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Learning about novel amine-adduct curing agents for epoxy resins: Butyl-glycidylether-modified poly(propyleneimine) dendrimers

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ABSTRACT

Novel butyl-glycidylether-modified poly(propyleneimine) dendrimers (PPIs) are prepared by reacting butyl glycidylether with PPI, which turn out to be able to cure bisphenol-A epoxy resin to an acceptable reaction extent. The nonisothermal reactions, dynamic mechanical properties and thermal stabilities of their cured epoxy resin are comparatively investigated with DSC, DMA and TGA, respectively. The model-fitting kinetic study demonstrates that Šesták–Berggren model can generally well simulate the reaction rates, and the isoconversional kinetic analysis with the Vyazovkin method indicates the curing agents, particularly their setric hindrance and the number of the –OH groups attached, greatly affect reaction kinetic schemes. Increasing the number of the BGE substituents attached to PPIs decreases the reactivity, glass- and beta-relaxation temperatures and thermal stability of the resulting epoxy systems, yet the intensity and width of the glass relaxation increase. This work offers a unique way of preparing modified-aliphatic-polyamine curing agents, and provides an opportunity to better learn about the amine-adduct curing agents which are widely used in room-temperature-cure epoxy coatings and adhesives from these good model compounds.

1. Introduction

Epoxy resins are widely used in protective coatings, adhesives, sealants, filling materials, structural materials, advanced composites, modeling compounds for electronic encapsulation, electrical insulation materials and so forth for more than 60 years, because they have high mechanical strength, excellent chemical resistance, good electrical properties, low shrinkage, strong adhesion to many different substrates, and easy processing [1–3]. To obtain well-balanced final properties, they must be converted from oligomers or monomers of low molecular weights into a highly crosslinked network polymer in the presence of curing agents via a variety of reaction mechanisms [4]. Naturally, curing agents play a paramount role in determining curing conditions, processing and, particularly, end-use properties of epoxy resins, for which reasons they have being revived a lot of interests for many decades.

On the other hand, dendrimers [5–7] belong to well-defined highly branched molecules emanating from a central core with a large number of functional terminals at their periphery. Owing to their unusual chemical and physical properties such as the extraordinarily high functionalities, versatile tuneability, unique rheology properties, optical-enhancement effects, self-assembly, and host–guest particulates [8], dendrimers have been attracting tremendous interests in the recent 26 years since the first successful achievement of poly(amidoamine) dendrimers (PAMAMs) by Tomalia and co-workers [7]. Furthermore, some dendrimers have been shown the promising potentials in biomedicines [9], functional materials [10], catalysts [11], etc. Quite recently, a few preliminary attempts have been made to use dendrimers as the modifiers for thermoplastic polymers and the curing agents for thermosets. For example, Tande et al. [12] used ester-terminated poly(propyleneimine) dendrimers to plasticize polyvinyl chloride (PVC) with the decreased glass-transition temperature found, which is due to the additional free volume provided by the dendrimers. Other reports indicated that PAMAMs and these of similar molecular structures [13–17] could effectively crosslink epoxy resins. These dendrimers also exhibit the advantages of lowered vapor pressure, alleviated toxicity, reduced unfavorable odor, retarded carbonation in air, and improved compatibility with epoxy resins over the conventional linear-aliphatic-amine curing agents of low molecular weights (e.g., ethylenediamine). Unfortunately, PAMAMs and like-structure dendrimers tend to thermally degrade at a reactively low temperature (i.e., 120 °C for PAMAMs) [7], which even lowers than the curing temperatures (sometimes as high as 250 °C [18]) of most epoxy formulations, as a consequence of the

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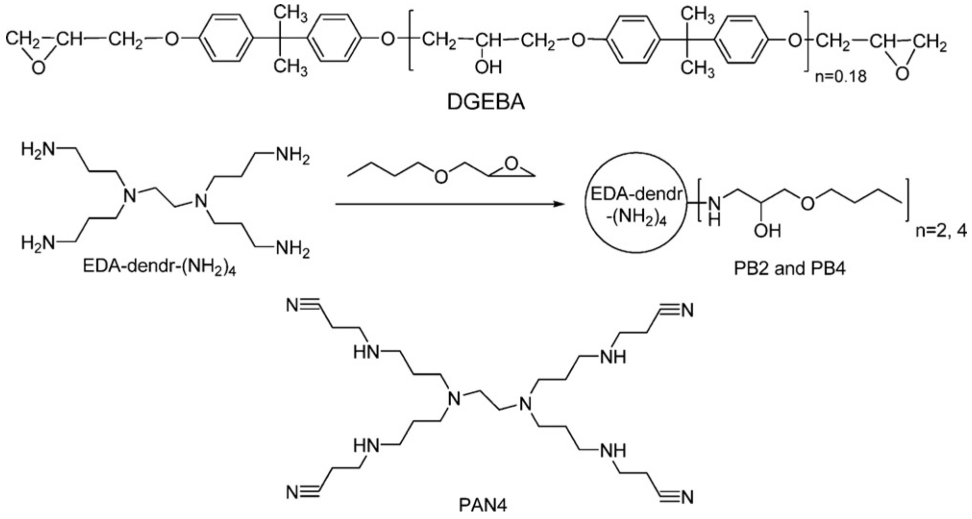


Scheme 1. Molecular structures of DGEBA, EDA-dendri-$(NH_2)_4$, PB2, PB4, PAN4, and epoxy resin (DGEBA).

retro-Michael addition of the weakened amidoamine linkages in their backbones [7]. This will adversely affect the curing reactions and further deteriorates the final properties of the epoxy resins.

Alternatively, amine-terminated poly(propyleneimine) dendrimers (PPIs) [19,20], consisting only of C–C and C–N linkages, take the advantages of excellent thermal stability (thermal decomposition temperature ≥300 °C [21]), lowered viscosity, and increased active-amine-hydrogen density over their PAMAM analogues. Thus, it is more promising for PPIs to serve as the curing agent for epoxy resins with improved properties. Furthermore, in principle it is also theoretically feasible to tailor the properties of the PPI-based epoxy curing agents such as compatibility, reactivity, pot life, crosslink density, flexibility, and solvent resistance via a number of chemical means to meet more specific requirements. In this respect, the chemical modification of PPIs may be a unique way to develop new curing agents with versatile properties. To the best of our knowledge, however, there are few fundamental and systematic studies on PPIs as the curing agents for epoxy resins to date [22–25], and in particular, there is a great demand for a better understanding of and reaching a deep insight into the effects of poly(propyleneimine) dendrimers and their modified products on the curing reactions and properties of epoxy resins. To this end, recently we have being performed a systematic study on this topic [23–25]. Our previous paper [23] focused on a novel curing agent for epoxy resins: the acrylonitrile-capped poly(propyleneimine) dendrimer (PAN4), see Scheme 1, which turned out to be able to well cure epoxy resins with the much decreased reactivity. The reason is that the electron-withdrawing acrylonitrile substituents on the amino functionalities lower the electron density on the resulting substituted-secondary amino groups, thus decreasing the nucleophilicity of the secondary amino functionalities.

As an extension of our previous work, this paper deals with novel curing agents for epoxy resins: butyl-glycidylether (BGE)-modified poly(propyleneimine) dendrimers (PB2 and PB4), with emphases on the nonisothermal reactions, dynamic mechanical properties, and thermal stability of the resulting epoxy resins. The primary objective of the present work is to clarify bonded BGE moieties, more bulk but less electron-withdrawing substituents (in fact slight electron-donating), on the properties of the resulting amine-adduct curing agents for epoxy resins. In industrial practices, BGE is frequently used to modify low-molecular-weight elementary polyamine curing agents to reduce their high volatilization and to improve other desired properties. This work will enrich our knowledge about the widely used but little fundamentally understood amine-adduct curing agents for epoxy resins [23,26], provide a better understanding of dendritic molecular architectures on the cure behaviors and properties of resulting epoxy systems, and further guide judicious molecular design and better applications of the new amine-adduct curing agents based on dendritic polyamines.

2. Experimental

2.1. Materials

Ethylenediamine (EDA) and acrylonitrile (Shanghai Reagent Co., Ltd., China) were purified by distillation prior to use. DGEBA, specific name: diglycidylether of bisphenol A (Heli Resin Co., Ltd., Suzhou, China), was dehydrated at 100 °C before use, with epoxide equivalent weight (EEW) of 196 g/eq. (data provided by the manufacturer). Butyl glycidylether, BGE (Huili Synthetic Materials Co., Ltd., Wuxi, China) was purified by distillation with an epoxy value of 0.695 mol/100 g. EDA-dendri-$(NH_2)_4$ (Scheme 1) was prepared in our lab with reference to published procedures [19,20].

2.2. Preparation of BGE-modified EDA-dendri-$(NH_2)_4$

The butyl-glycidylether-modified EDA-dendri-$(NH_2)_4$, PB2 and PB4 (Scheme 1), were prepared by reacting of BGE and EDA-dendri-$(NH_2)_4$ according to the mole ratio of epoxy to amine (N–H) = 1:2 for PB2 and 1:4 for PB4. To be more specific, BGE was added dropwise to continuously stirred EDA-dendri-$(NH_2)_4$ at 40 °C in 3 h according to the predesigned ratio, then the reaction mixture was heated to 50 °C, and held for additional 10 h. The final reaction product was discharged at room temperature to yield viscous colorless liquids (PB2 or PB4). The reactive hydrogen (N–H) equivalent weights of PB2 and PB4 were 94.5 and 215.5 g/eq., respectively.

2.3. Characterization

FTIR spectra of EDA-dendri-$(NH_2)_4$, PB2 and PB4 (thin films on KBr pallets) were recorded on a Nicolet^{TM} 5700 infrared spectrometer over the wavenumber of 4000–400 cm^{-1}.

Differential scanning calorimetry is the most convenient and powerful mean for studying highly exothermic reactions of epoxy resins due largely to its great accuracy and easy sample preparation [27]. Exotherms of the non-isothermal reactions as a function of time and temperature for DGEBA/EDA-dendri-$(NH_2)_4$, DGEBA/PB2, and DGEBA/PB4 were registered on a Perkin Elmer differential

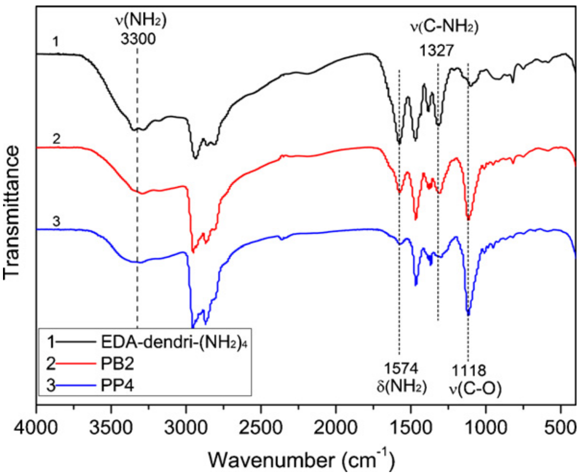


Fig. 1. FTIR spectra of EDA-dendri-$(NH_2)_4$, PB2 and PB4.

scanning calorimeter (DSC-7) for multiple heating rates of 5, 10, 15 and 20 °C/min from 25 to 250 °C/min under nitrogen flow of 20 ml/min. The stoichiometric DGEBA and EDA-dendri-$(NH_2)_4$, PB2 or PB4 were well mixed at room temperature as quickly as possible. Then, the approximately 10 mg of the fresh mixture was enclosed in a DSC aluminum pan, and immediately subjected to a heating run with a lidded empty pan as the reference.

Thermal stability of the cured epoxy resins was evaluated with a thermogravimetric analyzer (Pyris 1 TGA) at a constant heating rate of 10 °C/min from 40 to 850 °C in nitrogen (40 ml/min).

Dynamic mechanical properties of the completely cured epoxy specimens (35 mm × 10 mm × 2 mm) were examined using a dynamic mechanical analyzer (DMA Q800, TA Instruments) at the heating rate of 3 °C/min from −100 °C to well above the glass-transition temperatures (single cantilever/1 Hz).

3. Results and discussion

3.1. FTIR analysis of curing agents

Fig. 1 presents FTIR spectra of EDA-dendri-$(NH_2)_4$, PB2 and PB4, wherein the characteristic IR absorption bands are highlighted by dotted vertical lines. As seen in this figure, the primary amine functionality ($-NH_2$) of EDA-dendri-$(NH_2)_4$ can be confirmed by two characteristic adsorption bands: the strong dual peaks locating in 3350–3250 cm^{-1} owing to the stretch vibration of the NH_2– groups (ν_{NH2}), and the other band around 1574 cm^{-1} due to the scissor vibration of the primary amino groups (δ_{NH_2}). By contrast, for PB2 and PB4 the absorption bands around 1574 cm^{-1} and 1327 cm^{-1} originated from ν_{C-NH_2} decrease gradually with increasing the number of the BGE substituents on their molecules and eventually almost disappears, while that appearing around 1118 cm^{-1} associated with the combined vibration of ν_{C-O} increases accordingly. These drastic changes indicate BGE has preferentially reacted with the primary amino groups of EDA-dendri-$(NH_2)_4$, thereby producing the secondary amino functionalities in the PB2 and PB4 molecules. From the analysis above, we can infer that PB2 contains the approximately equal number of the primary and secondary amino functionalities, whereas PB4 bears almost solely the secondary amino functionalities.

3.2. Nonisothermal cure of epoxy resins

Shown in Fig. 2 are the nonisothermal DSC traces of the different reaction systems with the same heating rate of 10 °C/min (Fig. 2A) and the representative nonisothermal DSC curves of the

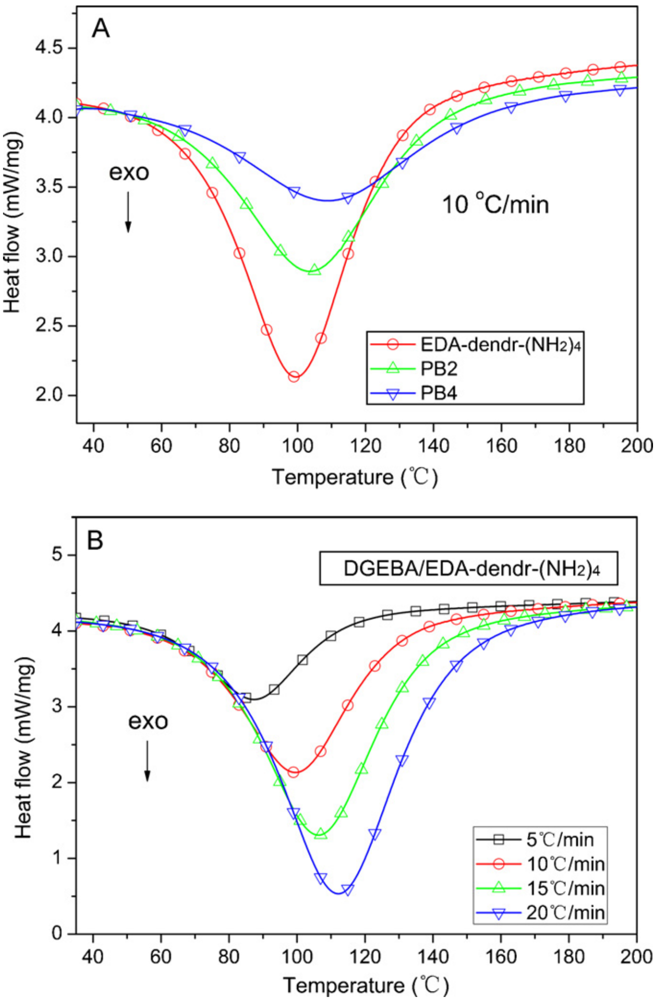


Fig. 2. Representative DSC thermographs of nonisothermal reactions. (A) DGEBA/EDA-dendri-$(NH_2)_4$ with the heating rate of 5, 10, 15 and 20 °C/min; B. DGEBA/EDA-dendri-$(NH_2)_4$, DGEBA/PB2 and DGEBA/PB4 with 10 °C/min.

DGEBA/EDA-dendri-$(NH_2)_4$ system with the different heating rates of 5, 10, 15 and 20 °C/min (Fig. 2B). Each of the DSC curves, irrespective of the reaction systems and the heating rates, exhibits a single exothermic peak without any shoulders, which likely mirrors the amino functionalities (N–H) of the same curing agents react with the epoxy resin, simultaneously [26] and thus the difference in their reactivity towards to the epoxy groups is insignificant for a kinetic modeling propose. In this regard, all these reactions can be considered as a single kinetic process from a statistic point of view.

In addition, as seen in Fig. 2A as the number of the BGE moieties increases, the exothermic peak of the corresponding reaction system shifts gradually to the increased-temperature regime, which indicates that the decreased reactivity of PB2 and PB4 compared to EDA-dendri-$(NH_2)_4$. This finding can also prove that the BGE-substituted secondary amino groups are less reactive than the corresponding primary amino groups, which disagrees the previous report that both the primary and secondary amino groups are equally reactive when reacting with the epoxy resin of TGDDM [28]. Meanwhile, the systematic decrease in the peak area can be observed, which is in response to the suppressed reaction exotherm in unit weight. On the other hand, for the same reaction system (Fig. 2B), increasing the heating rates results in the gradually broadened peak area and the increased peak temperature, which indicates that the increased percentage of the reactions will occur at a higher temperature within a shorter period of time.

Integration of the exothermic peaks shown in Fig. 2 gives rise to the reaction exotherm ΔH and the peak exotherm temperature T_p and Table 1 lists the obtained ΔH and T_p values for the different epoxy reaction systems with the various heating rates. Notice here that although ΔH in unit weight decreases appreciably as the number of the BGE moieties increases, ΔH for unit equivalent of epoxy groups is still in a narrow range (105–121 kJ/mol), which agrees with the typical range for typical epoxy-amine polymerizations (98–122 kJ/mol) [25,27]. This indicates that the enthalpy change associated with the ring-opening process of the epoxy-amine reactions is the primary contributing factor to the reaction exotherm, and furthermore the curing agents can well cure DGEBA to an acceptable reaction extent. For the same reaction system, the heating rates little affect ΔH, which implies that DGEBA can be cured to the essentially same reaction extent irrespective of the heating rate applied. Furthermore, in general ΔH (in kJ/mol) of the reactions slightly decreases with increasing the number of BGE moieties of the curing agents, which implicates that the epoxy-secondary amine reaction is less exothermic; nevertheless, the respective contributions of the primary and secondary amino groups of these curing agents to the reaction exotherms differ slightly. In fact, the difference in the reaction heat between epoxy-primary amine and epoxy-secondary amine reactions is usually neglected in other epoxy-primary amine systems, which also turned out to little influence kinetic analyses of epoxy reactions.

3.3. Rate equations

As regards reaction kinetic analysis of the thermosetting polymers, traditionally it is desirable to obtain a single rate equation to anticipate the progress of a specific reaction system and to predict reaction rate or conversion over a wide temperature and conversion range, especially beyond experiment observation limits. Thermal analysis of thermosetting reactions, particularly DSC kinetic analysis, is preferentially applied for this purpose. In DSC kinetic studies of epoxy resins, reaction exotherms are assumed to be directly proportional to extent of reaction or fractional conversion. Then, reaction rate can be parameterized as Eq. (1):

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H} = k(T)f(\alpha) \tag{1}$$

where t is the reaction time, ΔH the overall reaction heat, dH/dt the reaction heat flow, α the fractional conversion, $d\alpha/dt$ the reaction rate, and $f(\alpha)$ function associated with a specific reaction model. In reality, $f(\alpha)$ takes a large number of forms, which, sometimes, leads to casual the selection of a reaction model without rational discrimination. In this context, Málek method [29,30] is used to determine an appropriate reaction model $f(\alpha)$ and further to establish the explicit form of the rate equation. According to this method, apparent activation energy E_a should be independently calculated with another method, and subsequently two special functions ($y(\alpha)$ and $z(\alpha)$ [29,30]) can be constructed with which to identify a reaction model and to calculate model-related parameters:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)\exp(x) \tag{2}$$

$$z(\alpha) = \pi(x)\left(\frac{d\alpha}{dt}\right)\frac{T}{\beta} \tag{3}$$

In Eqs. (2) and (3), x is the reduced activation energy (E_a/RT), E_a the apparent activation energy, β the heating rate, R the universal gas constant (8.314 J mol^{-1} K^{-1}), T the absolute temperature (K), and $\pi(x)$ the temperature integral [31,32], which can be numerically approximated with adequate precision using a 4th-order rational equation of Senum and Yang [33]:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{4}$$

In this context, frequently cited peak-maximum-evolution Kissinger method [34] is used to evaluate E_a of the nonisothermal reactions studied. According to this method, one must conduct a set of experiments with different heating rates to produce a correlation of peak exothermic temperature T_p (Table 1) with β, and then use Kissinger equation [34] to relate them:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \text{Const.} - \frac{E_a}{RT_p} \tag{5}$$

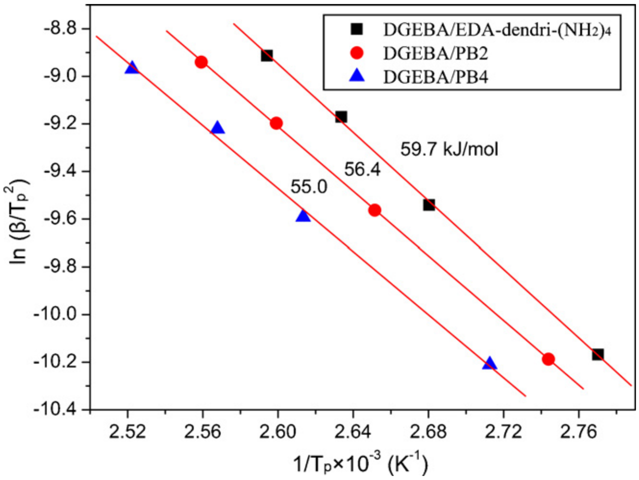
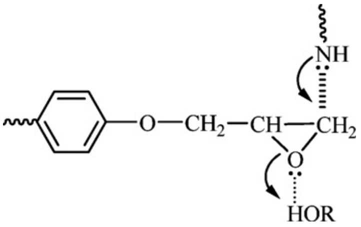


Fig. 3. Kissinger plots of $\ln(\beta/T_p^2)$ vs. $1/T_p$ for different epoxy-amine reactions.



Scheme 2. Epoxy-amine-hydroxyl trimolecular transition state.

From Eq. (5), E_a can be graphically determined from the slope of a linear plot of $\ln(\beta/T_p^2)$ against reciprocal T_p. As shown in Fig. 3, an excellent linear correlation between ($R > 0.998$) $\ln(\beta/T_p^2)$ can be established, and thus reciprocal T_p and the slopes of the fitted straight lines give rise to E_a. E_a is found to fall in a typical range (50–70 kJ/mol) for common epoxy-amine polymerizations [27]. Furthermore, by increasing the number of the BGE substituent of the curing agents from 0 to 2 to 4, E_a of the resulting reaction systems decreases from 59.7 to 56.4 to 55.0 kJ/mol. This finding is likely associated with the –OH groups from the curing agent (PB2 and PB4) which can additionally catalyze the further epoxy-amine reaction [35,36]. To be specific, see Scheme 2, the –OH groups can associate with the epoxy and amino groups to form an activated trimolecular epoxy-amine-hydroxyl intermediate whereby the energetic barrier for the epoxy-amine reactions is lowered.

It is worth pointing out that during the epoxy-amine reaction, the –OH groups will be produced which, like the –OH groups of PB2 and PB4, can catalyze the further reaction, too. Consequently, although our results reveal that the apparent activation energies, E_as, decrease in the order of DGEBA/EDA-

Table 1
Exothermic peak temperature (T_p) and reaction exotherm for different cure systems.

Formulation	β (°C/min)	T_p (°C)	ΔH (J/g)	ΔH (kJ/mol)
DGEBA/EDA-dendri-(NH_2)$_4$	5	87.9	510.9	118.6
	10	99.9	522.5	121.3
	15	106.6	520.4	120.8
	20	112.5	514.8	119.5
DGEBA/PB2	5	91.3	376.5	109.4
	10	104	388.8	112.9
	15	111.6	361.8	105.1
	20	117.6	394.2	114.5
DGEBA/PB4	5	95.9	255.5	105.1
	10	109.5	260.0	107.0
	15	116.3	263.2	108.3
	20	123.3	266.0	109.5

dendri-(NH_2)$_4$ < DGEBA/PB2 < DGEBA/PB4, the difference in their values is still rather trifle (<10%). Nevertheless, this result dose not implicit that the microscopic kinetic schemes (reaction mechanisms) of the different systems differ very slightly, but is due to the fact that the Kissinger equation can only give a single "averaged" E_a value for the whole process. The further discussion on the reaction mechanisms will be addressed in the following subsection by virtue of the model-free isoconversional kinetic analysis.

Then, introducing E_a and $d\alpha/dt$ of the values into Eqs. (2) through (4) produces the curves of the $y(\alpha)$ and $z(\alpha)$ functions, as shown in Fig. 4. Table 2 collects the characteristic conversions from this figure: α_M for $y(\alpha)$, α_p^∞ for $z(\alpha)$ and α_p for $d\alpha/dt$. We can find that they satisfy both $0 < \alpha_M < \alpha_p^\infty$ and $\alpha_p^\infty \neq 0.632$, which, according to Málek et al. [30], leads to the conclusion that the two-parameter autocatalytic model of Šesták–Berggren (the SB(m, n) model) [37] is more appropriate to use to fit the nonisothermal reaction rate. The SB(m, n) model can be expressed as

$$\frac{d\alpha}{dt} = Ae^{-x}\alpha^m(1-\alpha)^n \tag{6}$$

where m and n are the reaction orders, A the pre-exponent factor, and x the reduced activation, E_a/RT.

Transform logarithmically and rearrange Eq. (6), yielding

$$\ln\left[\left(\frac{d\alpha}{dt}\right)\exp(x)\right] = \ln A + n\,\ln[\alpha^{m/n}(1-\alpha)] \tag{7}$$

where n and $\ln A$ can be determined from the slope and intercept of the linear plot of $\ln(d\alpha/dt)\exp(x)$ vs. $\ln\alpha^{m/n}(1-\alpha)$ for $\alpha \in [0.1,0.9]$, respectively where m/n equals $\alpha_M/(1-\alpha_M)$ [29,30]. Table 2 also summarizes calculated m, n and $\ln A$ for the different reaction systems, and substitution of their averaged values and E_a into Eq. (6) produces the explicit rate equations: Eqs. (8)–(10) for DGEBA/EDA-dendri-(NH_2)$_4$, DGEBA/PB2 and DGEBA/PB4, respectively.

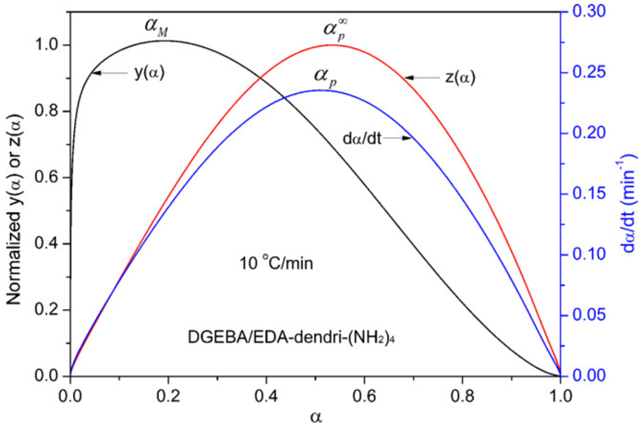


Fig. 4. Function curves of normalized $y(\alpha)$ and $z(\alpha)$, and experimental reaction rate $d\alpha/dt$ of representative DGEBA/EDA-dendri-(NH_2)$_4$ system with heating rate of 10 °C/min.

$$\frac{d\alpha}{dt} = 1.99\times10^8\exp\left(\frac{-59,730}{RT}\right)\alpha^{0.368}(1-\alpha)^{1.508}, \quad \alpha\in[0,1] \tag{8}$$

$$\frac{d\alpha}{dt} = 3.46\times10^7\exp\left(\frac{-56,350}{RT}\right)\alpha^{0.145}(1-\alpha)^{1.418}, \quad \alpha\in[0,1] \tag{9}$$

$$\frac{d\alpha}{dt} = 1.52\times10^7\exp\left(\frac{-55,010}{RT}\right)\alpha^{0.073}(1-\alpha)^{1.459}, \quad \alpha\in[0,1] \tag{10}$$

Fig. 5 compares the model-stimulated reaction rates and the experimental ones. From it, although a relatively greater deviation occurs for DGEBBA/PB4 at 20 °C/min (Fig. 5C), in general these rate equations can well predicate the reaction rates for the different heating rates. This discrepancy likely indicates that heating rates have some influences on the applicability of the SB(m, n) model for some epoxy-amine systems, which is likely due to the limitation of model-fitting methods which, in most cases, can only yields a single rate equation and are unlikely able to address all applied kinetic problems encountered. Despite that the further work is needed to identify the applicability of the SB(m, n) model to the high heating rates, our work clearly shows that the SB (m, n) model combined with the Málek method can still yield the acceptable kinetic prediction of the reactions if the heating rates do not exceed 15 °C/min.

As indicated by Eqs. (8)–(10), m tends to decrease in the order of DGEBA/PB4 < DGEBA/PB2 < DGEBA/EDA-dendri-(NH_2)$_4$, whereas n changes slightly, which quite resembles the case of the nonisothermal reactions of a partially reacted epoxy/anhydride system [38]. In some sense, this likely reflects that the reaction becomes less autocatalytic and tends to follow a single mechanism [39] as the number of the BGE moieties increases. Two main reasons could account for this finding. First, the BGE substitute attached to PB2 and PB4 considerably increases the steric hindrance of the substituted-amino functionalities and decreases the concentration and mobility of the reactive epoxy and amino groups. Second, the inherent –OH functionalities of PB2 and PB4 can additionally catalyze the further epoxy-amine reaction, which leads to the decreased percentage of the autocatalytic reactions and the increased percentage of the –OH catalyzed reaction. Noticeably, in comparison with our previous report on DGEBA cured with acrylonitrile-capped poly(propyleneimine) dendrimer (PAN4) [23], see Scheme 1, which, unlike PB2 and PB4, bears no –OH group at all, thus we can rationally infer that the substituted-secondary-amino functionalities can decrease the probability of the autocatalytic epoxy-amine reaction. Therefore, although more experimental proofs are required to clarify the influence of the different kinds of substituents on the amino functionalities on the

Table 2
Conversions, α_p, α_M, and α_p^∞ for peak values of $d\alpha/dt$, $y(\alpha)$ and $z(\alpha)$, respectively, along with calculated SB(m, n) model parameters, m, n and ln A.

Formulation	β (°C/min)	α_p	α_M	α_p^∞	n	m	ln A
DGEBA/EDA-dendri-$(NH_2)_4$	5	0.508	0.207	0.529	1.455	0.378	19.162
	10	0.509	0.194	0.535	1.484	0.358	19.092
	15	0.503	0.184	0.527	1.529	0.344	19.096
	20	0.507	0.188	0.524	1.564	0.362	19.090
DGEBA/PB2	5	0.499	0.122	0.527	1.396	0.195	17.430
	10	0.506	0.097	0.528	1.424	0.153	17.393
	15	0.499	0.088	0.524	1.447	0.140	17.373
	20	0.503	0.061	0.528	1.405	0.091	17.245
DGEBA/PB4	5	0.495	0.079	0.543	1.379	0.118	16.638
	10	0.495	0.045	0.539	1.439	0.068	16.519
	15	0.491	0.030	0.530	1.483	0.046	16.518
	20	0.473	0.038	0.525	1.534	0.061	16.479

curing behaviors of epoxy systems, the m value for the SB(m, n) model is likely linked with the ratio of the primary to secondary amino groups of the curing agents. Namely, the small the ratio of primary-amino groups to secondary ones, the smaller the m value.

To further examine the influence of the BGE substitutes on the reactivity of the curing agents, reaction rate constant k, a scaling factor for overall reaction rate, estimated from Eq. (2) are compared for the different temperatures. As shown in Table 3, $k(T)$ decreases with increasing the number of the BGE moieties of the curing agents; for example, k(80 °C) for DGEBA/EDA-dendri-$(NH_2)_4$ is about 2.62 times that of DGEBA/PB4. This indicates although the catalytic –OH groups from the curing agents are incorporated, the bulky BGE substitutes is more effective in decreasing the reactivity of the corresponding curing agents. In other words, the steric hindrance seems more influential than the catalytic effect of the –OH groups on the epoxy-amine reaction, which leads to the lowered reaction rate constant in response to the decreased reactivity of the curing agents.

3.4. Isoconversional kinetic analysis

Isoconversional kinetic analysis, without assuming any specific kinetic models, can provide us more straightforward information associated with thermosetting curing reactions, which, particularly, can reveal a dependence of effective activation energy on fractional conversion. Many studies frequently show that performing this analysis in thermally stimulated polymer processes, chemical, physical, or combined, can provide a useful clue about complexities involved in these processes [40]. More specifically, this analysis turns out to be especially useful in untangling complexities of epoxy cure reactions [41]. Furthermore, recently Vyazovkin's group successfully carried out this analysis to clarify the nitro substituent and its position on the benzene ring of the aromatic diamine curing agent on the nonisothermal curing behaviors of resulting epoxy systems [42–45]. Similarly, to obtain additional reaction kinetic information about the epoxy-amine reactions studied, we have also conducted the isoconversional kinetic analysis. Herein, the advanced isoconversional method, a nonlinear method, developed by Vyazovkin [46–48] is adopted for this purpose, because of its unparallel accuracy and wide applicability compared to other linear isoconversional methods frequented used. The analytic expressions for this method can be written by

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n} \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} = \min \tag{11}$$

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \tag{12}$$

where subscripts, i and j, denote thermal measurements with different temperature programs, $\Delta\alpha$ is the increment of conversion which is usually set as 0.02 sufficient to eliminate accumulative errors in E_α calculation, t is the time, and J is the temperature integral, which can be numerically evaluated with a trapezoid rule. According to the Vyazovkin method, a set of experiments should be carried out according to different temperature programs, and then E_α can be determined at any particular value of α by identifying a suitable E_a value which satisfies Eq. (11). Repeat this minimization procedure for each selected α, and will give rise to an $E_\alpha - \alpha$ dependence.

Fig. 6 shows the dependence of the fractional conversion (α) on the temperature for the different reaction systems with the heating rates of 5, 10, 15 and 20 °C/min. As the heating rate increases, the temperature for the same conversion increases accordingly, which indicates that the increased percentage of the epoxy-amine reactions will occur at a higher-temperature range. By applying the Vyazovkin method to the conversion-temperature data (Fig. 6), we can obtain the correlation of the effective activation energy with conversion for the different epoxy-amine systems considered. As presented in Fig. 7, E_α depends strongly on α and the different reaction systems exhibit the different $E_\alpha - \alpha$ profiles, which could probably reflect the change of reaction mechanisms (kinetic schemes) during the different stages of the reaction and the curing agents having profound influences on the reaction mechanisms of the curing systems. The detailed analysis of Fig. 7 is as follows.

In general, the E_α value increases in an order: DGEGA/EDA-dendri-$(NH_2)_4$ > DGEBA/PB4 > DGEBA/PB2. This observation is likely associated with the –OH groups inherent from the curing agents; furthermore, the increased setric hindrance of the BGE-

Table 3
Rate constants k at the various temperatures for different reaction systems.

System	Curing rate constant k (min^{-1}) at temperature (°C)						
	40	60	80	100	120	140	160
DGEBA/EDA-dendri-$(NH_2)_4$	0.0217	0.0859	0.291	0.867	2.31	5.59	12.5
DGEBA/PB2	0.0138	0.0505	0.160	0.447	1.13	2.60	5.54
DGEBA/PB4	0.0101	0.0360	0.111	0.303	0.746	1.69	3.53
DGEBA/PAN4[a]	0.00168	0.00581	0.0175	0.0468	0.1134	0.252	0.520

[a] Data quoted from Ref. [23].

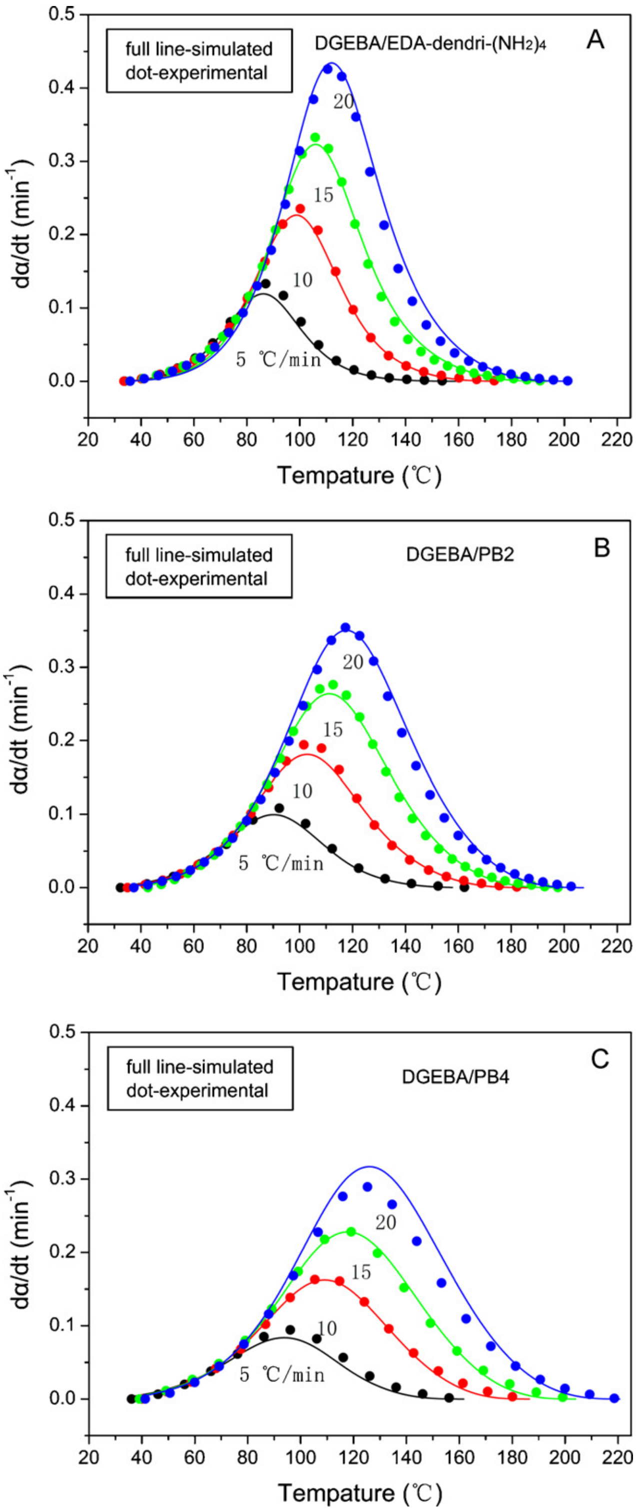


Fig. 5. Comparison of experimental rates and that predicated from SB(m, n) model.

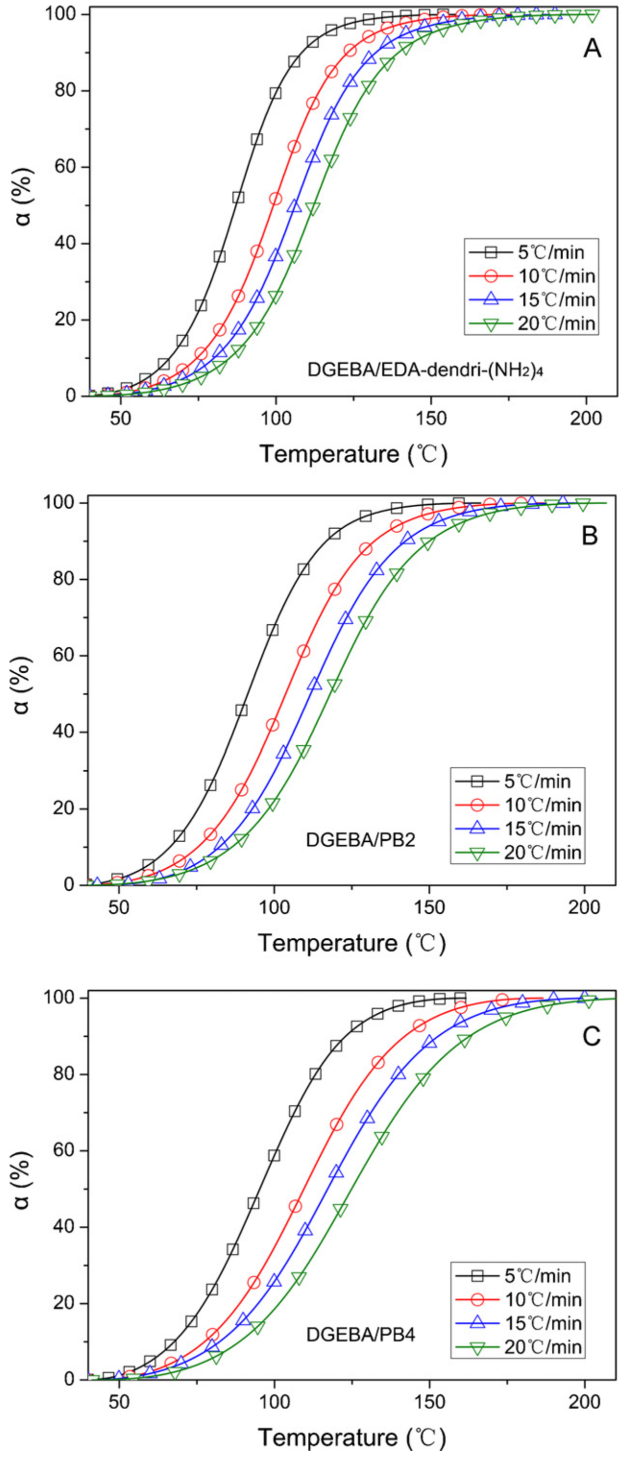


Fig. 6. Dependence of conversion on temperature for heating rates of 5, 10, 15 and 20 °C/min. (A) DGEB A/EDA-dendri-$(NH_2)_4$; (B) DGEBA/PB2; (C) DGEBA/PB4 at 10 °C/min.

substituted amino functionalities of the curing agents (PB2 and PB4) has certain contributions to this finding. To illustrate, as discussed in Section 3.3, the –OH groups can catalyze the epoxy-reaction reaction, which leads to the decreased apparent activation energy. As a result, the –OH groups from PB2 can additionally catalyze the curing reaction, which can also account for the much lower effective activation energy, E_α, observed in the DGEBA/PB2 system than that of the DGEBA/EDA-dendri-$(NH_2)_4$ system. Moreover, despite the fact that PB4 contains the much more –OH groups than PB2, E_α for DGEBA/PB4 is still higher than that for DGEBA/PB2. What leads to this anomaly? The reason may be that the majority of the amino functionalities of PB4 are attached with BEG moieties, which, in turn, causes the appreciably increased steric hindrance of the resulting secondary amino functionalities. Consequently, in the DGEBA/PB4 system, the number of the secondary amino groups is far greater than that of the primary ones which, in fact, can be neglected; therefore, the increased steric hindrance of the amino functionalities probably leads to the decreased reactivity of

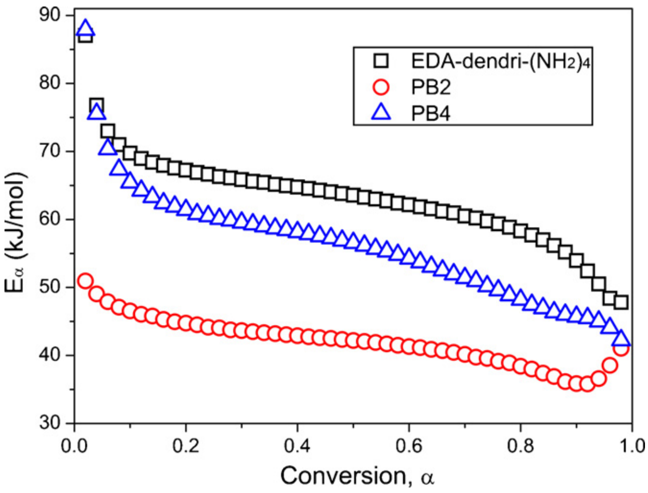


Fig. 7. Variation of effective activation energy (E_α) with fractional conversion for different reaction systems.

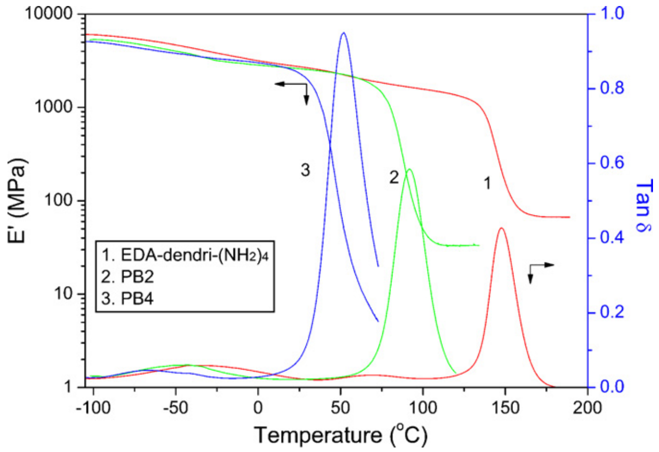


Fig. 8. Profiles of storage modulus E' and loss factor Tan δ vs. T for DGEBA completely cured with EDA-dendri-(NH_2)$_4$, PB2 and PB4.

PB4 than PB2. In contrast to the DGEBA/PB2 system in which the number of the primary and secondary amino groups are essentially equal as discussed in Section 3.1, thus the –OH groups inherent from PB2 can additionally catalyze the further reaction, in particular, the epoxy-primary amine reaction which is predominant at the early reaction stage. To summarize, the increased steric hindrance of the curing agents contributes positively to E_α, whereas the simultaneously incorporated –OH functionalities play a negative role, which will result in the competing mechanisms.

At the very beginning of the reaction, E_α of the different systems, especially the DGEBA/EDA-dendri-(NH_2)$_4$ and DGEBA/PB4 systems, drop quickly with increasing α. This can be attributed to the decreased viscosity of the system as the temperature increases, which makes the diffusion of the reactive groups (epoxy and amine) less restricted and thus lowers the activation energy associated with the diffusion. Notice here that initial E_α of the DGEBA/PB2 system is much lower than that of the other two. This observation suggests that the –OH groups from PB2 can markedly catalyze the corresponding epoxy-primary amine reaction, because the primary amino groups are much reactive than the secondary amino groups and the concentration of the primary amino groups is still high in the DGEBA/PB2 system. On the other hand, the unreached DGEBA/EDA-dendri-(NH_2)$_4$ system contains solely the primary amino groups, whereas the corresponding DGEBA/PB4 system contains almost only the BGE-substituted secondary amino groups and the corresponding secondary –OH groups. In this regard, although the –OH groups from PB4 can catalyze the epoxy-amine reaction, they also result in the much increased viscosity of the DGEBA/PB4 system due to the strong H-bonding among O and H atoms and the much increased molecular weight of PB4. Furthermore, the BGE-substituted secondary amino groups are less reactive than the primary amino groups. For the two reasons above, the epoxy-secondary amine reaction of the DGEBA/PB4 system manifests much increased E_α at the initial stage.

As the conversion further increases, E_α decreases gradually. This finding is likely associated with the increasingly restricted diffusion of the reactive groups, because the molecular weight and crosslink density increase rapidly with α. While the reaction preceding the high-conversion stage, a quick decrease in E_α value can be observed in the DGEBA/EDA-dendri-(NH_2)$_4$ system; conversely, a slight increase can be found in the DGEBA/PB2 system. The former can be explained as the impact of the diffusion near the glass-transition regime, but the latter is likely associated with the etherification of the epoxy groups at higher temperature ($T > 150\,^\circ$C) [49,50] which need overcome the much higher energetic barrier than the common epoxy-amine addition. For the DGEBA/PB4 system, the aforementioned tendency is not very distinctive, which likely results from the superposition or partial compensation of the etherification reaction and the diffusion affect near the end of the reaction.

From the analysis above, we can conclude that BGE moieties bonded to PB2 and PB4 have the great impact on the curing behaviors of the resulting reaction system, because they not only introduce the –OH groups, but increase the setric hindrance of the substituted secondary amino functionalities as well.

3.5. Dynamic mechanical properties

Fig. 8 displays the dynamic mechanical spectra for storage modulus E' and loss factor Tan δ against temperature T of the fully cured DGEBA/EDA-dendri-(NH_2)$_4$, DGEBA/PB2 and DGEBA/PB4 networks, and Table 4 summarizes the obtained characteristic relaxation temperature and modulus accordingly. From this figure we can detect a major relaxation process occurring in the network; i.e., E' decreases dramatically by a factor of > 100 in a relatively narrow temperature regime, while Tan δ goes through its maximum. These observations are indicative of the glass transition (α-transition) of the cured epoxy networks, which is owing to the cooperative motions of the whole network chains. Moreover, another relaxation process can be observed from -70 to $-30\,^\circ$C, which can be assigned to the β-transition of the epoxy-amine network as a result of the localized segmental motions (crank shaft) of the hydroxyl ether (–CH_2–CH(OH)CH_2O–) units in epoxy-amine networks [51–54], as illustrated in Scheme 3.

Further examine Fig. 8 and Table 4 and we can find that the temperature range and the intensity of the α and β transitions of the networks are strongly affected by the number of the BGE moieties bonded to the curing agents. To illustrate, as the number of BGE moieties of the curing agents increases from 0 to 2 to 4, the glass temperature of the networks decreases from 147.7 to 91.3 to 51.1 °C accompanied with the systematically increased amplitude and width. This finding is likely associated with the flexible pendent BGE terminals from PB2 and PB4 which increase the free volume, broaden the chain distribution of the resultant networks, and lower their crosslink densities, simultaneously. Interestingly, increasing the BGE moieties of the curing agents leads to the considerably increased peak height and the broadened temperature range of the glass transition near the room-temperature range, which likely suggests these curing agents may find some practical applications in the room-temperature-cure damping epoxy materials.

Table 4
Characteristic transition temperatures and modulus of different epoxy networks.

Formulation	DGEBA/EDA-dendri-$(NH_2)_4$	DGEBA/PB2	DGEBA/PB4
α-Relaxation (T_g)/°C	147.7	91.3	51.1
β-Relaxation (T_β)/°C	−34.5	−45.4	−65.5
Modulus at −100 °C/MPa	6024	5344	5046
Modulus at 20 °C/MPa	2811	2651	2562
Rubbery modulus E_r/MPa	67	33	<5
Crosslink density ν_e/mol m^{-3}	5958	3354	<566

As reported [55–59], crosslink density of cured epoxy resins can be estimated by

$$E_r = 3RT_r\nu_e \tag{13}$$

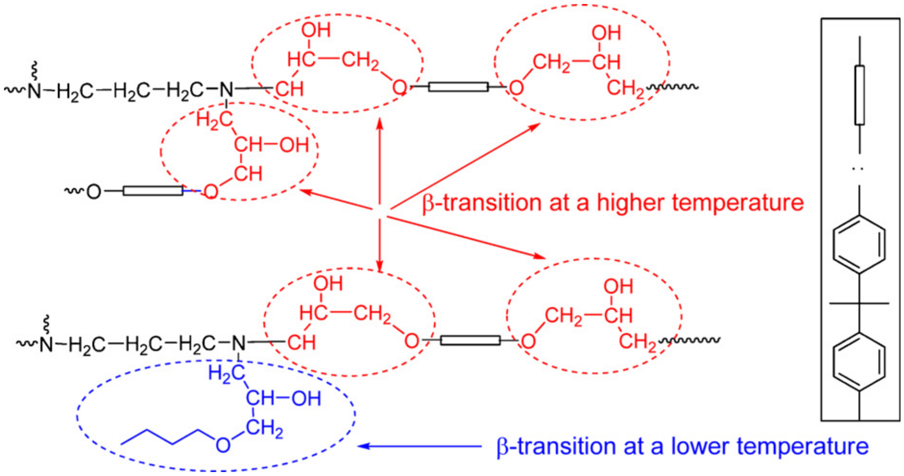
where E_r is the rubber modulus, R the universal gas constant, T_r the temperature corresponding to E_r, and ν_e the crosslink density. Table 4 also compares the obtained E_r, T_r and ν_e for the different epoxy networks, where T_r is regards as $T_g + 30$ °C. Clearly, as the number of the BGE moieties increases, the crosslink densities of the resultant epoxy networks decrease.

In addition to the aforementioned glass transition, the DGEBA/PB2 and DGEBA/PB4 networks manifest the decreased β-transition temperatures combined with the gradually decreased amplitudes compared with the DGEBA/EDA-dendri-$(NH_2)_4$ network. For example, an increase in the number of the BGE moieties from 0 to 2 to 4 corresponds to the decrease of the β-transition temperature of the corresponding network from −34.5 to −45.4 to −65.5 °C. This also indicates the gradually lowered activation energy of the β transition for the networks. The reason may be that the dangling BGE chain ends enhance the flexibility of the network and the movability of the $–CH_2–CH(OH)CH_2O–$ segments embedded in the networks by decreasing the crosslink density and by introducing the flexible $–CH_2–CH(OH)CH_2O–Bu$ segments. Note here that the relaxation of $–CH_2–CH(OH)CH_2O–Bu$ units of the pendent BGE terminals in the networks probably occurs at a much lower temperature region (<100 °C), so that the observed intensity of the β relaxation of the network (<100 °C) decreases with increasing the number of BGE moieties, as demonstrated in Scheme 3.

3.6. Thermal stability

The thermal stabilities of the cured DGEBA/EDA-dendri-$(NH_2)_4$, DGEBA/PB2 and DGEBA/PB4 systems are examined with TGA in N_2. Shown in Fig. 9A and B are the weight percentage and derivative weight percentage as a function of temperature, and presented in Table 5 are the temperatures for the different weight percentages accordingly. In general, the cured epoxy resins show the fairly good thermal stability, as indicated by the initial decomposition temperature T_i (for 0.5% weight loss) of all these epoxy systems higher than 220 °C with the temperature T_{max} for maximum decomposition rate in 372–380 °C (Fig. 9B) which decreases gradually with increasing the number of the bonded BGE segments of the curing agents. In contrast, these cured epoxy resins are much more thermally stable than that cured with PAMAMs [14] or silica-supported PAMAMs [13], in which cases the obvious weight loss can be detected in a much-lower temperature range (∼160 °C).

From T_i listed in Table 5, we can conclude the thermal stability of the different epoxy-amine systems increases in an order of DGEBA/PB4 < DGEBA/PB2 < DGEBA/EDA-dendri-$(NH_2)_4$. Generally, the thermal decomposition of amine-cured epoxy resins in an inert atmosphere [60,61] begins with the elimination of H_2O from the secondary alcohol groups $(–CH_2–CH(OH)–CH_2–)$, whereby the unsaturated double bonds resulting. After that, the residual starts to decompose with the liberation of volatile gases, followed by the vaporization and further carbonization of the remaining pyrolysates. By analogue, we can rationally infer that the elimination of water from the DGEBA/EDA-dendri-$(NH_2)_4$ network occurs at the higher temperature (about 276 °C), whereas the DGEBA/PB2 and DGEBA/PB4 networks dehydrate at the relatively low temperatures (248 and 220 °C). The probable reason is that the pendent aliphatic BGE chains $(–CH_2–CH(OH)CH_2O–Bu)$ in the cured epoxy resin are easier to dehydrate; meanwhile, the crosslink density of the resulting epoxy-amine network decreases. These likely lead to the easy liberation of H_2O of the PB2- and PB4-cured epoxy resins at the lower temperatures compared with that cured by EDA-dendri-$(NH_2)_4$. In addition, as listed in Table 5 the ash contents of the different at 800 °C vary with the curing agents, which suggests that the curing agent has some influences on the char formation process of the cured epoxy systems. For example, the ash contents of the different systems increase in the other of DGEBA/PB4 < DGEBA/EDA-dendri-$(NH_2)_4$ < DGEBA/PB2, which partially responds to the flame retardnance of the cured epoxy



Scheme 3. Schematic demonstration of origination of β-transition of epoxy networks.

Table 5
Temperatures for different weight percentages and maximum decomposition rates for different cured epoxy resins and corresponding ash contents for 800 °C.

Formulation	Temperature (°C) at varied weight loss fractions						Ash content (%)
	0.5%	10%	30%	50%	70%	T_{max}[a]	800 °C
DGEBA/EDA-dendri-(NH$_2$)$_4$	276.1	357.0	378.3	396.3	433.0	380.2	14.4
DGEBA/PB-2	247.6	344.3	372.3	390.7	432.1	378.3	16.1
DGEBA/PB-4	220.7	316.9	355.1	380.5	435.5	372.3	10.8

[a] T_{max} is the temperature for maximum thermal decomposition rate.

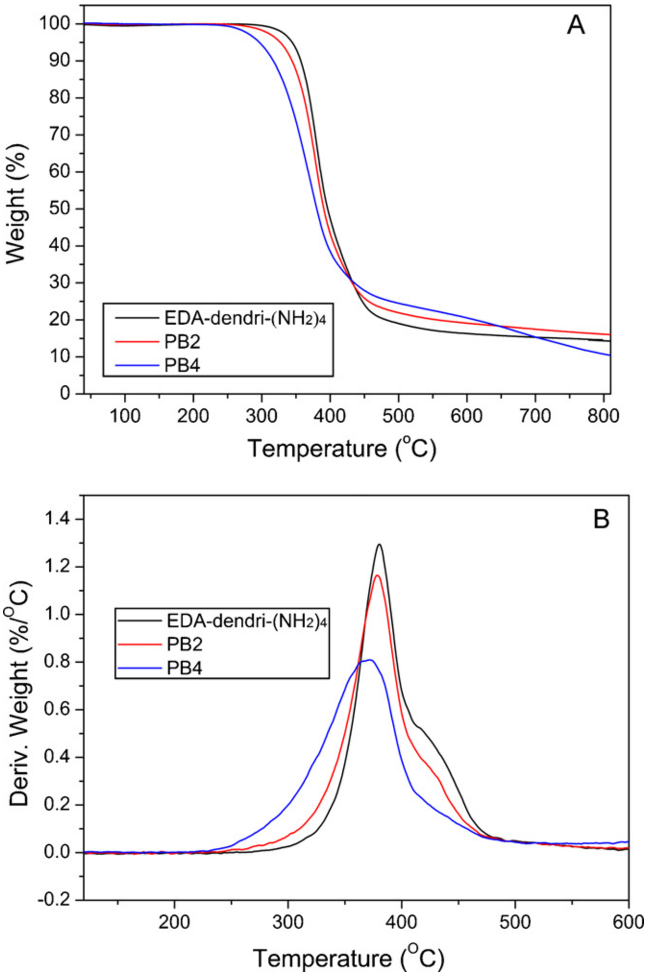


Fig. 9. TG thermographs of DGEBA/EDA-dendri-(NH$_2$)$_4$, DGEBA/PB2 and DGEBA/PB4 with heating rate of 10 °C/min. A. Weight percentage vs. temperature; B. derivative weight percentage vs. temperature.

resins. Although further work is required to clarify the mechanisms about the thermal decomposition process and the char formation of these cured epoxy resins, our result suggests introducing the flexible BGE chains in the amine curing agents and decreasing the crosslink density of the resulting network do not necessarily lead to the decreased ash contents of the cured epoxy after thermal decomposition at the high temperatures in an inert atmosphere.

4. Conclusions

We have successfully prepared the butyl-glycidylether-modified poly(propyleneimine) dendrimers (PB2 and PB4) and found they can well crosslink DGEBA nonisothermally with the overall reaction exotherm of 105–121 kJ/mol. The apparent activation energies of the DGEBA/EDA-dendri-(NH$_2$), DGEBA/PB2 and DGEBA/PB4 reactions were 59.7, 56.4 and 55.0 kJ/mol, respectively. By applying the Málek method, the Šesták–Berggren model was selected to model the reaction rate of the nonisothermal reactions with an good match achieved if the heating did not exceed 15 °C/min. Increasing the number of the BGE moieties bonded to the curing agents led to the lowered reactivity towards the epoxy resin and obscured the autocatalytic characteristic. The subsequent model-free kinetic analysis revealed that the –OH groups of the curing agents could lower the effective activation energy of the epoxy-amine reactions, whereas the steric hindrance of amino functionalities contributed to it negatively. In addition, as the number BGE moieties was increased, the glass- and β-transition temperatures, crosslink density and initial thermal decomposition temperatures of the corresponding networks decreased gradually; nevertheless, the cured epoxy resins still had the sufficient thermal good stability for <220 °C. Noticeably, PB2 and PB4, particularly PB4, could increase and broaden the damping of the cured epoxy resins near room-temperature range compared to EDA-dendri-(NH$_2$). To summarize, PB2 and PB4 show some potentials for room-temperature-cure epoxy coatings and adhesives with increased damping. This work provide a new possibility to develop the new epoxy curing agents with the unique molecular architectures by virtue of the chemical modifications of dendritic polyamines, and affords the deep insightful into the widely used amine-adduct curing agents for epoxy resins based on these novel amine adducts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2011.02.038.

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