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Synthesis of novel bisphenol containing phthalazinone and azomethine moieties and thermal properties of cured diamine/bisphenol/DGEBA polymers

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Abstract

A novel bisphenol(1,2-dihydro-2-(4-((4-hydroxy)phenyliminomethylidene)phenyl)-4-(4-((4-(4-hydroxy)phenyliminomethylidene)phenoxy)-phenyl)(2H)phthalazin-1-one, DPP) and a diamine(1,2-dihydro-2-(4-aminophenyl)-4-(4-(4-aminophenoxy)phenyl)(2H)phthalazin-1-one, DAP) were synthesized and characterized. The novel epoxy polymers containing phthalazinone and/or azomethine moieties were prepared by binary polymerization of DAP (or DPP) with diglycidyl ether of biphenyl A (DGEBA) and ternary polymerization of hybrid curing agents, DAP/DPP (DAP and DPP under different molar ratios) with DGEBA. The cure behaviors of these new epoxy systems were studied by dynamic differential scanning calorimeter (DSC) and Infrared (IR) scans. Especially, the activation energy of DAP/DGEBA calculated by Kissinger and Ozawa methods were 73.8 and 77.4 kJ/mol, respectively. For ternary epoxy system, it was found that hybrid curing agents of DAP/DPP exhibited significant associated effect on their reactivity towards the oxirane group. Glass transition temperatures (T_g's) of these new epoxy polymers were all above 150 °C from the results of DSC, and the initial thermal decomposition temperatures ($T_{d,5\%}$'s) and integral procedure decomposition temperatures (IPDT's) of these new epoxy polymers are above 350 and 850 °C, respectively from results of thermogravimetric analyses (TGA). These results show that new epoxy polymers containing phthalazinone and/or azomethine moieties exhibited excellent thermal properties. Especially, thermal properties of the ternary epoxy polymers could be modified by changing the content of DAP and DPP. The linear relationships between char yield ($Y_{c,wt\%}$) and the structural compositions of these new polymers (weight percentage of phthalazinone, azomethine and nitrogen, C/H weight ratio) were built.

Keywords: Nitrogen-containing epoxy polymer; Curing agent; Cure behavior

1. Introduction

Epoxy resins are widely used in industrial applications because of their great versatility, low shrinkage, good chemical resistance, outstanding adhesion and high-grade electrical insulation [1], but most of epoxy resins cannot meet the requirement of the advanced composite materials because they have not excellent overall properties such as thermal properties, toughness, flame-resistance as well as environmental consistency. Although halogen-containing epoxy resins are presently widely used for circuit board applications for their excellent flame retardancy, they have lower thermal properties and encounter a series of problems during decomposition or incineration, such as release of toxic, corrosive and halogenated gases as well as endocrine-disrupting chemicals [2,3]. Nowadays, people have to search or design new halogen-free flame-retardant epoxy systems with balanced properties [4].

Among all routes adopted up to now, two methods have been focused. One is covalent incorporation of phosphorus [5–23], and nitrogen [13,24–29] into the backbone of epoxy polymers. Phosphorus-containing epoxy polymers, which were studied intensively by Wang and Liu et al. [6–18,20], exhibit high flame retardancy, however, in general, the higher the content of phosphorus, the lower the thermal stability. Moreover, they also cause debatable environmental problems. These defects might not meet the requirement of the advanced composite materials. Nitrogen-containing flame-retardants [19] are gradually attracting greater attention because they have excellent heat-resistance, especially for the epoxy polymers containing triazine [13,25] or isocyanurate structures

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[24,26]. Furthermore, they are regarded as environmental consistency [19]. Thus, covalent incorporation of nitrogen into epoxy systems might be an effective method for high-performance epoxy polymers. The other halogen-free flame-retardant epoxy systems is inherently flame-retardant epoxy polymers [30], which contain highly aromatic bisphenols [31,32] or double bonds capable of undergoing Diels–Alder reaction [33,34], demonstrate excellent heat and flame-resistance, because these structures are favorable for formation of char residue and make limited oxygen index value (LOI) increase dramatically. These epoxy polymers may truly be called 'green materials' due to no additional flame-retardant elements in their structure. Thus, combination of the advantages of nitrogen and multiple-aromatic structures might be a new and effective way to develop the advanced epoxy-based composite materials.

Based on above concepts, two kinds of high nitrogen-containing multiple-aromatic structures (phthalazinone and azomethine linked by aromatic rings) were introduced into epoxy polymers to improve the thermal properties, one was a novel bisphenol, 1,2-dihydro-2-(4-((4-hydroxy)phenyliminomethylidene)phenyl)-4-(4-((4-(4-hydroxy)phenyliminomethylidene)phenoxy)phenyl)(2H)phthalazin-1-one (DPP), the other was a diamine, 1,2-dihydro-2-(4-aminophenyl)-4-(4-(4-aminophenoxy)phenyl)(2H)phthalazin-1-one (DAP). Both of them were synthesized from phenolphthalein and firstly used as curing agents for diglycidyl ether of biphenyl A (DGEBA). New epoxy polymers containing phthalazinone and/or azomethine structure were prepared by binary polymerization of DAP (or DPP)/DGEBA and ternary polymerization of DAP/DPP/DGEBA. We expected to develop high-performance epoxy polymers in a variety of properties by changing the content of ternary components, whose ingredients were easy to obtain in practice. The thermal properties of these new polymers such as glass transition temperature (T_g), 5 wt% decomposition temperature ($T_{d,5\%}$), char yield (Y_c wt%) and integral procedure decomposition temperature (IPDT) were intensively studied by DSC and TGA.

2. Experimental

2.1. Materials

All reagents and solvents were reagent-grade. Phenolphthalein, *p*-chloronitrobenzene, 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl ether (DDE) and 4,4′-diaminodiphenyl sulphone (DDS), 4-hydroxybenzaldehyde, hydroxylamine, hydrazine hydrate (85 wt% water solution) were used without purification. 1,4-Dioxane, dimethylformamide (DMF), dimethylsulphoxide (DMSO) were purified by standard methods before use. The liquid epoxy resin used in this study was a diglycidyl ether of biphenyl A (DGEBA, commercial name: NPEL-127E) from Nan Ya plastics of China with an equivalent epoxy molecular weight of 180 g/equiv.

2.2. Instrumentation

Infrared spectra were recorded by Vector 22 FTIR spectrophotometer (KBr pellet). ^{1}H NMR, ^{13}C NMR and ^{1}H–^{13}C COSY NMR were obtained with an Avance DMX 500 NMR spectrometer at 35 °C using DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed on a Flash EA1112 CHN–O-Rapid elemental analyzer using acetanilide as a standard. The melting point of monomers was determined by DSC method (Perkin–Elmer DSC 7 thermal analyzer) under a N_2 atmosphere at a heating rate of 10 °C/min. DSC scans for kinetics of DAP/DGEBA system (3.0–5.0 mg) were also conducted on the same thermal analyzer at heating rates of 5, 10, 15, and 20 °C/min, and N_2 was used as the carrier gas at a flow of 40 ml/min. Thermogravimetric analyses (TGA) were carried out on a Perkin–Elmer Pyris 1 under a N_2 atmosphere at a heating rate of 10 °C/min from 50 to above 850 °C.

2.3. Synthesis of diamine and bisphenol

2.3.1. Synthesis of 1,2-dihydro-4-hydroxyphenyl(2H)phthalazin-1-one (DHP)

The monomer DHP was synthesized from phenolphthalein by the method reported previously [35,36] (Yield 82%; mp 309–311 °C).

IR (KBr, cm^{-1}): 3150–3300 (N–H, O–H), 1644 (C=O), 1615 (C=N). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 12.742 (s, N–H), 9.811 (s, O–H), 8.342–8.325 (d, 1H), 7.874–7.906 (m, 2H), 7.730, 7.747 (d, 1H), 7.403, 7.420 (d, 2H), 6.926, 6.943 (d, 2H). Elemental analysis: $C_{14}H_{10}O_2N_2$ (238.246). Calcd C, 70.58%; H, 4.23%, N, 11.77%. Found: C, 70.47%; H, 4.37%, N, 11.88%.

2.3.2. Synthesis of 1,2-dihydro-2-(4-nitrophenyl)-4-(4-(4-nitrophenoxy)phenyl)(2H)phthalazin-1-one (DNP)

The compound DNP was synthesized by the reaction of DHP (23.8 g, 0.10 mol) and *p*-chloronitrobenzene (34.6 g, 0.22 mol) in DMF (150 ml) in the presence of potassium carbonate (31.0 g, 0.22 mol). The mixture was heated to 145–150 °C under a N_2 atmosphere and kept about 8–10 h. After cooling to the room temperature, the mixture was poured into the mixture of water/ethanol (50:50, v/v), filtered to give a yellow solid product and then recrystallined from ethanol (Yield 95%; mp: 236–237 °C).

IR (KBr, cm^{-1}): 1682 (C=O), 1513, 1345 (–NO_2), 1100–1300 (Ar-O-Ar). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 8.670 (d, 1H), 8.380, 8.361 (d, 2H), 8.276, 8.295 (d, 2H), 8.099, 8.118 (d, 2H), 7.896–7.917 (m, 2H), 7.853 (d, 1H), 7.735, 7.753 (d, 2H), 7.285, 7.302 (m, 2H), 7.160, 7.177 (d, 2H). Elemental analysis: $C_{26}H_{16}O_6N_4$ (480.436). Calcd C, 65.00%; H, 3.36%, N, 11.66%. Found: C, 65.17%; H, 3.37%, N, 11.71%.

2.3.3. Synthesis of 1,2-dihydro-2-(4-aminophenyl)-4-(4-(4-aminophenoxy)phenyl)(2H)phthalazin-1-one (DAP)

The obtained dinitro compound DNP 48.0 g (0.10 mol), 1.50 g Iron (III) chloride, 1.50 g active carbon and 300 ml

1,4-dioxane were introduced into a 1000 ml three-necked flask, then hydrazine hydrate (85 wt%, 60 ml) was added into the solution dropwise during 1 h period at 90 °C. After the addition was complete, the reaction was continued for another 4 h at reflux temperature. The mixture was filtered, and the product was obtained as pale yellow crystals from 1,4-dioxane/water (Yield 96%; mp 261–262 °C).

IR (KBr, cm^{-1}): 3460, 3406, 3367, 3338, 3229 (–NH_2), 1655 (C=O), 1622 (–NH_2), 1100–1300 (Ar-O-Ar). H NMR (500 MHz, DMSO-d_6, ppm): 8.407–8.390 (m, 1H), 7.910–7.924 (t, 2H), 7.752, 7.770 (d, 1H), 7.567, 7.583 (d, 2H), 7.242, 7.259 (d, 2H), 6.995, 7.012 (d, 2H), 6.838, 6.637 (d, 2H), 6.620, 6.637 (d, 4H), 5.293, 5.026 (s, 4H, NH_2). Elemental analysis: $C_{26}H_{20}O_2N_4$ (420.472). Calcd C, 74.27%; H, 4.79%, N, 13.33%. Found: C, 74.35%; H, 4.81%, N, 13.37%.

2.3.4. Synthesis of 1,2-dihydro-2-(4-(4-hydroxy)phenyliminomethylidene)phenyl)-4-(4-((4-(4-hydroxy)phenyliminomethylidene)phenoxy)phenyl)(2H)phthalazin-1-one (DPP)

DAP (42.1 g, 0.1 mol), 4-hydroxybenzaldehyde (24.4 g, 0.2 mol) and a catalytic amount of $ZnCl_2$ were dissolved in dry DMF (150 ml). The reaction mixture was stirred at 100 °C for 8 h, and then was poured into water (300 ml). The precipitate was collected by filtration and washed thoroughly by 95% ethanol (Yield: 95%, mp: 304–306 °C).

IR (KBr, cm^{-1}): 3369 (Ar-OH), 1646 (C=O), 1626 (C=N), 1235 (Ar-O-Ar, Ar-OH). ^1H NMR (500 MHz, DMSO-d_6, ppm): 10.153 (s, 2H, –OH), 8.500, 8.529 (d, 2H, CH=N), 8.449–8.462 (d, 1H), 7.976 (m, 2H), 7.776–7.823 (m, 5H), 7.694–7.726 (t, 4H), 7.316–7.341 (m, 4H), 7.153–7.190 (m, 4H), 6.890–6.921 (m, 4H). Elemental analysis: $C_{40}H_{28}O_4N_4$ (628.668). Calcd C, 76.42%; H, 4.49%, N, 8.91%. Found: C, 76.55%; H, 4.40%, N, 8.99%.

2.4. Preparation of samples for DSC and TGA

For binary curing system, the curing agent (DAP, DPP, DDS, DDM or DDE) was mixed with DGEBA at an equivalent molar ratio of 1:1. All diamines could mix very well with DGEBA under vigorous stirring at 120 °C. DPP was pulverized to fine powder, mixed with DGEBA under vigorous stirring at 100 °C. All samples were preserved in the refrigerator (−10 °C) for DSC test.

For ternary curing system, the hybrid curing agents DAP/DPP were prepared in various molar ratios (2, 1.5, 0.5, 0.3 and 0.125, corresponding molar ratio of reactive hydrogen of DPP, DAP and epoxy group are 8:2:10, 6:4:10, 5:5:10, 4:6:10 and 2:8:10, respectively, and denoted as AP1, AP2, AP3, AP4 and AP5, respectively). Desired amount of AP series and DGEBA were dissolved in DMF under 60 °C, and then mixture was vacuum dried at ambient temperature to obtain ternary systems. All samples were kept in the refrigerator (−10 °C) for DSC test.

Because it is difficult that DPP dissolves in DGEBA, prepolymerization of samples containing DPP is necessary. The procedure is as following: sample was dissolved in a small quantity of DMF (weight ratio of sample/DMF is about 1:1), heated to 150 °C under stirring. With the evaporation of DMF, the transparent sample was obtained. All these prepolymers were cured at 160 °C for 1 h and 200 °C for 2 h, the resulting polymers were used as samples for thermal properties analyses.

3. Results and discussion

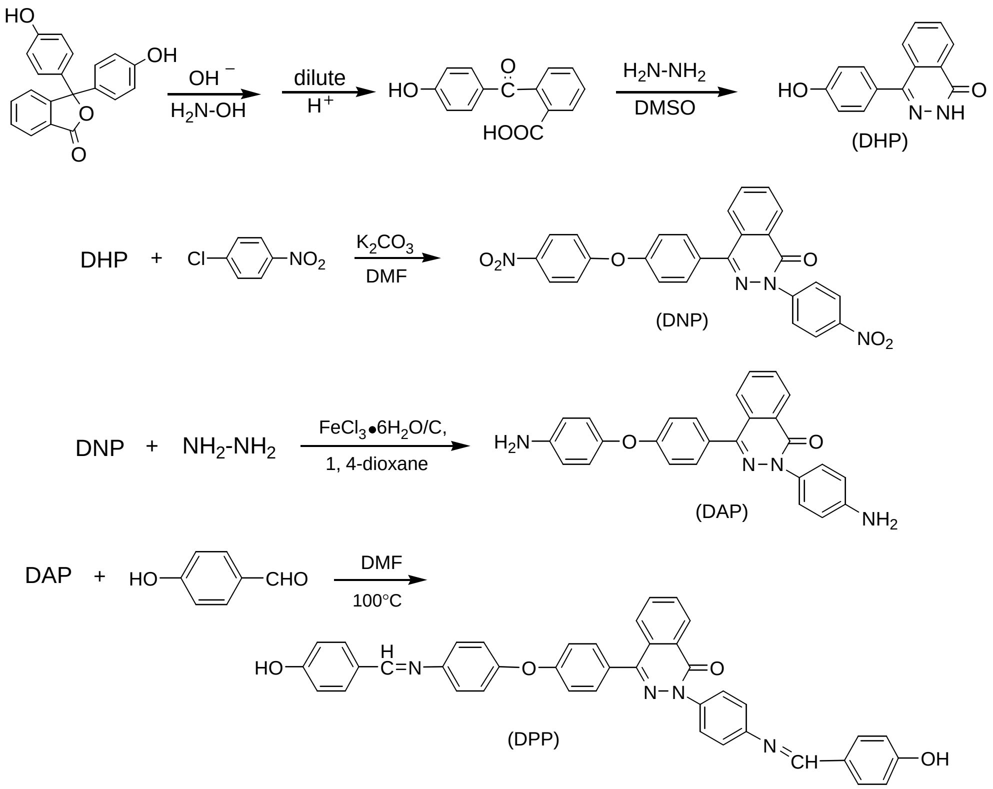
3.1. Synthesis and characterization

DHP, which has unsymmetrical heterocyclic bisphenol-like structure, was synthesized from phenolphthalein by two steps according to the methods described by Hubacher [35] and Hay [36], respectively (Scheme 1). In their reports, sulfolane was used as the solvent in the second step of 2-(4-hydroxybenzoyl)-benzoic acid with hydrazine monohydrate. In our experiment, we found DMSO could substitute sulfolane in this step without any loss of yield. The structure of DHP was proved by the results of IR, NMR and elemental analysis and consistent with literatures [36].

DAP, a diamine containing unsymmetrical phthalazinone structure, was synthesized first by Cheng et al. [37] and used as the materials for high-performance polyamides and polyimide with high strength and excellent thermal stability. In our study, DAP was synthesized by two steps: one was condensation of DHP with 4-chloronitrobenzene in the presence of potassium carbonate in DMF at 145–150 °C for about 8–10 h, it gave corresponding dinitro compound, DNP (Scheme 1). The other was reduction of DNP using NH_2–NH_2/$FeCl_3\cdot 6H_2O$ /reactive-C system in reflux 1,4-dioxane. We found NH_2–NH_2/$FeCl_3\cdot 6H_2O$/reactive-C system was an easy-prepared and effective reduction system for this reaction compared to the NH_2–NH_2/Pd–C system. The product DAP was recrystallized from DMF/H_2O (50:50, v/v). The results of IR, NMR and elemental analysis proved that the structures of DNP and DAP consisted with literatures [37].

A novel bisphenol, DPP, which contains phthalazinone moiety and azomethine linked by aromatic structure (Ar-CH=N–Ar), was first synthesized by the nucleophilic addition reaction of DAP and 4-hydroxybenzaldehyde in the presence of $ZnCl_2$ in DMF. The structure of this novel bisphenol was detailedly confirmed by FTIR, ^1H NMR, ^{13}C NMR, ^1H–^{13}C COSY NMR and elemental analysis.

The IR spectrum (Fig. 1) of this novel bisphenol exhibits the characteristic azomethine absorption in 1626 cm^{-1} and hydroxyl absorption in 3369 cm^{-1}. Fig. 2 shows the ^1H NMR spectrum of this novel bisphenol. The chemical shifts of protons belonging to OH and CH=N are in 10.153 and 8.500–8.529 ppm, respectively and consisted with other bisphenol containing azomethine structure [38,39]. Figs. 3 and 4 are the ^{13}C NMR and ^1H–^{13}C COSY (^1H, ^{13}C correlation spectroscopy) NMR spectra of DPP, respectively. Due to lots of carbon in the structure of DPP, the assignments in Fig. 3 are aided by the ^1H–^{13}C COSY NMR spectrum (Fig. 4). In a 2D NMR spectrum, it is common to plot the proton spectrum of DPP being studied along one axis and the carbon spectrum along the other axis. Each intensity spot on the two-dimensional plot indicates a carbon atom that bears the



Scheme 1. Synthetic routes of curing agents containing phthalazinone and/or azomethine moiety.

corresponding protons, whereas a carbon that has no hydrogen, such as a tertiary carbon (C1, C4, C9-11, C14, C17, C20, C25, C28, C31, C34, C39 and C42 in Fig. 3), does not have any spot in the ^{1}H–^{13}C COSY NMR spectrum. All the correlations were checked, and the assignments of all peaks are consistent with the structure of DPP.

From the viewpoint of molecular structure, DAP and DPP contain fairly a lot of aromatic rings as well as aromatic ether bonds, it will ensure improvement of thermal properties without decrease of toughness. At the same time, the presence of thermo-stable phthalazinone and/or azomethine moieties and their high nitrogen content (13.37 wt% for DAP and 8.91 wt% for DPP, respectively) will favor thermal stability and flame retardancy as well.

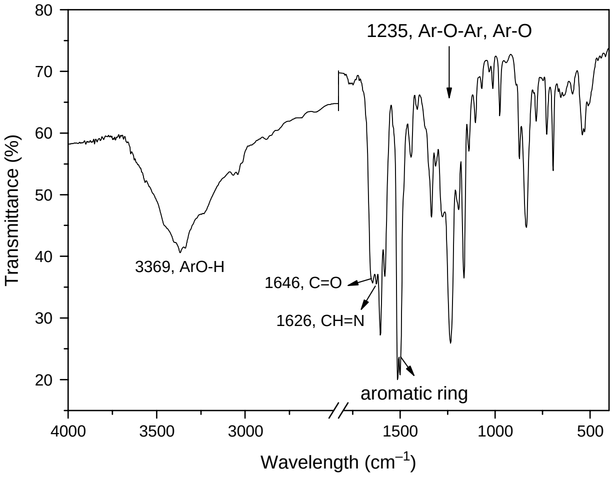


Fig. 1. IR spectrum of DPP.

3.2. Curing behaviors of DAP/DGEBA

The curing reaction of DAP/DGEBA was studied intensively by dynamic DSC and FTIR scans. Fig. 5 shows the dynamic DSC thermograms of DAP/DGEBA curing reaction at heating rate of 5, 10, 15 and 20 °C/min. It is seen that the cure exotherm shifts to higher temperatures with increasing heating rate. The temperature at which the maximum conversion rate occurs in the DSC curve (T_p) has a good linear correlation with different heating rates (the linear relation coefficient is 0.99) and the extrapolated at zero heating rate T_p is 160.3 °C which can be regarded as the suitable curing temperature for DAP/DGEBA. The DSC exothermic peak of DAP/DGEBA is very similar to that of other common aromatic diamine/DGEBA systems such as DDS/DGEBA and this curing system might be directly applied to the industrials.

To evaluate the kinetic parameters of DAP/DGEBA system, Kissinger [40] and Ozawa [41] methods were applied to calculate activation energy (E_a) because they are very simple ways to deal with the dynamic cure process of epoxy–amine system. The kinetic parameters obtained from these methods need not consider the heating rate, side reactions as well as the choice of the baseline.

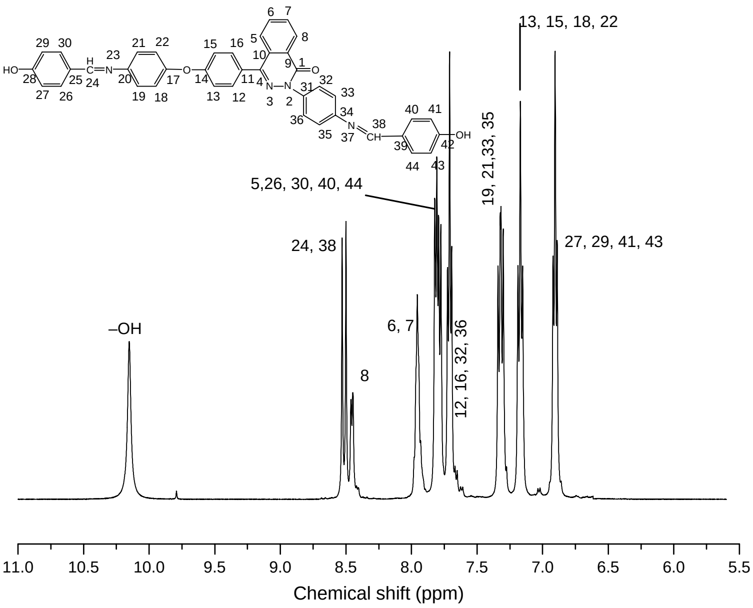


Fig. 2. ^{1}H NMR spectrum of DPP.

The Kissinger expression gives

$$-\ln\left(\frac{\varphi}{T_{\mathrm{p}}^{2}}\right)=\frac{E_{\mathrm{a}}}{RT_{\mathrm{p}}}-\ln\frac{AR}{E_{\mathrm{a}}} \tag{1}$$

where T_{p} is the temperature at which the maximum conversion rate occurs in the DSC curve, φ, A and R are heating rate, Arrenihus constant and ideal gas constant, respectively. Ozawa's equation can be expressed as follows

$$\ln\varphi=-1.052\frac{E_{\mathrm{a}}}{RT_{\mathrm{p}}}+\ln\frac{AE_{\mathrm{a}}}{R}-\ln f(\alpha)-5.331 \tag{2}$$

$f(\alpha)$ is a conversion-dependant function. The activation energy value (E_{a}) obtained from the slope of the $-\ln(\varphi/T_{\mathrm{p}}^{2})$ vs $1/T_{\mathrm{p}}$ plot and $-\ln\varphi$ vs $1/T_{\mathrm{p}}$ plot (Fig. 6) for this system are 73.8 and 77.4 kJ/mol, respectively, and these values are higher than the results of other common aromatic diamine-epoxy systems such as DDS/DGEBA systems (around 62–69 kJ/mol) [42]. It implies that DAP has low reactivity towards epoxy group and might be useful in tailoring the processing factors in the manufacturing process.

DSC method can only reflect the change of reaction indirectly through the collection of heat and thus there is a hysteresis in time while FTIR measurement provides a direct, real-time analysis of curing reaction that is widely interpretable in term of chemical structure [43].

Fig. 7(a) shows the infrared spectra of the DAP/DGEBA mixture in the range of 800–1700 cm^{-1}, which was heated in a

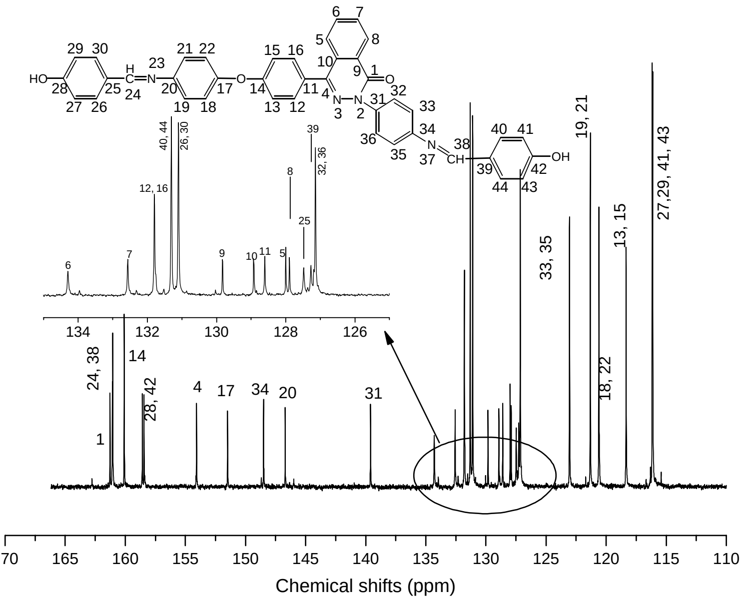


Fig. 3. ^{13}C NMR spectrum of DPP.

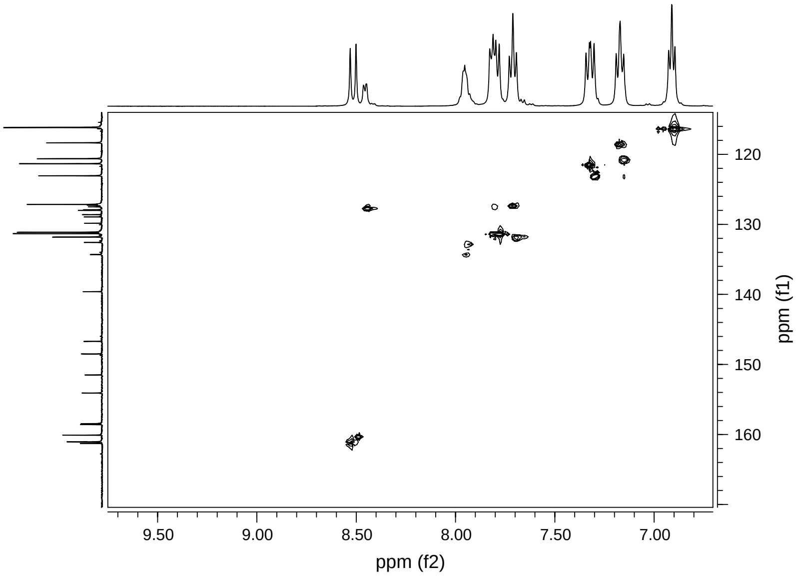


Fig. 4. ^1H–^{13}C COSY NMR spectrum of DPP.

heating rate of 20 °C/min and captured by real-time scanning of IR. One can clearly observe that intensities of peak at 915 cm^{-1}, the characteristic asymmetrical vibration of oxirane ring, sharply decrease with increasing cure temperature and finally disappear at about 300 °C. Moreover, the peaks at 1600–1630 cm^{-1} (in-plane bending vibration of –NH_2 of DAP, 1622 cm^{-1}, and herein is covered partly by the vibration peaks of aromatic and phthalazinone ring) become 'thin' with increasing cure temperature because of the disappearance of amine with increasing of temperature. From Fig. 7(b), one can see that five peaks in 3200–3500 cm^{-1} (stretching vibration of –NH_2) of the uncured DAP/DGEBA become a wide peak, and shift to higher wave numbers gradually. It indicates that the amine group disappears and the generated secondary hydroxyl groups form due to the cleavage of the oxirane rings. From the results of in situ FTIR determination, the formation of crosslinking points in the curing process of DAP/DGEBA system mainly ascribes to the reaction of amine and oxirane group.

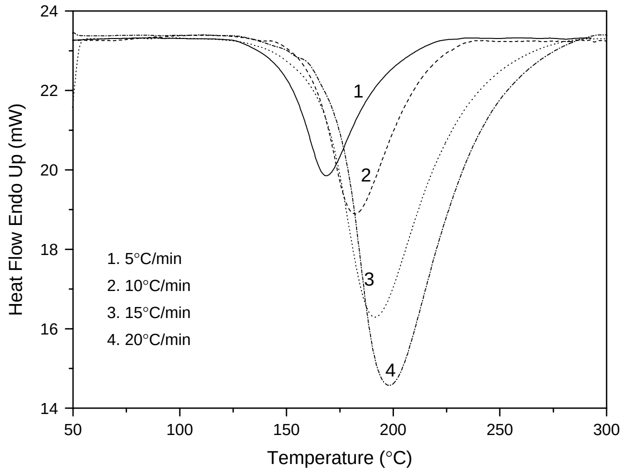


Fig. 5. Dynamic DSC thermograms of the DAP/DGEBA reactions at heating rates of 5, 10, 15 and 20 °C/min under N_2.

3.3. Cure behaviors of DAP/DPP/DGEBA system

It is well known that the curing procedures for thermally curing epoxy resins based on various compositions are often determined from the DSC exothermic peaks. Moreover, the position and area of exothermic peak also represent the reactivity of the compositions under thermal curing. Herein,

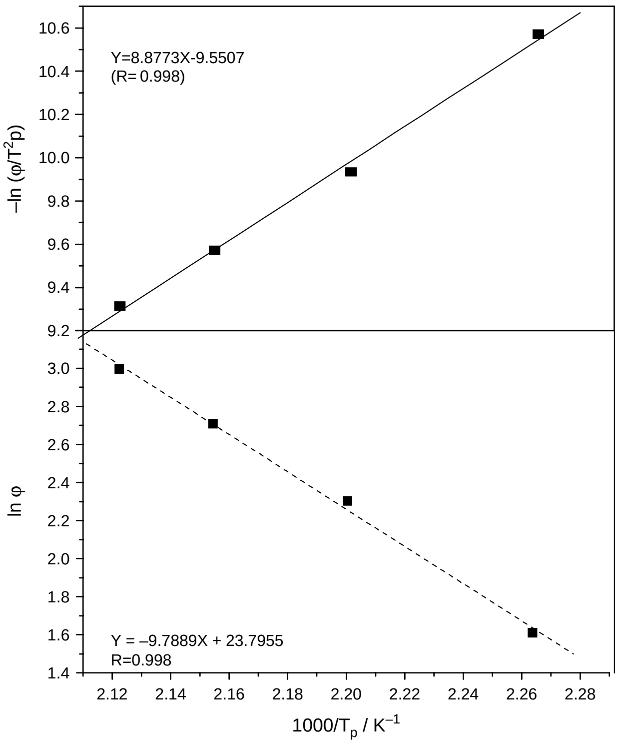


Fig. 6. The plots of $-\ln(\varphi/T_p^2)$ vs $1/T_p$ and $\ln\varphi$ vs $1/T_p$ for DAP/DGEBA curing reaction at various heating rates.

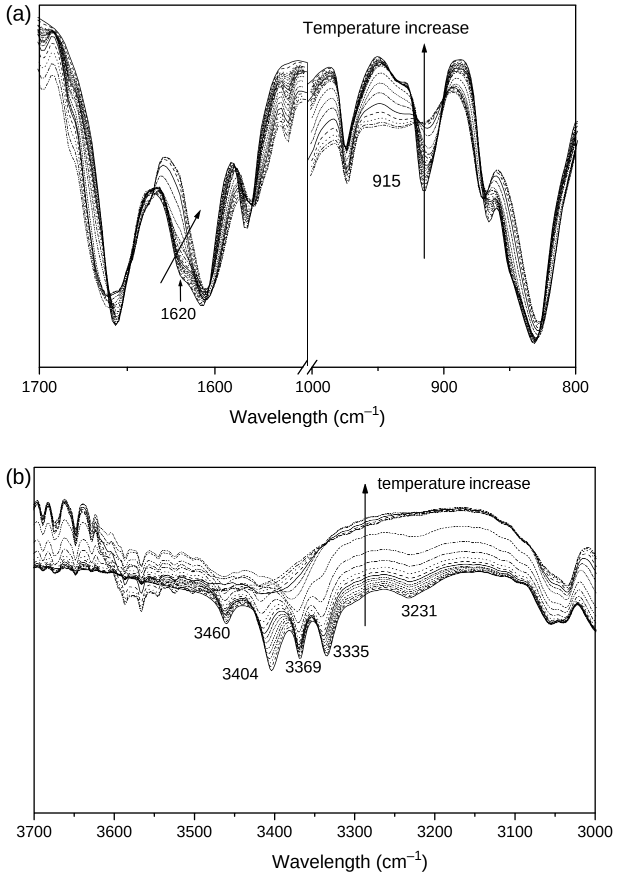


Fig. 7. FTIR in situ spectrum of DGEBA/DAP curing reaction in a heating rate of 20 °C/min. (a) 800–1700 cm^{-1}; (b) 3000–3700 cm^{-1}.

DAP and DPP were blended in a given molar ratio and used as hybrid curing agents for DGEBA, and the cure behaviors of ternary polymerization system consisting of DAP, DPP and DGEBA (AP1–AP5 /DGEBA) were evaluated by dynamic DSC scans at a heating rate of 15 °C/min under nitrogen.

As shown in Fig. 8, the DSC exothermic peak of the DPP/DGEBA (curve b) is so wide and irregular (from about 170 to 300 °C), and T_p is about 220 °C. It means that this reaction is complicated and DPP seems very difficult to react with oxirane group. Decrease of the reactivity of hydroxyl group towards oxirane group might result from the steric hindrance due to high melting point of DPP and its poor solubility in DGEBA. This deduction is supported by the fact that a small endothermal peak exists near the melting point of DPP (about 307 °C in curve b), which infers that DPP could not dissolve well in DGEBA.

It is interesting that 2-methylimidazole could accelerate the polymerization of DPP and DGEBA. The DSC exothermic peak (from about 100 to 180 °C, Fig. 8, curve a) and T_p (154 °C) of the DPP/DGEBA/2-methylimidazole (0.15% weight of sample) are narrower and lower than those of DPP/DGEBA, respectively, and that no endothermal peak appears at high temperature implies that DPP could polymerize with DGEBA completely in the presence of 2-methylimidazole. This is because the curing reaction of DPP/DGEBA was accelerated dramatically by 2-methylimidazole and a great deal of reaction heat were released in a short time, which made the temperature of the curing system increased dramatically and DPP dissolved in DGEBA very well and then reacted with DGEBA completely.

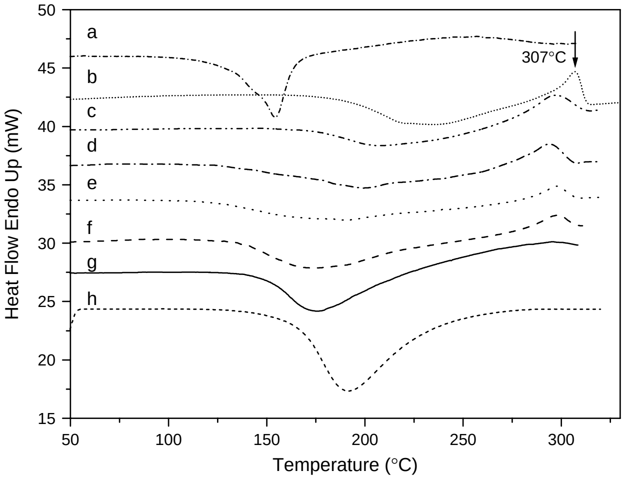


Fig. 8. The DSC thermograms of DGEBA cured with (a) DPP/2-methylimidazole (0.15% weight of DPP and DGEBA); (b) DPP; (c) AP1; (d) AP2; (e) AP3; (f) AP4; (g) AP5 and (h) DAP under N_2 at a heating rate of 15 °C/min.

Both the starting curing temperatures and T_ps of the ternary systems (Fig. 8 curves c–g) shift to low temperatures with increasing molar content of DAP. It indicates that the reactivity of hybrid curing agent towards oxirane group ascends with increasing molar content of DAP. The endothermic peaks at the end of the exothermic curve (curves c–g) also shift to lower temperatures slightly and become smaller with decreasing molar content of DPP. When the molar ratio of DAP/DPP are 0.3 and 0.125 (Fig. 8 curves f and g), T_p for AP4/DGEBA and AP5/DGEBA systems are 174 and 175 °C, respectively and even lower than that of DAP/DGEBA system (191 °C, curve h). This implies that these hybrid curing agents exhibit significant associated effect on their reactivity towards oxirane group.

A method to ensure that the ternary system copolymerize completely is prepolymerization of above ternary systems in DMF, in which DPP is easy to be dissolved. Thus these ternary systems are convenient to be applied without obvious change of manufacturing technology.

3.4. Thermal properties of the cured polymers

3.4.1. Glass-transition temperature's (T_gs)

T_gs of the cured polymers (DAP, AP1-AP5 and DPP/DGEBA) were measured from a second heating trace with DSC at a heating rate of 20 °C/min (Fig. 9). All above epoxy polymers exhibit high T_gs with the range of 157–204 °C. One can see that the T_g value (204 °C, Fig. 9 curve a) of the cured DAP/DGEBA polymer is very high, and close to that of the cured DDS/DGEBA polymer (214 °C) and higher than those of the cured DDM, DDE and DPP/DGEBA polymers (165, 158 and 157 °C, respectively, see Table 1). Although

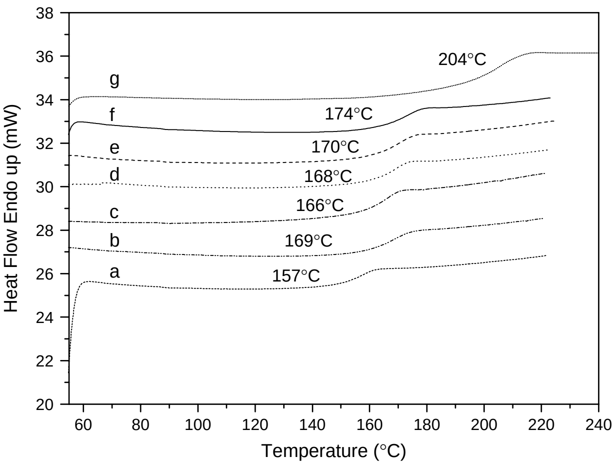


Fig. 9. The DSC thermograms of the cured epoxy polymers under N_2 at a heating rate of 20 °C/min. (a) DPP/DGEBA; (b) AP1/DGEBA; (c) AP2/DGEBA; (d) AP3/DGEBA; (e) AP4/DGEBA; (f) AP5/DGEBA and (g) DAP/ DGEBA.

DAP and DPP have longer molecular length than DDM, DDE and DDS and contain soft aromatic ether bond, they still have fairly high T_gs.

The obvious difference on T_gs of DAP/DGEBA and DPP/DGEBA polymers may attribute to two aspects, the reaction nature of amino and hydroxyl groups towards oxirane group and molecular length of DAP and DPP. For DPP/DGEBA system, if there is no further reaction between the unreacted oxirane group and the generated secondary hydroxyl group of products, the DPP/DGEBA polymer is linear polymer with high molecular weight (Fig. 10(a)), which often is referred to as poly(hydroxyethers) [44,45]. In fact, the generated secondary hydroxyl group could react with the unreacted oxirane group under high temperature, thus the crosslinking points were produced. With regard to the crosslinking density, the cured DPP/DGEBA polymer may less than the cured DAP/DGEBA polymer because three-dimensional chain extension will occur at the beginning of DAP and DGEBA reaction (Fig. 10(b)) on the fact that secondary amine groups formed in the reaction show the same reactivity towards the oxirane group as the primary amine presented initially. The other reason accounting for the difference of T_gs is different molecular length of DPP and DAP. It is evident that the space gap between the crosslinking points of the cured DPP/DGEBA polymer is longer averagely than those of the cured DAP/DGEBA polymer. The longer the space gap between the crosslinking points, the more the free volume of a polymer, and the lower the T_g. Due to their longer molecular length and lots of ether bonds, it is reasonable to deduce that the cured DAP and DPP/DGEBA polymers might be tougher than the cured DDM, DDE and DDS/DGEBA polymers.

In order to balance the overall properties of the cured polymers, change of structure and crosslinking density of network are effective methods. If we combine two kinds of networks together demonstrated in Fig. 10(a) and (b), the crosslinking density might be decreased with decreasing in content of DAP due to the decrease of the crosslinking points and the increase of space gap between the crosslinking points.

Actually, the ternary polymerization systems (DAP/DPP/DGEBA) were developed for this aim.

These ternary systems had been expected to adjust the thermal or mechanical properties by altering networking structure of the resulting polymers, which could be achieved through changing the molar ratios of DAP/DPP. With the increase of molar fraction of DAP, the T_gs of these ternary polymers (AP1–AP5/DGEBA) increase slightly in the narrow range of 165–175 °C but still close to the T_g of the cured DPP/DGEBA polymer (157 °C). In other words, T_gs of these copolymers do not distribute evenly between 157 and 204 °C as our original expectation. The non-sensitive relationship of T_gs towards the networking structure of the copolymers reveals that introduction of DPP with longer molecular length has more impacts on the chain structures of the copolymers. However, imperfect curing technique may be responsible for this result because all samples were cured in the same conditions, which may not the optimum conditions for embodiment of the effect they should play.

It is noted that the aforementioned ternary epoxy polymers are also potentially useful for advanced ‘green’ composite matrices because their high T_gs (about 170 °C) and excellent thermal stabilities, which will be discussed in the following.

Table 1
Thermal stability parameters for the cured epoxy resins

The cured epoxy resin	T_g(°C)	$T_{d,5\%}$ (°C)	Y_c% (850 °C)	T_{max} (°C)	A^*	K^*	IPDT (°C)
DAP/DGEBA	204	375	23.14	389	0.642	1.564	845
AP1/DGEBA	174	354	33.00	412	0.664	1.988	1093
AP2/DGEBA	170	361	40.07	415	0.698	2.347	1364
AP3/DGEBA	168	353	43.55	399	0.719	2.536	1500
AP4/DGEBA	166	365	45.75	423	0.739	2.627	1584
AP5/DGEBA	169	367	46.99	419	0.736	2.763	1667
DPP/DGEBA	157	357	49.31	415	0.754	2.891	1770
DDM/DGEBA	165[a]	382	16.13	394	0.558	1.407	671
DDE/DGEBA	158[a]	366	15.19	385	0.546	1.386	648
DDS/DGEBA	214[b]	389	11.50	420	0.537	1.259	587

[a] The curing process: 80 °C/2 h + 150 °C/4 h.
[b] The curing process: 110 °C/2 h + 200 °C/4 h.

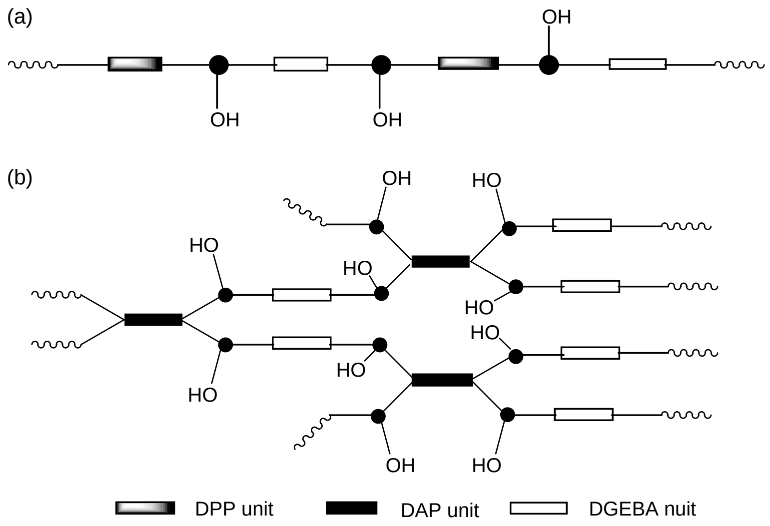


Fig. 10. Schematics of local thermoset network structures of the cured (a) DPP/DGEBA polymer and (b) DAP/DGEBA polymer in the early stage of polymerization.

3.4.2. Thermal stabilities of the cured polymers from TGA

Thermal stabilities of the epoxy polymers were assessed by thermogravimetric analyses (TGA) with the following parameters: 5 wt% decomposition temperature ($T_{d,5\%}$), and integral procedure decomposition temperature (IPDT). $T_{d,5\%}$ indicates the apparent thermal stability of the cured epoxy polymers. IPDT proposed early by Doyle [46] can be discussed in a quantitative thermal analysis containing the char residue of the resulting materials at high temperatures.

From the TGA results, the IPDT is calculated by the following equation [47]

$$\text{IPDT}(^\circ\text{C}) = A^* K^* (T_f - T_i) + T_i \tag{3}$$

where A^* is the area ratio of total experimental curve divided by total TGA thermogram, K^* is the coefficient of A^*, T_i and T_f are the initial and final experimental temperature, respectively. Figs. 11 and 12 show the TGA thermograms of the binary (DAP, DPP, DDM, DDE and DDS/DGEBA) and ternary epoxy polymers (AP1–AP5/DGEBA), respectively. The corresponding data of $T_{d,5\%}$ and IPDT of these epoxy polymers are listed in Table 1.

For binary epoxy polymers, $T_{d,5\%}$ values (Table 1) of the DAP/DGEBA and DPP/DGEBA polymers are 375 and 357 °C, respectively, which are close to the DDM/DGEBA (382 °C), DDE/DGEBA (369 °C) and DDS/DGEBA (389 °C) polymers. However, the IPDT values of the DAP/DGEBA and DPP/DGEBA polymers are 845 and 1770 °C, respectively, which are much higher than those of the DDM, DDE and DDS/DGEBA polymers. These indicate that the introduction of phthalazinone and azomethine structure can improve the inherent thermal stability of the thermosets dramatically.

For the ternary epoxy polymers, $T_{d,5\%}$ values of all epoxy polymers are above 350 °C, at the same time, the char yield (Y_c wt%, 850 °C) increases with increasing molar content of DPP. These reveal that all of them have excellent thermal stability, and introduction of DPP favors the formation of char residue.

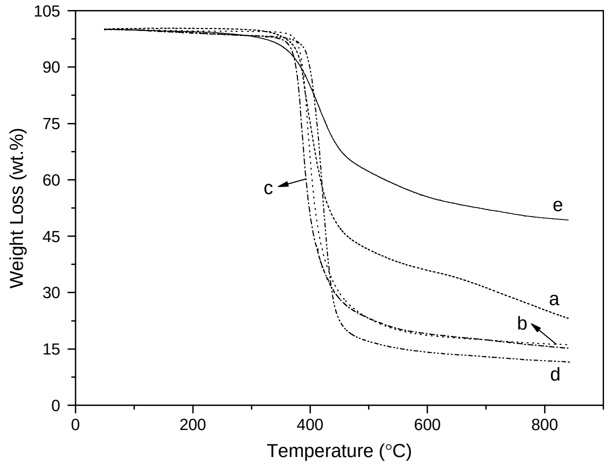


Fig. 11. TGA thermograms of the cured polymers (a) DAP/DGEBA; (b) DDM/DGEBA; (c) DDE/DGEBA; (d) DDS/DGEBA and (e) DPP/DGEBA. In N_2, 10 °C/min.

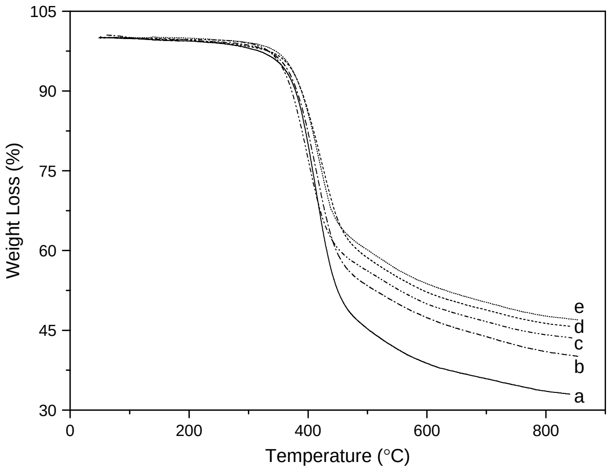


Fig. 12. TGA thermograms of the ternary cured polymers (a) AP1/DGEBA; (b) AP_2/DGEBA; (c) AP3/DGEBA; (d) AP4/DGEBA; (e) AP5/DGEBA; in N_2, 10 °C/min.

Compared with the structure of DAP, DPP has more aromatic rings and azomethine moieties which had been proved to form char residue during decomposition [48]. The IPDT values of all ternary polymers vary between that of the DAP/DGEBA (845 °C) and DPP/DGEBA (1770 °C) polymers. Thus we can modulate the thermal stabilities of the ternary epoxy polymers by changing the molar ratio of DAP/DPP, and this might have instructional sense to control the properties of the resulting epoxy polymers.

It is interesting that the char yields and IPDT of these ternary epoxy polymers are close to those of the DPP/DGEBA polymer (49.31% and 1700 °C, respectively), as T_gs of these ternary epoxy polymers do. This means that introduction of DPP into epoxy backbone changes the original structure of DAP/DGEBA polymer dramatically.

3.4.3. Relationship of structure and thermal properties of the epoxy polymers

From the above discussion, the binary epoxy polymers (DAP and DPP /DGEBA) and the ternary epoxy polymers (AP1–AP5/DGEBA) have excellent thermal properties due to the introduction of the unsymmetrical heterocyclic bisphenol structure (phthalazinone) and azomethine moieties. According to Van Krevelen's theory [49], increase in the char formation will depress the flammability of the materials, and the char residue on pyrolysis is linearly proportional to the limited oxygen index (LOI) for halogen-free polymers. That is, LOI value of halogen-free polymers could be predicted by the determination of the char residue. Lin [50] and Chen [51] et al. have proved that the LOI value of epoxy polymers correlates with the charring performance, and report [30] pointed out the epoxy polymers would have high LOI values and excellent flame-resistance if they have high char yield (generally above 40%). Thus, we could predict the LOI value of the polymers if the quantitative relationships of the structure and char residue were built. Herein, we expected to build the quantitative relationships between structure and char yield of these epoxy polymers, which will be beneficial to future exploration.

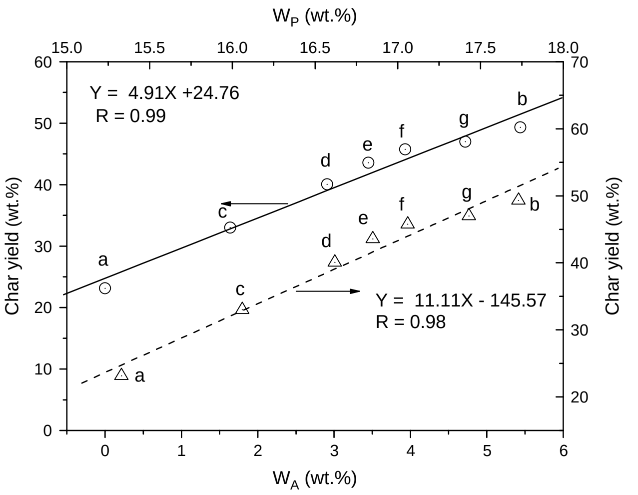


Fig. 13. The relationships between char yields (Y_c) and content of phthalazinone, azomethine in the binary and ternary cured polymers. (a) DAP/DGEBA; (b) DPP/DGEBA; (c) AP1/DGEBA; (d) AP2/DGEBA; (e) AP3/DGEBA; (f) AP4/DGEBA and (g) AP5/DGEBA.

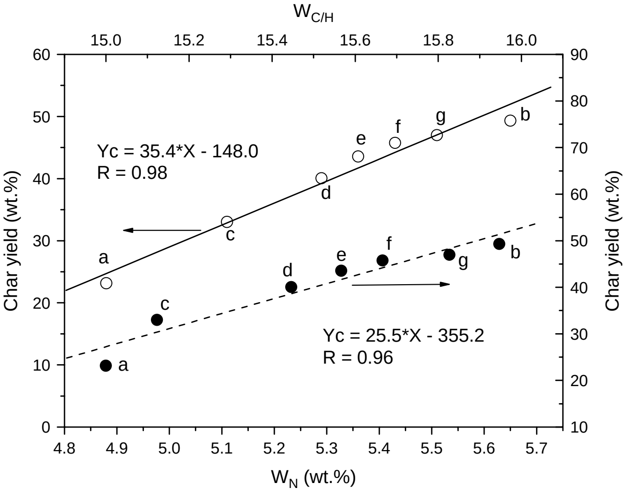


Fig. 14. The relationships between char yields (Y_c) and weight percent of nitrogen (wt%), C/H weight ratio in the binary cured polymers and ternary cured polymers. (a) DAP/DGEBA; (b) DPP/DGEBA; (c) AP1/DGEBA; (d) AP2/DGEBA; (e) AP3/DGEBA; (f) AP4/DGEBA and (g) AP5/DGEBA.

The relationships between char yield (Y_c) and weight percent of phthalazinone (W_P, the weight percentage of phthalazinone in a sample) and azomethine (W_A, the weight percentage of azomethine in a sample) in the binary and ternary epoxy polymers are shown in Fig. 13. It can be seen that Y_c have good linearity with W_P and W_A, Y_c increase with increasing weight percent of phthalazinone and azomethine structures. From the slope (4.91 for Y_c vs W_P and 11.11 for Y_c vs W_A) of two lines, we conclude that azomethine group may facilitate char formation more readily than phthalazinone group do.

The relationships between Y_c and weight percent of nitrogen (W_N, the weight percentage of nitrogen in a sample), C/H weight ratio ($W_{C/H}$, the weight ratio of carbon and hydrogen in a sample) in the binary and ternary cured polymers are shown in Fig. 14. It can be seen that char yield (Y_c) increase linearly with the increase of the content of nitrogen as well as C/H weight ratio. That is, high nitrogen content and C/H weight ratio are benefit to form char residue.

From the above results, if the Van Krevelen's theory could be applied to our system, we can build directly the relationship between LOI value and the structure of the epoxy polymers and predict the properties of the resulting epoxy polymers based on this relationship. It will be discussed particularly in the other paper.

4. Conclusions

In this paper, a novel bisphenol (DPP) containing phthalazinone and azomethine moieties was successfully synthesized from 4-hydroxybenzaldehyde and diamine (DAP). New epoxy polymers were prepared by binary polymerization of DAP (or DPP)/DGEBA and ternary polymerization of DAP/DPP/DGEBA. It was found that hybrid curing agents of DAP/DPP exhibited significant associated effect on their reactivity towards oxirane group. The thermal properties include T_g, $T_{d,5\%}$ and IPDT of these new epoxy systems were over 150, 350 and 850 °C, respectively.

The linear relationships of char yields (Y_c) and the structural compositions of the binary and ternary epoxy polymers (content of phthalazinone, azomethine and nitrogen, C/H weight ratio) were built for understanding the relationship between structure and properties for these new epoxy polymers.

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