAP system.

Thermal properties of the cured resins

Glass transition temperatures (T_g s) of the cured TMBP/DAP system with 0, 5, 10, and 20 wt % HPCTP were measured from a first heating trace with DSC at a heating rate of 20°C/min (Fig. 8). All cured epoxy resins exhibited very high T_g s that ranged from 202 to 235°C. One can see that T_g value (curve 1 in Fig. 8) of the cured TMBP/DAP was 235°C and higher than that of the cured DGEBA/DAP (204°C)²⁵ we reported early. Compared with DGEBA, TMBP has a rigid biphenyl structure and bulky tetramethyl structure, which can inhibit the chain movement in some extent. T_g value of the cured TMBP/DAP/HPCTP (5 wt %) was 234°C and almost the same as that of the cured TMBP/DAP, while T_g values of the resultant thermosets with 10 and 20 wt % HPCTP were 221°C and 202°C respectively, and the corresponding T_g s range became

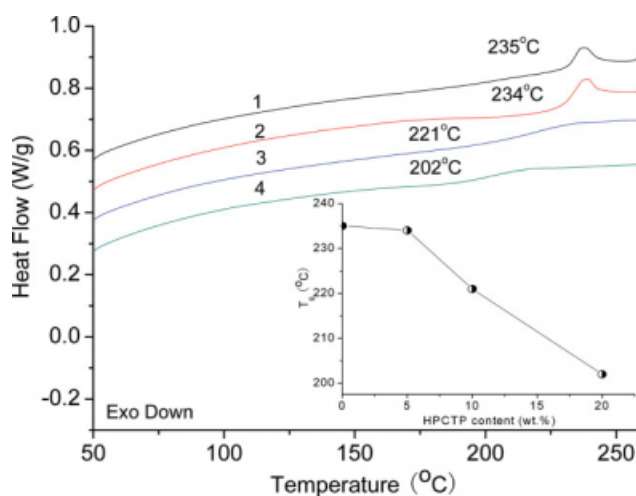


Figure 8 Glass transition temperatures (T_g s) of the cured epoxy resins. Line-1: 0 wt % HPCTP, Line-2: 5 wt % HPCTP, Line-3: 10 wt % HPCTP, and Line-4: 20 wt % HPCTP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

wider than those of the cured TMBP/DAP with 0 and 5 wt % HPCTP. The depression of T_g with loading HPCTP can be attributed to two possible reasons. Firstly, HPCTP can inhibit the cure reaction, which supported by the aforementioned kinetic analyzes, resulting in a comparative lower crosslinking density in the epoxy matrix. Secondly, HPCTP with unique bulky cyclic structure in the epoxy matrix may cause more free volumes and decreases the entanglement of polymer chains. Thus it favors to the movement of the segmental motion of the polymer (i.e. plasticization effect), which was supported by the $E_\alpha \sim \alpha$ dependence of TMBP/DAP/HPCTP (10 wt %) system.

Thermal stabilities of the aforementioned epoxy resins were assessed by TGA. The 5 wt % decomposition temperature ($T_{d,5 \text{ wt } \%}$), the maximum decomposition temperature (T_{max}), and char residue at 850°C ($Y_{c, \text{wt } \%}$) were determined. All thermal parameters were collected in Table I. Due to highly aromatic structure of TMBP and DAP, $T_{d,5 \text{ wt } \%}$ and $Y_{c, \text{wt } \%}$ of the cured TMBP/DAP were 347°C and 28.0 wt % respectively and very high. $T_{d,5 \text{ wt } \%}$ of the pure HPCTP (curve 1 in Fig. 9) was 337°C and slightly lower than that of the cured TMBP/DAP. Comparative low initial decomposition temperature of a flame retardant is useful to the exertion of its nonflammability because it can decompose in advance of the matrix during combustion and release flame resistant substances to protect the matrix. That is, HPCTP is a suitable flame retardant for TMBP/DAP system. Moreover, the range of decomposition temperature between $T_{d,5 \text{ wt } \%}$ and T_{max} of HPCTP was rather small, and the residual char was also quite low (only 2.8 wt % at 500°C). Presumably, HPCTP can retard

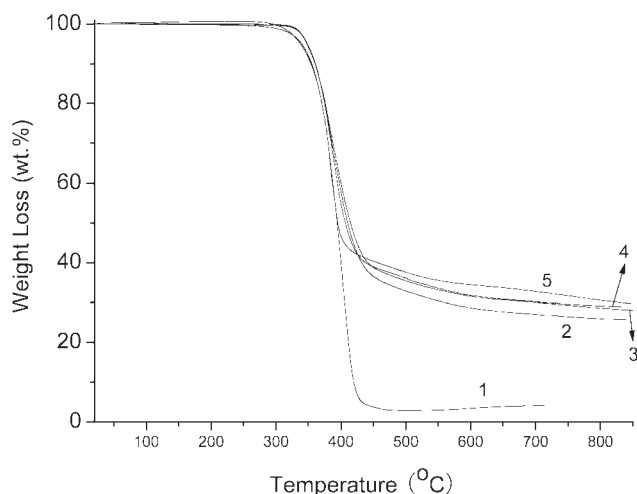


Figure 9 Weight loss of pure HPCTP (Line-1) and the cured epoxy resins from TGA are Line-1: 0 wt % HPCTP, Line-2: 5 wt % HPCTP, Line-3: 10 wt % HPCTP, and Line-4: 20 wt % HPCTP.

TABLE I
Thermal Parameters of the Cured TMBP/DAP/HPCTP Epoxy Resins

HPCTP content (wt %)	T_g (°C, DSC)	$T_{d,5 \text{ wt } \%}$ ^a (°C)	T_{max} ^b	$Y_{c, \text{wt } \%}$ (850°C)
0	235	347	384	25.6
5	234	347	387	28.0
10	221	347	390	28.9
20	202	341	384	29.7
Pure HPCTP	–	337	403	2.8 ^c

^a 5 wt % decomposition temperature ($T_{d,5\%}$), indicates the apparent thermal stability of the epoxy thermosets.

^b T_{max} indicates the temperature of maximum decomposition rate.

^c Determined at 500°C.

flame by a gas-phase mechanism by releasing of non-flammable gas which can dilute air and absorb heat energy in combustion. Combination of HPCTP with TMBP/DAP together may favor to exert synergistic effect of a solid-phase and gas-phase mechanisms on the improvement of the flame resistance since the cured TMBP/DAP system favors to char formation.

Introducing 5, 10, and 20 wt % HPCTP into TMBP/DAP system did not cause dramatic change of $T_{d,5\%}$ (347–341°C) and T_{max} (384–390°C) due to adjacent $T_{d,5\%}$ and T_{max} values of HPCTP and the cured TMBP/DAP system. That is, HPCTP did not weaken the thermal properties of the cured TMBP/DAP system. With loading HPCTP from 0 to 20 wt %, $Y_{c, \text{wt } \%}$ of the resultant thermosets presented an increase from 25.6 to 29.7 wt %. Thus it is clear that introduction of HPCTP facilitated the formation of char residue which favored to flame resistance effectively.

Due to excellent thermal properties of the cured TMBP/DAP/HPCTP system, they are potentially useful for advanced “green” composite matrices.

CONCLUSIONS

New inherently flame retardant epoxy system composed of TMBP, DAP, and HPCTP was prepared. The cure kinetic, and thermal properties of the TMBP/DAP with and without HPCTP were reported. Kinetic analysis results indicated that E_α decreased with increasing α for TMBP/DAP system because diffusion-controlled reaction dominated the curing reaction gradually in the later cure stage, while TMBP/DAP/HPCTP (10 wt %) system gave an increase phenomenon of $E_\alpha \sim \alpha$ dependence in the later cure stage ($\alpha \geq 0.60$) due to kinetic-controlled reaction in the later cure stage. The existence of HPCTP dramatically changed the physical state of the curing system and inhibited the cure reaction. These cured epoxy resins had very high glass transition temperatures (202–235°C), excellent thermal

stability with high 5 wt % decomposition temperatures (>340°C) and high char yields (>25.6 wt %) which is indicative of good flame retardancy. These epoxy materials may be attractive for use as high-performance “green” electronic products because of their outstanding properties and the absence of a halogen element.

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