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Novel crosslinkable epoxy resins containing phenylacetylene and azobenzene groups: from thermal crosslinking to flame retardance

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Abstract

Several kinds of novel flame-retardant-free and thermo-crosslinkable epoxy resins (EPs) containing azobenzene or/and phenylacetylene groups have been synthesized and characterized, and the flame retardant properties as a result of thermal crosslinking during combustion were investigated in detail. Crosslinking behaviors were tested by simultaneous thermogravimetry–differential scanning calorimetry (TGA–DSC). Thermal stabilities were investigated by thermogravimetric analysis (TGA). Flame retardance of the resulting EPs was evaluated through LOI tests, and combustion behaviors were studied via cone calorimetry and micro-combustion calorimetry (MCC), which further confirmed that flame retardance of these EPs was significantly improved, despite the absence of conventional flame retardant. Py–GC/MS analysis was used to investigate the degradation mechanism of these epoxy resins, and the results confirmed that the flame-retardant activity of epoxy resins mainly took effect in the condensed phase. The chemical constitution of the char layers were investigated by XPS and Raman spectrum. The co-crosslinking behavior between azobenzene and phenylacetylene groups was predicted and confirmed, which led to the most compact char layer, therefore resulted in the best flame retardance of these EPs.

Keywords

Epoxy resin; Crosslinking; Flame retardance; Carbonization

1. Introduction

Epoxy resin (EP), also known as polyepoxides, are a class of reactive prepolymers or polymers with epoxide groups, which have long been considered as one of the most extensively applied thermosetting polymers due to their excellent mechanical and chemical properties, good heat and solvent resistance, remarkable adhesive strength, and ease of curing and processing. EP have found wide applications in our daily life, such as adhesives, coatings, electronic/electrical industry, construction and transportation [1]. Unfortunately, like many other polymer materials, EP is easy to be ignited and will not self-extinguish after ignition, which greatly restricts their applications in many areas that require flame resistance and thermal stability [2].

In order to improve the flame retardance of EP, traditional methods are incorporating flame retardants, including flame-retardant epoxy monomer/oligomer or curing agent by chemical linking, and flame-retardant additives by physical blending into the material matrix [3-11]. Among them, halogen-containing flame retardants, which have long been proved particularly effective for EP, like tetrabromobisphenol A (TBBPA), 2,2,6,6-tetrabromo-3,3,5,5-tetramethyl-4,4-biphenol (TBTMBPA) and their epoxide derivatives, have been widely used for the past decades [2]. However, halogen-containing flame retardants will produce toxic and corrosive smoke during combustion that will cause environmental and health hazards, which lead to the prohibition of their further use [2, 12]. Therefore, the harmfulness of the flame retardants to the natural ecosystem and human health should be the top priority in both research and industry fields. The trade-off between flammability and the toxicity of flame retardant is designing and synthesizing new kinds of inherent flame-retardant EP that totally without halogen and possess desired flame retardance at the same time [13-16]. Many studies were reported for the design and synthesis of

flame-retardant EP by incorporating phosphorus-containing moieties into the main-chain or side pendant, including phosphine oxide, phosphates, phosphazenes, and some phosphorylated and phosphonylated derivatives[17-21]. However, these phosphorus-containing epoxy resins hardly gain high weight content of phosphorus, resulting in relatively lower flame retardance. Also, environmental and ecological stresses from the raw materials for these phosphorus-containing intermediates (phosphorus trichloride and phosphoryl chloride for instance), cannot be overlooked, thus new methods of flame retardance have been attracting more and more attention. Triazole-containing epoxy resins and polyesters were believed to be able to convert from triazole to indole while releasing N_2 at high temperature, and thanks to the aromatization tendency of indole groups, triazole-containing epoxy resins will possess great flame retardance as well [22, 23]. Also the inert N_2 could act as the diluent agent for both oxygen and combustible volatiles. Crosslinking between the unsaturated bonds, such as carbon–carbon double/triple bond at certain temperature, for instance, before or during the maximum decomposition of the polymer, is believed in enhancing the thermal stability and promoting aromatization and carbonization of the polymer, therefore increasing the decomposition residue, which shall play positive role on flame retardance. Deoxybenzoin-based epoxy resins were reported to have great flame retardance and thermal stability because of the conversion of deoxybenzoin to diphenylacetylene at 300~500 ℃, and diphenylacetylene would further crosslink together during combustion, by which aromatization and carbonization would be resulted, thus a compact char layer was formed, isolating oxygen and heat transfer, and endowing the material great flame retardance [24, 25]. Phenylacetylene groups were also reported to be able to occurred crosslinking reaction at high temperature and improve the flame retardance of PET-based copolyesters [26-29]. Azobenzene-containing copolyesters would also occur high temperature crosslinking reaction during combustion, from which compact char

layers were formed and then flame retardance of the material was improved [30]. Azobenzene is a chemical compound composed of two phenyl rings linked by a N=N double bond, derivatives of which are usually incorporated into polymer chains as photo-responsible moieties or liquid crystalline mesogens. Interestingly, although azo compounds exhibit combustibility, a number of symmetrical and unsymmetrical azo-alkanes were reported as flame retardants or flame-retardant synergists for polyolefins [31-33].

Considering that the crosslinking behaviors of azobenzene and phenylacetylene groups may have some effect on EPs, in this work, several flame-retardant EPs based on azobenzene or/and phenylacetylene groups were synthesized and characterized. Crosslinking behaviors between these groups were investigated, and the flame retardance of EPs was also evaluated as a consequence. At last, a plausible mechanism from crosslinking toward carbonization and flame retardance was proposed.

2. Experimental

2.1 Materials

Diglycidyl ether of bisphenol A (DGEBA, E-44, epoxy equivalent = 0.44 mol/100g) was purchased from Feicheng Deyuan Chemical Co., Ltd. (Feicheng, China). 4- phenylethynylphthalic anhydride (PEPA, 99.9%) was kindly supplied by Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou, China). *O*-phthalic anhydride (*o*-PA, 99.5%), *p*-nitrobenzoic acid (99.5%), *d*-glucose (99.5%), acetic acid (99.5%), sodium hydroxide (＞96.0%) and epichlorohydrin (ECH, 99.5%) were all provided by Chengdu Kelong Chemical Co., Ltd. (Chengdu, China) and used as received. Dimethyl sulfoxide (DMSO, 99.5%) and dichloromethane (DCM, 99.5%) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China) and used without further purification.

2.2 Synthesis of the crosslinkable epoxy

2.2.1 Synthesis of 4,4'-(diazene-1,2-diyl) dibenzoic acid (Azo-DBA)

Azo-DBA was synthesized via a classic method as can be seen in Scheme 1[34]: in a three-necked bottle, 15g of *p*-nitrobenzoic acid (0.090 mol) and 50g of NaOH (1.25 mol) were mixed in 225 mL of water and heated to 70 °C until the solid dissolved. Then hot glucose aqueous solution (100 g of glucose in 15 mL of water) was added dropwise into the above mixture at 70 °C under mechanical stirring, whereupon a yellow precipitate was obtained, which immediately changed to a brown solution upon further addition of glucose. Then a steam of air was passed into the mixture for 3 h and a light brown precipitate was obtained. The precipitate was filtered, dissolved in water, and acidified with 25 mL of acetic acid, thus a light pink precipitate was obtained. The raw product was filtered, washed with 400 mL of water, and dried in an oven to obtain Azo-DBA (yield 9 g, 74.2 %). ^{1}H NMR (DMSO-d_6) δ (ppm): 8.17 (4H, Ar-H), 8.01 (4H, Ar-H), 13.28 (2H, COOH). ^{13}C NMR (DMSO-d_6) δ (ppm): 123.3 (Ar), 131.2 (Ar), 133.8 (Ar-C-COOH), 154.6 (Ar-C-N=N), 167.1 (-COOH).
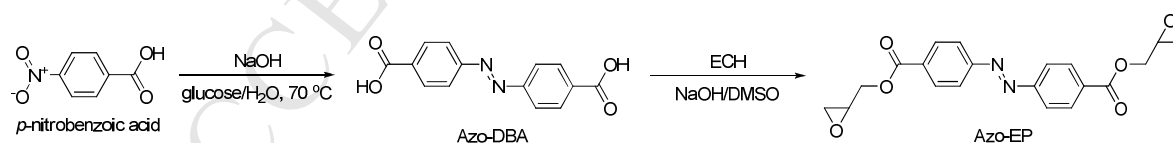
Scheme 1. Synthesis route of Azo-DBA and Azo-EP.

2.2.2 Synthesis of bis(oxiran-2-ylmethyl) 4,4'-(diazene-1,2-diyl) dibenzoate (Azo-EP)

Azo-EP was synthesized from Azo-DBA as seen in Scheme 1. In a three-necked bottle, 2g of Azo-DBA

(7.4 mmol) was dissolved in 40 mL of DMSO at 120 °C under mechanical stir, and a homogenous dark brown solution was obtained. Then 25 mL of epichlorohydrin (ECH) was added into the solution, whereupon a brown precipitate was obtained. Then the reaction mixture were stirred at 120 °C for 30 min, again a homogenous dark brown solution was obtained. When the above mixture was cooled to 50 °C, 1 mL of sodium hydroxide (1 mol/L) solution was added, then the mixture were stirred at 50 °C for 3h. 300 mL of water was added into the solution, a salmon pink precipitate was obtained. The raw product was filtered, washed with 400 mL of water, and dried in an oven to obtain Azo-EP (yield 2.4 g, 85 %, m. p. 120 °C). ^{1}H NMR (DMSO-d_6) δ (ppm): 8.05 (4H, Ar-H), 8.23 (4H, Ar-H), 4.15, 4.35, 4.70 (4H, COO-C$\underline{H}_2$-C$_2$H$_3$O), 3.39 (2H, COO-CH$_2$-C$\underline{H}$-CH$_2$O), 2.78, 2.88 (4H, COO-CH$_2$-CH-C$\underline{H}_2$O). ^{13}C NMR (DMSO-d_6) δ (ppm): 44.7 (COO-CH$_2$-CH-$\underline{C}$H$_2$O), 49.4 (COO-CH$_2$-$\underline{C}$H-CH$_2$O), 66.3 (COO-$\underline{C}$H$_2$-C$_2$H$_3$O), 123.5 (Ar), 131.2 (Ar), 132.3 (Ar-$\underline{C}$-COO), 154.8 (Ar-$\underline{C}$-N=N), 165.3 (Ar-$\underline{C}$OO).
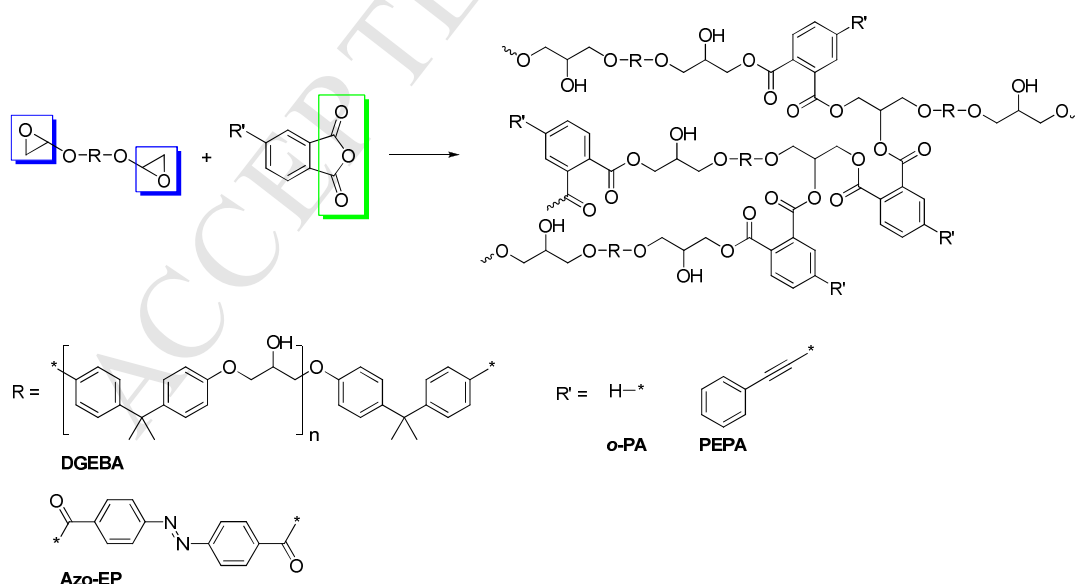
2.3 Curing

2.3.1 DGEBA based epoxy resins cured by *o*-phthalic anhydride (*o*-PA) and 4-phenylethynylphthalic anhydride (PEPA)

The cured epoxy resins were obtained by thermally curing. DGEBA and *o*-PA were mixed at 60 °C in an equivalent ratio of epoxy to anhydride as 1:1, then the mixture were cured at 160 °C for 6 h to obtain the cured resin (DGEBA-PA). DGEBA and PEPA were mixed at 80 °C in an equivalent ratio of epoxy to anhydride as 1:1, then the mixture were cured at 180 °C for 2 h and then at 200 °C for 6 h and post-cured at 220 °C for 2 h. Then the cured epoxy with crosslinkable phenylacetylene group (DGEBA-PEPA) was

obtained.

2.3.2 Azo-EP based epoxy resins cured by *o*-PA and PEPA

The cured Azo-EP resins were also obtained by thermally curing. As Azo-EP was really viscous while melted, which would make it impossible to blend with the curing agents directly. Therefore, the curing agents were dissolved in certain solvents, then Azo-EP was added and mixed to obtain a homogeneous solution. *O*-PA was dissolved in DCM firstly; Azo-EP was then added into the solution under magnetic stirring at an equivalent ratio of epoxy to anhydride as 1:1. The above solution was heated to 40 °C until all the DCM was evaporated, then a well-blended mixture of Azo-EP and *o*-PA was obtained. The mixture was melted at 130 °C, then cured at 150 °C for 6h. Same procedure for the pre-mixing and curing of Azo-EP-PEPA was carried out. Curing processes of DGEBA and Azo-EP based epoxy resins at the presence of anhydride hardeners were showed in Scheme 2.

Scheme 2. Curing processes of DGEBA-PA (DGEBA+*o*-PA), DGEBA-PEPA (DGEBA+PEPA),

Azo-EP-PA (Azo-EP+*o*-PA) and Azo-EP-PEPA (Azo-EP+PEPA)

Figure 1 showed the dynamic DSC thermograms for the curing process of Azo-EP-PA and Azo-EP-PEPA. As can be seen, both curing systems show a single exothermic peak corresponding to the curing reactions. The endothermic peak of Azo-EP-PA and Azo-EP-PEPA before the exothermic peak belongs to the melting process of Azo-EP and the curing agents. So the ideal curing procedure was settled based on the DSC data.
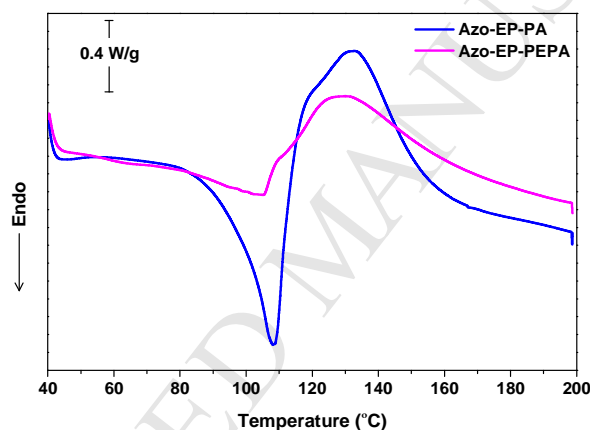

Fig. 1. DSC thermograms for the thermal curing reactions of Azo-EP-PA and Azo-EP-PEPA.

Non-isothermal curing behaviors of Azo-EP-PA and Azo-EP-PEPA were studied by DSC measurement; and detailed curing kinetics data were investigated by Kissinger's and Crane's methods, as illustrated in the Supporting Information.

2.4 Characterization

Nuclear magnetic resonance (NMR). The ^{1}H NMR and ^{13}C NMR data was obtained at room temperature

by a Bruker AVANCE AVII 400 NMR instrument, with tetramethylsilane as the internal stand.

Simultaneous thermogravimetry–differential scanning calorimetry (TGA–DSC). Crosslinking behavior was performed on a METTLER TOLEDO simulataneous TGA-DSC (TGA/DSC1/1100LF) with 5 ± 0.25 mg of samples at a heating rate of 10 °C min^{-1} in N$_2$. The temperature error is about ± 0.1 °C.

Differential scanning calorimetry (DSC). The thermal curing study of DGEBA and Azo-EP with *o*-PA and PEPA was carried out on a TA Q200 DSC apparatus with 5 ± 0.25 mg of samples at a heating rate of 10 °C min^{-1} in N$_2$. Thermal transition temperatures were also measured by DSC.

Thermoravimetric analysis (TGA). Thermal decomposition behavior of all the samples was conducted on a NETZSCH TGA (209 F1) under nitrogen atmosphere at a heat rate of 10 °C min^{-1} with ± 0.1 °C temperature error. The testing samples were weighed as 5 ± 0.5 mg.

Limiting oxygen index test (LOI). The LOI test measurements were performed on the Oxygen Index Flammability Gauge (HC–2C) according to ASTM D 2863–97. The cured samples were cut to a size of $130 \times 6.5 \times 3.2$ mm^3.

Microscale combustion calorimeter (MCC). The heat release capacity (HRC), peak heat release rate (PHRR) and total heat release (THR) were measured by a FTT–0001 calorimeter with 10 ± 0.5 mg of samples at a heating rate of 1 °C min^{-1}.

Cone calorimetry. The heat release rate (HRR), total heat release (THR) and the burning residues were measured by an FTT cone calorimeter (Fire Test Technology, UK) according to ISO 5660-1 at a heat flux 35 kW/m^2. The samples were directly cured in a mold with an inside size of $100 \times 100 \times 3$ mm^3.

Scanning electron microscopy (SEM). After the cone calorimetry, morphologies of the cryogenically fractured surface of the burning residual were collected and observed using scanning electron microscopy

(JEOL JSM 5900LV) with an acceleration of 10 kV. Gold was sprayed on the surface before observation.

X-ray photoelectron spectroscopy (XPS). XPS tests of thermal treated samples (400 °C under N_2 atmosphere for 10 min) wer conducted on a XSAM80 (Kratos Co., UK), using AlKα excitation radiation (hv-1486.6eV).

Raman spectroscopy measurement of thermal treated samples (400 °C under N_2 atmosphere for 10 min) were carried out at room temperature with LabRAM HR800 laser Raman spectrometer (SPEX Co., USA) by a 532 nm helium-neon laser line.

Pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS). The degradation procedure of these samples was investigated with a CDS 5200 pyrolyzer equiped with a DANI MASTER GC–TOF–MS gas chromatography-mass spectrometer.

3. Result and discussion

3.1 Crosslinking behavior

In order to verify the hypothesis that azobenzene and phenylacetylene containing EP would conduct crosslinking reactions in certain temperature range, the thermal behaviors of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA were characterized by simultaneous thermogravimetry-differential scanning calorimetry (TGA-DSC) in N_2 (Figure 2). For the DSC thermogram of DGEBA-PEPA, a notable exothermal process was observed starting at 330 °C, and reached its maximum at 370 °C, which was attributed to the crosslinking reaction of phenylacetylene group [26]. While on the contrary, no exothermal process was observed for DGEBA-PA. For Azo-EP-PA, a similar exothermal process like that of DGEBA-PEPA was observed, and the difference was that the initial crosslinking temperature of Azo-EP-PA

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was 260 °C, which was much lower than that of DGEBA-PEPA (330 °C). This phenomenon was attributed to that the crosslinking activity of azobenzene groups is much higher than that of phenylacetylene groups, decided by the different chemical structures of these groups, and this led to the difference of the maximum temperature (320 *versus* 370 °C, respectively).
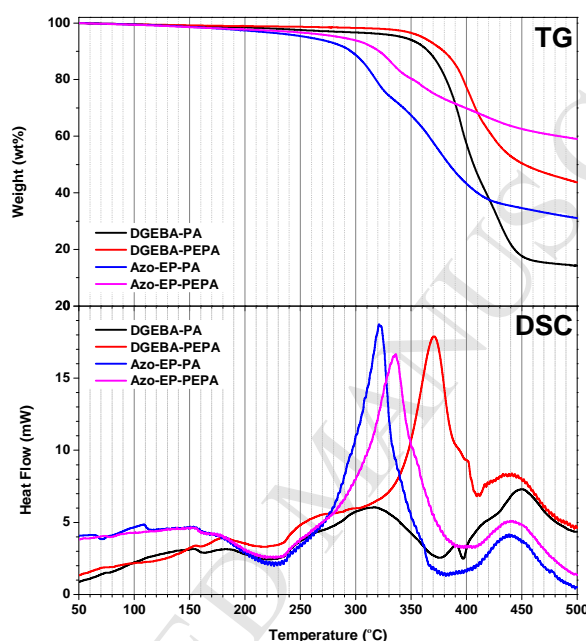

Fig. 2. TGA-DSC thermograms of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA.

For Azo-EP-PEPA, interestingly, the starting temperature of crosslinking observed at the DSC curve was 260 °C, which was nearly the same as that of Azo-EP-PA; while the maximum temperature was 336 °C, which was higher than that of Azo-EP-PA. This was explained as following: the existence of both azobenzene and phenylacetylene led to co-crosslinking reaction between these two crosslinkable groups, which would delay the occurrence of the maximum temperature of Azo-EP-PEPA than that of Azo-EP-PA. As a result, residues at 500 °C for these crosslinkable EPs were much higher than that of DGEBA-PA,

suggesting that the crosslinking would accelerate the process of carbonization, which was extremely important for char-forming flame retardance. However, further evidence is needed for the co-crosslinking reaction.

3.2 Thermal stability

TGA results of all samples under nitrogen atmosphere were obtained and curved in Figure 3. $T_{5\%}$ (the temperature where 5 wt% of weight lost, defined as the initial decomposition of the testing sample), T_{max} (the temperature at maximum weight loss rate), and the residue after test were all summarized in Table 1. For the TGA thermograms of DGEBA-PA and DGEBA-PEPA, one single decomposition process was observed, and T_{max} values were much close to each other. However, the incorporation of PEPA endowed DGEBA-PEPA a higher $T_{5\%}$ (355.6 °C) than that of DGEBA-PA (345.5 °C), owing to the crosslinking behavior of phenylacetylene groups started at 330 °C, which would lead to the formation of thermal stable crosslinking structures, and further decreased the weight loss rate at T_{max}. As for the decomposition residue, as predicted, it greatly increased from 6.2 to 38.1 wt%, suggesting that the crosslinking of phenylacetylene groups would further promote aromatization and carbonization, which exhibited a positive effect on flame retardance. For the thermograms of Azo-EP-PA and Azo-EP-PEPA, compared to that of DGEBA-PA, $T_{5\%}$ of these two samples both decreased. This could be explained that, because of lower thermal stability of Azo-EP monomer () that the decomposition of azobenzene groups occurred at relatively low temperature [35, 36], the incorporation of azobenzene group decreased the thermal stability at the beginning of decomposition. However, $T_{5\%}$ of Azo-EP-PEPA (296.4 °C) was higher than that of Azo-EP-PA (262.1 °C), suggesting that the incorporation of phenylacetylene group would lead to co-crosslinking behavior between azobenzene and phenylacetylene groups, which would decrease the decomposition of azobenzene groups,

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therefore a significant improvement in decomposition residue was also observed (from 29.7 wt% to 48.2
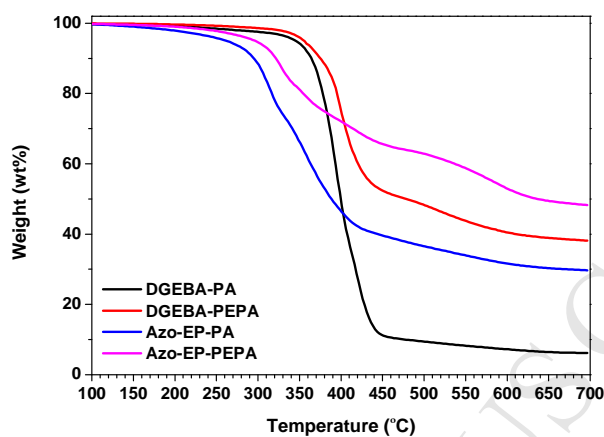
wt%).

Fig. 3. TGA thermograms of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA.

Table 1 TGA data of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA.

Samples	$T_{5\%}$ (°C)^a	T_{max} (°C)^b	The rate of T_{max} (wt%/min)	Residue at 700 °C (wt%)
DGEBA-PA	345.5	394.0	16.3	6.2
DGEBA-PEPA	355.6	397.0	10.5	38.1
Azo-EP-PA	262.1	358.0	3.9	29.7
Azo-EP-PEPA	296.4	362.0	2.6	48.2

^{a}$T_{5\%}$ defined as the temperature at which 5 wt% weight loss occurred.

^{b}T_{max} defined as the temperature at maximum weight loss rate.

3.3 Flame Retardance and Burning behavior

The limiting oxygen index (LOI) indicated the minimum oxygen concentration (vol%) which could

support the combustion of a certain material. Therefore, the LOI of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA was tested for estimating their flame retardance, which was 21, 27, 24.5, 27.5 % respectively. As a result, the incorporation of azobenzene or/and phenylacetylene groups all increased the LOI value of epoxy resins. For DGEBA-PA, when the testing oxygen concentration was higher than 22, the sample was ignited quickly and no extinguishing behavior was observed until the whole sample was burned out. However, for DGEBA-PEPA tested at an oxygen concentration of 27, when the sample was ignited, flame propagation was very slow, then the flame gradually diminished and finally extinguished. For Azo-EP-PA and Azo-EP-PEPA samples, similar combustion process as DGEBA-PEPA was observed, while interestingly, an intumescent phenomenon was observed as shown in Figure 4, which was due to the release of inert gases such as N_2 from azobenzene group during combustion[35, 36]. The inert gases released acted as either the blowing agent to intumesce the char layer, or diluent for the combustible volatiles and oxygen. The maximum LOI value, as predicted, was obtained from Azo-EP-PEPA, which was in accord with TGA–DSC and TGA results.

DGEBA-PA   DGEBA-PEPA   Azo-EP-PA   Azo-EP-PEPA

Fig. 4. Burning residues after LOI test of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA

Microscale Combustion Calorimeter (MCC) is an important measurement that investigate the thermal combustion behavior of materials in microscale. During MCC tests, volatile products of the samples are

burned and corresponding heat release data recorded (which should correspond to the flammability properties of the decomposition products generated during TGA testing). In this case, MCC results of all samples were obtained, and the heat release rates (HRR) were curved in Figure 5. A reduction of both peak heat release rate (PHRR) and total heat release (THR) was observed for the samples with the incorporation of crosslinkable groups. Notably, Azo-EP-PEPA, due to the potential co-crosslinking behavior between azobenzene and phenylacetylene groups, exhibited the minimum THR (6.5 kJ/g) and PHRR (90.1 W/g), which all greatly decreased from those of DGEBA-PA. Moreover, the incorporation of azobenzene group (Azo-EP-PA) led to lower THR and PHRR than that of phenylacetylene group (DGEBA-PEPA), which was because that the crosslinking process of azobenzene occurred early than that of phenylacetylene, therefore leading to an earlier formation of char layer than that of DGEBA-PEPA. However, as can be seen from the HRR curve, PHRR of azobenzene containing epoxy resins occurred earlier than those of DGEBA-PA and DGEBA-PEPA, which was because of the earlier decomposition of azobenzene groups; and the incorporation of phenylacetylene group would defer the earlier heat release by the co-crosslinking behavior between azobenzene and phenylacetylene groups, which was in accord with the TGA–DSC and TGA results.
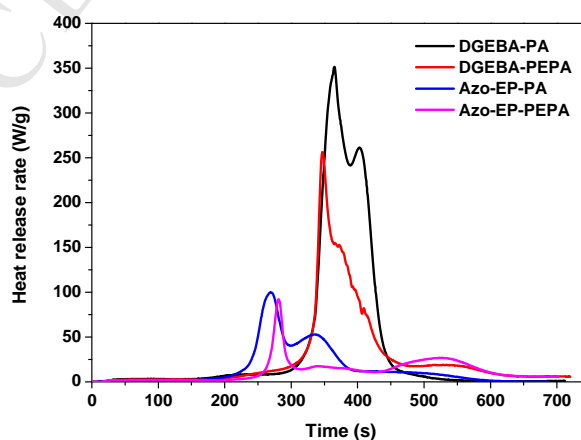
Fig. 5. HRR curve of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA from MCC at a heating

rate of 1 °C min^{-1}.

The cone calorimeter test, which is an oxygen consumption technique similar to the real fire[37], was

used to evaluate the combustion performance of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and

Azo-EP-PEPA (Figure 6), the detailed data were collected in Table 2. The heat release rate (HRR), in

particular the peak value of HRR (PHRR), was considered as the most important parameter to evaluate fire

safety of the flame retardant materials, which determined rate of flame spread[38, 39]. One who lowered the

PHRR could slow down the flame spread and decrease fire hazard of the resulting materials. From Figure

6(a), PHRR of both Azo-EP-PA and Azo-EP-PEPA decreased significantly: PHRR of Azo-EP-PA was

about 343 kW/m^2, approximately half of that of DGEBA-PA. For Azo-EP-PEPA, PHRR further decreased

to 288 kW/m^2, which was only 42 % of that of DGEBA-PA. However, for DGEBA-PEPA, PHRR was

much higher than that of DGEBA-PA. This abnormal phenomenon was explained as following, during

combustion, the crosslinking reaction of phenylacetylene group and the decomposition of the epoxy resin

matrix happened at the same temperature range, which would lead to a competition between crosslinking

and decomposition, thus aromatization and the subsequent char formation were retarded. Nevertheless, the

incorporation of azobenzene group effectively reduced the HRR of the relevant EP and slow down the flame

propagation, and the cooperation between azobenzene and phenylacetylene groups endowed EP the best

flame retardance. Also, with the incorporation of crosslinkable groups, the total heat release (THR)

decreased significantly: the value of DGEBA-PA was 49.3 MJ/m^2; while the values for DGEBA-PEPA,

Azo-EP-PA and Azo-EP-PEPA were 46.9, 43.6 and 24.9 MJ/m^2, respectively (Figure 6(b)). The mass

curves of these samples (Figure 6(c)) were similar to the THR ones: Azo-EP-PEPA exhibited the highest

burning residues of 52 wt%, meaning least fuel generation and feeding-back during combustion, which was

in accordance with the TGA results.

However, for DGEBA-PEPA and Azo-EP-PA, both the burning residue and the THR value of

DGEBA-PEPA was higher than that of Azo-EP-PA, this was explained as follows: since the char forming

ability of phenylacetylene group was better than that of azobenzene group (as could be proved from the

previous research about the application of phenylacetylene and azobenzene groups in copolyesters, when the

content of the crosslinking group was the same, the burning residue of phenylacetylene containing

copolyester was higher than that of the azobenzene containing one[26, 33]), the burning residue of

DGEBA-PEPA was higher than that of Azo-EP-PA. However, because of the competition between

crosslinking of phenylacetylene group and the decomposition of EP matrix, the THR of DGEBA-PEPA was

also higher than that of Azo-EP-PA. Consequently, the cone calorimetric results strongly showed that these

thermal crosslinkable EPs exhibited low flammability, without the incorporation of traditional

flame-retardants.

For the digital photos and SEM images of the burning residues after cone calorimetry of these samples

(Figure 7), DGEBA-PA was almost burned out after the test, and many isolated coal-dust-like residues was

observed from the SEM images, thus made the char layer the most porous one. The char layer of

DGEBA-PEPA was improved by the crosslinking of phenylacetylene group, which also made the char layer

more compact than that of DGEBA-PA, as could be seen from the SEM image. However, because of the

competition between the crosslinking reaction and decomposition, most of the crosslinkable moieties

decomposed and burned out before the formation of crosslinking and carbonization. The char layer of

Azo-EP-PA looked much better than that of DGEBA-PEPA, which was because of the earlier crosslinking of azobenzene group. Since the decomposition of azobenzene group would lead to the release of N_2, however, some gas holes was observed from the char layer, thus made the char layer looser than that of DGEBA-PEPA, as shown in the SEM image. For Azo-EP-PEPA, because of the co-crosslinking between azobenzene group and phenylacetylene group, the char layer was the most intact and compact one, thus endowed Azo-EP-PEPA the best flame retardance.
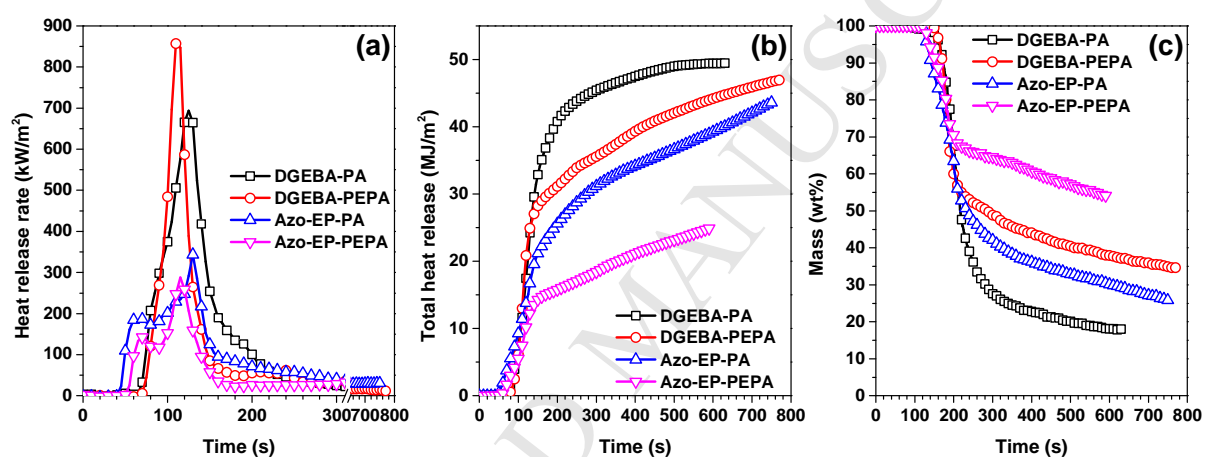
Fig. 6. Cone calorimetric results of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA: (a) heat release rate, (b) total heat release and (c) residue mass.

Table 2 Detailed combustion results of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA obtained from cone calorimetry

	DGEBA-PA	DGEBA-PEPA	Azo-EP-PA	Azo-EP-PEPA
TTI (s)[a]	63	62	39	45
PHRR (kW/m^2)	694	857	344	289
Averaged HRR (kW/m^2)	77	61	58	42

FIGRA (kW/m^{2}s)^b	5.6	7.8	2.6	2.5
Time to PHRR (s)	125	110	130	115
THR (MJ/m^2)	49.3	46.9	43.6	24.9
Residue (wt%)	17	33	23	52

[a] TTI stands for the time to ignition.

[b] FIGRA is calculated by dividing the value of PHRR by the time to PHRR.
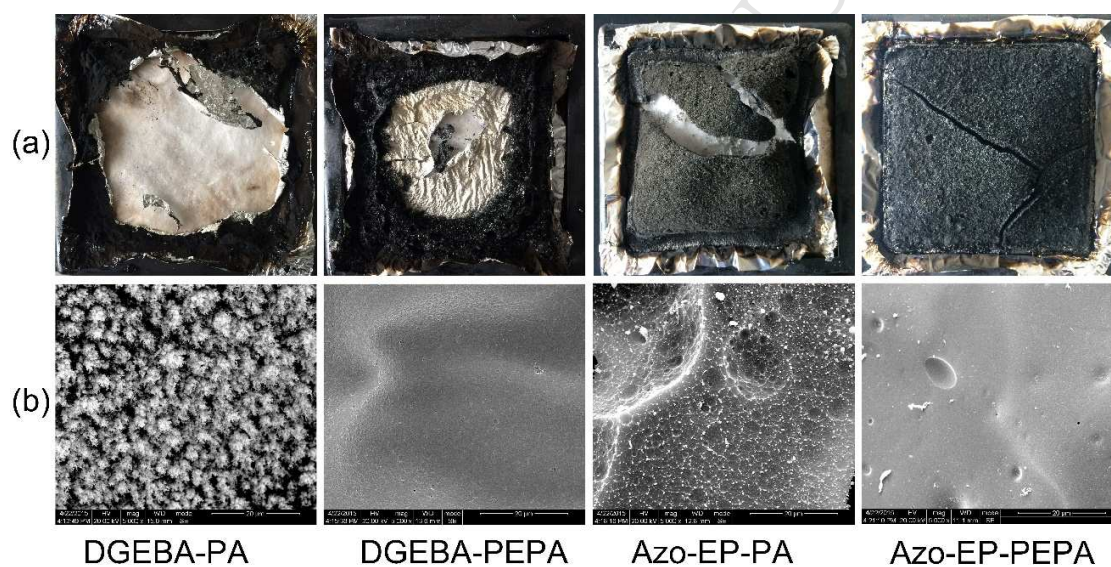
Fig. 7. Burning residues after cone calorimetry of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and

Azo-EP-PEPA: (a) digital photographs, (b) SEM images of the cryogenically fractured surfaces.

3.4 Char formation

As for charring flame retardant, the forming of compact char layer during combustion is very important

for material to self-extinguish. This critical layer can prohibit the spread of flammable volatiles generated

from the decomposition of material into the flame zone, correspondingly can prevent the transfer of heat and

oxygen. Therefore, in order to investigate the relationship between the crosslinked structure and the char formation, as well as the flame-retardant mechanism, the chemical structures of the residue char after thermal treatment under N_2 were studied in detail.

The chemical constitution of the decomposition residue after isothermal treatment (400 °C under N_2 atmosphere for 10 min) for DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA were investigated by XPS. The C_{1s} and N_{1s} XPS results were presented in Table 3 and Table 4; also the simulation curves of C_{1s} and N_{1s} were presented in Figure 8 and Figure 9, respectively. As illustrated, the decomposition residue was mainly consisted of C–C, C–O and C–N bonds. Among them, C–C bond was the maximum one in content for all these samples, which constructed the basis of the decomposition residue. C–O bond, mostly coming from the epoxy matrix and the ester linkage, was also detected in all these samples. Compared between DGEBA-PA and DGEBA-PEPA, the content of C–O in DGEBA-PEPA was much higher than that of DGEBA-PA. Thanks to the crosslinking behavior of PEPA, by which more compact char layer was formed, the decomposition of the epoxide crosslinked network decreased.

As for Azo-EP-PA and Azo-EP-PEPA, the content of C–O in Azo-EP-PEPA was also higher than that of Azo-EP-PA. The co-crosslinking behavior between azobenzene group and phenylacetylene group would lead to the formation of a more compact char layer and then decrease the decomposition of the matrix. With the incorporation of azobenzene group, C–N and N–N bonds were detected in both the C_{1s} and the N_{1s} results. As can be seen from the N_{1s} result, the content of N–N bond in Azo-EP-PA was much lower than that of Azo-EP-PEPA. With the incorporation of PEPA, the co-crosslinking reaction would happen between azobenzene and phenylacetylene group, which would reduce the decomposition of azobenzene groups, thus increase of the content of N-N bond was observed.
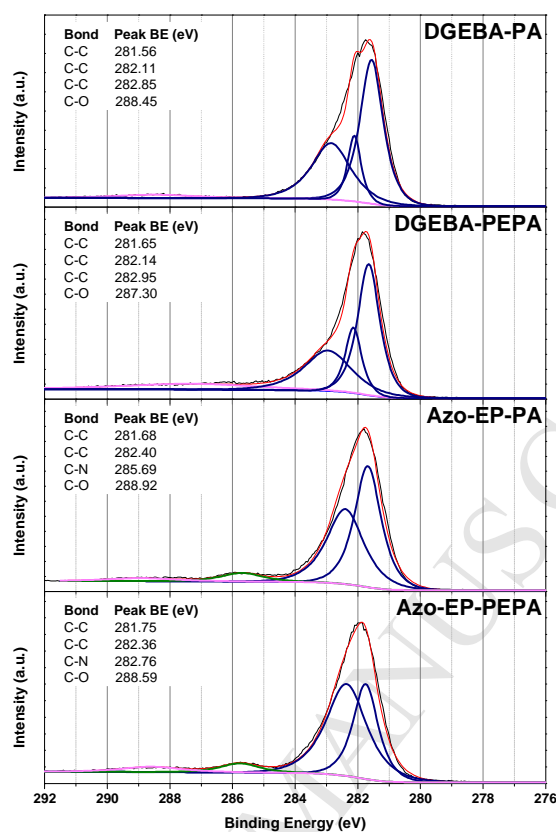
Table 3 Results for C_{1s} XPS of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA isothermal treated at 400 °C under N_2 atmosphere for 10 min.

Samples	C–C Area (%)	C–O Area (%)	C–N Area (%)
DGEBA-PA	95.96	4.06	0
DGEBA-PEPA	88.51	11.46	0
Azo-EP-PA	91.57	3.02	5.41
Azo-EP-PEPA	90.08	4.68	5.24

Table 4 Results for N_{1s} XPS of Azo-EP-PA and Azo-EP-PEPA isothermal treated at 400 °C under N_2 atmosphere for 10 min.

Samples	N–N Area (%)	N–C Area (%)
Azo-EP-PA	76.53	23.47
Azo-EP-PEPA	87.10	12.90

Fig. 8. C_{1s} XPS spectra of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA isothermal treated

at 400 °C under N_2 atmosphere for 10 min.
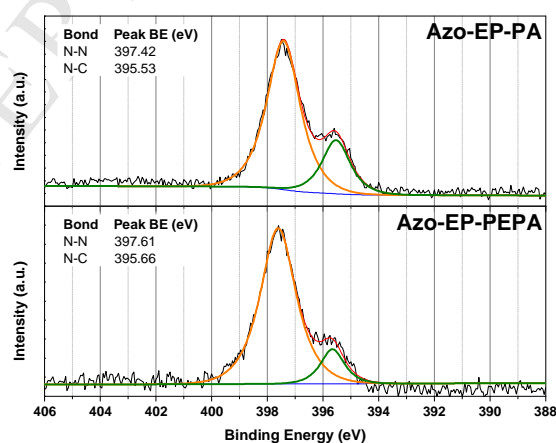
Fig. 9. N_{1s} XPS spectra of Azo-EP-PA and Azo-EP-PEPA isothermal treated at 400 °C under N_2 atmosphere

for 10 min.

Raman spectroscopy provides a suitable method to characterize the different types of the carbonaceous materials. Therefore, the decomposition residues of DGEBA-PEPA and Azo-EP-PEPA after thermal treatment were inspected. As shown in Figure 10, the peak at about 1580 cm^{-1}, corresponding to the stretching vibration with E_{2g} symmetry in the sp^2 hybridized carbon atoms in a graphite layer[26], decreased in Azo-EP-PEPA, compared with that of DGEBA-PEPA. The incorporation of azobenzene group would lead to the co-crosslinking reaction between the azobenzene and the phenylacetylene groups, which would result in the formation of heterocyclic char layer, rather than carbonaceous graphite. The peak at about 1100 cm^{-1}, corresponding to the stretching vibration of aliphatic carbon chain, also decreased in Azo-EP-PEPA compared with that of DGEBA-PEPA, this was due to the same reason for the above phenomenon.
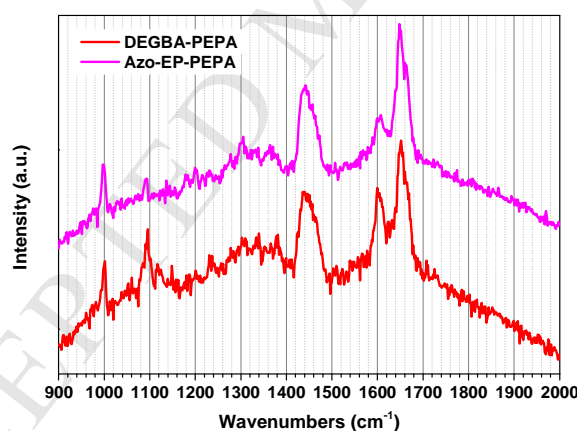
Fig. 10. Raman spectra for the residue after thermal treatment of DGEBA-PEPA and Azo-EP-PEPA.

In order to elucidate the degradation mechanism, fast pyrolysis of these samples have been carried out at 400 °C in a Py-GC/MS equipment for DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA, and the volatile products were thoroughly analysed. The GC curves of these samples were shown in Figure 11,

and detailed data were listed in Table 5. As can be seen from Figure 11, the volatiles from DGEBA-PA were

the most complex one. However, after the incorporation of crosslinkable groups, the volatile products

became less and simpler. The crosslinking behavior could form char layers as physical barrier to prevent the

degradation of the matrix, which was in accord with the afore-mentioned TGA and MCC results, that the

quantity of volatile components of the crosslinkable epoxy resins degradation decreased. As for Azo-EP-PA

and Azo-EP-PEPA, N-containing volatile products were detected in Azo-EP-PA; while for Azo-EP-PEPA,

such products were much less than that of Azo-EP-PA. This would be another proof that azobenzene and

phenylacetylene groups could conduct co-crosslinking behavior during degradation. From Table 5, main

volatile products of these samples were all the hardener molecules degraded from the crosslinked network of

epoxy resins, volatilized from small amount of unreacted hardeners, or generated from the initial

degradation of the ester linkages [40]. For DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA, combining the

XPS and Raman results on the chemical constitution of the condensed residues, the crosslinking and

carbonization processes were concluded as illustrated in Scheme 3, char layers were finally formed to

prevent further degradation of the matrix.
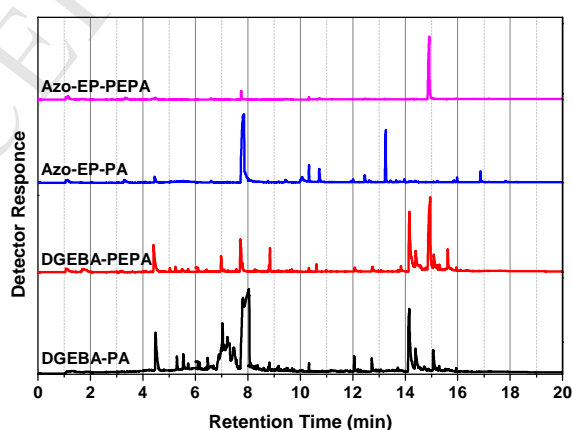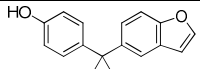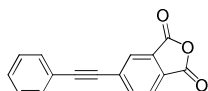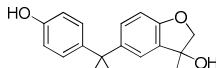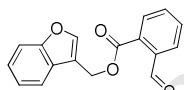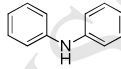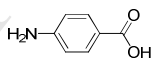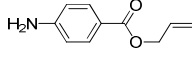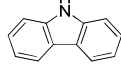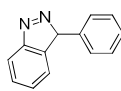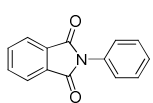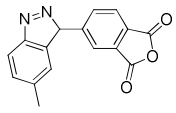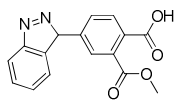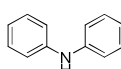

Fig. 11. The pyrogram of the pyrolysis products.

Table 5 Compounds identified in the pyrograms of DGEBA-PA, DGEBA-PEPA, Azo-EP-PA and Azo-EP-PEPA

Samples	Retention Time (min)	M	Assigned Structure
DGEBA-PA	4.5	118	
	5.3	120	
	5.5	134	
	6.5	122	
	6.9	122	
	7.2	162	
	7.8	134	or
	8.1	148	
	12.1	212	
	13.9	228	
	14.4	252	
	15.2	266	
DGEBA-PEPA	4.4	94	
	7.0	136	
	7.7	160	
	7.8	148	

	14.4	252	
	14.9	248	
	15.1	284	
	15.7	280	
Azo-EP-PA	4.4	94	
	7.8	169	
	7.9	148	
	10.0	137	
	10.7	177	
	12.0	167	
	12.5	194	
	13.3	223	
	15.8	278	
	16.9	296	
Azo-EP-PEPA	4.4	94	
	7.7	148	
	10.4	169	

| 14.9 | 248 | |
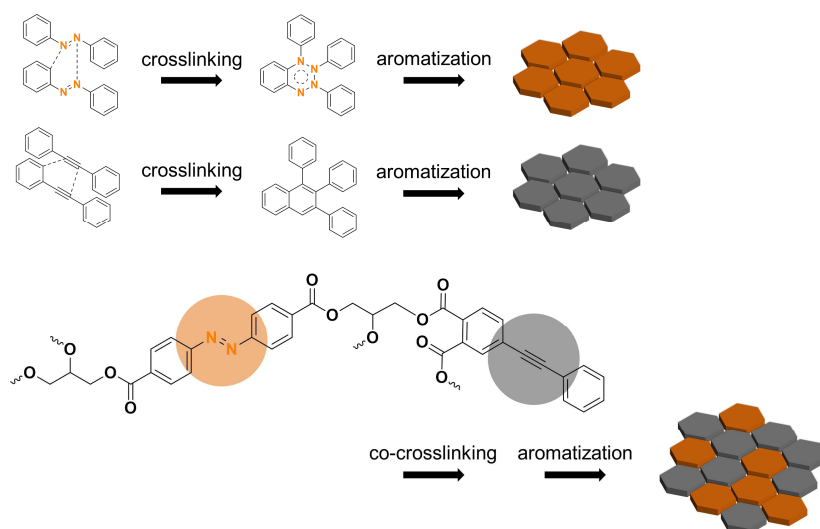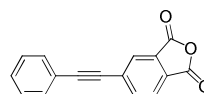
Scheme 3. Crosslinking toward aromatization processes of azobenzene and phenylacetylene groups, and the co-crosslinking behavior between the two crosslinkable groups thereof.

4. Conclusions

In summary, novel thermal crosslinkable epoxy resins with two different kinds of crosslinkable groups have been synthesized successfully, and their crosslinking behaviors, flame retardance, thermal stabilities and the corresponding flame-retardant mechanism were investigated in detail. Crosslinking behaviors of azobenzene and phenylacetylene groups were confirmed by TG–DSC, and the co-crosslinking reaction between the former two crosslinkable groups were confirmed by TG–DSC, XPS, and Raman test together, which all played a positive role on flame retardance, and also resulted in the improvement in char formation both under decomposition and combustion. Flame-retardant test results suggested that, with the incorporation of crosslinkable groups, flame retardance of these EPs were all be improved significantly. LOI

value was increased from 21% of DGEBA-PA to 27.5% of Azo-EP-PEPA, HRC, PHRR and THR of crosslinkable EPs from MCC test were all immensely decreased, PHRR of crosslinkable EPs from cone calorimetric test was also greatly decreased, except for that of DGEBA-PEPA because of the competition between crosslinking of phenylacetylene group and the decomposition of EP matrix. Condensed phase flame-retardant mechanism was proved by the degradation procedure of these crosslinkable epoxy resins, which was obtained from the Py-GC/MS analysis. Therefore, the formation of the compact char resulting from the crosslinking reactions were considered as the key points to the flame retardance of EPs when subjected to the fire, despite the absence of any normal flame retardant. It is believable to make a significant and fruitful attempt to improve the flame retardance of EP.

Supporting Information

Non-isothermal curing behaviors of Azo-EP-PA and Azo-EP-PEPA.

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