Article

Synthesis, Thermal Properties and Curing Kinetics of Hyperbranched BPA/PEG Epoxy Resin

Tossapol Boonlert-uthai [ID]**, Chavakorn Samthong and Anongnat Somwangthanaroj** *[ID]

Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University,
Bangkok 10330, Thailand; tossapol.bu@gmail.com (T.B.-u.); tao_hp_@hotmail.com (C.S.)
* Correspondence: anongnat.s@chula.ac.th; Tel.: +66-2218-6860

check for updates

Abstract: The hyperbranched epoxy resins (HBE) composed of bisphenol A (BPA) and polyethylene glycol (PEG) as reactants and pentaerythritol as branching point were successfully synthesized via $A_2 + B_4$ polycondensation reaction at various BPA/PEG ratios. The ^{13}C NMR spectra revealed that the synthesized HBE mainly had a dendritic structure as confirmed by the high degree of branching (DB). The addition of PEG in the resin enhanced degree of branching (DB) (from 0.82 to 0.90), epoxy equivalent weight (EEW) (from 697 g eq^{-1} to 468 g eq^{-1}) as well as curing reaction. Adding 5–10 wt.% PEG in the resin decreased the onset and peak curing temperatures and glass transition temperature; however, adding 15 wt.% PEG in the resin have increased these thermal properties due to the lowest EEW. The curing kinetics were evaluated by fitting the experimental data of the curing behavior of all resins with the Šesták–Berggren equation. The activation energy increased with the increase of PEG in the resins due to HBE's steric hindrance, whereas the activation energy of HBE15P decreased due to a large amount of equivalent active epoxy group per mass sample. The curing behavior and thermal properties of obtained hyperbranched BPA/PEG epoxy resin would be suitable for using in electronics application.

Keywords: hyperbranched epoxy; curing kinetics; polyethylene glycol; thermal properties

1. Introduction

Epoxy thermoset has become the most recognized adhesive and is widely used in demanding industries such as aerospace, automotive, building and construction, and electrical and electronics industries. For the electrical and electronics industries, especially hard disk drive (HDD) production, thermoset epoxy has been used to adhere the important parts, such as head gimbal assembly (HGA) used for reading and writing the digital data on a disk in HDD. The physical, thermal, mechanical, thermomechanical, and rheological properties of the thermoset epoxy used in HDD should be investigated in order to match the HGA process in HDD production. Generally, the commercial epoxy adhesive is based on diglycidyl ether of bisphenol A (DGEBA) because of high thermal and mechanical properties, good weather and chemical resistances, low shrinkage, and high adhesion strength [1–3]. However, the unmodified epoxy has some disadvantageous properties, i.e., inherent brittleness and low toughness, limiting its utilization for the advanced applications which require high mechanical performance. Thus, the modification of epoxy by an incorporation of toughening agent and plasticizer was investigated and the natures of these fillers are of great importance affecting the final properties of the cured epoxy-based adhesive products.

In the present, hyperbranched polymers are novel three-dimensional macromolecules and are produced in a one-step procedure by multiplicative growth from a multi-functional core to form the repeated branching units via polycondensation of AB_x monomers [4–9]. If x ≥ 2 and functional group of A molecule reacts only with functional group of B molecule, the production of highly branched

polymers is ensured. Hyperbranched epoxy resins are easy to synthesize, have low viscosity, high solubility and large number of end functional groups; therefore, they are widely produced and developed for industrial scale productions and applications, such as oil field chemical, additive and resin for waterborne applications, dispersion agent, rheology modifier, and crosslinker for elastomer [9]. The most important feature of hyperbranched polymer is their degree of branching (DB) and branching factor classified into dendritic (D), linear (L), and terminal (T) units in the macromolecular structure [10].

Furthermore, glass transition temperature (T_g) is the most important thermal property for a dendritic polymer. There is a relationship between DB and T_g [11–14]. It can be found that T_g gradually decreased with increasing DB. This can be explained by the fact that a greater degree of branching means more junction points and terminal units which lead to large numbers of free volume between branching chains, resulting in high flexibility [11–16]. Recently, there was a study to control epoxy equivalent weight (EEW) and performance of hyperbranched epoxy resins. It was found that T_g and mechanical properties of the cured hyperbranched epoxy/DGEBA composites were tuned by the EEW of hyperbranched epoxy resin and these properties were firstly increased and then decreased [17]. Moreover, it was found that the hyperbranched resin can act as toughener to enhance the mechanical property of the thermoset [18–22].

De and Karak [4,5] synthesized the hyperbranched epoxy resins by $A_2 + B_3$ and $A_2 + B_4$ polycondensation reactions between triethanol amine and in situ prepared diglycidyl ether of bisphenol A (DGEBA), and between pentaerythritol and in situ prepared DGEBA, respectively. It was found that the hyperbranched epoxy resin which was synthesized via one-step polycondensation and the aliphatic–aromatic moiety in the hyperbranched structure offer a high-performance toughened thermoset. Moreover, both reaction time and amount of B_4 moiety affected DB, EEW, as well as thermal and mechanical properties. These properties were firstly enhanced and then reduced with increase in reaction time and the amount of B_4 moiety. The properties of A_2B_4 hyperbranched epoxy thermoset were better than the properties of A_2B_3 hyperbranched epoxy thermoset, especially lower curing time and mechanical properties, such as toughness, elongation at break and adhesion strength.

There are several studies examining the addition of polyethylene glycol in the epoxy resins to improve low impact resistance of DGEBA by decreasing T_g of the thermoset [23–26]. However, in epoxy blended with low epoxy content, crystallization can occur when PEG content increases and it can decrease and hinder the cure reaction. In addition, if PEG is excessively added in the system, melting occurs, which reduces the thermal stability of the thermoset [26,27]. The physical properties of the cured epoxy depend on the structure of crosslinking network, curing temperature and curing time [28–31]. The relationship between network formation and final properties of the epoxy network is important in order to achieve the desired high-performance thermoset. The curing kinetics of the epoxy adhesive has been studied and analyzed via different techniques such as differential scanning calorimetry (DSC), dielectric relaxation spectroscopy, and gel permeation chromatography (GPC) [32].

This research aimed to obtain the epoxy adhesive whose properties are suitable for electronics application. The hyperbranched epoxy resins (HBE) were synthesized through $A_2 + B_4$ polycondensation reaction varying the ratios of aliphatic PEG and aromatic-containing bisphenol A (BPA) in A_2 part. The chemical structures and degree of branching of the synthesized HBE resins were confirmed by FTIR, ^{1}H and ^{13}C NMR, and GPC. The curing behavior of HBE having different PEG fractions in their structures was also investigated by DSC. The curing kinetics was evaluated by fitting the experimental data with the auto-catalyzed reaction model.

2. Materials and Methods

2.1. Materials

Bisphenol A (BPA) used as A_2 monomer for preparing the in-situ generated DGEBA monomer was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and was purified by recrystallization from toluene before using. Epichlorohydrin (ECH) as epoxidation reagent was obtained from Tokyo

Chemical Industry Co., Ltd. Pentaerythritol (PE) used as B_4 branch generating unit for reacting with the in-situ generated DGEBA was purchased from Tokyo Chemical Industry Co., Ltd., Japan and was purified by recrystallization from ethanol prior to use. Polyethylene glycol (PEG400, Mw = 400 g/mol) as A_2 monomer was purchased from Sigma-Aldrich, St. Louis, MI, USA. Sodium hydroxide (NaOH) as base catalyst and sodium chloride (NaCl) were obtained from Ajax Finechem, Australia. Hydrobromic acid (HBr), acetic acid, potassium hydrogen phthalate, methyl violet, and chlorobenzene were used to determine epoxy equivalent weight (EEW) of the hyperbranched epoxy resins and were purchased from Tokyo Chemical Industry Co., Ltd., Japan. Diethylenetriamine (DETA) as amine curing agent was brought from Tokyo Chemical Industry Co., Ltd., Japan. Solvents were analytical grades and used as received.

2.2. Synthesis of HBE Resins

The hyperbranched epoxy resins were synthesized via the $A_2 + B_4$ polycondensation reaction [5] using BPA and PEG400 as A_2 monomers and PE as B_4 monomer (10 wt.% of total A_2 monomer content). Mass ratios of BPA and PEG400 were varied at 100:0, 95:5, 90:10 and 85:15. The molar ratio of A_2 monomer to ECH was fixed at 1:2. Five grams of BPA, 0.50 g of PE and 10.82 g of ECH were stirred using a magnetic bar in a two-necked round bottom-flask equipped with condenser and dropping funnel. When the mixture temperature was reached from room temperature to 60 °C, 5N aqueous NaOH solution (1.852 g equivalent to the hydroxyl groups) was added into the mixture drop wisely through the dropping funnel until the mixture temperature reached 110 °C (addition time was about 30 min). The reaction temperature was kept at 110 °C for 4 h. Afterwards, the mixture was immediately quenched in an ice bath to terminate the reaction and allowed to settle in a separation funnel. The organic layer was separated from the aqueous layer and purified by shaking with 15 wt.% NaCl solution followed by distilled water until its pH was 8–9. Eventually, the organic solution was dried under vacuum at 70 °C until the weight of the dried sample was constant. The synthesized resins were the viscous transparent liquids. The formulations for the synthesis of hyperbranched epoxy resins are tabulated in Table 1.

Table 1. The mixture composition for synthesis of hyperbranched epoxy resins and for curing reaction.

| Resin | Synthesis | | | | Curing [a] |
| | B4 | A2 | | End Group | DETA (g) |
	PE (g)	BPA (g)	PEG (g)	ECH (g)	
HBE	0.50	5.00	-	10.82	0.059
HBE5P	0.50	4.75	0.25	10.65	0.062
HBE10P	0.50	4.50	0.50	10.48	0.073
HBE15P	0.50	4.25	0.75	10.30	0.088

[a] weight of the resin was 2.00 g.

2.3. Preparation of Cured HBE

The synthesized HBE resins were homogenously mixed with DETA by mechanically stirring at room temperature for 10 min. The ratio of HBE to DETA was 1:1 molar ratio of active functional groups. The weight of amine curing agent of each system could be calculated by Equation (1). Epoxy Wt is weight of epoxy and phr amine is evaluated by Equation (2). Moreover, epoxy equivalent weight (EEW) of the mixture and NH-group equivalent can be calculated by Equations (3) and (4), respectively. Table 1 shows the composition of different formulations with respect to epoxy equivalent weight of resin.

$$\text{curing agent Wt} = \frac{\text{epoxy Wt} \times \text{phr amine}}{100} \tag{1}$$

$$\text{phr amine} = \frac{\text{NH equivalent}}{\text{EEW}} \times 100 \tag{2}$$

$$\text{EEW of mixture} = \frac{\text{Total Wt}}{\frac{Wt_a}{EEW_a} + \frac{Wt_b}{EEW_b}} \tag{3}$$

$$\text{NH equivalent} = \frac{\text{Mw of amine curing agent}}{\text{Amount of NH-group}} \tag{4}$$

2.4. Characterization of HBE Resins

FT-IR spectra of the synthesized HBE resins were recorded by a PerkinElmer FT-IR System in a wavenumber range of 400–4000 cm^{-1}, attenuated total reflectance (ATR) mode and resolution of ± 2 cm^{-1}. NMR (500 MHz) spectrometer from Varian Unity Inova was used to record the ^{1}H NMR and ^{13}C NMR spectra of the resins by using CDCl$_3$ as solvent and TMS as reference. For degree of branching (DB), the degree of branching of a linear polymer equals 0, while a perfect dendrimer has a DB of 1. DB is the ratio of the sum of integration of dendritic and terminal units to the sum of integration of all repeating units in the structure, measured from ^{13}C NMR technique [4,5,8,9], as shown in Equation (5).

$$\text{DB (\%)} = \frac{D + T}{D + T + L} \times 100 \tag{5}$$

The epoxy equivalent weight (EEW) of the resins was calculated using the standard test methods (ASTM D 1652) [33]. The molecular weight distribution was measured by gel permeation chromatography (GPC), Shimadzu/LC-10ADvp, using a refractive index (RI) detector and CH$_3$Cl as mobile phase operated at 40 °C with 1 mL/min. The Mark–Houwink calibration curve correction method was used for standard calibration.

The curing behavior of HBE resins was characterized by differential scanning calorimetry (DSC), DSC 1 STARe Mettler-Toledo, under a nitrogen atmosphere. First, the non-isothermal curing behavior was measured in a range of 25–200 °C and a heating rate of 10 °C/min in order to evaluate the suitable curing temperature [34]. Isothermal curing kinetics was performed at various curing temperatures ranging from 70 to 100 °C. Moreover, the glass transition temperature (T$_g$) of the cured epoxy adhesive was also measured by non-isothermal DSC measurement from −30 to 200 °C at a heating rate of 10 °C/min.

2.5. Kinetic Analysis

This research determined the kinetic parameters of thermal curing under isothermal condition, which is a conventional method to monitor the curing kinetics [35]. The kinetic parameters included pre-exponential factor (A), activation energy (E$_a$), and reaction order (n).

Both overall heat released and cure rate from heat flow can be measured via DSC. The curing kinetics can be expressed in the following equation:

$$\frac{dQ}{dt} = Q_r \frac{d\alpha}{dt} = Q_r k(T) f(\alpha) \tag{6}$$

where dQ/dt is the heat flow, Q$_r$ is the total heat released after the reaction was complete, dα/dt is the rate of reaction or curing rate, α is the degree of cure, k(T) is the rate constant, T is the absolute temperature, and f(α) is the reaction model. The degree of cure at time *t* from the isothermal analysis was defined as,

$$\alpha = \frac{H(t)}{H_T} \tag{7}$$

when H(t) is the heat of reaction at a certain time t and H_T is the total heat of reaction. The rate constant can be replaced by an Arrhenius equation. Therefore, Equation (6) can be rearranged as shown in Equation (8):

$$\frac{d\alpha}{dt} = A\exp(-\frac{E_a}{RT})f(\alpha) \tag{8}$$

where A is the pre-exponential factor, E_a is the activation energy, and R is the gas constant ($8.314 \text{ kJ kmol}^{-1} \text{ K}^{-1}$).

The kinetic parameters will be meaningless if the reaction model is not suitably used [36]. Generally, three reaction models are classified by characteristic of reaction profile. Vyazovkin et al. recommended how to decide the reaction model by visually inspecting the isothermal reaction profile [37]. The first model is the accelerating model in which the rate increases continuously with rising degree of cure and approaches maximum at the end of the cure state. This type can be explained by a power law model:

$$f(\alpha) = n\alpha^{(n-1)/n} \tag{9}$$

where n is a constant. The second model is the decelerating model in which the maximum rate is at the initial reaction and it decreases continuously while the degree of cure increases. This type is a common reaction model as expressed in Equation (10):

$$f(\alpha) = (1-\alpha)^n \tag{10}$$

where n is the reaction order. The third model is a sigmoidal model in which the rate has the accelerating and decreasing behaviors at the initial and final stages, respectively. This type is the auto-catalyzed reactions, which is known as Šesták–Berggren model [38] as shown in Equation (11):

$$f(\alpha) = \alpha^m (1-\alpha)^n \tag{11}$$

where n and m are the reaction orders relating to the effects of unreacted reactants and catalytic effect of the product of the reaction, respectively.

Generally, the curing kinetics of the epoxy system can be explained by the autocatalytic model [39] as expressed by Kamal's equation:

$$\frac{d\alpha}{dt} = (k_1(T) + k_2(T)\alpha^m)(1-\alpha)^n \tag{12}$$

where $k_1(T)$ and $k_2(T)$ are the rate constants and m and n are the reaction orders. When combining Equations (8), (11) and (12) and simplifying the calculations [40], the curing kinetics could best be described by Šesták–Berggren model [41] and the kinetic model is shown in Equation (13).

$$\frac{d\alpha}{dt} = k(T)\alpha^m (1-\alpha)^n \tag{13}$$

k(T), m and n can be calculated by MATLAB program (version: R2018b) and the activation energy (E_a) can be determined from taking natural logarithm to Arrhenius's equation as shown in Equation (14):

$$\ln k(T) = \ln A - \frac{E_a}{RT} \tag{14}$$

E_a and lnA can be evaluated from the slope and y-intersection of graph plotted between lnk(T) versus 1/T.

3. Results and Discussions

3.1. Synthesis and Characterization of the Hyperbranched Epoxy Resins

The synthesis of HBE resin began with the polymerization of BPA and PEG using NaOH as base catalyst. The possible synthesized products included diglycidyl ether of polyethylene glycol (DGEPEG), diglycidyl ether of bisphenol A, and diglycidyl ether copolymer of bisphenol A and polyethylene glycol (DGECBAPEG) [42] as displayed in Scheme 1. These in situ products were produced at reaction temperature of 60 °C. When the reaction temperature was heated at 110 °C, A_2 monomers reacted with pentaerythritol (B_4) monomer via $A_2 + B_4$ polycondensation reaction to form the hyperbranched epoxy resins, as shown in Scheme 2. Concurrently, epichlorohydrin as epoxidation reagent converted the terminal hydroxyl groups of HBE resins to terminal epoxy groups. The features of the synthesized epoxy resin were investigated by FT-IR and NMR techniques. The FT-IR spectra showed the important functional groups of all resins (Figure 1). There were the stretching vibrations (ν_{max}/cm^{-1}) of the following feature: 3450 (O–H), 3050 (aromatic C–H), 2970 (aliphatic C-H), 1620 (aromatic C=C), 1249 (C–O), 1040 (C–C), and 915 (oxirane) [4,5]. The FT-IR results of all samples were similar, and it was hardly inspected to identify new chemical bonds. Therefore, the inspection of the chemical bond should be identified via NMR analysis.
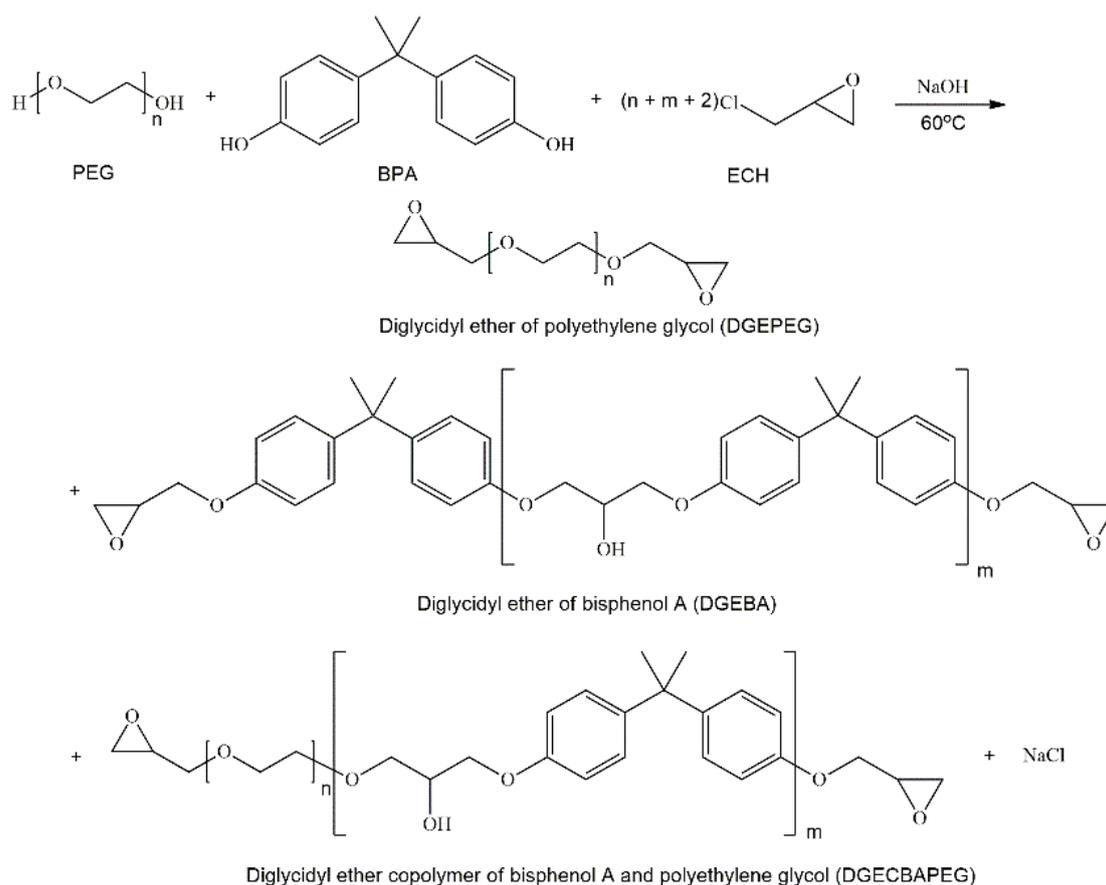
Scheme 1. Formation of in situ diglycidyl ether of polyethylene glycol (DGEPEG), in situ diglycidyl ether of bisphenol A, and in situ diglycidyl ether copolymer of bisphenol A and polyethylene glycol (DGECBAPEG).
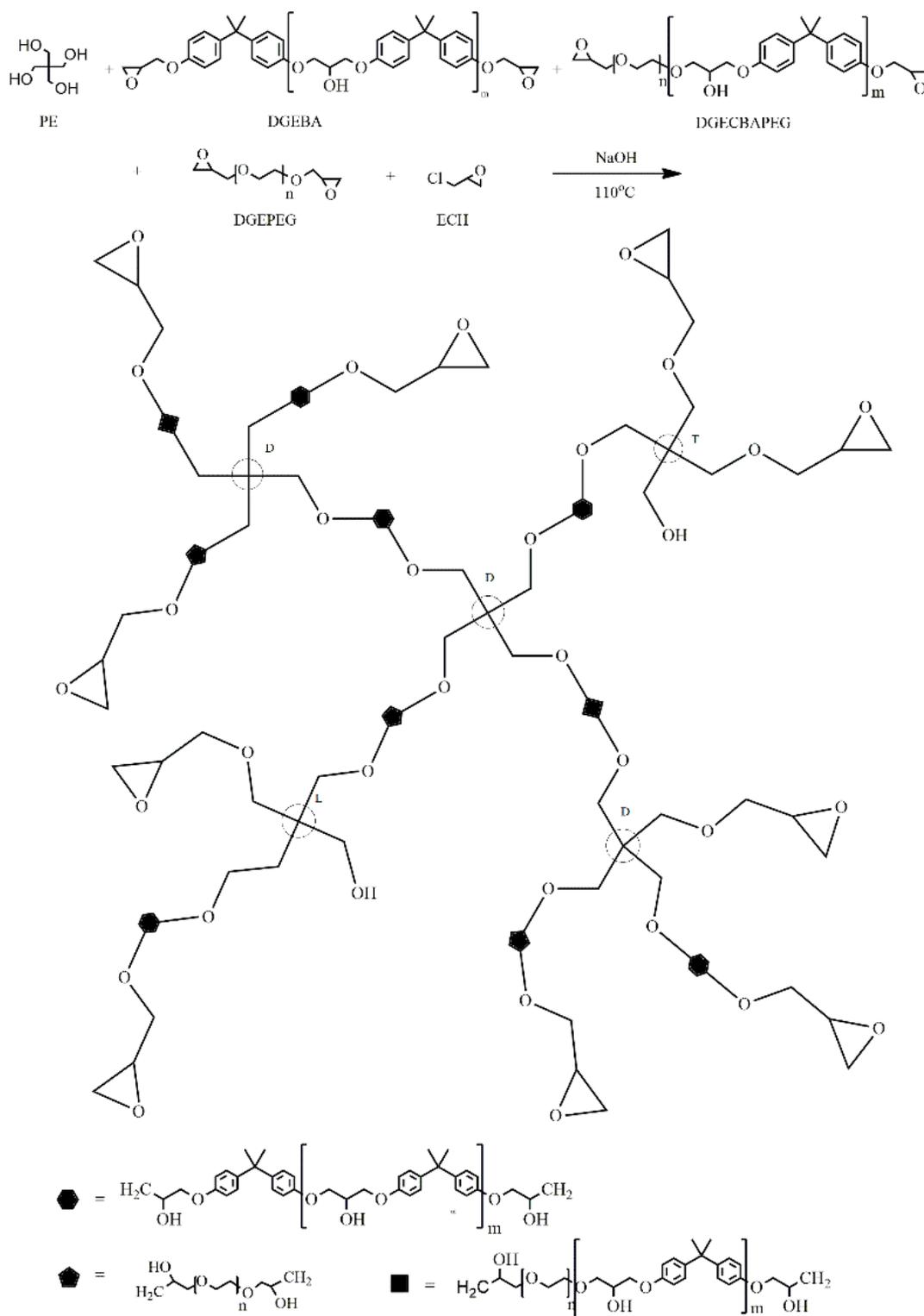
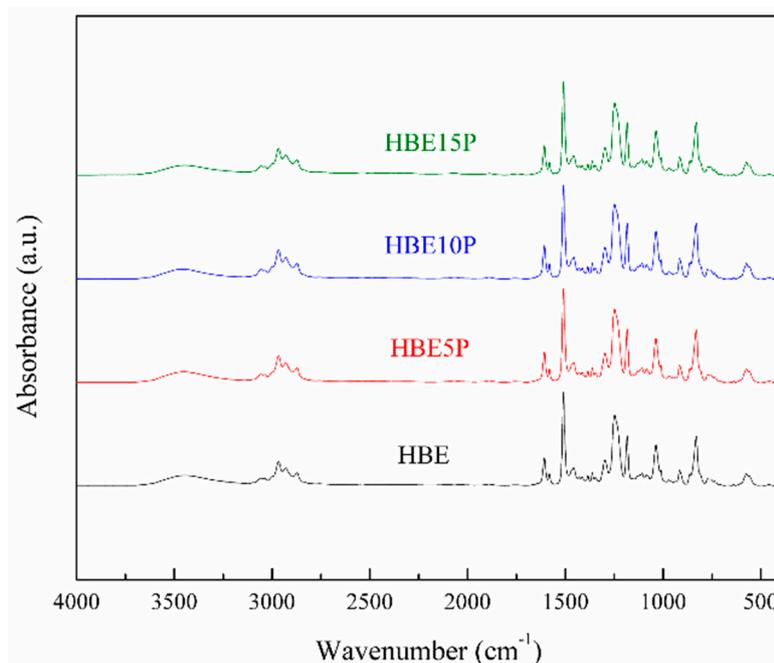**Scheme 2.** Synthesis of the hyperbranched epoxy resin and its possible structure.

Figure 1. FTIR spectra of hyperbranched epoxy resins (HBE) at various polyethylene glycol (PEG) contents.

The ^{1}H-NMR spectra (Figure 2), δ_H (ppm), of HBE resin implied the following structural feature: 1.62 (3H, CH$_3$), 2.76 and 2.90 (2H, oxirane), 3.38 (1H, oxirane), 3.65 (2H, CH$_2$–pentaerythritol unit), 3.70–3.80 (2H, 4CH$_2$ of the substituted and unsubstituted pentaerythritol), 3.9 (2H, CH$_2$–oxirane), 4.10 (2H, CH$_2$–bisphenol-A unit), and 4.15 (1H, OH), 4.20 (1H, CHOH), 6.82 (4H, Ph), and 7.08 (4H, Ph).
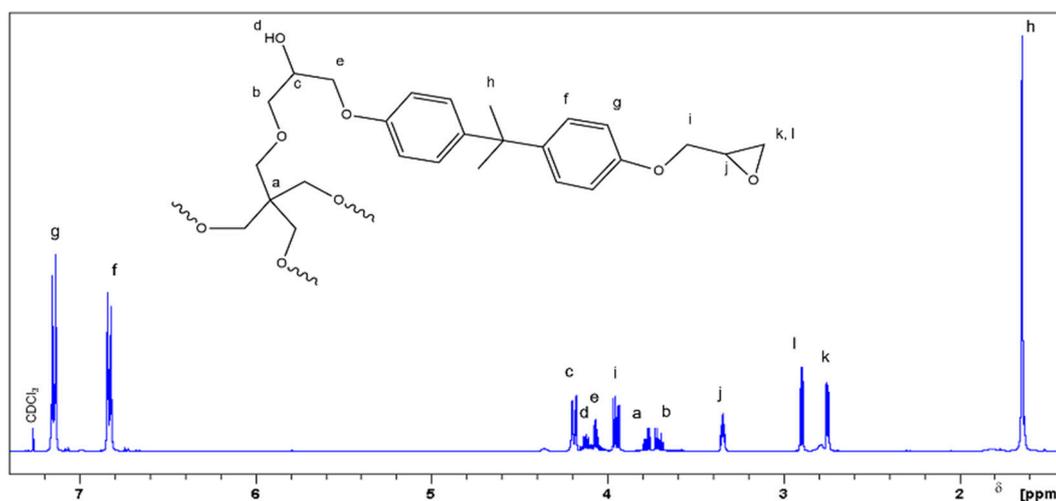

Figure 2. ^{1}H NMR spectrum of HBE resin.

The ^{1}H-NMR spectra (Figure 3), δ_H (ppm), of HBE5P resin implied the following structural feature: 1.62 (3H, CH$_3$), 2.78 and 2.90 (2H, oxirane), 3.38 (1H, oxirane), 3.60 (2H, CH$_2$-polyethylene glycol), 3.65 (2H, CH$_2$–pentaerythritol unit), 3.70–3.80 (2H, 4CH$_2$ of the substituted and unsubstituted pentaerythritol), 3.9 (2H, CH$_2$–oxirane), 4.08 (2H, CH$_2$–bisphenol-A unit), and 4.15 (1H, OH), 4.20 (1H, CHOH), 6.82 (4H, Ph), and 7.08 (4H, Ph).
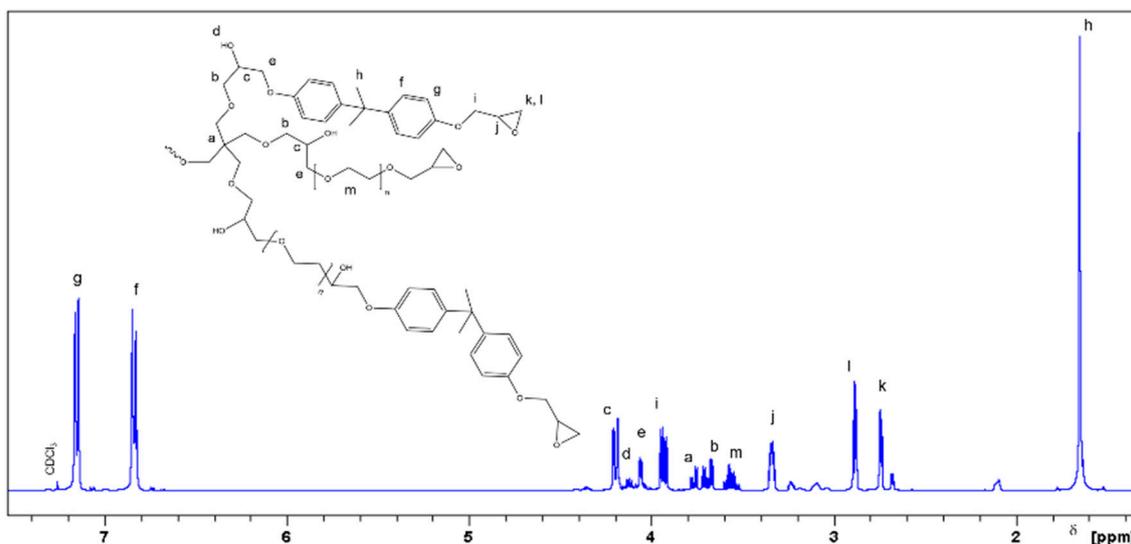
Figure 3. ^{1}H NMR spectrum of HBE5P resin.

The ^{13}C NMR spectrum (Figure 4), δ_C (ppm), of HBE resin implied the following structural feature: 31.0 (CH$_3$, bisphenol-A unit), 41.0 (C, isopropylidiene of bisphenol-A unit), 44.0 (CH$_2$, oxirane), 44.0–47.0 (central C of pentaerythritol unit), 50.0 (CH, oxirane), 51.0 (CH$_2$–oxirane), 62.0–67.0 (CH$_2$–O units and CHOH unit), 68.0 (CH$_2$, pentaerythritol unit), and 114.0, 127.0, 143.0 and 156.0 (4C, Ph).

Figure 4. ^{13}C NMR spectrum of HBE resin.

The ^{13}C NMR spectrum (Figure 5), δ_C (ppm), of HBE5P resin implied the following structural feature: 31.0 (CH$_3$, bisphenol-A unit), 41.0 (C, isopropylidiene of bisphenol-A unit), 44.0 (CH$_2$, oxirane), 44.0–47.0 (central C of pentaerythritol unit), 50.0 (CH, oxirane), 51.0 (CH$_2$–oxirane), 62.0–67.0 (CH$_2$–O units and CHOH unit), 68.0 (CH$_2$, pentaerythritol unit), an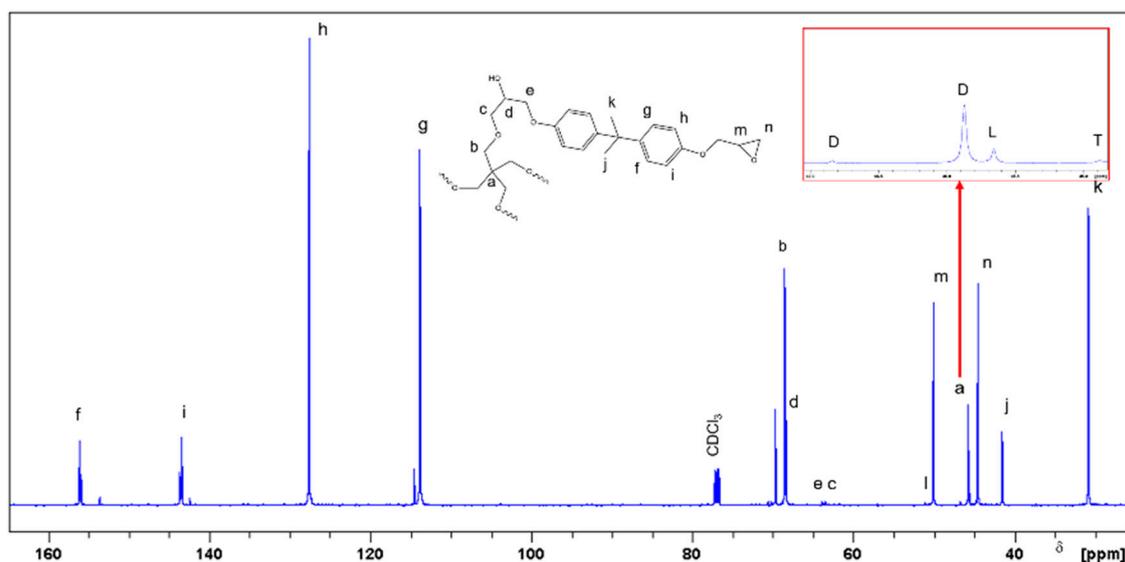d 114.0, 127.0, 143.0 and 156.0 (4C, Ph). For the ^{1}H-NMR and ^{13}C NMR spectra of HBE10P and HBE15P resins, there were the same peak, indicating the important chemical bonding; therefore, this research shows only the spectrum of HBE5P resins.
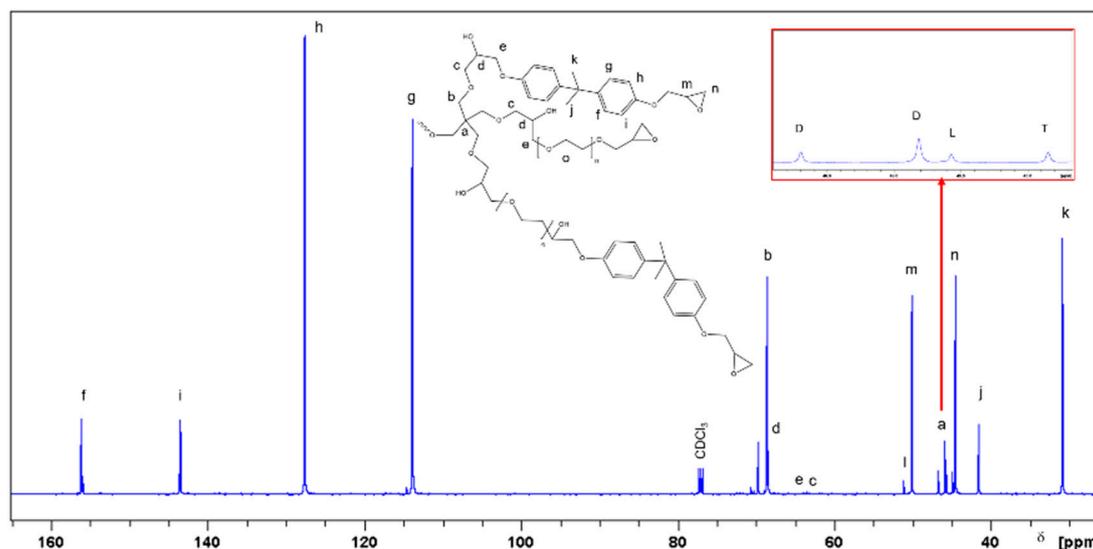
Figure 5. ^{13}C NMR spectrum of HBE5P resin.

The degree of branching (DB) of the hyperbranched epoxy resins with various ratios of BPA and PEG was investigated from the ^{13}C NMR spectra (Figures 4 and 5) using the four units of central carbon atoms of pentaerythritol [5] (δ_C(HBE) = 44.9, 45.6, 45.9, and 46.8 ppm and δ_C(HBE5P) = 44.8, 45.6, 45.8, and 46.7 ppm). The DB was calculated using Equation (5) and the integration values of these peaks were tabulated in Table 2. It was found that all synthesized resins had the hyperbranched structure because DB > 0.5 [9]. The DB values of each formula with and without polyethylene glycol in their structure were hardly different; however, dendritic units decreased and terminal units increased because in situ DGECBAPEG was formed and it might reduce the amount of in situ epoxide group, hindering the generation of branching unit.

Number average molecular weight (M_n), weight average molecular weight (M_w) and dispersity (Đ) of the resins are listed in Table 2. The molecular weight of the resin decreased when adding 5 wt % PEG and increased when the PEG amount was further increased (10–15 wt.%), implying an increase of molecular weight. Moreover, the glass transition temperature of the resin decreased with increase of PEG due to the effect of branching density [43] and the internal plasticized effect of PEG.

Table 2. Dendritic (D), linear (L), and terminal (T) units (%), degree of branching (DB), and physical properties of HBE, HBE5P, HBE10P, and HBE15P resins.

Resin	Branching Structure				M_W (g mol^{-1})	M_n (g mol^{-1})	Đ	T_g (°C)	EEW (g eq^{-1})
	D (%)	L (%)	T (%)	DB					
HBE	77.80	18.14	4.06	0.82	4148	3425	1.211	−9	697
HBE5P	64.65	17.23	18.12	0.83	4014	3363	1.194	−14	663
HBE10P	73.13	10.15	16.72	0.90	4049	3384	1.197	−19	564
HBE15P	76.86	10.92	12.23	0.89	4124	3386	1.218	−20	468

3.2. Curing Behavior of the Hyperbranched Epoxy

The curing study of the hyperbranched epoxy resins cured with diethylenetriamine was investigated by DSC technique. Firstly, curing behavior should be determined to obtain the onset and peak temperatures as well as the heat of reaction of epoxy mixture by non-isothermal DSC method, as shown in Figure 6 and Table 3. Even though chain entanglement occurred in every system, the onset and peak temperatures decreased with increase of PEG in the resins in the case of the resin with 0–10 wt.% PEG because the long-chain structure of PEG acted as plasticizer, increasing the mobility of the polymer chains. However, at 15 wt.% PEG in the resin, the effect of chain entanglement during crosslinking dominated; therefore, the onset and peak temperatures of the resin with 15 wt.% PEG

obviously increased [44]. Moreover, the high concentration of PEG chains in the system would delay the curing reaction [45]. Moreover, the heat of reaction increased with increase of PEG due to reduced EEW of the resins in which the active epoxide ring increased. In addition, glass transition temperature (T_g) of the epoxy thermoset with 0–10 wt.% PEG decreased because of more flexible PEG and an increase in DB [12–14], whereas T_g of HBE15P thermoset increased exceedingly owing to high crosslink density which could be interpreted from high heat of reaction [46].
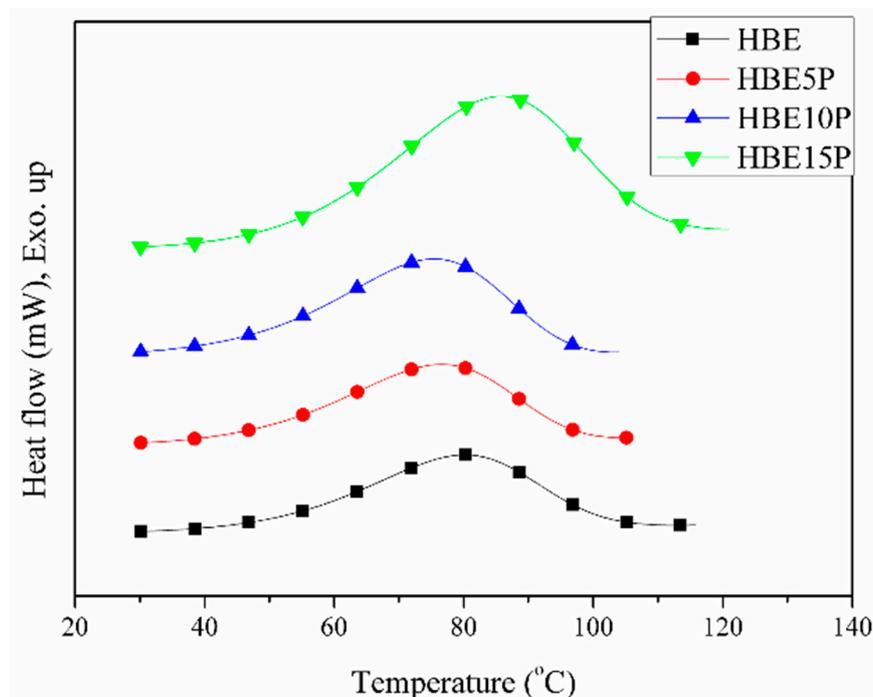

Figure 6. The curing behavior of HBE, HBE5P, HBE10P, and HBE15.

3.3. Curing Kinetics of the Hyperbranched Epoxy

The curing time of the hyperbranched epoxy at 70, 80, 90, and 100 °C as tabulated in Table 3 was determined by isothermal DSC method. The curing time of all cured hyperbranched epoxy mixtures decreased with increasing curing temperature. This can be attributed to high mobility of epoxy molecules which decreased viscosity, accelerated the rate of cure and reduced the curing time [1].

Table 3. The curing behavior and thermal properties of HBE, HBE5P, HBE10P, and HBE15P.

Parameter	HBE	HBE5P	HBE10P	HBE15P
Onset temperature (°C)	50.74	48.10	46.16	53.44
Peak temperature (°C)	79.96	76.95	75.47	85.43
Heat of reaction (J g^{-1})	205.16	242.65	258.19	307.13
Curing time at 70 °C (sec)	1,058	1,055	872	1,173
Curing time at 80 °C (sec)	933	968	817	997
Curing time at 90 °C (sec)	870	911	700	735
Curing time at 100 °C (sec)	613	773	597	515
T_g (°C)	77.90	72.79	51.82	109.41

The kinetic parameters (k, n, and m) were evaluated by fitting the experimental data (cure rate and degree of cure) with Equation (13) via MATLAB program. The results of fitting the data and the equation model are shown in Table 4 and Figure 7. In order to avoid the relative experimental errors for model fitting, the degree of cure should be selected in a range of 0.05–0.95 [37]. It was found that the coefficient of determination (r^2) of all results was high enough (>0.90), indicating that the

experimental data can fit well with the theoretical model in which the rate has the accelerating and decreasing behaviors at the initial and final stages, respectively. It was suggested that the rate constant (k) was a function of curing temperature in which it increased when the temperature increased.

Table 4. The curing kinetic parameters of the hyperbranched epoxy at several curing temperatures.

Parameter	HBE	HBE5P	HBE10P	HBE15P
		70 °C		
k	0.115	0.297	0.145	0.118
n	0.894	1.288	0.882	0.944
m	0.040	0.281	0.059	0.064
r^2	0.999	0.990	0.998	0.999
		80 °C		
k	0.201	0.899	0.349	0.268
n	1.143	1.630	1.120	1.253
m	0.050	0.278	0.122	0.142
r^2	0.999	0.987	0.998	0.998
		90 °C		
k	0.311	1.943	0.631	0.410
n	1.321	2.060	1.302	1.242
m	0.047	0.490	0.160	0.061
r^2	0.999	0.991	0.996	0.997
		100 °C		
k	0.725	2.401	1.308	0.889
n	1.646	1.928	1.622	1.493
m	0.257	0.262	0.147	0.136
r^2	0.994	0.947	0.927	0.982
E_a (kJ mol^{-1})	63.38	75.56	76.52	69.02
r^2	0.975	0.936	0.996	0.987

Moreover, the rate constant of the HBE with PEG resins was higher than those without PEG (i.e., HBE) because of a high degree of branching and low entangle structure [47]. The rate constant of HBE5P was the highest, meaning that its cure rate was very fast; however, its curing time was not the lowest because high crosslink network structures slowed down the cure reaction. Furthermore, n order (effect of unreacted materials on the reaction) and m order (catalytic effect of the products on the reaction) of each cured hyperbranched epoxy at the same isothermal temperature were insignificantly different, except HBE5P whose n and m values increased when the temperature increased. The n and m values of HBE5P were higher than those in other systems. It implied that the cure rate of HBE5P is the fastest in the initial stage and then the rate was the slowest at the final stage due to the diffusion control from high crosslink structure [34,48]. In addition, the activation energy of the epoxy at several curing temperatures was calculated from Equation (14) and listed in Table 4. It was found that the activation energy increased with increase of PEG in the resins due to the steric hindrance of PEG structure [49,50], whereas the activation energy of HBE15P decreased because HBE15P had a large amount of equivalent active epoxy group per mass sample (low EEW) which facilitated the curing reaction due to the weakening in the interaction of the molecular chain [17,51].
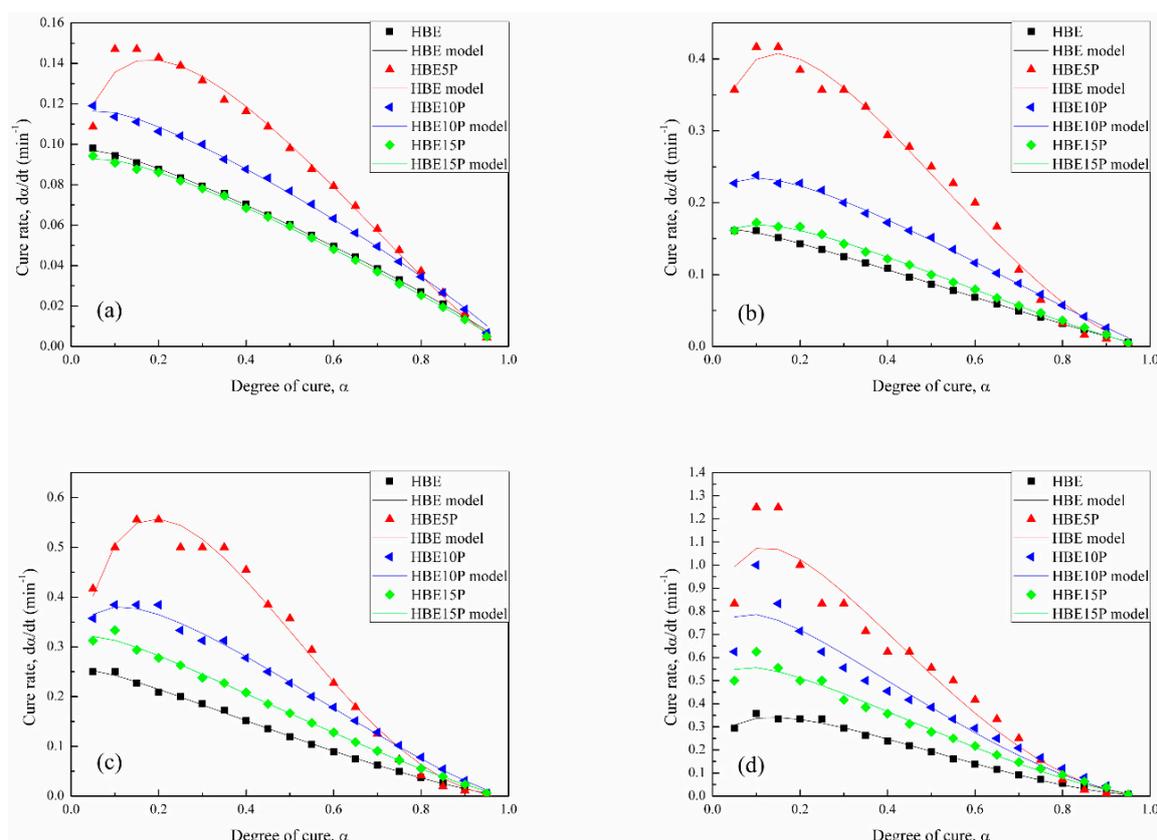
Figure 7. The cure rate and degree of cure of HBE with various PEG contents at (**a**) 70 °C, (**b**) 80 °C, (**c**) 90 °C, and (**d**) 100 °C. Symbol shows experimental result and solid line is model fitting.

4. Conclusions

In this study, the hyperbranched epoxy resins were synthesized by $A_2 + B_4$ polycondensation reaction with various ratios of polyethylene glycol (PEG) to bisphenol A (BPA). The characterization and feature of synthesized resins were evidently identified by FTIR and NMR analysis. The addition of PEG in the resin enhanced degree of branching, epoxy equivalent weight, and curing reaction. Adding 5–10 wt.% PEG in the resin reduced the onset and peak curing temperatures and glass transition temperature; however, the resin with 15 wt.% PEG showed the increase in these thermal properties due to the lowest epoxy equivalent weight. The curing behavior of all resins followed the auto-catalyzed reaction model (Šesták–Berggren equation). The activation energy increased with increase of PEG in the resins due to the steric hindrance of PEG structure, whereas the activation energy of HBE15P decreased due to a large amount of equivalent active epoxy group per mass sample.

Author Contributions: Conceptualization, T.B.-u. and A.S.; methodology, T.B.-u. and A.S.; investigation, T.B.-u. and A.S.; data analysis, T.B.-u.; writing—original draft preparation, T.B.-u.; writing—review and editing, C.S. and A.S.; supervision, A.S.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Golaz, B.; Michaud, V.; Leterrier, Y.; Månson, J.A. UV intensity, temperature and dark-curing effects in cationic photo-polymerization of a cycloaliphatic epoxy resin. *Polymer* **2012**, *53*, 2038–2048. [CrossRef]
2. Kotch, T.G.; Lees, A.J.; Fuerniss, S.J.; Papathomas, K.I. Luminescent organometallic complexes as visible probes in the isothermal curing of epoxy resins. *Chem. Mater.* **1992**, *4*, 675–683. [CrossRef]

3. Yu, J.; Huang, X.; Wang, L.; Peng, P.; Wu, C.; Wu, X.; Jiang, P. Preparation of hyperbranched aromatic polyamide grafted nanoparticles for thermal properties reinforcement of epoxy composites. *Polym. Chem.* **2011**, *2*, 1380–1388. [CrossRef]

4. De, B.; Karak, N. Novel high performance tough hyperbranched epoxy by an $A_2 + B_3$ polycondensation reaction. *J. Mater. Chem. Part A* **2013**, *1*, 348–353. [CrossRef]

5. De, B.; Karak, N. Ultralow dielectric, high performing hyperbranched epoxy thermosets: Synthesis, characterization and property evaluation. *RSC Adv.* **2015**, *5*, 35080–35088. [CrossRef]

6. Emrick, T.; Chang, H.T.; Fréchet, J.M.J. The preparation of hyperbranched aromatic and aliphatic polyether epoxies by chloride-catalyzed proton transfer polymerization from AB_n and $A_2 + B_3$ monomers. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 4850–4869. [CrossRef]

7. Emrick, T.; Chang, H.-T.; Frechet, J.M.J. An $A_2 + B_3$ approach to hyperbranched aliphatic polyethers containing chain end epoxy substituents. *Macromolecules* **1999**, *32*, 6380–6382. [CrossRef]

8. Gong, W.; Mai, Y.; Zhou, Y.; Qi, N.; Wang, B.; Yan, D. Effect of the degree of branching on atomic-scale free volume in hyperbranched poly [3-ethyl-3-(hydroxymethyl) oxetane]. A positron study. *Macromolecules* **2005**, *38*, 9644–9649. [CrossRef]

9. Seiler, M. Hyperbranched polymers: Phase behavior and new applications in the field of chemical engineering. *Fluid Phase Equilibr.* **2006**, *241*, 155–174. [CrossRef]

10. Mai, Y.; Zhou, Y.; Yan, D.; Lu, H. Effect of reaction temperature on degree of branching in cationic polymerization of 3-ethyl-3-(hydroxymethyl) oxetane. *Macromolecules* **2003**, *36*, 9667–9669. [CrossRef]

11. Khalyavina, A.; Häußler, L.; Lederer, A. Effect of the degree of branching on the glass transition temperature of polyesters. *Polymer* **2012**, *53*, 1049–1053. [CrossRef]

12. Luo, X.; Xie, S.; Liu, J.; Hu, H.; Jiang, J.; Huang, W.; Gao, H.; Zhou, D.; Lü, Z.; Yan, D. The relationship between the degree of branching and glass transition temperature of branched polyethylene: Experiment and simulation. *Polym. Chem.* **2014**, *5*, 1305–1312. [CrossRef]

13. Luo, X.; Xie, S.-j.; Huang, W.; Dai, B.-n.; Lu, Z.-y.; Yan, D.-y. Effect of branching architecture on glass transition behavior of hyperbranched copolystyrenes: The experiment and simulation studies. *Chin. J. Polym. Sci.* **2016**, *34*, 77–87. [CrossRef]

14. Shi, Y.; Cao, X.; Luo, S.; Wang, X.; Graff, R.W.; Hu, D.; Guo, R.; Gao, H. Investigate the glass transition temperature of hyperbranched copolymers with segmented monomer sequence. *Macromolecules* **2016**, *49*, 4416–4422. [CrossRef]

15. Pongsa, U.; Samthong, C.; Somwangthanaroj, A. Direct functionalization with 3,5-substituted benzoic acids of multiwalled carbon nanotube/epoxy composites. *Polym. Eng. Sci.* **2013**, *53*, 2194–2204. [CrossRef]

16. Pongsa, U.; Somwangthanaroj, A. Effective thermal conductivity of 3,5-diaminobenzoyl-functionalized multiwalled carbon nanotubes/epoxy composites. *J. Appl. Polym. Sci.* **2013**, *130*, 3184–3196. [CrossRef]

17. Wang, Y.; Chen, S.; Chen, X.; Lu, Y.; Miao, M.; Zhang, D. Controllability of epoxy equivalent weight and performance of hyperbranched epoxy resins. *Compos. Part B Eng.* **2019**, *160*, 615–625. [CrossRef]

18. Buonocore, G.G.; Schiavo, L.; Attianese, I.; Borriello, A. Hyperbranched polymers as modifiers of epoxy adhesives. *Compos. Part B Eng.* **2013**, *53*, 187–192. [CrossRef]

19. Flores, M.; Fernández-Francos, X.; Ramis, X.; Serra, A. Novel epoxy-anhydride thermosets modified with a hyperbranched polyester as toughness enhancer. I. Kinetics study. *Thermochim. Acta* **2012**, *544*, 17–26. [CrossRef]

20. Santiago, D.; Fernández-Francos, X.; Ramis, X.; Salla, J.M.; Sangermano, M. Comparative curing kinetics and thermal–mechanical properties of DGEBA thermosets cured with a hyperbranched poly(ethyleneimine) and an aliphatic triamine. *Thermochim. Acta* **2011**, *526*, 9–21. [CrossRef]

21. Xu, P.; Cong, P.; Li, D.; Zhu, X. Toughness modification of hyperbranched polyester on epoxy asphalt. *Constr. Build. Mater.* **2016**, *122*, 473–477. [CrossRef]

22. Boogh, L.; Pettersson, B.; Månson, J.-A.E. Dendritic hyperbranched polymers as tougheners for epoxy resins. *Polymer* **1999**, *40*, 2249–2261. [CrossRef]

23. Guo, Q.; Harrats, C.; Groeninckx, G.; Koch, M.H.J. Miscibility, crystallization kinetics and real-time small-angle X-ray scattering investigation of the semicrystalline morphology in thermosetting polymer blends of epoxy resin and poly (ethylene oxide). *Polymer* **2001**, *42*, 4127–4140. [CrossRef]

24. Horng, T.J.; Woo, E.M. Effects of network segment structure on the phase homogeneity of crosslinked poly (ethylene oxide)/epoxy networks. *Polymer* **1998**, *39*, 4115–4122. [CrossRef]

25. Kalogeras, I.M.; Roussos, M.; Christakis, I.; Spanoudaki, A.; Pietkiewicz, D.; Brostow, W.; Vassilikou-Dova, A. Dielectric properties of cured epoxy resin+ poly (ethylene oxide) blends. *J. Non Cryst. Solids* **2005**, *351*, 2728–2734. [CrossRef]

26. Luo, X.; Zheng, S.; Zhang, N.; Ma, D. Miscibility of epoxy resins/poly (ethylene oxide) blends cured with phthalic anhydride. *Polymer* **1994**, *35*, 2619–2623. [CrossRef]

27. Sixun, Z.; Naibin, Z.; Xiaolie, L.; Dezhu, M. Epoxy resin/poly(ethylene oxide) blends cured with aromatic amine. *Polymer* **1995**, *36*, 3609–3613. [CrossRef]

28. Jagadeesh, K.S.; Gururaja Rao, J.; Shashikiran, K.; Suvarna, S.; Ambekar, S.Y.; Saletore, M.; Biswas, C.; Rajanna, A.V. Cure kinetics of multifunctional epoxies with 2, 2′-dichloro-4, 4′-diaminodiphenylmethane as hardener. *J. Appl. Polym. Sci.* **2000**, *77*, 2097–2103. [CrossRef]

29. Liaw, D.J.; Shen, W.C. Curing of acrylated epoxy resin based on bisphenol-S. *Polym. Eng. Sci.* **1994**, *34*, 1297–1303. [CrossRef]

30. Roşu, D.; Mustată, F.; Caşcaval, C.N. Investigation of the curing reactions of some multifunctional epoxy resins using differential scanning calorimetry. *Thermochim. Acta* **2001**, *370*, 105–110. [CrossRef]

31. Montserrat, S.; Málek, J. A kinetic analysis of the curing reaction of an epoxy resin. *Thermochim. Acta* **1993**, *228*, 47–60. [CrossRef]

32. Karayannidou, E.G.; Achilias, D.S.; Sideridou, I.D. Cure kinetics of epoxy–amine resins used in the restoration of works of art from glass or ceramic. *Eur. Polym. J.* **2006**, *42*, 3311–3323. [CrossRef]

33. ASTM International. *Standard Test Methods for Epoxy Content of Epoxy Resins*; ASTM D1652-97; ASTM International: West Conshohocken, PA, USA, 1997.

34. Cai, H.; Li, P.; Sui, G.; Yu, Y.; Li, G.; Yang, X.; Ryu, S. Curing kinetics study of epoxy resin/flexible amine toughness systems by dynamic and isothermal DSC. *Thermochim. Acta* **2008**, *473*, 101–105. [CrossRef]

35. Sbirrazzuoli, N.; Vyazovkin, S. Learning about epoxy cure mechanisms from isoconversional analysis of DSC data. *Thermochim. Acta* **2002**, *388*, 289–298. [CrossRef]

36. Ghaffari, M.; Ehsani, M.; Khonakdar, H.A.; Van Assche, G.; Terryn, H. The kinetic analysis of isothermal curing reaction of an epoxy resin-glassflake nanocomposite. *Thermochim. Acta* **2012**, *549*, 81–86. [CrossRef]

37. Vyazovkin, S.; Burnham, A.K.; Criado, J.M.; Pérez-Maqueda, L.A.; Popescu, C.; Sbirrazzuoli, N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta* **2011**, *520*, 1–19. [CrossRef]

38. Perez-Maqueda, L.A.; Criado, J.M.; Sanchez-Jimenez, P.E. Combined kinetic analysis of solid-state reactions: A powerful tool for the simultaneous determination of kinetic parameters and the kinetic model without previous assumptions on the reaction mechanism. *J. Phys. Chem. A* **2006**, *110*, 12456–12462. [CrossRef]

39. Kamal, M.R. Thermoset characterization for moldability analysis. *Polym. Eng. Sci.* **1974**, *14*, 231–239. [CrossRef]

40. Kamal, M.R.; Sourour, S. Kinetics and thermal characterization of thermoset cure. *Polym. Eng. Sci.* **1973**, *13*, 59–64. [CrossRef]

41. Pongsa, U.; Samthong, C.; Praserthdam, P.; Somwangthanaroj, A. Influence of diaminobenzoyl-functionalized multiwalled carbon nanotubes on the nonisothermal curing kinetics, dynamic mechanical properties, and thermal conductivity of epoxy-anhydride composites. *J. Appl. Polym. Sci.* **2016**, *133*. [CrossRef]

42. Badr, M.M.; Amer, A.A.; Shehat, A.S. Synthesis and characterization of waterborne epoxy resins for coating application. *Austr. J. Basic Appl. Sci.* **2010**, *4*, 1376–1382.

43. Svoboda, P. Influence of branching density in ethylene-octene copolymers on electron beam crosslinkability. *Polymers* **2015**, *7*, 2522–2534. [CrossRef]

44. Beamish, J.A.; Zhu, J.; Kottke-Marchant, K.; Marchant, R.E. The effects of monoacrylated poly(ethylene glycol) on the properties of poly(ethylene glycol) diacrylate hydrogels used for tissue engineering. *J. Biomed. Mater. Res. Part A* **2010**, *92*, 441–450. [CrossRef] [PubMed]

45. Zhang, C.; Liu, X.; Liu, H.; Wang, Y.; Guo, Z.; Liu, C. Multi-walled carbon nanotube in a miscible PEO/PMMA blend: Thermal and rheological behavior. *Polym. Test.* **2019**, *75*, 367–372. [CrossRef]

46. Samthong, C.; Laine, R.M.; Somwangthanaroj, A. Synthesis and characterization of organic/inorganic epoxy nanocomposites from poly(aminopropyl/phenyl)silsesquioxanes. *J. Appl. Polym. Sci.* **2013**, *128*, 3601–3608. [CrossRef]

47. Nabae, Y.; Kakimoto, M.-A. Design and Synthesis of Hyperbranched Aromatic Polymers for Catalysis. *Polymers* **2018**, *10*, 1344. [CrossRef] [PubMed]

48. Deng, Y.; Martin, G.C. Diffusion and diffusion-controlled kinetics during epoxy-amine cure. *Macromolecules* **1994**, *27*, 5147–5153. [CrossRef]

49. Lin, M.-S.; Jeng, K.-T.; Huang, K.-Y.; Shih, Y.-F. Optically clear simulataneous interpenetrating polymer networks based on poly(ethylene glycol) diacrylate and epoxy. II. Kinetic study. *Polym. Sci. Part A Polym. Chem.* **1993**, *31*, 3317–3325. [CrossRef]

50. Yu, A.Z.; Sahouani, J.M.; Webster, D.C. Highly functional methacrylated bio-based resins for UV-curable coatings. *Prog. Org. Coat.* **2018**, *122*, 219–228. [CrossRef]

51. El-hefian, E.A.; Nasef, M.M.; Yahaya, A.H. Rheological and morphological studies of chitosan/agar/ poly (vinyl alcohol) blends. *J. Appl. Sci. Res.* **2010**, *6*, 460–468.