

Preparation of a branched amine and physical and thermal studies of epoxy compositions including the amine compound

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ABSTRACT: A branched amine, abbreviated as EATP, was synthesized by reacting ethylene diamine with methyl acrylate, followed by reaction with xylylene diamine via a two-step process. The prepared EATP (in the range of 5–30 parts per resin) was added to epoxy compositions with bisphenol A epoxy resin and a curing agent, xylylene diamine. The epoxy compositions were cured at high temperatures and processed for flexural strength testing and dynamic mechanical analysis. The results showed that the flexural strength was improved by 13% when 10% EATP was present in the epoxy matrix, but there was a decrease in $\tan \delta$ and storage modulus values. Moreover, the degree of fire hazard of the epoxy compositions and EATP was studied by measuring the heat release rate (HRR). The reduction in the HRR with higher amounts of EATP in the epoxy indicated that the xylylene groups of EATP enhance the thermal stability of the resin. © 2018 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2018**, *135*, 46233.

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INTRODUCTION

Epoxy resins have high chemical and heat resistance, as well as good mechanical and thermal properties. Consequently, they have a wide range of industrial applications, including semiconductor encapsulants, adhesives, coatings, and automobile and aerospace parts.^{1,2} Epoxy polymers are generally synthesized by reacting epoxy resins with amine or maleic anhydride hardeners.^{3,4} It is known that epoxy polymers form three-dimensional networks and that the crosslinking density of these polymers depends on the number of glycidyl ether groups in the resin.⁵ When epoxy resins react with amine hardeners, one proton on the nitrogen atom of the hardener binds with one glycidyl ether to form a polymer network.⁶ Based on the location of functional groups in the molecule,⁷ amine hardeners can be categorized as poly(ether amines); polyamides; amidoamines; ethylene amine derivatives such as diethylenetriamine (DETA), triethylenetetramine (TETA), and lupasol; cycloaliphatic amines [bis(*p*-aminocyclohexyl)methane (PACM)] and diaminocyclohexane (DACH)]; and aromatic amines such as 4,4'-methylene-diamine (MDA) and diaminodiphenyl sulfone (DDS).

Extensive research has been carried out on amine hardeners for both petroleum-based and biobased epoxy resins.⁸ Jeffamine, a poly(ether amine), has long pot life, low viscosity, and flexible properties but has low crosslinking density and poor mechanical properties when cured with epoxy resins.^{9–11}

In the case of ethylene diamines such as DETA or TETA, controlling the reaction becomes difficult because of high reaction rates. Lupasol hardeners, one of the most widely used branched ethylene diamine derivatives, have many advantages over other ethylene amines but do not have good mechanical properties as they only have hyperbranched alkyl chains.^{12,13} Cycloaliphatic amines can be cured faster than poly(ether amines), but a disadvantage is that the resulting products are brittle.¹⁴ As aromatic amine derivatives cure slowly upon reacting with epoxy resins, they require high temperatures to form epoxy polymers. However, the cured polymers have a high glass-transition temperature (T_g) and good mechanical properties. Moreover, the polymers show high thermal stability and high activation energy of thermal decomposition, in addition to good adhesion onto substrates.^{15,16}

In this study, aromatic xylylene functional groups were introduced into an ethylene diamine derivative precursor to yield an amine hardener with multiaromatic functionalized amines as well as a flexible ethylene diamine linker. By dynamic mechanical analysis (DMA), flexural strength measurements, and micro-combustion calorimetry (MCC) methods, it was confirmed that the presence of xylylene groups leads to good mechanical properties, improved thermal stability, and excellent fire resistance.

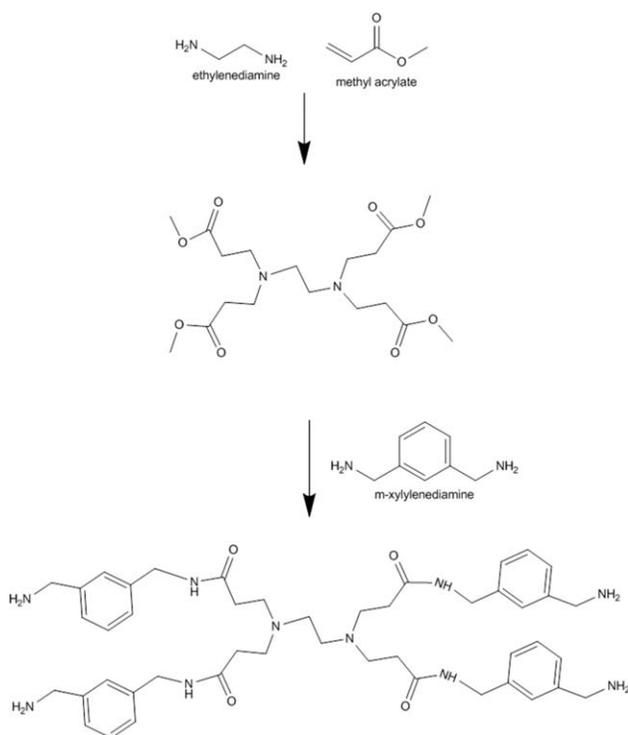


Figure 1. Reaction scheme for the synthesis of TEAT and EATP.

EXPERIMENTAL

Materials

Diglycidylether of bisphenol A epoxy resin (DGEBA, YD-128) with an epoxy equivalent weight (E.E.W.) of 187 g/eq was purchased from Kukdo Chemical Co. (South Korea, Seoul). Ethylene diamine, xylylene diamine, and methyl acrylate were obtained from Sigma-Aldrich (St. Louis, Missouri).

Preparation of Branched Amine Compound

A two-step reaction was carried out as shown in Figure 1. For step 1, 500 mL of methanol was taken in a 1 L three-neck round-bottom flask and placed in an ice bath. Then, 9.7 mL (0.14 mol) of ethylene diamine was added, followed by the dropwise addition of 60 mL (0.72 mol) of methyl acrylate for 1 h. The reaction was carried out for 3 days at 45 °C. Residual methanol and methyl acrylate were evaporated. Excess methanol was added to the obtained product, tetramethyl-3,3',3'',3'''-(ethane-1,2-diylbis(azanetriyl))tetrapropionate (TEAT), and evaporated three times to remove unreacted methyl acrylate. TEAT obtained as a liquid was analyzed using electrospray ionization mass spectrometer (ESI-MS), elemental analysis, and NMR and used in the second step without further purification.

¹H-NMR of TEAT [300 MHz, CDCl₃, δ (ppm)]: 3.67 (12H, s), 2.75 (8H, t), 2.49 (8H, t), 2.41 (4H, t). Elemental analysis for (C₁₈H₃₂N₂O₈) (calc'd) was C = 53.44 (53.46), H = 8.12 (7.92), N = 7.28 (6.93); and ESI-MS for (C₁₈H₃₂N₂O₈, mass + proton)⁺ was 405.2 *m/z*.

For step 2, TEAT (114 g, 0.282 mol) and xylylene diamine (186 mL, 1.41 mol) were stirred in a flask for 10 h at 80 °C. The unreacted xylylene diamine was evaporated in a rotary evaporator. The product, 3,3',3'',3'''-[ethane-1,2-diylbis(azanetriyl)]tetrakis[N-[3-(aminomethyl)benzyl]propanamide] (EATP), obtained as a liquid, was characterized using ¹H-NMR, ¹³C-NMR, and elemental analysis. EATP was used to prepare different epoxy compositions with bisphenol A epoxy resin, xylylene diamine, and varying concentrations of EATP.

¹H-NMR of TEAT [300 MHz, DMSO-d₆, δ (ppm)]: 8.46 (4H, s), 7.3-7.0 (16H, t), 4.24 (8H, t), 3.68-3.66 (16H, t), 2.72 (8H, t), 2.31 (4H, t). Elemental analysis for (C₄₆H₆₄N₁₀O₄) (calc'd) was C = 68.61 (67.29), H = 8.14 (7.86), N = 17.71 (17.06); and ESI-MS for (C₄₆H₆₄N₁₀O₄, mass + proton)⁺ was 821.5 *m/z*.

Preparation of Epoxy Compositions

The epoxy compositions were prepared by stoichiometrically mixing DGEBA and the curing agent, xylylene diamine, with different concentrations of EATP [5–30 parts per resin (phr)]. The equivalent ratio of epoxy versus curing agent is calculated by eq. (1), and the composition details are listed in Table I.

$$\frac{[100 \text{ g (epoxy resin)}]/[187 \text{ g (eq. of epoxy resin)}]}{\times 34.05(\text{AHEW}) \times \text{molar ratio}} \quad (1)$$

where AHEW is the amine hydrogen equivalent weight, and the molar ratio is 0.05, 0.1, 0.2, or 0.3. A mixture of xylylene diamine and EATP was stirred with a mechanical stirrer at 80 °C. Stirring was continued for an additional 20 min at 40 °C under vacuum. The amine compounds in the reactor were cooled to room temperature, followed by the addition of DGEBA, and stirred at 40 °C for 20 min under vacuum. The prepared epoxy compositions were poured into a metal mold and heated at 80 °C for 30 min, 110 °C for 1 h, and 140 °C for 1 h to complete the curing process. The heating parameters were based on differential scanning calorimetry (DSC), as shown in Figure 2 and Table II.

Characterization

The synthesized product, TEAT, was analyzed using ESI-MS for elemental analysis (EA, elemental analyzer, Flash 2000, Thermo Scientific, Waltham, MA) and ¹H-NMR Bruker Avance, 300 MHz spectrometer (Billerica, MA). EATP was analyzed by gas chromatography (GC, Agilent 7890A, DB-1 column, FID

Table I. Prepared Epoxy Compositions

Component	RF (reference)	XP5	XP10	XP20	XP30
Epoxy resin (g)	100	100	100	100	100
Xylylene diamine (g)	18.21	17.30	16.39	14.57	12.75
EATP (g)	— (0 phr)	2.74 (5 phr)	5.48 (10 phr)	10.97 (20 phr)	16.45 (30 phr)

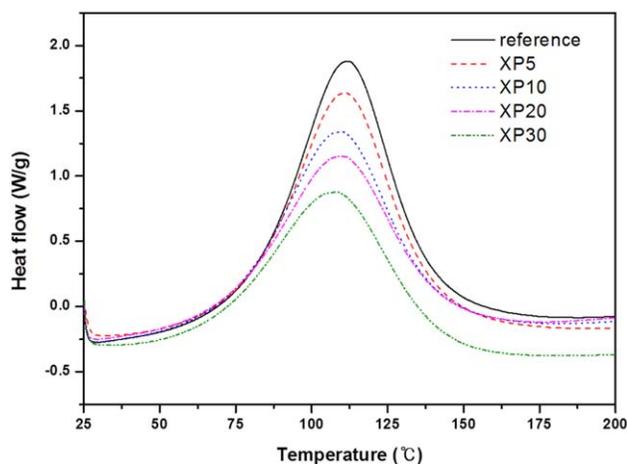


Figure 2. DSC curve of epoxy compositions. [Color figure can be viewed at wileyonlinelibrary.com]

detector, Wilmington, DE), elemental analysis, and FT-NMR. The reactivity of the epoxy compositions was monitored by DSC (Q-2000, TA Instruments, New Castle, DE). The temperature of the DSC instrument was increased at a heating rate of 10 °C/min from 25 to 300 °C to obtain the reaction enthalpy (ΔH) and peak temperature (T_{peak}) required to determine the optimum curing conditions. The flexural strength of the cured epoxy compositions was measured with a universal testing machine (UTM), as described by the ASTM D 790M method. The test specimens were molded to a size of 60 mm \times 25 mm \times 3 mm. The flexural strength test was repeated 10 times for each sample to obtain an average value. The thermal degradation activation energy of the epoxy compositions was measured by thermogravimetric analysis (TGA/Q-500, TA Instruments) under nitrogen gas with a heating rate of 2, 5, 10, and 20 °C/min. Dynamic mechanical analysis was carried out to measure the viscoelastic properties of the cured compositions with a Q-800 (TA Instruments). The test specimen was processed to a size of 60 mm \times 12 mm \times 3 mm and mounted on the dual cantilever probe of the Q-800. The test was performed at a heating rate of 2 °C/min from 25 to 250 °C at a frequency of 1 Hz and amplitude of 10 μ m to obtain the storage modulus, loss modulus, and $\tan \delta$ data. The thermal stability of each composition was measured by microcombustion calorimetry (FAA-PCFC, Fire Testing Technology, London, UK) in the temperature range of 250–650 °C to obtain the heat release rate (HRR).

Table II. Thermal Data for Epoxy Compositions Obtained by DSC Experiments

	RF (reference)	XP5	XP10	XP20	XP30
T_{onset} (°C)	73.88	72.26	70.48	68.63	65.31
T_{peak} (°C)	112.19	110.20	109.73	109.94	108.05
ΔH (J/g)	511.6	468.3	418.5	375.9	348.6

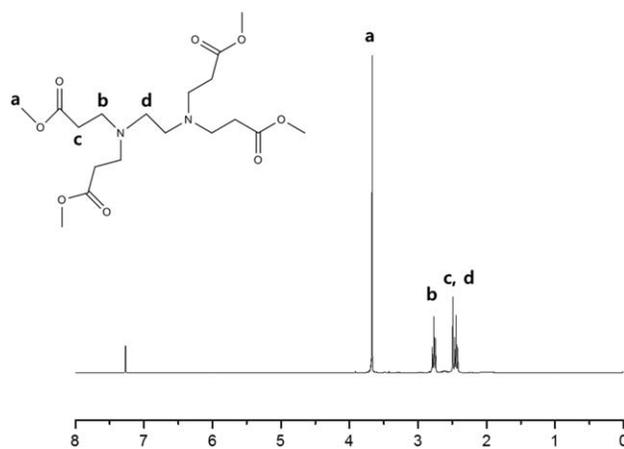


Figure 3. $^1\text{H-NMR}$ spectrum of TEAT.

RESULTS AND DISCUSSION

Structural Analysis of the Prepared Precursor and the Multifunctional Amine

The peak areas of the reactants (ethylene diamine and ethyl acrylate) and products in step 1 were monitored by GC with respect to time. The GC data showed four different peaks at the initial stages of the reaction. Although four ethyl acrylates are theoretically able to bind to one ethylene diamine, four peaks were observed at retention times of 51, 61, 63, and 68 min. When the reaction was allowed to progress further, all of the peaks disappeared except for the peak at 68 min. The ESI-MS data showed that the theoretical mass (+1) of TEAT is 405.2 m/z . As shown in Figure 3, TEAT was characterized by $^1\text{H-NMR}$ analysis.

The ESI-MS profile of EATP showed a peak at 821.5 m/z for the ideal mass (+1). In addition to $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ was used to better characterize the EATP. Individual peaks from both NMR studies are assigned in Figure 4.

Figure 5 shows a comparison between the FTIR spectra of TEAT and EATP, which indicates that the reaction was complete. The C=O amide peak of EATP appeared at 1650 cm^{-1} , whereas the C=O ester peak of TEAT at 1739 cm^{-1} disappeared. Also, the primary amine of EATP is observed at 3288 cm^{-1} , and the aromatic C–H bending modes were observed at 702, 788, and 800 cm^{-1} .

Thermal and Kinetic Studies of Epoxy Compositions

Figure 2 shows the DSC curves of the epoxy compositions at heating rates of 10 °C/min. The curing conditions of these epoxy compositions were determined by the T_{peak} values from these results. The T_{peak} of the compositions shifted from 112 °C (reference) down to 108 °C (XP30) in proportion to the concentration of EATP in the composition. The detailed information is collected in Table II.

The activation energy of each composition was calculated from T_{peak} obtained by DSC analysis when increasing the heating rate from 2 to 20 °C/min. The activation energies were obtained using Kissinger's equation and from the T_{peak} and heating rate values in eq. (2):

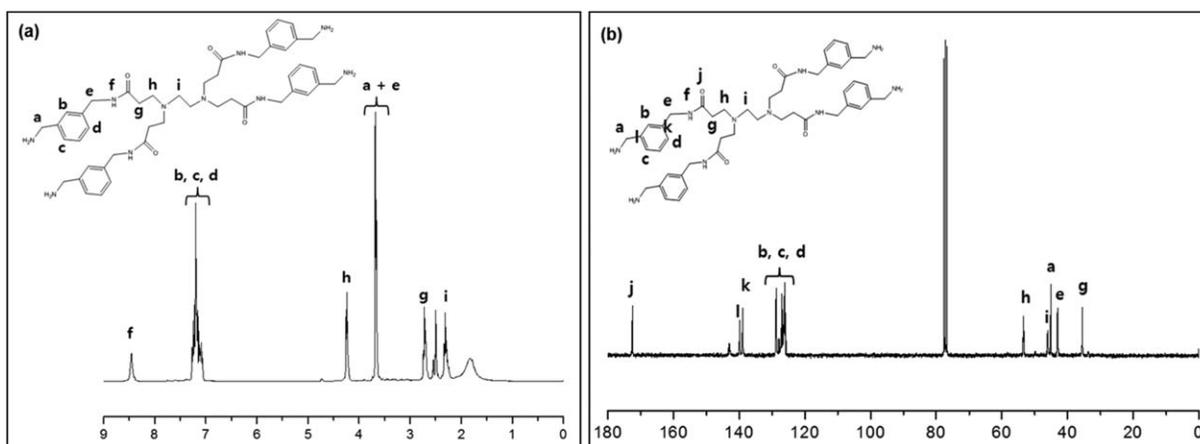


Figure 4. (a) ^1H -NMR spectrum of EATP; (b) ^{13}C -NMR spectrum of EATP.

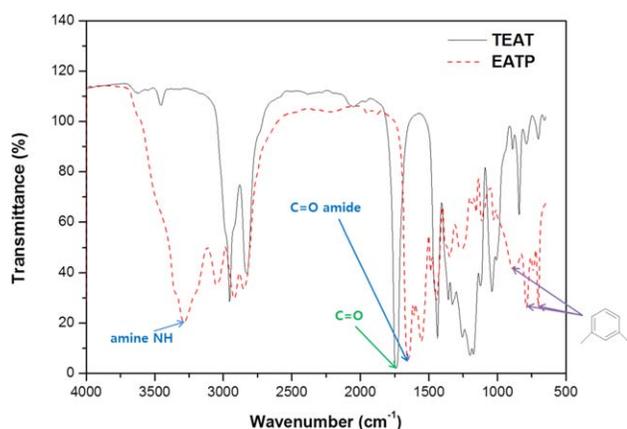


Figure 5. FTIR spectra of TEAT and EATP. [Color figure can be viewed at wileyonlinelibrary.com]

$$-\ln(\theta/T_{\text{peak}}^2) = E_a/RT_{\text{peak}} - \ln(AR/E_a) \quad (2)$$

where θ is the heating rate (K/min), A is the pre-exponential factor, R is the universal gas constant (J/K mol), and E_a is the

activation energy (kJ/mol). An example in Figure 6(a) shows a change in T_{peak} brought about by a difference in the heating rate. Figure 6(b) displays a straight line, the slope of which is the activation energy fitted by $-\ln(\theta/T_{\text{peak}}^2)$ versus $1/RT_{\text{peak}}$. The thermal data in Table III indicate that there is no substantial difference between the calculated activation energies (47.5–49.6 kJ/mol) for different concentrations of EATP.

Mechanical Properties of the Epoxy Compositions

The flexural strength of the cured epoxy compositions (Figure 7) increased in proportion to the concentration of EATP. Specifically, when 10% of EATP was added to the composition, the flexural strength showed the highest value of 115 MPa, which is >12% of that for the reference specimen. The results indicate that the four rigid xylylene amine groups of EATP provide stiffness and enhance the flexural strength. The crosslinking density of EATP measured by dynamic mechanical analysis decreased in proportion to the EATP concentrations, as shown in Table IV. This indicates that the multiamine functional groups do not significantly impair the rigidity of the epoxy polymer at room temperature. However, the internal soft ethylene diamine acryl

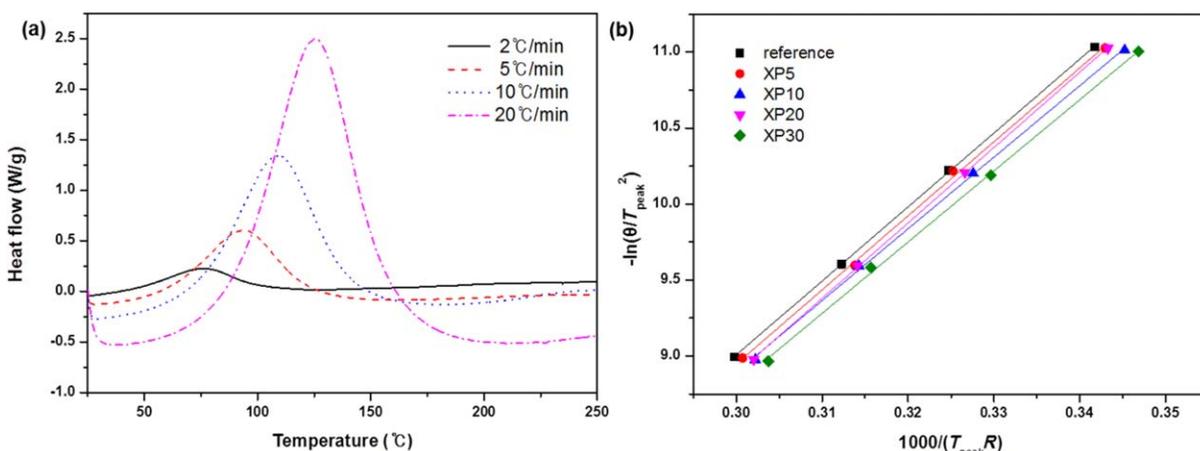
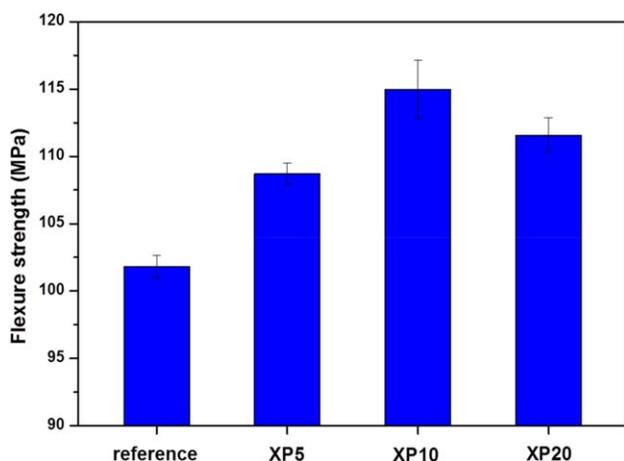


Figure 6. (a) T_{peak} change with different heating rates for XP10; (b) fitted line using the Kissinger equation, where $y = -\ln(\theta/T_{\text{peak}}^2)$, $x = 1/RT_{\text{peak}}$. [Color figure can be viewed at wileyonlinelibrary.com]

Table III. DSC Data for Epoxy Compositions

Sample	Heating rate (°C/min)				Activation energy (kJ/mol)
	2	5	10	20	
Reference	79.0	97.4	112.2	128.2	48.7
XP5	77.7	96.8	110.2	127.0	47.7
XP10	75.4	94.2	109.7	125.0	47.1
XP20	77.4	95.3	109.9	125.2	49.6
XP30	73.8	91.9	108.1	122.2	47.5

Under heating rate, data are T_{\max} (°C).

**Figure 7.** Flexural strength of epoxy compositions. [Color figure can be viewed at wileyonlinelibrary.com]

groups linked to four xylylene amines caused a decrease in the storage modulus. Moreover, the ethylene diamine acryl groups also reduced the $\tan \delta$, which is related to the glass-transition temperature (Table IV).

Viscoelastic Properties of Epoxy Compositions with DMA

The cured epoxy compositions were analyzed by DMA to observe the change in the storage modulus and $\tan \delta$, which represents the glass-transition temperature (T_g), as shown in Figure 8 and Table IV. The stiffness was increased with increasing EATP content, from 2257 (reference) to 2609 MPa for XP30 at 30 °C, because of the increase in the number of rigid xylylene groups in EATP. However, the storage modulus (E') of the epoxy compositions with higher concentrations of EATP showed

a decrease at lower temperatures in the range 80–140 °C near the transition from the glassy state to the rubbery state. With increasing temperature, the $\tan \delta$ values also decreased proportionally with increasing amounts of EATP. The decrease in T_g could be attributed to the decrease in the crosslinking density, as given by eq. (3)¹⁷:

$$\nu = Er/3RT \quad (3)$$

where ν is the crosslinking density, Er is the rubbery elastic storage modulus (MPa), T (K) is the absolute temperature corresponding to the measured storage modulus, and R is the ideal gas constant (L MPa/K mol). In the present study, the temperature corresponding to the rubbery region, T_r was chosen to be ($T_g + 40$ °C) for substitution in the equation. Table IV shows that the crosslinking density reduces from 1.19 for the reference sample (RF) to 0.66 for XP30 because of the bulky nature of the curing agent.

Therefore, as shown in Figure 8, the storage modulus of the networked polymer is high at room temperature, but reduces rapidly with an increase in temperature, due to its bulky and flexible geometry.

Analysis of Thermal Degradation Activation Energy by TGA

The thermal degradation activation energies of the epoxy compositions were calculated using the data obtained from TGA analysis, for the same samples at different heating rates from 2 to 20 °C/min. The change in T_{peak} due to the different heating rates was applied to the Kissinger equation [(eq. (4))¹⁸:

$$-\ln(\theta/T_{\text{peak}}^2) = E_a/RT_{\text{peak}} - \ln(nAR/W_m^{n-1}) \quad (4)$$

where θ is the heating rate, n is the apparent reaction order, R is the universal gas constant, T_{peak} is the temperature at which

Table IV. DMA Data for Epoxy Compositions Including EATP

Data	RF (reference)	XP5	XP10	XP20	XP30
E' at 30 (°C)	2257	2322	2339	2524	2609
E'' max (°C)	128.7	123.3	113.3	107.8	103.8
$\tan \delta_{\text{max}}$ (°C)	134.8	129.9	121.2	115.7	113.5
Crosslink density (mol/cm ³)	1.19	1.00	0.80	0.79	0.66

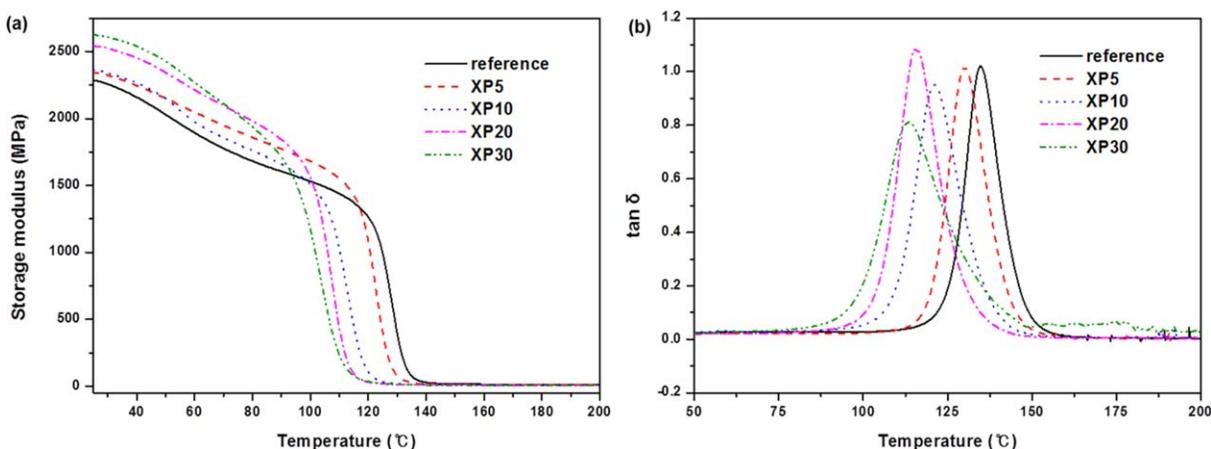


Figure 8. DMA data for epoxy compositions: (a) storage modulus and (b) $\tan \delta$. [Color figure can be viewed at wileyonlinelibrary.com]

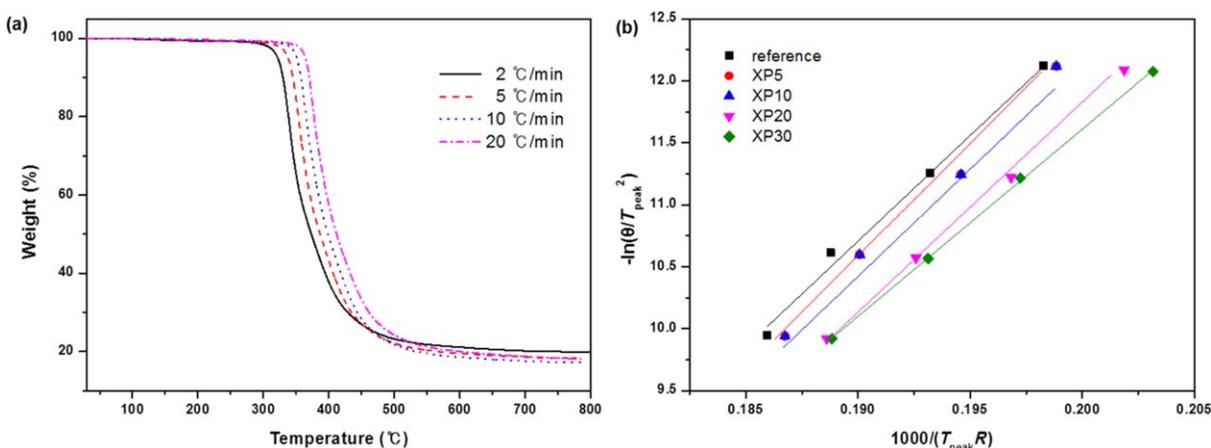


Figure 9. (a) TGA data for XP30 at different heating rates; (b) plot of $-\ln(\theta/T_{peak}^2)$ versus $1000/(RT)$ of epoxy compositions. [Color figure can be viewed at wileyonlinelibrary.com]

the maximum degradation rate occurs, A is the pre-exponential factor, and W_m is the weight of the sample at the maximum rate of weight loss. Therefore, the displayed slope between $-\ln(\theta/T_{peak}^2)$ and $1/RT_{peak}$ is the thermal degradation activation energy (Figure 9 and Table V). Based on the calculated activation energies, it is stated the thermal stability of the epoxy compositions increased when lower concentrations of EATP (≤ 10 phr) were added. However, when higher

concentrations of the flexible portion of the hardener (XP20 and XP30) were added, there was a drastic decrease in thermal stability.

Effect of EATP on Fire Resistance

As epoxy compositions have high resistance to fire, they are widely used in the automobile and aerospace industries. Heat release rate (HRR) is often used to predict the flammability or

Table V. Thermal Degradation Activation Energies Obtained by Kissinger's Equation by TGA

Sample	Heating rate (°C/min)				Activation energy (kJ/mol)
	2	5	10	20	
Reference	333.6	349.5	364.1	373.9	171.6
XP5	331.9	345.1	359.8	371.0	175.8
XP10	330.2	342.0	355.3	368.2	181.4
XP20	322.8	338.1	351.5	364.7	162.6
XP30	319.1	336.8	349.8	363.9	151.2

Under heating rate, data are T_{peak} (°C).

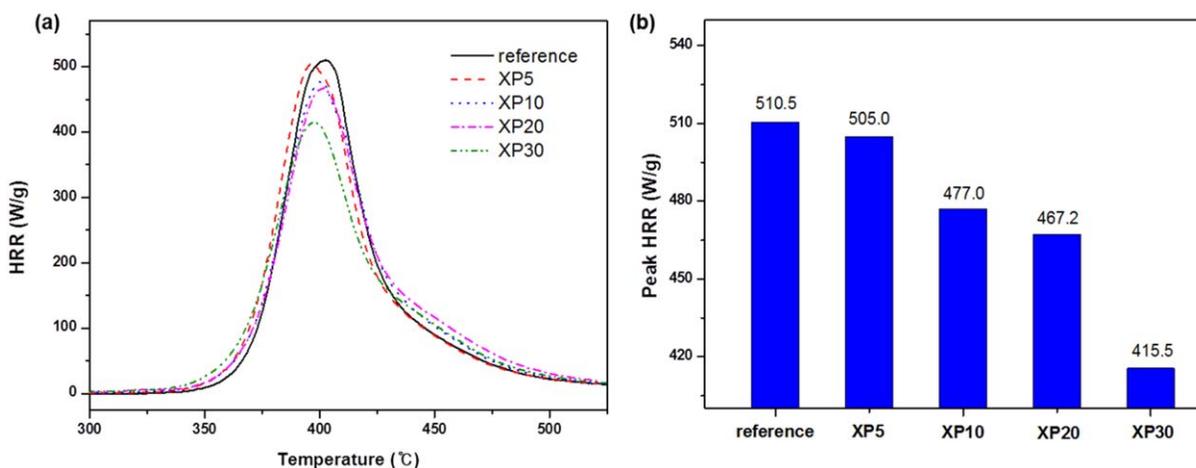


Figure 10. (a) HRR versus temperature of epoxy compositions; (b) peak HRR of epoxy compositions. [Color figure can be viewed at wileyonlinelibrary.com]

degree of fire hazard of a material in terms of reaction to fire (or flammability) rather than fire endurance.¹⁹ The variation in the HRR of epoxy compositions at different concentrations of EATP was analyzed using a microcalorimeter. A lower HRR is desirable since higher HRR values result in fire deaths caused by the release of toxic gases. Figure 10(a) displays the plot of HRR versus temperature, while Figure 10(b) shows the peak HRR of the samples. The data reveal that lower peak values of HRR are obtained for higher concentrations of EATP in epoxy compositions. Therefore, the addition of aromatic amines to ethylene diamine provides a geometry favorable for lowering the flammability values for not only EATP but also epoxy compositions with EATP.

CONCLUSIONS

In this study, a branched amine modified with xylylene diamine was synthesized via a two-step reaction. The structures of the prepared products were analyzed with FTIR, ¹H-NMR, and ¹³C-NMR. Furthermore, the final branched amine product was added to epoxy compositions and cured respectively for the tests of their physical properties and thermal heat resistance. As found by DSC, the activation energies of the epoxy compositions with EATP are in the range of 47.5–49.6 kJ/mol. Moreover, the thermal degradation activation energies of the compositions were carried out with TGA. The results show that the thermal stability of the compositions increases until the amount of EATP is increased to 10%, but decreases as the amount of EATP added exceeds 10%. The compositions including 10% or less than 10% of EATP show an increase in flexural strength, while the glass-transition temperature ($\tan \delta$ obtained by DMA) decreases in proportion to the amount of EATP added. However, the HRR data confirmed that the flammability of the compositions decreased with increasing amounts of EATP.

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