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Kinetics of curing and thermal degradation of hyperbranched epoxy (HTDE)/diglycidyl ether of bisphenol-A epoxy hybrid resin

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Abstract Hyperbranched epoxy resin (HTDE) has relatively low viscosity and high molecular mass and holds great promise as a functional additive for enhancing the strength and toughness of thermosetting resins. In this work, the curing and thermal degradation kinetics of HTDE/diglycidyl ether of bisphenol-A epoxy (DGEBA) hybrid resin were studied in detail using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) techniques by Coats–Redfern model. The effect of molecular mass or generation and content of HTME on the activation energy, reaction order, and curing time were discussed; the results indicated that HTDE could accelerate the curing speed and reduce the activation energy and reaction order of the curing reaction.

Keywords Hyperbranched epoxy resin · Kinetics · Curing · Thermal degradation · DSC · TG

Introduction

Epoxy resins are one of the most versatile polymers and are widely used in applications such as coatings, encapsulations, structural composites, and adhesives [1] because the cured thermosetting polymer can be tailored to suit specific performance characteristics. As a result of their high-crosslink density and aromatic backbone, most epoxy resins are rigid materials and fail by brittle fracture [2]. In order to obtain epoxy resins suitable for high-tech applications, such as print circuit boards, electronic components, and aerospace composites and functional coatings [3, 4], a toughening agent is often required during their formation. However, many toughening agents decrease the strength of epoxy resins to some extent, including tensile strength and flexural strength of the cured materials [5–7]. So a novel toughening approach which does not impair the strength of epoxy resins is very important.

Hyperbranched polymers are of interest for many applications because they are easier to synthesize than dendrimers and yet possess a highly branching structure. In particular, hyperbranched polymers have better solubility and lower viscosity than linear polymers with similar molecular mass and repeat unit structure, so these materials have potential as thermoplastic tougheners for thermosets [8–11]. Hyperbranched aliphatic epoxy resin [12–14] with high epoxy equivalent mass can effectively increase the toughness of cured material but will decrease the strength by 20%. However, hyperbranched aliphatic epoxy resin [15, 16] with low epoxy equivalent mass and low viscosity can increase effectively several times the toughness of epoxy resins and enhance their tensile and flexural strength by over 20%. So a study of curing kinetics and thermal degradation kinetics of the hyperbranched epoxy/diglycidyl ether of bisphenol-A epoxy

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(DGEBA) hybrid resin will be important for the extended application of epoxy resin.

Theory and model of curing and thermal degradation kinetics

The glycidyl group is highly strained and readily reacts with curing agents by nucleophilic attack on the α-carbon of the epoxy group. A range of chemical agents with active hydrogen atoms can be used to cure epoxy resins, although the most important curing reactions occur with amines. Here, the overall curing process involves an attack of the amine group on the terminal carbon atom of the glycidyl unit, which subsequently converts the epoxide to a hydroxyl group [17]. According to Bouer [2], the curing reaction involves a complex intermediate, stabilized by the formation of a hydrogen-bonded species. This hydrogen bonding causes the electron deficient epoxy complex to become more susceptible to nucleophilic attack by the incoming amino group.

Since the curing process actually produces hydroxyl groups that can act as the hydrogen bonding species, the epoxy-amine reaction becomes autocatalytic as it proceeds [2]. Hence, the overall mechanism of epoxy reaction relies on the presence of free-proton donors and the formation of a stabilized complex intermediate. It is important to understand how the epoxy network develops kinetically, as this is related to the final network structure and determines the physical and engineering properties [18]. To measure epoxy curing kinetics, the reaction process must be monitored as the material transforms from liquid to rubber state and/or to vitrified state. Differential scanning calorimetry (DSC) is the most widely used method for monitoring the curing process [19–21]. In addition, DSC may be operated in the dynamic mode with a constant scanning rate (heating or cooling) or in the isothermal mode for a given curing temperature. Thermogravimetric analysis (TG) also is an important tool for studying thermal degradation kinetics of hyperbranched polymers.

In the dynamic mode, a temperature scan of the catalyzed epoxy monomer sample produces an exothermic curing peak in the DSC trace. Many dynamic models [22] have been used to calculate the activation energy of the reaction based on the known reaction order. Study of the curing and thermal degradation kinetics of HTDE/DGEBA hybrid resin has not been reported before and its reaction order is unknown, therefore, Coats–Redfern [23] model should be the right choice. Coats–Redfern model showed that analysis of scanning curve obtained at a constant scanning rate can give average activation energy E as

$$\ln[g(a)/T^2] = \ln[(AR/\Phi E)/(1-2RT/E)] - E/(RT) \quad (1)$$

$$\text{when } n = 1, g(a) = -\ln(1-\alpha);$$

$$\text{when } n \neq 1, g(a) = [1-(1-\alpha)^{1-n}]/(1-n)$$

where Φ is the heating rate, T is the temperature, A is the frequency factor, R is the gas constant, E is the reaction activation energy, n is reaction order, and α is conversion degree. Thus a plot of $\ln[g(a)/T^2]$ against $1/T$ should result in a straight line with slope $-E/R$ from which the activation energy can be calculated, then the reaction order can be obtained according to relationship of $g(a)$ and n.

Experimental

Materials

The epoxy resin used was liquid diglycidyl ether of bisphenol-A (DGEBA) (E 51 Dongfeng Chemical Corp. China) containing 5.1 mmol epoxy group per gram of resin. The curing agent was DETA-AN which was produced by the addition reaction of equal molar acrylonitrile (AN) and diethylene triamine (DETA).

The hyperbranched epoxy resin (HTDE) consists of a highly branched aromatic polyester backbone. The characteristics of the HTDE were shown in Table 1, and the viscosity of the HTDE was measured by a Brookfield DV-II +Pro Viscometer with RV-S06 spindle in 298 K and 20 r min^{-1} of rotational speed. The molecular mass

Table 1 Properties of the HTDE and DGEBA

HTDE	Molecular mass/g mol^{-1}	Epoxy equivalent mass/g mol^{-1}	Viscosity/cp	Molecular mass distribution/Mw/Mn
HTDE-1(G1)[a]	1400	312.5	550	1.11
HTDE-2(G2)	3400	400.0	700	2.06
HTDE-3(G3)	7400	454.5	500	1.88
HTDE-4(G4)	15500	526.3	350	1.83
DGEBA	392	196.1	15,600	2.50

[a] HTDE-*n*, *n* refers to the generation of hyperbranched polymers

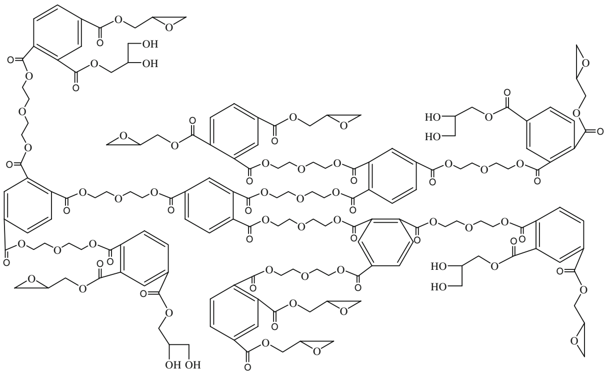

Fig. 1 Ideal molecular structure of HTDE-2

distribution was measured by Agilent 1100 Series HPLC, the Agilent PLgel 5um MIXED-C as GPC fixed phase, and the tetrahydrofuran (THF) as flowing phase. The structure of the HTDE-2 was shown in Fig. 1. The HTDE was prepared from the carboxy-terminated hyperbranched precursor in our lab [24].

Experimental apparatus

DV-II +Pro Viscometer (Brookfield Engineering LABS), 1100 Series HPLC (Agilent), NETZSCH DSC204 F1, and NETZSCH TG209 (NETZSCH Gerätebau GmbH.).

Curing kinetics of HTDE/DGEBA hybrid resin

The HTDE/DGEBA hybrid resin samples were prepared by blending the HTDE in DGEBA at about 5–10 K through stirring with glass stick. The modified resin was mixed with a stoichiometric amount DETA-AN by continuously stirring the mixture for 5 min under 283 K, 5–10 mg of the mixture was placed in the DSC crucible, and the scanning procedure was carried out with NETZSCH DSC204 F1. A dynamic DSC scanning was carried out up to 523 K at heating rate 5.0 K min^{-1} and nitrogen atmosphere flow rate 20 ml min^{-1}.

The effect of molecular mass of HTDE on the curing kinetics was based on the 9%HTDE/91%DGEBA hybrids which show best comprehensive mechanical performance [15, 16]. Moreover, the mechanical performance of HTDE-2/DGEBA hybrid resins is better than those of HTDE-1/DGEBA, HTDE-3/DGEBA, and HTDE-4/DGEBA hybrid resin. The effect of HTDE content on the curing kinetics was, therefore, mainly inferred from HTDE-2/DGEBA hybrid resins system. The curing curves and integral curves of all the samples were shown in Figs. 2 and 3, respectively.

From Figs. 2 and 3, some typical data of curing process were obtained and are shown in Table 2, including T_i the initial curing temperature, T_p the peak curing temperature, T_t completing curing temperature, curing time, and the conversion α_p of the T_p.

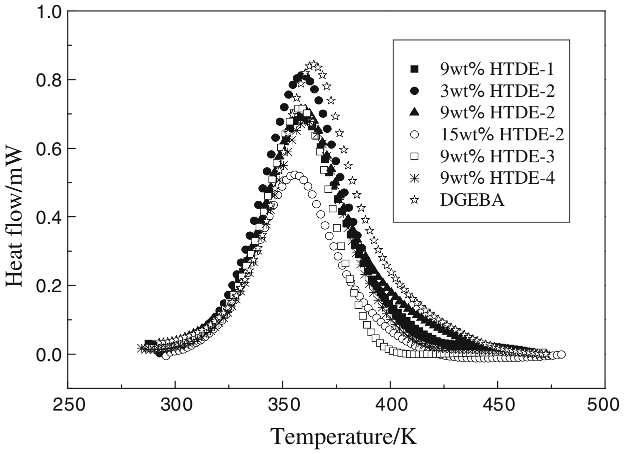

Fig. 2 DSC curves of HTDE/DGEBA hybrid resins

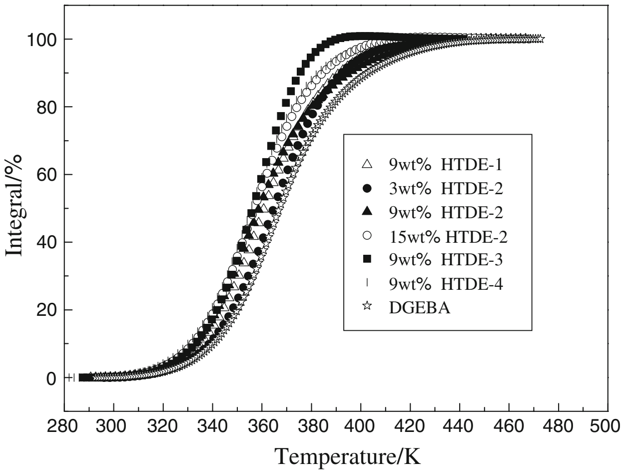

Fig. 3 Conversion-temperature curves of HTDE/DGEBA hybrid resins

Curves of $\ln[g(a)/T^2]$ against $1/T$ were also obtained by Coats–Redfern method during curing process of mass fraction 9%HTDE-1/DGEBA hybrid resin (shown in Fig. 4). The curing kinetics data of mass fraction 9%HTDE-1/DGEBA hybrid resin were shown in Table 2 from Fig. 4, while the regress coefficient of the curve was −0.998. Curing kinetics data of other hybrid resin systems also were obtained and shown in Table 2 by a similar process.

From Fig. 2 and Table 2, with the increase of molecular mass or generation of hyperbranched epoxy resins, the exothermic energy and curing reaction time decrease, curing reaction activation energy increases first and then decreases, temperature ($\mathrm{T_p}$) at maximum curing reaction rate decreases, but curing reaction order is constant. The exothermic energy, curing reaction order, and curing reaction activation energy of hybrid resin systems decrease

Table 2 Typical curing kinetics data of DGEBA and HTDE/DGEBA hybrid resins

Typical data	DGEBA	HTDE-1 9%	HTDE-2 3%	HTDE-2 9%	HTDE-2 15%	HTDE-3 9%	HTDE-4 9%
T_i/K	302.7	301.7	302.0	301.6	301.1	300.7	300.6
T_p/K	364.5	359.7	359.8	358.5	355.8	357.3	358.4
T_t/K	439.7	419.7	417.5	422.6	414.1	411.7	423.9
Curing range/K	137	118	115.5	121	113	110	123.3
Curing time/min	27.4	23.6	23.1	24.2	22.6	22.0	24.6
α_p	0.45	0.47	0.47	0.42	0.47	0.52	0.48
ΔH/J g^{-1}	479.8	400.2	448.0	391.8	312.7	387.1	381.6
Reaction order (n)	1.90	1.60	1.67	1.60	1.55	1.60	1.60
Ea/kJ mol^{-1}	78	69	75	71	70	70	65
Regress (R)	−0.997	−0.998	−0.999	−0.993	−0.998	−0.998	−0.993
Standard deviation (SD)	0.247	0.109	0.1099	0.264	0.097	0.059	0.274

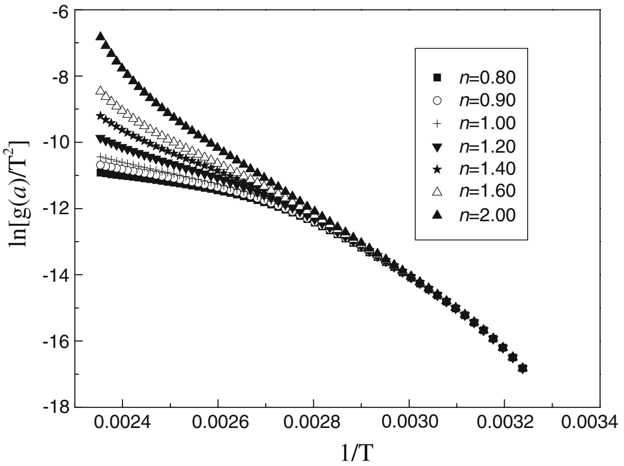

Fig. 4 Simulation curves of mass fraction 9%HTDE-1/DGEBA hybrid resin by Coats–Redfern method

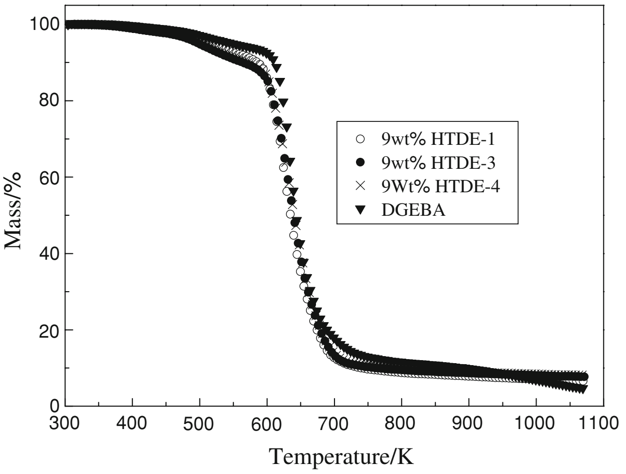

Fig. 5 Effect of HDTE generation on TG curves of their hybrid resins

with the increase of hyperbranched epoxy resins content. During the curing reaction of epoxy resins, the exothermic energy evolution recorded by DSC is proportion to the extent of consumption of the epoxide group in the epoxy resins or the reactive groups in the curing agent, that is, the released heat is proportion to the extent of the reaction. The relative content of epoxy group of hyperbranched epoxy resin is lower than that of DGEBA. Moreover with the increase of molecular mass or content of hyperbranched epoxy resins, their relative content of epoxy group decreases. So, exothermic energy, curing reaction order, and activation energy of hybrid resin systems are less than those of DGEBA. The decrease of curing time of hybrid resins with hyperbranced epoxy resin results from the following two reasons. First, the viscosity of hyperbranched epoxy resin is lower than that of DGEBA, low viscosity helps molecule or group to move and react, so with the decrease of viscosity, the reaction activation energy of hybrid resin systems decreases and the curing curve moves to low temperature. On the other hand, the presence of many hydroxyl groups in hyperbranched epoxy resin can accelerate the curing reaction between epoxy group and amine curing agent [2, 24].

According to Arrhenius equation, reaction activation energy increases with the increase of their viscosity, HTDE-2/E51 hybrid resin has larger viscosity, therefore, its reaction activation energy is bigger (Table 1).

Thermal degradation kinetics of HTDE/DGEBA hybrid resin

All TG analyses were performed on a NETZSCH TG209 (NETZSCH Gerätebau GmbH.) instruments. Samples of 10–15 mg were heated to 1,100 K under a nitrogen at a flow rate of 20 ml min^{-1} and at heating rate 10.0 K min^{-1}.

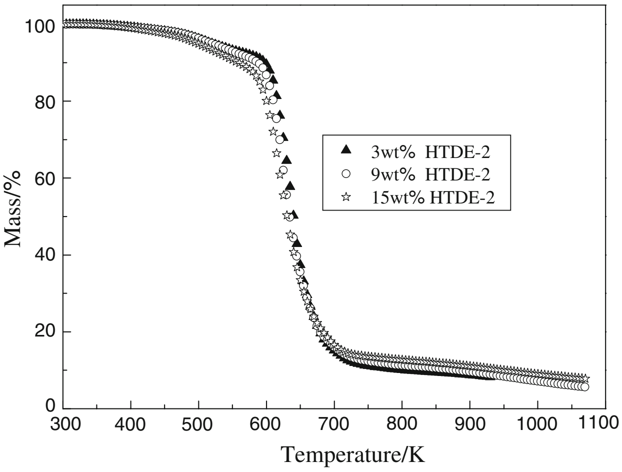

Fig. 6 Effect of HTDE-2 content on TG curves of their hybrid resins

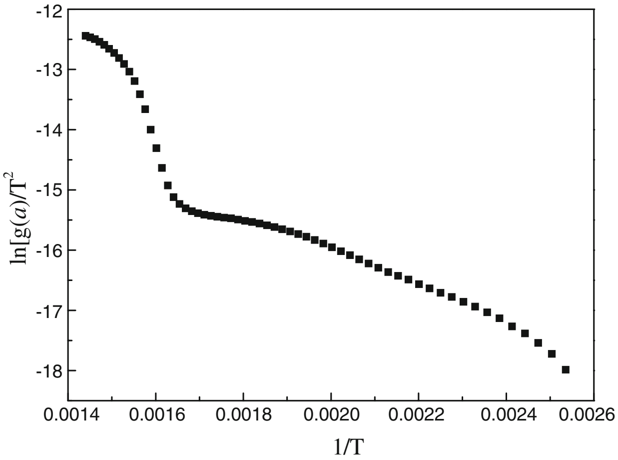

Fig. 7 Plot of $\ln[g(a)/T^2]$ against $1/T$ by Coats–Redfern method in DGEBA system

The effect of molecular mass or generation and content of hyperbranched epoxy resins (HTDE) on their thermal degradation curves was shown in Figs. 5 and 6.

Relative mass loss data were obtained and shown in Table 3 from Figs. 5 and 6. With the increase of molecular mass or generation and content of hyperbranched epoxy resins in hybrid resins system, hydroxyl content of hybrid resins system should increase because ring-close degree of hyperbranched epoxy resin was lower than that of DGEBA epoxy resin, therefore, initial thermal degradation temperature (temperature at 5% mass loss) of HTDE/DGEBA hybrid resins decreased. But the residual char yield increases for higher rigid group content of hyperbranched epoxy resin compared with that of DGEBA epoxy resin from Table 3.

Thermal degradation kinetics data of the HTDE/DGEBA hybrid resins can also be calculated by Coats–Redfern model. Assuming the conversion of thermal degradation reaction of hybrid resins is 100% at 1,100 K, the residual char yield can be deducted. Thermal degradation reaction of epoxy resin results from random fracture mechanics reaction [25–28], so its reaction order customarily is considered as 1. The plot of $\ln[g(a)/T^2]$ against $1/T$ of DGEBA during thermal degradation was shown in Fig. 7 according to reaction order of 1 by Coats–Redfern model.

All activation energy data of DGEBA and HTDE/DGEBA hybrid resin were obtained and shown in Table 3 by Coats–Redfern model. The two slopes of the plot indicate that thermal degradation reaction of DGEBA occur in two steps and has two distinct thermal degradation activation energy (Fig. 7). The temperature and mass loss of the turning point were 594.2 K and 6.96%, respectively, in Fig. 7. The thermal degradation reaction under 594.2 K corresponds to dehydration of the hydroxyl groups of epoxy resin and is related to chemical bond fracture of epoxy resin at over 594.2 K. So with the increase of molecular mass or generation and content of hyperbranched epoxy resins in the hybrid resins system, the activation energy of low temperature reaction (E_{a_1}) changed only a bit, but the activation energy of high temperature reaction (E_{a_2}) changed markedly because of the multi-effects of intramolecular cavity density, rigid group density, epoxy equivalent mass of hyperbranched epoxy resin, and crosslink density of hybrid resins.

Table 3 Properties of TG curves and kinetics data of HTDE/DGEBA hybrid resin

Typical data	DGEBA	HTDE-1 9%	HTDE-2 3%	HTDE-2 9%	HTDE-2 15%	HTDE-3 9%	HTDE-4 9%
Temp. 5% mass loss/K	548.7	519.5	519.9	519.2	499.2	498.2	508.8
Temp. 10% mass loss/K	611.7	586.5	598.9	585.7	562.3	565.2	572.8
Temp. max. degrad. rate/K	641.9	623.1	638.8	621.5	613.0	617.0	614.2
Residual mass at 1100 K/%	4.73	6.61	5.12	6.67	7.79	7.73	8.12
E_{a_1}/kJ mol^{-1}	24	22	19	21	21	21	21
Regress (R_1)	−0.987	−0.990	−0.995	−0.998	−0.998	−0.997	−0.997
E_{a_2}/kJ mol^{-1}	118	90	106	95	83	87	89
Regress (R_2)	−0.968	−0.980	−0.977	−0.974	−0.984	−0.988	−0.989

Conclusions

Curing kinetics and thermal degradation kinetics of hybrid resin systems are studied by DSC, TG using Coats–Redfern model. With the increase of molecular mass or generation of hyperbranched epoxy resins, the exothermic energy and curing reaction time decrease, curing reaction activation energy increases first and then decreases, temperature at maximum curing reaction rate decreases, while curing reaction order remains constant. The exothermic energy, curing reaction order, and curing reaction activation energy of hybrid resin systems decrease with the increase of hyperbranched epoxy resins content. The thermal degradation reaction of pure DGEBA epoxy resin system and hybrid resin systems include a low temperature section under 594 K and a high temperature section over 594 K. Activation energy of the thermal degradation reaction of hybrid resin systems are almost equal to that of pure DGEBA epoxy resin system in the low temperature section, but in the high temperature section, activation energy is lower than that of pure DGEBA epoxy resin system. Moreover, activation energy of thermal degradation reaction of hybrid resin systems decreases with the increase of hyperbranched epoxy resins content.

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