

Curing Kinetics and Mechanism of Novel High Performance Hyperbranched Polysiloxane/Bismaleimide/Cyanate Ester Resins for Resin Transfer Molding

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ABSTRACT: Curing kinetics and mechanism determine the structure and property of thermosetting resins and related composites. The curing kinetics and mechanism of a novel high performance resin system based on hyperbranched polysiloxane (HBPSi), 2,2'-diallylbisphenol A modified bismaleimide (BD), and cyanate ester (CE) resins for Resin Transfer Molding (RTM) technique were systemically studied by Differential Scanning Calorimetry (DSC), Fourier Transform Infrared (FTIR) spectra, and torque rheometer. Results show that the addition of HBPSi to BD/CE resin not only decreases the initial curing temperature and apparent activation energy, but also changes the curing mechanism,

and thus the structure and properties of resultant crosslinked networks. An "Interpenetrating network (IPN)-coupling structure" is proposed to be formed in the HBPSi/BD/CE system, which is different from traditional "IPN" structure in BD/CE resin. The simulation of curing reaction suggests that the variety of the curing activity leads to the difference between the curing behaviors of BD/CE and HBPSi/BD/CE resins, which is in good agreement with FTIR and DSC analyses. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 304–312, 2011

Key words: curing mechanism; hyperbranched polysiloxane; bismaleimide/cyanate ester resin; rheology

INTRODUCTION

Resin transfer molding (RTM) has been the subject of attraction increasing attentions since 1990s owing to its many competitive advantages, such as close-mold forming, accurate control of composition, simple processing procedure, and one-time network formation,^{1–4} and thus becomes a promising process with a great potential to produce advanced composites at a low cost.

Fabricating a composite by RTM technique involves introducing a reactive resin at an injection temperature into a closed mold containing fabric preforms, and then curing the resin,^{5,6} so that the rheology and curing kinetics of the matrix resin

show more importance for RTM technique than that of traditional molding processes. During mold filling, the inception of a chemical reaction in the resin takes place, and the viscosity of the resultant resin increases with filling time, consequently, a premature gelation of the resin may occur and leads to an incomplete mold filling. Therefore, accurate prediction and precise control of the curing reaction of a resin during the mold-filling process is critical for achieving product consistency and process efficiency. In addition, a complete characterization of the curing behavior and its kinetics of the resin during the mold-filling stage can provide useful information of the relation between the processing variables and the material properties.

Recently, a novel kind of high performance resins made up of hyperbranched polysiloxane (HBPSi), 2,2'-diallylbisphenol A modified bismaleimide (BD), and cyanate ester (CE) for RTM technique was developed by our research group,⁷ which is coded as HBPSi/BD/CE. Uncured HBPSi/BD/CE resins have significantly low viscosity and suitable pot life, meanwhile cured HBPSi/BD/CE resins exhibit excellent integrated properties including thermal, mechanical, and dielectric properties, suggesting a great potential for fabricating advanced structural and functional composites via RTM technique. However, the curing behavior, kinetics, and mechanism of HBPSi/BD/CE system have not been investigated clearly, so it is not possible to effectively control the

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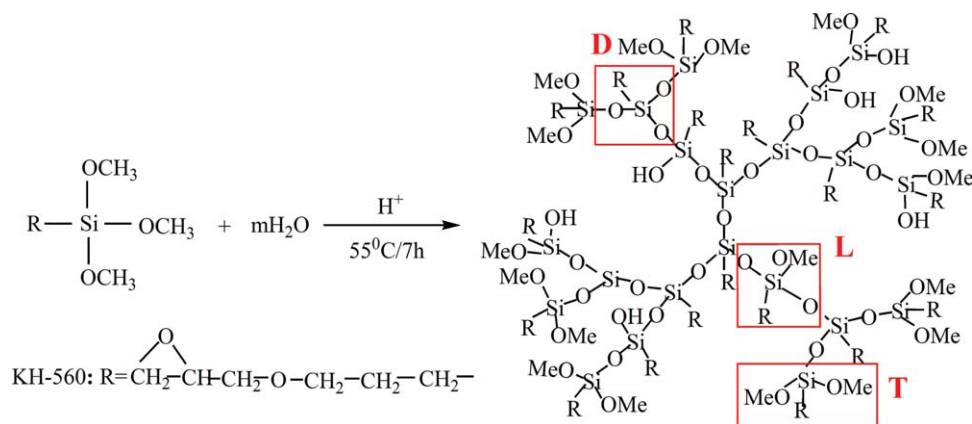
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Scheme 1 Synthesis of hyperbranched polysiloxanes via hydrolyzation of γ -glycidoxypropyltrimethoxysilane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

curing reaction of HBPSi/BD/CE system, and thus the structure and property of resultant crosslinked network. Therefore, it is of great interest to intensively investigate the curing behavior, kinetics, and mechanism of HBPSi/BD/CE system.

In this article, various technologies including differential scanning calorimetry (DSC), online Fourier Transform Infrared (FTIR) spectra, and HAAKE torque rheometer were employed to evaluate the curing behavior and kinetics of HBPSi/BD/CE system, importantly, a new curing mechanism is proposed, which is different from that of BD/CE.

EXPERIMENTAL

Raw materials

The 4,4'-bismaleimidodiphenylmethane (BDM) was supplied by HuBei Fengguang Chemicals (China). The 2,2'-diallylbisphenol A (DBA) was purchased from Laiyu Chemical Factory (China). The 2,2'-bis(4-cyanatophenyl) isopropylidene (CE) was the commercial product of Zhejiang Shengda Chemicals (China).

Hyperbranched polysiloxane (HBPSi) was synthesized via the hydrolyzation of γ -glycidoxypropyltrimethoxysilane by us as described in Scheme 1.⁷ Its ¹H NMR spectrum was recorded on a Bruker WM300 (Germany) with CDCl₃ as the solvent and internal standard, and the results are: 0.67 (\equiv Si-CH₂-), 1.719(-CH₂-CH₂-CH₂-), 2.6 and 3.14 (CH-O-CH₂-CH), 2.8 (>CH-O-CH₂), 3.5 (-O-CH₃, -O-CH₂-CH₂-), 3.75 (-CH₂-O-CH₂-). The ²⁹Si NMR spectrum of HBPSi is shown in Figure 1. HBPSi has three different chemical shifts at -67.99, -66.21, and -65.39 ppm, which can be assigned to dendritic (D), linear (L), and terminal (T) unit, respectively. The absolute molecular weight (M_w) of HBPSi was measured by Multiangle Laser

Light Scattering (MALLS, USA), the M_w of HBPSi is 1500–2000, and d_n/d_c value is 0.0772.

Preparation of BD/CE and HBPSi/BD/CE resins

Table I gives the formulation of each resin. Appropriate quantities of BDM and DBA were placed in a three-necked flask with a mechanical stirrer and a thermometer. The mixture was heated to 135°C and maintained within that temperature range with stirring until a clear brown homogeneous liquid was obtained. The mixture was maintained at that temperature for an additional 30 min to obtain a transparent liquid, which was BD prepolymer.

BD prepolymer was cooled to 100°C, and then preweighted CE was added into the flask with stirring for 30 min to obtain a brown-red transparent liquid, coded as BD/CE prepolymer.

BD prepolymer was cooled to 100°C, and then preweighted CE and HBPSi were added into the flask with stirring for 30 min to obtain a brown-red transparent liquid, coded as HBC-1, HBC-2, or HBC-3 prepolymer, respectively.

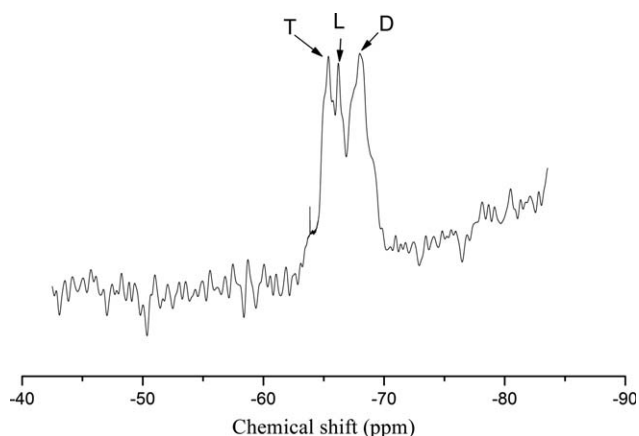


Figure 1 ²⁹Si NMR spectrum of HBPSi.

TABLE I
Four Formulations of BD/CE and HBPSi/BD/CE Resins

System	Weight (g)			
	BDM	DBA	CE	HBPSi
BD/CE	100	86	25	0
HBC-1	100	86	25	10
HBC-2	100	86	25	15
HBC-3	100	86	25	20

Characterizations

A DuPont (USA) Model 2910 DSC was used to analyze the curing kinetics of resins by assuming proportionality between the heat evolved during curing procedure. A sample with a weight of 0.9–1.5 mg was sealed in a hermetic pan and heated from 25 to 330°C at five different heating rates, taking values of 5, 10, 15, 20, and 25°C min⁻¹.

FTIR spectra were recorded between 400 and 4000 cm⁻¹ with a resolution of 2 cm⁻¹ on a Nicolet FTIR 5700 spectrometer (USA). Each sample was prepared by coating a liquid resin on a KBr plate. To monitor the curing behavior of BD/CE, the vibration bands of =C–H, –OCN and triazine ring at 828, 2276, and 1562 cm⁻¹, respectively, are chosen to calculate their separate relative content (R_C). It should be noted that the absorption peak attributing to –OCN group splits into a doublet owing to the chemical environment of the polymer, so its whole big peak is integrated. The band at 2970 cm⁻¹ assigning to methyl herein is regarded as the reference because it is assumed to be unchanged during the curing process. Thus, the respective R_C of =C–H, –OCN and triazine ring groups can be calculated according to eq. (1):

$$R_C = \frac{(A_{\text{peak}}/A_{\text{methyl}})_{T,t}}{(A_{\text{peak}}/A_{\text{methyl}})_{T,t=0}} \quad (1)$$

where A_{peak} and A_{methyl} are the areas of the vibration bands of each chosen peak and methyl, respectively, T is the curing temperature, and t is the time of curing.

Torque rheometer was performed using a HAAKE PolyLab QC (Germany). Each sample with a weight of (45 ± 0.5) g was tested at different temperatures with a revolution speed of 40.0 L min⁻¹.

RESULTS AND DISCUSSION

DSC analyses

The DSC thermograms for BD/CE and HBPSi/BD/CE prepolymers at a heating rate of 10°C min⁻¹ are given in Figure 2. Each prepolymer shows an exo-

thermic peak, however, all peaks for HBPSi/BD/CE prepolymers slightly shift toward higher temperature compared with that of BD/CE, suggesting that there is additional reaction in the HBPSi/BD/CE system which will be illuminated by the corresponding dynamically scanned FTIR spectra later.

In addition, it can be seen that the width of the whole exothermic peak of each HBPSi/BD/CE prepolymer is narrower than that of BD/CE prepolymer, but the former has small curing enthalpy than the latter (the baseline was traced from 90 to 320°C). It indicates that the curing of HBPSi/BD/CE prepolymer avoids heat accumulation and thermal explosion, and thus becomes controllable. Obviously it is a very attractive feature for fabricating composites, especially those with big thickness. This phenomenon can be interpreted by the special structure of HBPSi. It is known that hybranched polymers usually exhibit spheroidal configuration. Although they have large density of terminal active groups grafted on the shell, their branched molecular chains are too short to entangle, so they usually show high reactivity only at high temperature.^{8,9} In the case of HBPSi/BD/CE resins, the existence of many terminal epoxy groups in HBPSi provides great possibilities to adapt to the needs of curing reaction.

To further study the effect of HBPSi on the curing reaction of BD/CE prepolymer, the kinetic parameters such as the reaction order (n), kinetic constant (A), and activation energy (E) for the whole reaction of BD/CE and HBC-2 system are calculated by employing Kissinger method [eq. (2)] and Crane equation [eq. (3)].^{10–12}

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

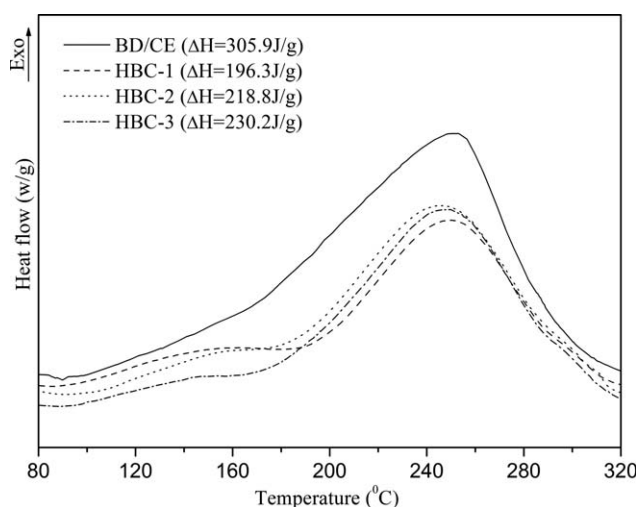


Figure 2 DSC thermograms of BD/CE and HBPSi/BD/CE prepolymers at a heating rate of 10°C min⁻¹.

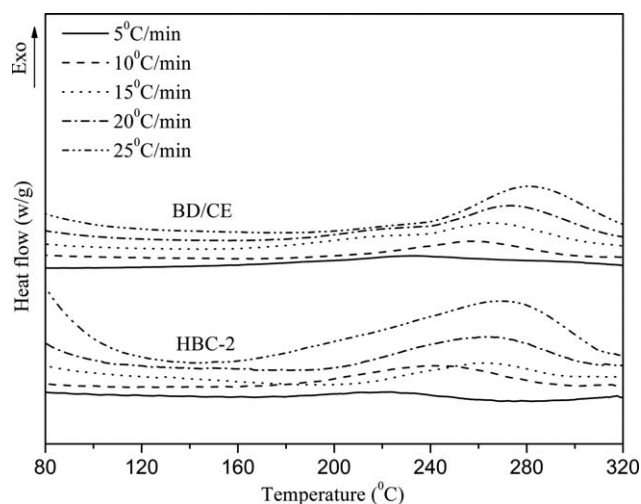


Figure 3 Dynamic DSC scans at different heating rates for BD/CE and HBC-2 prepolymers.

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 BD/CE and HBC-2 prepolymers under different heating rates are shown in Figure 3, 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 4 and 5, respectively. The calculated results of E , A , and n are summarized in Table II.

BD/CE and HBC-2 have similar reaction orders (0.89, 0.87), indicating that both of them follow the first-order reaction. While HBC-2 has smaller apparent activation energy (58.6 kJ mol^{-1}) than BD/CE

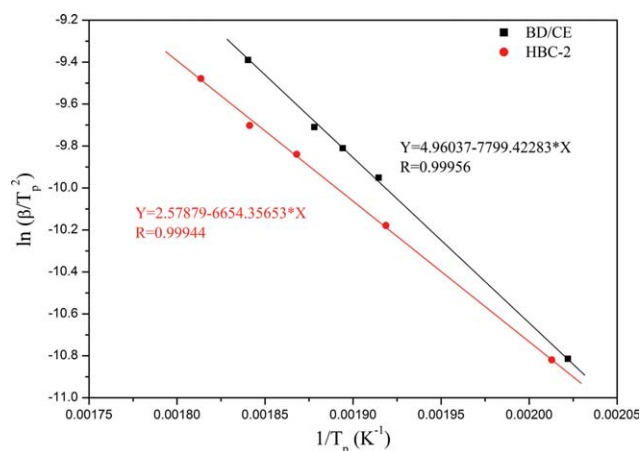


Figure 4 Overlay plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for BD/CE and HBC-2 prepolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

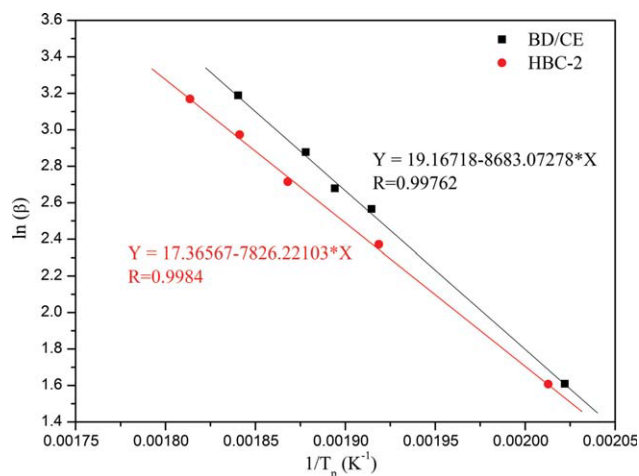


Figure 5 Overlay plots of $\ln(\beta)$ versus $1/T_p$ for BD/CE and HBC-2 prepolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

prepolymer, suggesting that the curing reaction of HBC-2 is easier to occur than that of BD/CE prepolymer. On the other hand, HBC-2 has bigger pre-exponential factor than BD/CE, reflecting that the molecules in HBC-2 have much bigger possibility to collide each other for curing than those in BD/CE because there are more active groups in HBPSi/BD/CE system.

Based on above DSC analyses, it is concluded that compared with BD/CE, HBPSi/BD/CE system has different curing kinetics by decreasing the apparent activation energy, and thus leading to the improvement in activity of the curing reaction.

FTIR analyses

To further discuss the difference of curing kinetics between BD/CE and HBPSi/BD/CE resins, FTIR analyses for BD/CE and HBC-2 resins were carried out. Figure 6 shows the FTIR spectra of BD/CE and HBC-2 resins after being cured with different curing procedures. The absorption peak at 828 cm^{-1} is attributed to the bending vibration of the $=C-H$ groups of maleimide in BDM, while the peak assigning $-OCN$ or triazine group appears at 2276 or 1562 cm^{-1} , respectively. Because the absorption peak of $Si-O-Si$ in the FTIR spectrum usually splits into a doublet (or several peaks) of partially resolved peaks depending on the chemical environment of the polymer, or overlaps with other peaks,¹³ so which can

TABLE II
Kinetic Parameters Obtained by Kissinger Method and Crane Equation

System	E (kJ mol^{-1})	A (S^{-1})	n
BD/CE	67.0	1.83×10^6	0.89
HBC-2	58.6	2.00×10^6	0.87

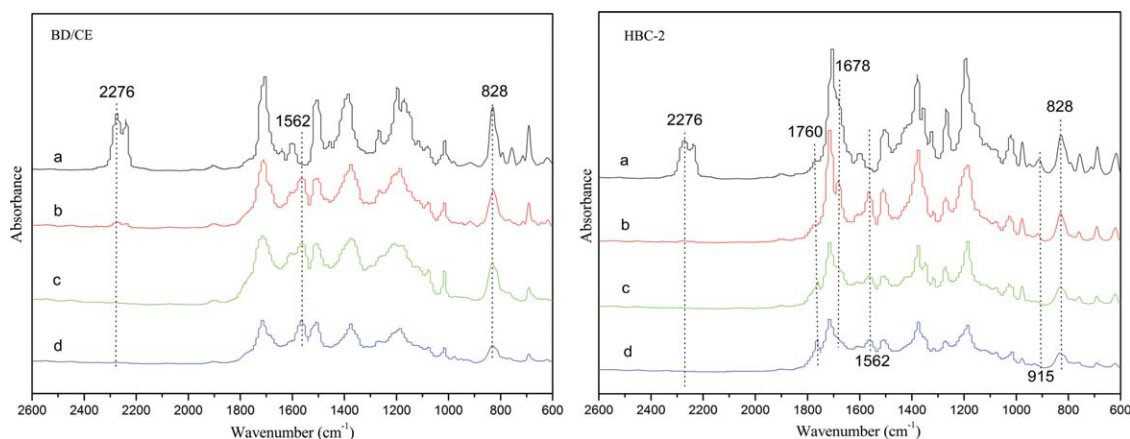


Figure 6 FTIR spectra of BD/CE and HBC-2 resins cured via different procedures: (a) 130°C/0.5 h; (b) 130°C/0.5 h + 170°C/2 h; (c) 130°C/0.5 h + 170°C/2 h + 200°C/2 h; (d) 130°C/0.5 h + 170°C/2 h + 200°C/2 h + 220°C/2 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

not be used to evaluate the curing behavior, and thus the characteristic absorption peak (915cm^{-1}) attributing to the epoxy groups in HBPSi is selected to observe the change of HBPSi during the curing procedure.

Figure 7 plots the relative contents of the $=\text{C}-\text{H}$, $-\text{OCN}$, and triazine ring groups as a function of temperature for BD/CE and HBPSi/BD/CE-2 resins during the curing process according to FTIR spectra. Compared with BD/CE resin, the variety of FTIR spectra of HBC-2 resin with the progress of curing is more complicated. First, in the case of BD/CE resin, $-\text{OH}$ groups in DBA have significant catalytic role on the cyclotrimerization of $-\text{OCN}$ groups,^{14,15} so after being cured at low temperature ($\leq 170^\circ\text{C}$), the stretching vibration absorption peak (2276cm^{-1}) of $-\text{OCN}$ groups decreases rapidly, and the R_C value of $-\text{OCN}$ groups decreases from 100 to 15%; mean-

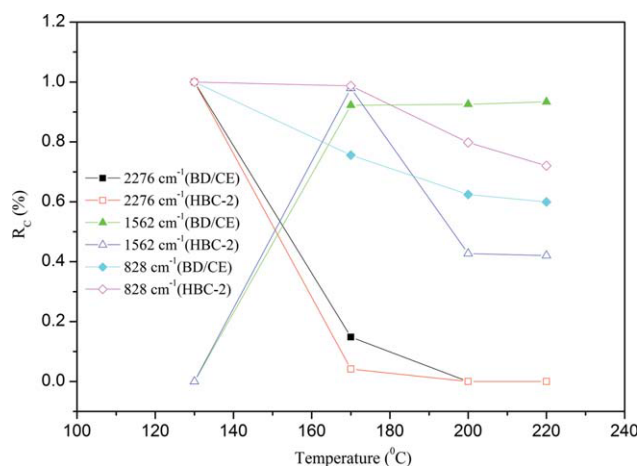
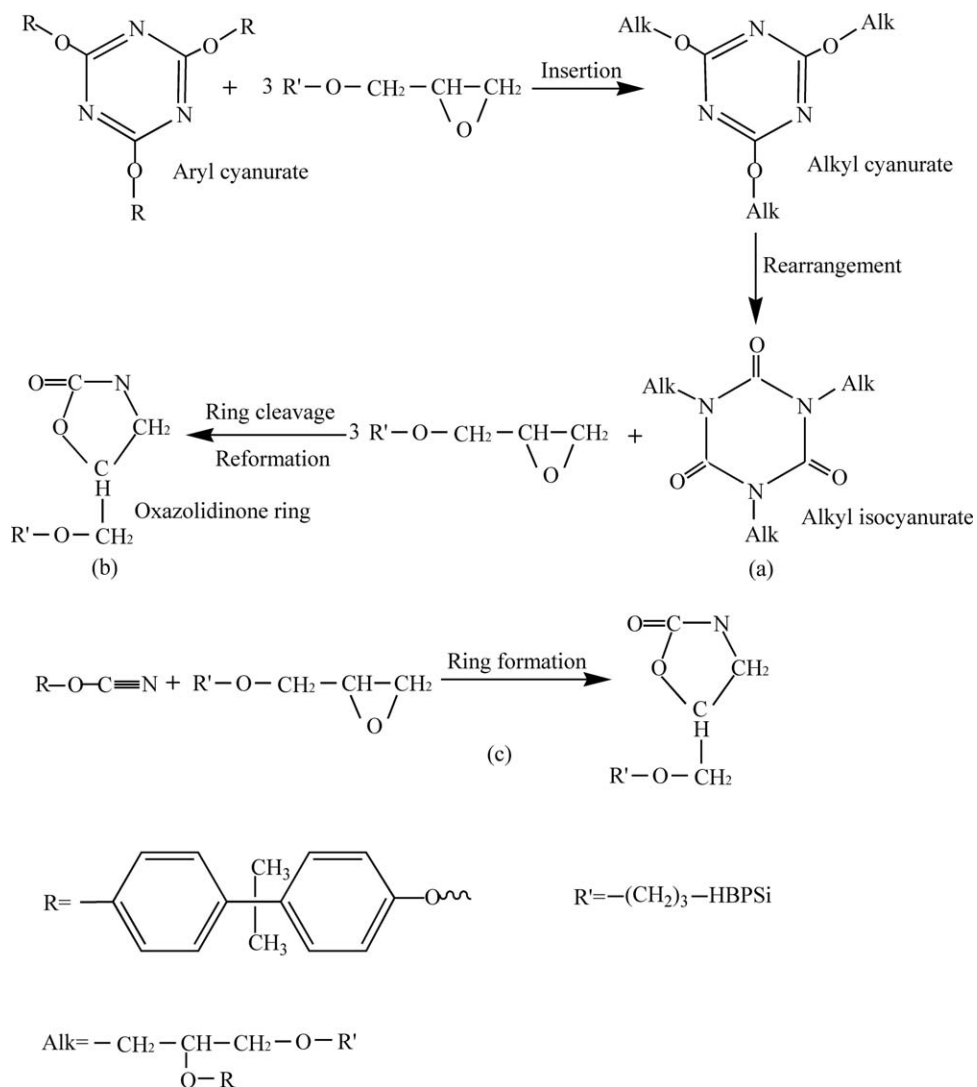


Figure 7 The relative content of $=\text{C}-\text{H}$, $-\text{OCN}$, or triazine ring groups as a function of temperature for BD/CE and HBC-2 resins cured via different procedures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

while the absorption of triazine groups increases, and the R_C value of triazine groups is 92% at this point, indicating the formation of triazine network by the cyclotrimerization of $-\text{OCN}$ groups. However, the stretching vibration absorption peak of $-\text{OCN}$ groups in HBC-2 resin decreases from 100 to 4%, much faster than that in BD/CE resin, because a large number of $\text{Si}-\text{OH}$ groups in HBPSi can also catalyze the cyclotrimerization of $-\text{OCN}$ groups. Meanwhile the absorption peak of epoxy group (915cm^{-1}) declines, and a new absorption peak attributing to isocyanurate band appears at 1678cm^{-1} , reflecting the formation of isocyanurate resulting from the reaction between triazine group of CE and epoxy group of HBPSi as shown in Scheme 2(a).¹⁶ Second, after being cured at 200°C , the stretching vibration absorption peak of $-\text{OCN}$ group in BD/CE resin completely disappears, for example, the R_C value of $-\text{OCN}$ and triazine groups are 0 and 100%, respectively. In contrast, for HBC-2 resin after being cured at 200°C , the absorption peaks of $-\text{OCN}$, epoxy, and isocyanurate groups entirely disappear, while a new additional peak at 1760cm^{-1} appears, which is usually referred to oxazolidinone. The oxazolidinone is generally associated to isocyanurate ring cleavage/rearrangement or direct ring formation as shown in Scheme 2(b,c).¹⁷ It is worth noting that the peak of the triazine ring does not increase with the consuming of the $-\text{OCN}$ group as that of BD/CE resin, and the R_C value of triazine ring reduces to 43%. Further increasing the curing temperature to 220°C , more amount of triazine ring is consumed; meanwhile the peak at 1760cm^{-1} still keeps on increasing, reflecting that there indeed exist reactions discussed above.

It is well known that the curing of a thermosetting resin can be divided into two stages, that is, the kinetics controlled one followed by diffusion controlled stage.¹⁸ Because $\text{Si}-\text{OH}$ group in HBPSi and



Scheme 2 Coreactions between HBPSi and CE.

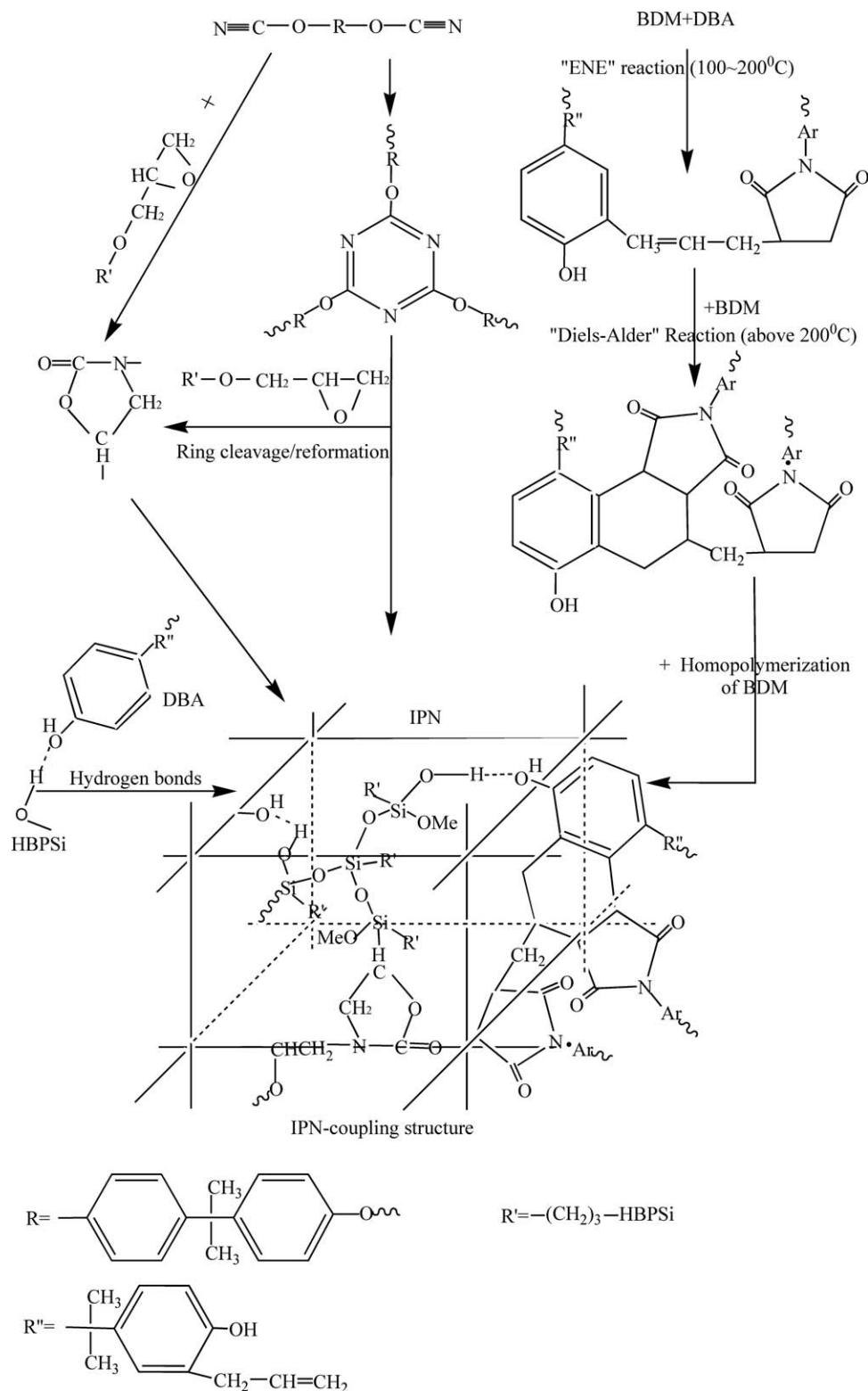
—OH group in DBA can catalyze the cyclotrimerization of —OCN groups, the diffusion controlled stage of HBPSi/BD/CE tends to occur earlier or at lower temperature compared with that of BD/CE, and thus the copolymer of BDM and DBA is blocked with the homopolymer of BDM, as a result, the R_C of =C—H groups in maleimide rings of HBPSi/BD/CE system (72%) is much higher than that of BD/CE (60%).

For the curing mechanism of BD/CE, many researchers believe that BD and CE crosslink to form two discrete networks which interpenetrated with each other in the cured resin,^{19,20} briefly, it is an IPN structure. In the case of HBPSi/BD/CE, it is worthy to note that there are the self-polymerization of Si—OH groups,²¹ and the hydrogen bonds resulting from phenol group in DBA and Si—OH group in HBPSi, so besides above IPN structure in BD/CE, HBPSi plays a coupling or bridge role. In detail, HBPSi connects to the CE resin network by the

chemical reaction between epoxy and —OCN; meanwhile, HBPSi connects to the BD resin network through hydrogen bonds, and thus makes the entire system form a complex “IPN-coupling structure” (Scheme 3), which is different from traditional IPN structure.

Rheology analyses

Controlling the rheology of thermosets during fabrication is crucial to their end-use performance. Torque rheometer has been demonstrated as an effective technique for evaluating the variety of viscosity during the polymer processing by the change of torque.²² It is believed that with the progress of curing, the molecular chains change from linear structure to three-dimensional network, leading to increased viscosity and torque, so the point when the torque starts to increase can be regarded as the sign of the beginning of crosslinking reaction. In addition, the



Scheme 3 Formation of IPN-coupling structure for HBPSi/BD/CE system.

increasing rate of torque can reflect the pace of crosslinking reaction, that is, the slope of the curve represents the curing rate.²³

The plots of dependence of torque on time at 200°C of BD/CE and HBPSi/BD/CE resins with the

same weight are depicted in Figure 8. The torque of BD/CE linearly increase with initial increase in the length of time, and then reaches the maximum value at about 22 min, which represents the curing time of the resin. As a contrast, each curve of HBPSi/BD/

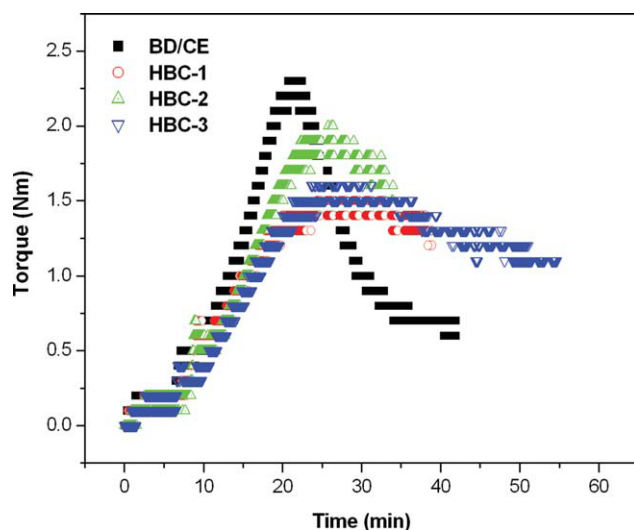


Figure 8 The torque as a function of time for various prepolymers at 200°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CE system also shows similar shape as BD/CE does, however, HBPSi/BD/CE system has longer curing time than BD/CE resin. This phenomenon is easily understood, because the former has higher curing temperature than the latter as discussed in the part of curing behavior.

Because the first stage of the curing is controlled by the kinetics, the curing rate of HBPSi/BD/CE system is almost the same as that of BD/CE resin. But with the progress of curing, the complex curing mechanism of HBPSi/BD/CE system indeed reduce its curing rate in the diffusion stage compared with that of BD/CE resin. These data are in agreement with DSC analyses.

With a further increased length of time, the torque decreases quickly, suggesting that some materials in the crosslinked network decompose. It is proved that the curing mechanism of BD system contains the copolymerization between BDM and DBA, and the self-polymerization of BDM. The former occurs at temperature as low as around 110°C, and the latter takes place at a relatively higher temperature. However, when the BD/CE mixture is put into an environment with very high temperature, above two reactions compete with each other, a small amount of free DBA tends to be left alone, as a result, the torque of BD/CE decreases quickly with the extension of time after the maximum torque. This phenomenon supplies very useful information for curing BD/CE resin, specifically, BD/CE resin needs to be cured by a multi-step procedure containing the step at low temperature and that at high temperature to guarantee the complete copolymerization between DBA and BDM. Note that this information

also proves the necessity of conducting rheology analyses.

From the intensity of the maximum torque, the crosslinking degrees of four resins follow the order of BD/CE > HBC-3 > HBC-2 \approx HBC-1. This ascertains to their different curing mechanisms. As discussed above, BD/CE resin is an IPN network made up of rigid maleimide groups and triazine rings, some of which are replaced by tough oxazolidinone rings and polyether structures when HBPSi is added to BD/CE resin, so HBPSi/BD/CE system tends to have lower crosslinking degree than the latter. However, when the content of HBPSi is large enough, the molecular chains of HBPSi are easier to connect with each other via the self-polymerization of Si—OH groups, resulting in improved crosslinking degree.

CONCLUSIONS

BD/CE and HBPSi/BD/CE resins have significantly different curing behaviors and mechanisms. For BD/CE, its curing mechanism is that BD and CE crosslink to form two discrete networks which interpenetrate with each other in the cured resin; consequently, it is an IPN structure. In the case of HBPSi/BD/CE, besides above IPN structure in BD/CE, a complex “IPN-Coupling structure” is proposed because HBPSi performs as a coupling or bridge role to connect both CE resin network and BD resin network, which still need further study.

Compared with BD/CE, Hbpsi/BD/CE system has decreased initial curing temperature and apparent activation energy.

Rheology analyses supply additional information for curing BD/CE, which needs to be cured by a multi-step procedure to guarantee the complete copolymerization between DBA and BDM.

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