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Polymer 42 (2001) 8339–8347

polymer

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Curing behavior of tetrafunctional epoxy resin/hyperbranched polymer system

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Received 27 October 2000; received in revised form 7 May 2001; accepted 18 May 2001

Abstract

The effects of hyperbranched polymers (HBPs) on the cure behavior of tetrafunctional epoxy resin were investigated using differential scanning calorimetry (DSC) and FT-IR spectroscopy and compared with those of the linear analog. The hydroxyl terminal groups of the HBP initiated the cure reaction through proton donor–acceptor complex. The heat of cure in epoxy/HBP system was higher than that in epoxy/linear polymer system. The activation energy for cure reaction was lower in epoxy/HBP system. When the hydroxyl terminal groups of the HBP were transformed into benzoate groups, the induction time for cure reaction became much longer and the heat of cure was reduced. The isothermal kinetic parameters were obtained from Kamal equation, where the overall reaction order was ca. 1.5. As the cure reaction proceeded, the characteristic peaks of epoxy ring were decreased and H-bonded C=O peak was increased. The intensity of the H-bonded C=O peak was increased with increasing amount of the HBP. © 2001 Published by Elsevier Science Ltd.

Keywords: Hyperbranched polymer; Cure behavior; Tetrafunctional epoxy resin

1. Introduction

Nonlinear polymers such as dendrimers and hyperbranched polymers (HBPs) have attracted considerable interest during recent years. Dendrimers are built of AB_x type ($x \geq 2$) monomers attached in layers around a central core, where each layer is called a generation. They have perfectly branched structures. HBPs are related to dendrimers in the sense that they are based on the similar AB_x monomers, but with the differences that they have randomly branched structures and contain linear segments. Dendrimers can be obtained through multi-step divergent [1–3] or convergent growth approach [4–6]. However, HBPs can be easily synthesized through one-step polymerization process [7,8], and hence HBPs are often cheaper to produce and more available in large-scale applications. Because of their highly functionalized globular structures, HBPs exhibit different properties from those of linear polymers of the same molar mass, such as low entanglement in the solid state [9], high solubility in various solvents and low melt viscosity [10–12].

The large number of terminal groups allows the use of HBPs as cross-linking agents. Hult et al. [13] used hyperbranched aliphatic polyesters as curing agents in the coating resin formula. The resin could be UV cured, and the glass transition temperature of the cured films was correlated to the difference in the structure of terminal groups in the resin. A combination of enhanced reactivity and reduced viscosity for alkyd resins has been achieved by using hyperbranched polyesters [14–16]. Shi and Rånby [17–19] also studied hyperbranched methacrylated polyesters and their use in photo-polymerization of films and fiber-reinforced polymer composites. The resins exhibited low viscosities and short curing times.

Although the use of HBPs as curing agents has somewhat been carried out, there is very limited information concerning the cure kinetics and the cure mechanism in the system. The comparison between the effects of HBP and linear polymer on the cure behavior has scarcely been performed. Therefore, it is the purpose of this study to investigate the effects of HBPs on the cure kinetics and the cure mechanism and to compare the effects with those of a linear analog. This study also aims for studying the relationship between structure and property.

A hyperbranched aliphatic polyester, which was synthesized from an AB_2 type monomer and a B_3 type core, was used. The change of the terminal groups was performed with

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PII: S0032-3861(01)00365-2

Table 1
Physical properties of EPON HPT 1071 epoxy resin

Physical form	Dark colored solid
Epoxy equivalent weight	150–170
Melting point (ASTM D3461, Mettler, 1°C/min)	50°C
Melt viscosity at 110°C	18–22 P (Brook field)
T_g	23°C (DSC)

a view to elucidating the effects of the terminal groups on the cure mechanism. A linear analog was synthesized from an AB type monomer and a B_2 type core, where the branching was perfectly suppressed and the backbone was very similar to those of the HBPs. A tetrafunctional epoxy resin was chosen as the matrix resin. Tetrafunctional epoxy resins have been widely used as high performance composite matrices in aerospace/aircraft industries [20–24].

The size and the spherical configuration of the HBP eliminate the detrimental particle filtering effect observed with other conventional toughening systems. It is believed that the hyperbranched aliphatic polyester can play the role of toughening agent as well as the role of cross-linking agent in this system.

2. Experimental

2.1. Materials

2,2-Bis(methylol)propionic acid (bis-MPA) was used as an AB_2 type monomer and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylol propane, TMP) was used as a B_3 type core moiety. *p*-Toluenesulfonic acid (*p*-TSA) was used as an acid catalyst. Benzoyl chloride, 4-dimethyl aminopyridine (DMAP) and triethylamine (TEA) were used to change the terminal groups of the HBP. All of these chemicals were purchased from Aldrich and used without further purification. Hydroxypivalic acid (AB type monomer) and 2-ethyl-2-methyl-1,3-propanediol (B_2 type core) were purchased from Tokyo Chemical Industry (Japan) and used to synthesize the linear analog of the HBP.

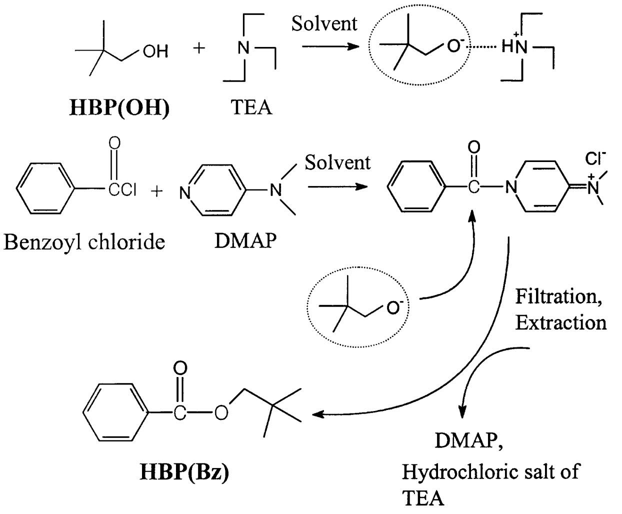


Fig. 1. Schematic diagram for the transformation of the terminal groups of HBP(OH).

The epoxy was EPON HPT 1071 supplied by Shell Chemical. This resin was technical grade of *N*,*N*,*N*′,*N*′-tetraglycidyl-α,α′-bis-(4-aminophenyl)-*p*-diiso-propylbenzene. Since the resin has low moisture gain and high glass transition temperature, it has been widely used as a high performance matrix for hot/wet conditions. Table 1 represents the physical properties of EPON HPT 1071. The epoxy equivalent weight (EEW) of the resin was ca. 160.

2.2. Sample preparation

2.2.1. Synthesis of HBPs

Bis-MPA (149 mmol, 20.0 g), TMP (7.1 mmol, 0.953 g) (in stoichiometric correspondence to the perfect third generation, i.e. bis-MPA:TMP = 21:1) and *p*-TSA (0.100 g) were well mixed in a three-necked flask equipped with a nitrogen inlet, a drying tube and a mechanical stirrer. The flask was placed in an oil bath previously heated to 140°C, and the mixture was left to react for 3 h under stirring. The nitrogen stream was turned off and the flask was connected to a vacuum line for 2 h. The molecular weight of the synthesized HBP was evaluated using a matrix-assisted laser desorption–ionization time-of-flight (MALDI/TOF) mass spectrometer, i.e. $M_n = 1688$ g/mol. The hydroxyl terminal groups of the HBP were transformed into benzoate groups (Bz) using TEA and DMAP as catalysts. The procedure for the change of the terminal groups of the HBP is schematically outlined in Fig. 1.

2.2.2. Synthesis of linear polyester (LPE)

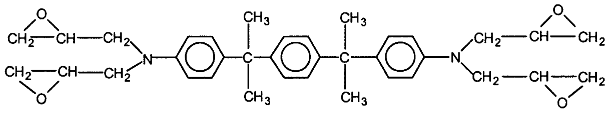
Hydroxypivalic acid (80.9 mmol, 9.556 g), 2-ethyl-2-methyl-1,3-propanediol (3.85 mmol, 0.455 g) and *p*-TSA (48 mg) were well mixed in a three-necked flask equipped with a nitrogen inlet, a drying tube and a mechanical stirrer. The flask was moved to an oil bath at 130°C. The mixture was left to react for 2 h under nitrogen atmosphere. Subsequently, the flask was connected to a vacuum line for 2 h. The molecular weight of LPE was also evaluated using a MALDI/TOF mass spectrometer, i.e. $M_n = 1445$ g/mol.

2.2.3. Preparation of sample mixtures for cure

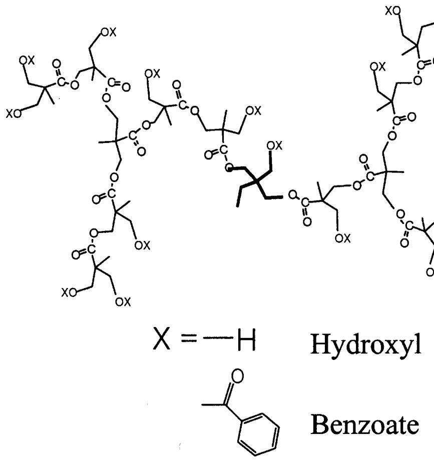
The molar ratios of epoxide/hydroxyl groups in samples were made as 1/1, 1/0.71, and 1/0.54. The samples were denoted as EHA, EHB, EHC in HPT 1071/HBP(OH) system, EBA, EBB, EBC in HPT 1071/HBP(Bz) system, and ELA, ELB, ELC in HPT 1071/LPE system, respectively. The sample mixtures were prepared by dissolving the epoxy resin and the curing agent in acetone, then evaporating the solvent in a vacuum oven at room temperature.

2.3. Instrumental analysis

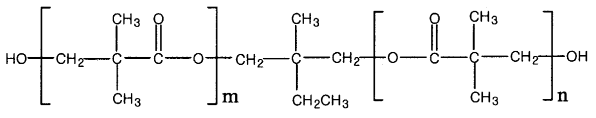
Thermal analysis was performed with a TA instrument.



(a) EPON HPT 1071



(b) HBP



$$HO-\left[CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-O\right]_m-CH_2-\underset{CH_2CH_3}{\overset{CH_3}{C}}-CH_2-\left[O-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_2\right]_n-OH$$

(c) LPE

Fig. 2. Chemical structures of epoxy resin, HBPs, and LPE.

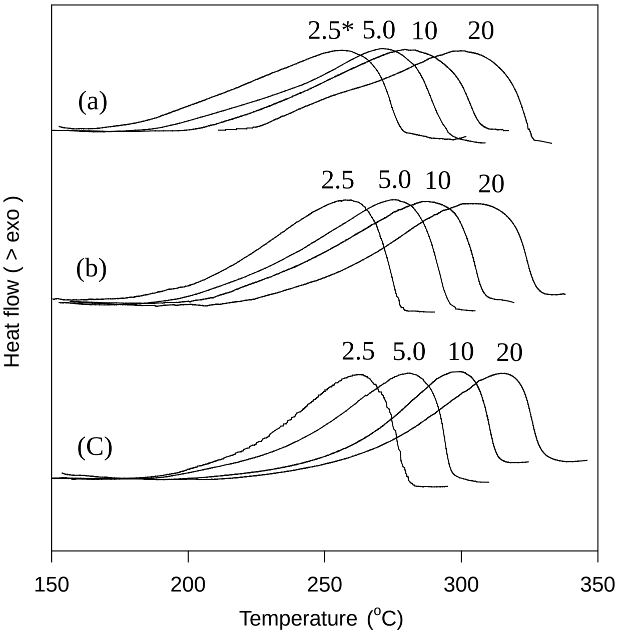


Fig. 3. Dynamic DSC thermogram of HPT 1071/HBP(OH) system: (a) EHA; (b) EHB; (c) EHC; *heating rate (°C/min).

The dynamic DSC experiments were conducted with heating rates of 2.5, 5.0, 10, and 20°C/min. The heat of cure reaction was determined from the area under the cure exotherm. The isothermal DSC experiments were carried out in the temperature range of 220–250°C/min. This temperature range was chosen from the results that below the range, curing rate was too late to detect curing behavior, whereas curing exothermic peak was shown and a small amount of thermal degradation occurred over the range.

Infrared spectra were recorded on a Bomem MB 100 Fourier transform infrared (FT-IR) spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. IR spectra were obtained in the absorption mode at a resolution of 2 cm^{-1} and 16 scans. The sample mixture was coated on KBr pellet and the sample was cured on a heating block equipped with a temperature controller.

3. Results and discussion

We have recently reported the synthetic process and the microstructure of the HBP used in this study and its application to blends with semi-crystalline polymers [25,26]. The chemical structures of HBPs, LPE and HPT 1071 resin are illustrated in Fig. 2. The degree of branching (DB) of the HBP was determined to be 0.44 by the inverse gated decoupling ^{13}C NMR technique. The molar ratios of epoxy/hydroxyl groups were prepared using the microstructure of HBP and EEW of the epoxy resin.

3.1. Dynamic DSC experiment

The dynamic DSC thermograms of HPT 1071/HBP(OH) system are illustrated in Fig. 3. Table 2 presents the exothermic peak temperature (T_p), conversion at the peak (α_p), and heat of cure (ΔH) in the HPT 1071/HBP(OH) system. At a constant concentration of the HBP, the initial curing temperature and the peak temperature increased with increasing the heating rate. At the same heating rate, the exothermic peak temperature increased with decreasing the amount of HBP. The heat of cure was independent of the heating rate at a constant concentration of HBP. On the other hand, the heat of cure increased with decreasing the concentration of the curing agent. This arose from the relatively increased composition of epoxide groups with decreasing amount of the curing agent in unit sample amount. When the cure enthalpies were normalized with the mole-epoxide, the enthalpies were reduced with decreasing concentration of the curing agent as can be seen by ΔH_n values. This phenomenon means that the initial concentration of the hydroxyl groups was associated with the extent of cure. In the early stage of cure reaction, the amount of the hydroxyl groups generated from epoxy rings was small, and

Table 2
Peak temperature (T_p), conversion at the peak (α_p), heat of cure (ΔH) and the normalized heat of cure (ΔH_n) in the dynamic DSC experiments of HPT 1071/HBP(OH) system

Sample	Property	Heating rate (°C/min)			
		2.5	5.0	10	20
EHA	T_p (°C)	253.0	264.2	282.1	302.2
	α_p	0.65	0.67	0.63	0.65
	ΔH (J/g)	367.4	359.8	363.2	368.2
	ΔH_n (kJ/mole-epoxide)	97.6	95.5	96.4	97.8
EHB	T_p (°C)	257.1	272.9	288.1	306.1
	α_p	0.72	0.73	0.73	0.71
	ΔH (J/g)	373.7	380.1	378.7	374.2
	ΔH_n (kJ/mole-epoxide)	87.8	89.3	89.0	87.9
EHC	T_p (°C)	264.1	282.2	296.0	313.2
	α_p	0.78	0.78	0.77	0.76
	ΔH (J/g)	382.1	387.5	385.2	381.3
	ΔH_n (kJ/mole-epoxide)	82.9	84.1	83.6	82.7

hence the hydroxyl groups of the HBP mainly initiated the cure process. Since the reactivity of the hydroxyl groups of the HBP (primary alcohol) was somewhat higher than those generated from epoxy rings (secondary alcohol), the cure reaction proceeded better with increasing composition of the HBP.

Table 3 shows T_p, α_p, and ΔH_n in HPT 1071/LPE system. The T_ps were higher than those of HPT 1071/HBP(OH) system. The normalized cure enthalpies were lower than those of HPT 1071/HBP(OH) system, which means the extent of cure in this system was less than that in HPT 1071/HBP(OH) system. It is thought that the lower viscosity of HPT 1071/HBP(OH) system facilitated the molecular motion of the functional groups and elevated the extent of cure.

The extents of cure at the peaks of the exotherms were almost constant and independent of the heating rate at a given concentration of curing agent. Ozawa [27–29] suggested an equation concerning the relationship among heating rate, peak temperature, and activation energy on the assumption that the extent of cure at the peak temperature is constant and irrespective of the heating rate. Therefore, it is possible to evaluate the activation energy for cure reaction using Ozawa equation:

$$\log \Phi = C - 0.4567E_a/RT_p \tag{1}$$

where Φ is the heating rate, E_a the activation energy, and T_p the peak temperature. E_a can be obtained from the slope of $\log \Phi$ vs. $1/T_p$. Duswaalt [30] reported that the activation energy obtained from Eq. (1) would be in a precision of 3% and an accuracy of 10%. Fig. 4 shows the plot of $\log \Phi$ vs. $1/T_p$ in HPT 1071/HBP(OH) system. Exothermic peak temperatures varied in a predictable manner with the heating rate. The activation energies in these systems are listed in Table 4. The activation energies of epoxy/hydroxyl group system were higher than those of epoxy/amine system [23]. The activation energies were decreased with increasing concentration of the curing agent in all cases. One of the reasons is the increased primary alcohol–epoxide reaction. The reason is also associated with the increment of the amount of proton donor materials (i.e. curing agents), which facilitates the cure reaction through donor–acceptor complex. The curing agent reacts with the complex through nucleophilic addition. Fig. 5 illustrates proton donor–acceptor complex in these systems. The activation energies of HPT 1071/HBP(OH) system were lower than those of

Table 3
Peak temperature (T_p), conversion at the peak (α_p), and the normalized heat of cure (ΔH_n) in the dynamic DSC experiments of HPT 1071/LPE system

Sample	Property	Heating rate (°C/min)			
		2.5	5.0	10	20
ELA	T_p (°C)	256.0	268.3	285.1	305.2
	α_p	0.68	0.70	0.71	0.69
	ΔH_n (kJ/mole-epoxide)	92.1	92.7	93.4	94.0
ELB	T_p (°C)	261.3	275.4	292.2	309.3
	α_p	0.75	0.77	0.76	0.77
	ΔH_n (kJ/mole-epoxide)	82.3	82.9	83.8	83.4
ELC	T_p (°C)	268.4	285.7	299.0	316.3
	α_p	0.82	0.81	0.83	0.81
	ΔH_n (kJ/mole-epoxide)	73.1	74.2	73.9	74.9

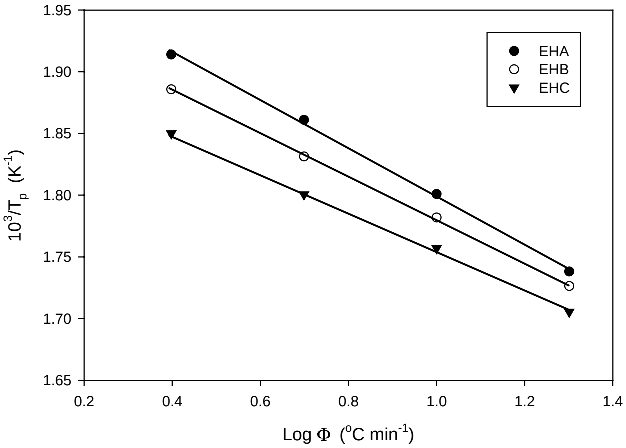


Fig. 4. Reciprocal peak temperature as a function of logarithm heating rate.

Table 4
Activation energies of HPT 1071/HBP(OH) and HPT 1071/LPE systems in the dynamic DSC experiments

Sample	E_a (kcal/mol)
EHA	23.7
EHB	24.8
EHC	25.5
ELA	24.2
ELB	25.3
ELC	26.5

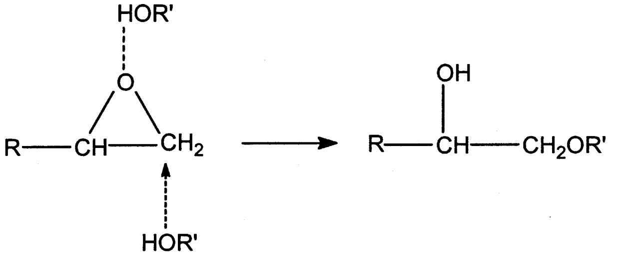


Fig. 5. Proton donor–acceptor complex in epoxy/hydroxyl groups curing system.

HPT 1071/LPE system. The HBP(OH) is easy to form intramolecular proton donor–acceptor complex owing to the large number of vicinal hydroxyl groups, whereas the relatively long chain of LPE restricts the intramolecular polar interaction. The large amount of LPE is also required for the desired molar ratio of epoxide/hydroxyl groups because of the lower functionality. In this case, the main chain of LPE acts as a steric hindrance for the intermolecular polar interaction. As previously stated, the lower viscosity of HBP(OH) system also facilitates the molecular motion of functional groups and elevates the reactivity. Therefore, the HBP(OH) system has lower activation energy and higher heat of cure.

In order to certify that the curing reaction was initiated not by self-ring opening reaction but by hydroxyl terminal groups of HBP(OH), the hydroxyl groups were transformed into benzoate groups (Bz) by organic synthetic methods. Dynamic DSC thermograms of HPT 1071/HBP(Bz) system are presented in Fig. 6. As can be seen from Fig. 6, the induction time for cure reaction was more increased than that of HPT 1071/HBP(OH) system. Table 5 shows the exothermic peak temperature and the heat of cure at a heating rate of 10°C/min in HPT 1071/HBP(Bz) system. The peak temperature and the initial curing temperature were much higher than those of HPT 1071/HBP(OH) system. Therefore, it is obvious that the hydroxyl terminal groups of HBP(OH) initiated the curing reaction. The ΔH_n in HPT 1071/HBP(Bz) system was less than that in HPT 1071/HBP(OH) system. Unlike HPT 1071/HBP(OH) system, ΔH_n increased with decreasing concentration of HBP(Bz). In this case, there were little initial hydroxyl groups. Therefore, the self-ring opening reaction of the epoxy resin was predominant during initial cure time and the reaction was easier in the larger amount of epoxy resin.

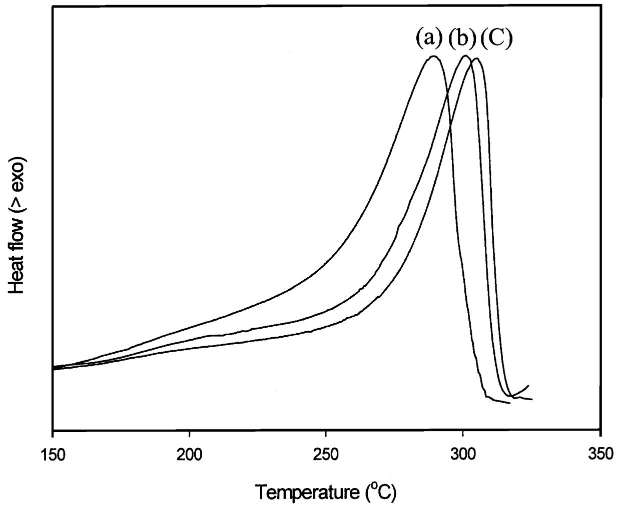


Fig. 6. Dynamic DSC thermogram of HPT 1071/HBP(Bz) system at a heating rate of 10°C/min: (a) EBA; (b) EBB; (c) EBC.

Table 5
The peak temperature (T_p), the normalized heat of cure (ΔH_n) of HPT 1071/HBP(Bz) system at a heating rate of 10°C/min

	T_p (°C)	ΔH_n (kJ/mole-epoxide)
EBA	294.7	67.6
EBB	301.0	69.3
EBC	304.9	71.2

3.2. Isothermal DSC experiment

The cure rate was determined directly from DSC thermograms using the following equation:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{H_{com}} \tag{2}$$

where α is the extent of cure, H_{com} the complete heat of cure obtained from 10°C/min scans. Since the heat of cure was almost constant and independent of the heating rate at a given concentration of curing agent, the reference heat of cure was arbitrarily selected as the value obtained from a heating rate of 10°C/min. The maximum cure rates in HPT 1071/HBP(OH) system are shown as a function of reciprocal cure temperature in Fig. 7. The maximum cure rates increased with increasing cure temperature at a given epoxy concentration. The maximum cure rates also increased with the increase of HBP(OH) concentration.

In order to get the degree of conversion, the DSC curves

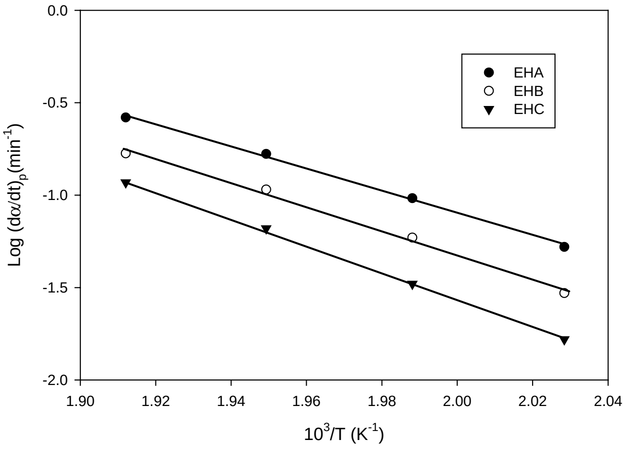


Fig. 7. The maximum cure rates as a function of reciprocal cure temperature in HPT 1071/HBP(OH) system.

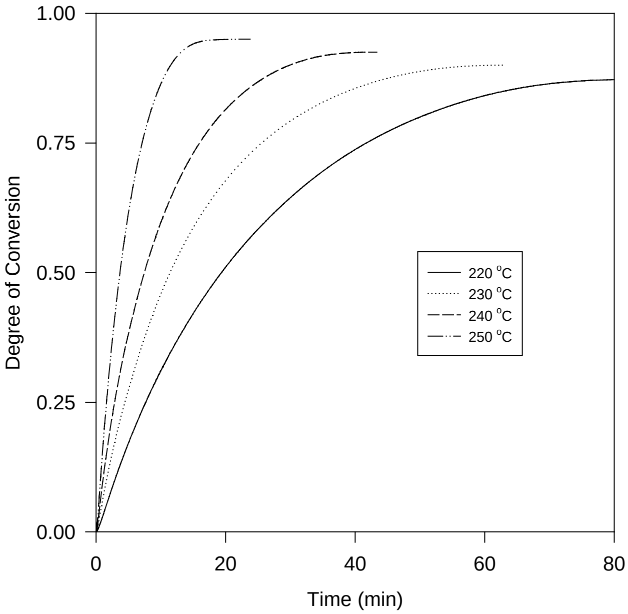


Fig. 8. Degree of conversion as a function of cure time for EHA.

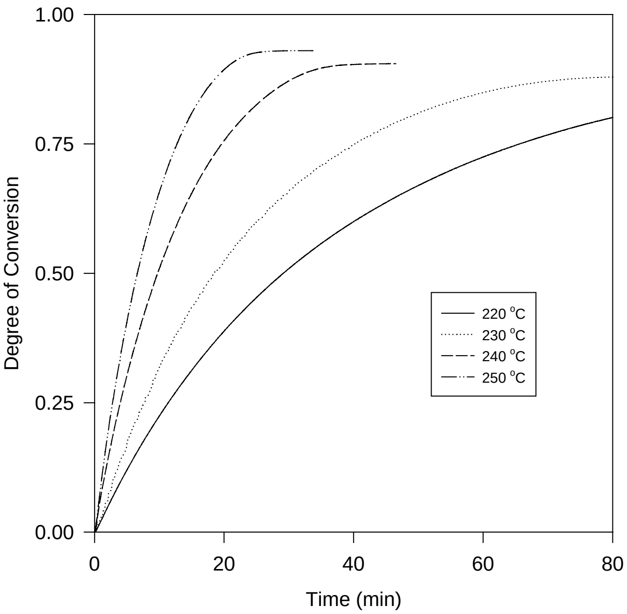


Fig. 9. Degree of conversion as a function of cure time for ELA.

were integrated and the partial areas as a function of time were normalized with respect to H_{com} and sample weight. The degree of conversion of EHA and ELA is presented in Figs. 8 and 9. The degree of conversion of HBP(OH) system was higher than that of LPE system at a given curing time, which means HBP(OH) had shorter curing times. As the reaction temperature decreased, the degree of conversion also decreased.

Isothermal kinetic parameters were obtained from Kamal equation [31,32]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{3}$$

where k_1 and k_2 are the kinetic rate constants, m and n the kinetic exponents. This equation has been widely used for auto-catalyzed reactions. Table 6 presents the isothermal kinetic parameters of HPT 1071/HBP(OH) system. In epoxy/amine system, the overall reaction order $(m + n)$ is known as 2 [33]. However, in this case, the value was ca. 1.5. The m-value increased with increasing temperature and increasing amount of the curing agent, whereas n-value showed the opposite behavior. Considering these results, m is thought to be related with maximum reaction rate and n is considered to be related with post-cure reaction. The k_1 and k_2 were increased with increasing temperature and increasing concentration of the curing agent. HPT 1071/LPE system showed similar m- and n-values to those of HPT 1071/HBP(OH) system. However, the k_1 and k_2 were lower than those of HPT 1071/HBP(OH) system.

Table 6
Isothermal kinetic parameters of HPT 1071/HBP(OH) system

Sample	Temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})	m	n
EHA	220	0.0251	0.0656	0.29	1.28
	230	0.0602	0.0821	0.45	1.13
	240	0.1253	0.0935	0.63	0.93
	250	0.1602	0.1036	0.76	0.79
EHB	220	0.0215	0.0512	0.18	1.33
	230	0.0412	0.0697	0.38	1.16
	240	0.0805	0.0832	0.52	1.03
	250	0.1307	0.0922	0.68	0.84
EHC	220	0.0112	0.0408	0.12	1.38
	230	0.0237	0.0556	0.29	1.23
	240	0.0455	0.0712	0.43	1.06
	250	0.0861	0.0803	0.60	0.91

3.3. FT-IR analysis

FT-IR spectra of HPT 1071 and HBPs are shown in

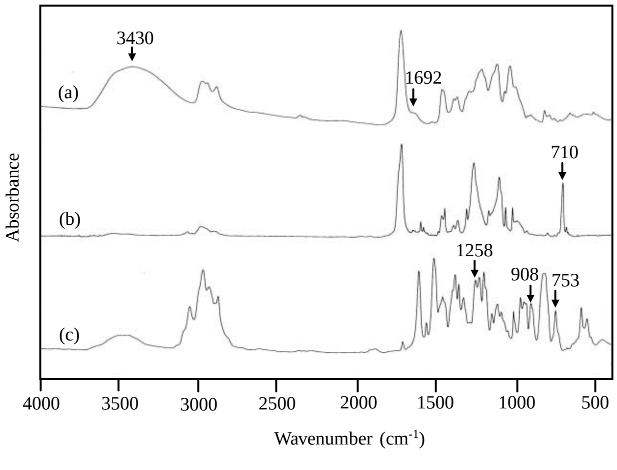


Fig. 10. FT-IR spectra of HPT 1071 and HBPs: (a) HBP(OH); (b) HBP(Bz); (c) HPT 1071.

Table 7
Principal vibrational bands of HPT 1071 and HBPs

HPT 1071		HBP(OH)		HBP(Bz)	
ν (cm^{-1})	Assignment	ν (cm^{-1})	Assignment	ν (cm^{-1})	Assignment
3047 (s)[a]	Aromatic C–H str., epoxy ring C–H str.	3430 (s,b)	O–H str.	2000–1800 (w)	Summation bands
2928 (s)	Aliphatic C–H str.	1727 (vs)	Free C=O str.	1725 (vs)	C=O str. (benzoate)
2871 (s)	(N)–C–H str.	1692 (w,b)	H-bonded C=O str.	1602 (m), 1585 (m)	Sym. ring str.
2000–1800 (w)	Summation bands	1471 (m)	CH_2 scissors def.		
1613 (s)	Sym. ring str.	1456 (m)	CH_3 asym. def.	1491 (w)	Different ring str.
1463 (m)	‘Sideways’ ring bend	1396 (m)	CH_3 sym. def.	1472 (m), 1452 (m)	‘Sideways’ ring bend + CH_3 asym. bend
1331 (m)	C–N str.	1220 (s)	C–C–O asym. str.		
1258 (m)	Epoxy sym. C–O–C str.	1046 (s)	1° alcohol C–O str.	1374 (m)	CH_3 sym. bend
1154 (w)	Aromatic ring def.	828 (w)	CH_3 rock	1270 (s)	Benzoate ester C–O str.
908 (m)	Epoxy asym. C–O–C str.	639 (w,b)	1° alcohol C–OH def.	1112 (s)	OCH_2 str.
821 (s)	Aromatic ring C–H def.			1071 (m), 1027 (m)	Ring C–H bend
753 (m)	Epoxy half-ring str.			710 (s)	Ring C–H wag

[a] Intensity: s, strong; m, medium; w, weak; v, very; b, broad.

Fig. 10. The principal vibrational bands of HPT 1071/HBP system and their assignments are listed in Table 7. The stretching band of the hydroxyl terminal groups of HBP(OH) was observed near 3430 cm^{-1} and disappeared from the FT-IR spectrum of HBP(Bz). The broad peak near 1692 cm^{-1} was assigned to H-bonded C=O stretching vibration. In the spectrum of HBP(Bz), the peak at 710 cm^{-1} was due to the terminal benzene ring C–H wagging vibration. The shoulder peak at 1692 cm^{-1} disappeared because of the absence of H-bonding. Therefore, it is believed that the transformation of the terminal groups was successfully performed. In the spectrum of HPT 1071, the characteristic

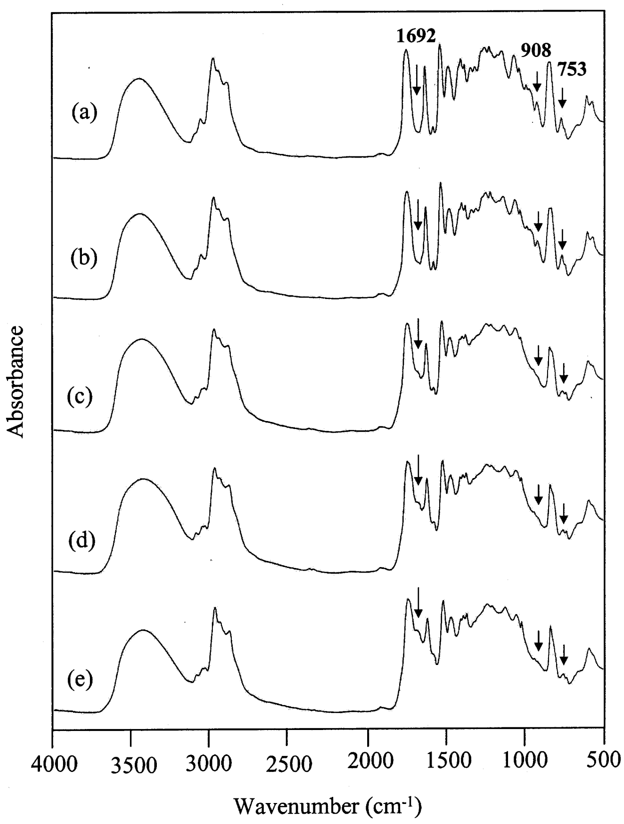


Fig. 11. FT-IR spectral change of EHA at 240°C with increasing cure time: (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min; (e) 60 min.

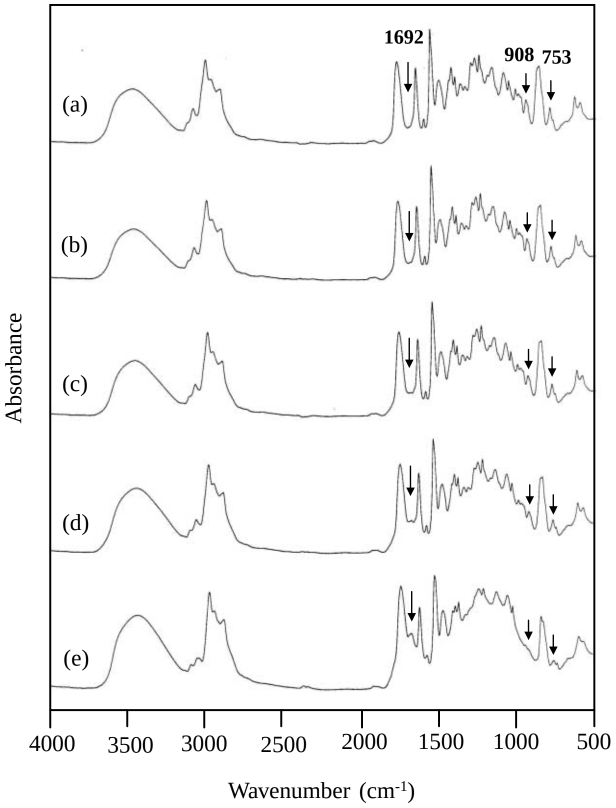


Fig. 12. FT-IR spectral change of EHC at 240°C with increasing cure time: (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min; (e) 60 min.

peaks of epoxy ring were observed at 1258, 908, and 753 cm^{-1}. As the cure reaction proceeded, the intensities of these peaks were decreased owing to the breaking of epoxy ring.

The FT-IR spectral changes of EHA and EHC with increasing curing time are illustrated in Figs. 11 and 12. As the concentration of curing agent increased, the characteristic peaks of the epoxy ring disappeared more rapidly. The peaks near 1200 cm^{-1} were increased, which were due to the stretching of C–O–C groups generated from cure reaction.

It is noteworthy that the peak of H-bonded C=O groups was increased and the peak of free C=O groups (1727 cm^{-1}) somewhat shifted to higher wavenumber (1731 cm^{-1}) with increasing curing time. The ring opening of the epoxy group was mainly caused by the reaction with the hydroxyl group of HBP(OH). On that reaction, one hydroxyl group was generated as a result of the consumption of one hydroxyl group. Therefore, the increase in the concentration of the hydroxyl groups was not severe. The reason that the intensity of H-bonded C=O peak increased with the progress of curing is rather related with the increase of the intermolecular H-bonds between C=O groups of HBP(OH) and hydroxyl groups generated from epoxy ring. The amount of HBP(OH) in EHA was less than that of epoxy resin because of the high functionality of HBP(OH). In that case, it was somewhat difficult to form the intermolecular H-bond in the early stage of curing. As the curing time increased, the hydroxyl groups generated from the ring opening of epoxy resin played the role of a bridge between HBPs and facilitated the intermolecular H-bond. Judging from Figs. 11 and 12, the intramolecular H-bond within HBPs was obviously rare at the initial stage of curing. It seems that the intermolecular H-bond was more important factor in total H-bonds. High temperature might cause the self-ring opening reaction of the epoxy group in some degree, which could increase the number of hydroxyl groups and enhance H-bonds. The peak of the free C=O groups which were not H-bonded shifted to somewhat higher wavenumber owing to the restricted environment generated from the cross-linking reaction.

As the concentration of HBP(OH) was increased, the intensity of the peak at 1692 cm^{-1} was more intense at the end of cure reaction. In case of EHC, the number of the hydroxyl groups of the HBP was less than that of epoxide groups. The hydroxyl groups generated from the ring opening of the epoxy groups were involved in cure reaction through the ring opening of other epoxy groups or the etherification of two hydroxyl groups. Therefore, the chance of the intermolecular H-bond was reduced, resulting in the less intensity of the H-bonded C=O peak than that in EHA.

HPT 1071/LPE system showed similar behaviors to those of HPT 1071/HBP(OH) system. However, the intensities of H-bonded C=O peak were slightly lower than those in HPT 1071/HBP(OH) system.

4. Conclusions

The effect of hyperbranched aliphatic polyester on the cure behavior of tetrafunctional epoxy resin was studied and compared with that of the linear counterpart. In the dynamic DSC experiment of epoxy/HBP(OH) system, the heat of cure was independent of heating rate at a given composition and reduced with decreasing concentration of HBP(OH). The hydroxyl terminal groups of HBP(OH) initiated the cure reaction through proton donor–acceptor complex. The low viscosity and the large number of vicinal hydroxyl groups in HBP(OH) facilitated the molecular motion and the polar interaction, and resulted in lower activation energies than those of LPE system. In epoxy/HBP(Bz) system, the induction time for cure reaction was much more increased than that in epoxy/HBP(OH) system. The heat of cure in epoxy/HBP(Bz) system was less than that in epoxy/HBP(OH) system. Unlike the epoxy/HBP(OH) system, the heat of cure was increased with decreasing concentration of the HBP(Bz). The epoxy ring opening reaction was predominant in the initial cure process of epoxy/HBP(Bz) system. The isothermal kinetic parameters were obtained from Kamal equation. While $m + n$ value has been known as 2 in epoxy/amine system, the value in epoxy/hydroxyl group system was evaluated to be approximately 1.5. The k_1 and k_2 values were increased with increasing temperature and increasing curing agent amount. As the cure reaction proceeded, the characteristic peaks of epoxy ring were decreased and H-bonded C=O peak was increased. The intensity of the H-bonded C=O peak was increased with increasing amount of the HBP. The free C=O peak shifted to slightly higher wavenumber owing to the restricted structure.

Acknowledgements

This research has been carried out by Research Institute of Engineering Science (RIES) and the authors gratefully acknowledge the research support of RIES.

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