### Polymer 51 (2010) 4776-4783

Contents lists available at ScienceDirect

### Polymer

journal homepage: www.elsevier.com/locate/polymer

# Phosphorus-containing liquid cycloaliphatic epoxy resins for reworkable environment-friendly electronic packaging materials

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#### ARTICLE INFO

Article history: Received 6 May 2010 Received in revised form 12 August 2010 Accepted 17 August 2010 Available online 24 August 2010

*Keywords:* Epoxy resin Synthesis Electronic packaging

#### ABSTRACT

Novel thermally reworkable, phosphorus-containing, di- and tri-functional liquid cycloaliphatic epoxy resins were designed and synthesized. Their chemical structures were characterized by means of MS, FTIR, <sup>1</sup>H NMR and <sup>31</sup>P NMR methods. After curing, the products were transparent and stable up to 220 °C, while exhibited quick thermal decomposition at the temperature range of 255–280 °C. The removal test showed that, after heat-treatment at 260 °C in air atmosphere for only 4 min, the residual char on the glass substrate could be easily wiped off. This unique degradation behavior was attributed to the synergistic effect of two factors: the thermally-labile phosphate groups evenly distributed within the three-dimensional network and the in-situ catalyzing of phosphate and ester groups, as evidenced by the results of molecular modeling, isothermal TGA and FTIR spectra. In addition, compared to the commercial cycloaliphatic epoxy resin ERL-4221, the newly synthesized epoxy resins had increased limiting oxygen index (LOI) by 31%. The combination of excellent reworkability, non-halogen flame retardancy, high glass transition temperature of 227 °C and high mechanical modulus endows them the potential for environment-friendly microelectronic and optoelectronic packaging applications.

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### 1. Introduction

Cycloaliphatic epoxy resins are thermosetting materials widely employed as encapsulants in microelectronic industry, e.g. direct chip attach (DCA), chip scale package (CSP) and chip on board for multichip modules (MCM), or as underfill adhesive in flip chip technology to help evenly distribute stress caused by thermal cycling, improve heat shock properties, and enhance the reliability of the solder interconnects [1–7]. However, after curing, epoxy resins polymerize to form crosslinking network structure. The intractability makes them extremely difficult for the disposal, recycling and reuse of scrapped electronic products. Moreover, even large amount of electronic wastes have been generated during the production process since, when the components are encapsulated using conventional epoxy resins, the high decomposition temperature of over 300 °C and insoluble and infusible nature make the disassembly and repair almost impossible. This problem is especially severe for the MCM and integrated optoelectronic module packagings, in which multiple chips or optoelectronic

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devices are mounted onto one high-density board. If one chip is damaged, the whole expensive integrated module has to be discarded. It has been reported that the manufacturing loss due to defective electronic components could be over 30% for MCM packaging [8]. In this regard, electronic packaging materials, which can offer reworkability and enable the convenient removal and replacement of faulty chip without damaging the other components and circuit board, are strongly desired to meet environmental protection and cost-saving requirements [9–13].

To make an epoxy resin reworkable, the method can be adopted to introduce either chemical or thermally-labile group into the crosslinking structure. Under controlled condition, the weak bonds decompose to make network collapse and the decreased physical properties such as shearing strength and modulus can permit localized removal of a defective chip. Buchwalter et al reported epoxy resins containing acetal and ketal linkages, which could be degraded by applying acid-containing solvent [14], but the aggressive acid is not convenient for the localized operation of integrated circuit. Thereafter, Ober [15,16], Shirai [17], and Wong [18,19] et al developed thermally reworkable epoxies containing secondary/tertiary ester or carbamate groups, which could decompose in the favorable temperature range from 200 to 300 °C. In our previous report, the cured cycloaliphatic diepoxides





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containing secondary and tertiary carbon—ether linkages started to decompose at 220 and 239 °C, respectively [20].

Besides the desired temperature, another key target for reworkable epoxy is the decomposition rate and temperature sensitivity in order to suit the quick, clean and localized rework process. Nevertheless, although current reworkable epoxies have the decomposition temperatures within 200-300 °C, from the viewpoint of practical application, their degradation rates are still slow and the pyrolysis temperature ranges are relatively wide.

In addition, as electronic encapsulating materials, a great concern about cycloaliphatic epoxies is their flammability. Typical cycloaliphatic epoxy like ERL-4221 only has the LOI value of about 18. Bromine-containing epoxies have satisfied flame retardant property, but the highly toxic hydrogen bromide, dibenzo-p-dioxin and dibenzo-furan released during combustion have restricted their applications due to the environmental reason [21,22]. Alternatively, organophosphorus epoxy resins are receiving much attention because of their good flame retardant ability and the fire-extinguishing mechanism which the incombustible phosphorous char serving as an outer flame protection barrier, and therefore release much less toxic gas and smoke into the atmosphere relative to the brominated analogues [23–26].

On the other hand, it is noteworthy that polymers containing phosphate bonds usually possess relatively low thermal degradation temperature [27-29]. Keeping the above suggestions in mind, the present work was undertaken to design and synthesize new phosphorus-containing cycloaliphatic di- and tri-functional epoxy resins with a combination of several favorable characteristics in one epoxy molecule. After curing, the weak phosphate bond evenly distributed within the crosslinking network can act as sensitive temperature trigger to initiate thermal decomposition in the event of necessity; the introduction of phosphorus element may result in apparent enhancement in flame retardant property; the liquid state at room temperature prior to curing and high glass transition temperature after curing can be expected owing to their cycloaliphatic structures. Their synthesis and characterizations, thermally reworkability, flame retardancy and mechanical properties as well as decomposition mechanism were investigated and discussed in detail.

### 2. Experimental

### 2.1. Materials

Phenylphosphoryl dichloride, phosphoryl trichloride, Cyclohex-3-enyl-1-methanol and OXONE (a monopersulfate compound:  $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ ) were purchased from Aldrich Chemical Company and used without further purification. Hexahydro-4-methylphthalic anhydride (HMPA) and 2-ethyl-4-methylimidazole (EMI) were used as curing agent and curing accelerator, respectively. Commercial epoxy resin ERL-4221 was employed here for the purpose of comparison with the newly synthesized two epoxy resins. Their chemical structures are given in Table 1. Other chemical reagents were of analytical reagent grade and used as received.

### 2.2. Synthesis

## 2.2.1. Synthesis of bis(cyclohex-3-enylmethyl)phenyl phosphate (Olefin I)

Into a 500-ml four-neck round-bottom flask equipped with a mechanical stirrer, a thermometer and an addition funnel with drying tube, cyclohex-3-enyl-1-methanol (62.5 g, 0.558 mol), dichloromethane (50 ml) and triethylamine (38.2 ml, 0.258 mol) were charged. Under the nitrogen atmosphere, to the above

### Table 1

Chemical structures of ERL-4221, HMPA and EMI used in this study.



solution, phenylphosphoryl dichloride (39.0 g, 0.186 mol) was added. Then the reaction was allowed to proceed at room temperature for 36 h. The resultant mixture was washed successively with dilute HCl and Na<sub>2</sub>CO<sub>3</sub> aqueous solution and finally deionized water to neutrality. The organic phase was dried over MgSO<sub>4</sub>. After filtration, the filtrate was evaporated on a rotary evaporator. The residue was distilled under reduced pressure to remove the excess cyclohex-3-enyl-1-methanol (at  $60-62 \,^{\circ}$ C, 6 Torr) and there was obtained 60.6 g liquid product. Yield: 91%. FTIR (cm<sup>-1</sup>): 3026, 2927, 2839, 1651, 1595, 1490, 1435, 1289, 1211, 1046, 1023, 943, 766. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS, ppm): 7.19–7.39 (m, 5H, Ar-H), 5.70 (m, 4H,=CH–), 4.07 (m, 4H, –CH<sub>2</sub>–O), 1.33–2.18 (m, 14H, –CH<sub>2</sub>–, –CH–).

# 2.2.2. Synthesis of bis(3,4-epoxycyclohexylmethyl)phenyl phosphate (Epoxide I)

Into a 1000 ml four-necked round-bottom flask quipped with a mechanical stirrer, a pH meter and a dropping funnels were charged Olefin I (7.6 g, 20 mmol), CH<sub>2</sub>Cl<sub>2</sub> (90 ml), acetone (90 ml), and 18-crown-6 ether (0.9 g). Under the nitrogen atmosphere and vigorously stirring at about 50 °C, OXONE (45.0 g, 75 mmol) and ethylenediaminetetraacetic acid (0.06 g, 0.2 mmol) in 240 ml of deionized water were added. The reaction was continued for 24 h, and then the organic phase was collected and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic portions were combined, washed with deionized water, and dried over MgSO<sub>4</sub>. After filtration, the filtrate was evaporated on a rotary evaporator to give 6.4 g liquid. Yield: 74%. HRMS (*m*/*z*): calcd for C<sub>20</sub>H<sub>27</sub>O<sub>6</sub>P 394.3975; found, 394.1586 [M]<sup>+</sup>. FTIR (cm<sup>-1</sup>): 2925, 1595, 1490, 1439, 1279, 1213, 1046, 1025, 943, 904, 808, 788, 769. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS, ppm): 7.16-7.36 (m, 5H, Ar-H), 3.91 (m, 4H, -CH<sub>2</sub>-O), 3.15 (m, 4H, C-H on epoxide ring), 1.05–2.13 (m, 14H, -CH<sub>2</sub>-, -CH-). <sup>31</sup>P NMR  $(CDCl_3/phosphoric acid, ppm): -6.03$  (a single peak).

### 2.2.3. Synthesis of tri(cyclohex-3-enylmethyl) phosphate (Olefin II)

The similar epoxidation procedure to that for Olefin I was carried out except that the phosphoryl chloride compound used was phosphoryl trichloride instead of phenylphosphoryl dichloride. A liquid product Olefin II was obtained. Yield: 89%. FTIR (cm<sup>-1</sup>): 3022, 2914, 2838, 1650, 1436, 1281, 1016, 876, 654. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS, ppm): 5.66 (s, 6H, =CH–), 3.93 (m, 6H,  $-CH_2-0$ ), 1.30–2.15 (m, 21H,  $-CH_2-$ , -CH-).

# 2.2.4. Synthesis of tri(3,4-epoxycyclohexylmethyl) phosphate (Epoxide II)

The preparation procedure of Epoxide II was similar to that of Epoxide I except that the olefin compound used was tri(cyclohex-3-enylmethyl) phosphate instead of bis(cyclohex-3-enylmethyl) phenyl phosphate. There was obtained 6.8 g liquid. Yield: 78%. HRMS (*m/z*): calcd for C<sub>21</sub>H<sub>33</sub>O<sub>7</sub>P 428.4550; found, 428.1859 [M]<sup>+</sup>. FTIR (cm<sup>-1</sup>): 2928, 1438, 1263, 1019, 960, 979, 810, 786, 745. <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS, ppm): 3.82 (m, 6H,  $-CH_2-O$ ), 3.17 (m, 6H, CH on epoxide ring), 1.03–2.19 (m, 21H,  $-CH_2-$ , -CH-). <sup>31</sup>P NMR (CDCl<sub>3</sub>/ phosphoric acid, ppm): -3.54 (a single peak).

### 2.3. Curing of epoxides

Epoxide and HMPA were homogeneously mixed with a molar stoichiometric ratio of 1:0.8 at room temperature. Into this mixture 0.5 wt% of 2-ethyl-4-methylimidazole was added as curing accelerator. Sample bars for dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermal gravimetry analysis (TGA) and LOI tests were obtained by curing in a mold with specific dimension and cured at 140 °C for 2 h, at 170 °C for 4 h, and post cured at 190 °C for another 2 h. As a comparison, the commercial diepoxide ERL-4221 was also mixed with HMPA and 2-ethyl-4-methylimidazole with the same ratio and cured under the same conditions.

### 2.4. Measurements

Mass spectra were obtained on a Bruker Microtof-Q spectrometer for electrospray ionization in positive and negative modes. The mass-to-charge (m/z) ratios of the ions were determined with a quadrupole mass spectrometer, which was scanned from 65 to 2000 amu. The polarity of the ions detected was rapidly switched between + and -, and the data were recorded.

Fourier-transform infrared spectra (FTIR) were recorded on a Nicolet 5700 spectrometer. Liquid samples were measured by casting film on KBr salt tablets, whereas solid samples were measured using pallets prepared by compressing the dispersed mixture of sample and KBr powder.

<sup>1</sup>H NMR and <sup>31</sup>P NMR were recoded on an INOVA-400 NMR spectrometer (Varian) using CDCl<sub>3</sub> as solvents, tetramethylsilane (TMS) and phosphoric acid as internal standards, respectively.

DSC curves were recorded on a NETZCH DSC 204 thermal analyzer using  $N_2$  as a purge gas (20 ml/min) at a heating rate of 10 °C/min. About 5–10 mg cured product was put into the aluminum pan for DSC measurement.

DMA measurements were conducted on an apparatus (TA DMA Q800) at a heating rate of 2 °C/min and at a frequency of 1 Hz under a nitrogen atmosphere. The tests were carried out in the single cantilever mode using the specimens with dimension of  $2 \times 6 \times 40 \text{ mm}^3$ .

TGA measurements were performed on a NETZSCH TG 209 thermal analyzer under both nitrogen and air atmosphere over a temperature range of 25–800 °C with a heating rate of 10 °C/min and the gas flow rates of 60 ml/min.

Computational calculations were performed using Gaussian 03W program package. The optimized geometries and energies were calculated with the 6-31G (d)-level calculations based on the restricted Hartree-Fock calculation method.

LOI tests were performed according to the standard of ISO4589-1984 with test specimen bar of 12 cm in length, 6.5 mm in width and 3.0 mm in thickness. The samples were ignited by a Bunsen burner vertically, and the flame was removed and the timer was started. The concentration of oxygen was raised if the specimen was extinguished before burning 5 cm or 3 min.



Scheme 1. Synthetic routes of two phosphorous-containing epoxides.

The oxygen content was adjusted until the limiting concentration was determined. For each sample, ten specimen bars were measured, and the obtained LOI values were averaged. The standard deviations were found to be within  $\pm 0.2$ .

Viscosities of epoxides were measured using a rotary viscometer (NDJ-1) over the temperature range of 25–85 °C.

### 3. Results and discussion

### 3.1. Synthesis and characterization

The synthesis of two cycloaliphatic epoxides containing phosphate ester linkages is presented in Scheme 1, which mainly consists of two steps: synthesis of olefins and then epoxidations of olefins to give the epoxides.

The synthesis of olefin was the typical nucleophilic substitution reaction of phosphoryl chloride with cyclohex-3-enyl-1-methanol. Because phosphoryl chlorides were sensitive to water, all the regents should be purified carefully according to the standard methods prior to use. Epoxides were prepared according to the Prileshajev epoxidation reaction of corresponding olefins [30]. The organic peracids are commonly used oxidation regents, but usually they are required to be excess to obtain a complete conversion of C=C double bond into epoxide group, which results in large amounts of acid waste [31]. Alternatively, in this study, inorganic oxidant OXONE was adopted to prepare the epoxides. After reaction was finished, it was very convenient to remove Oxone residues by simply washing with deionized water.



Fig. 1. <sup>1</sup>H NMR spectra of Olefin I and Epoxide I.



Fig. 2. <sup>1</sup>H NMR spectra of Olefin II and Epoxide II.

In the FTIR spectrum of Olefin I, the peak at 1651 cm<sup>-1</sup> was corresponded to the C=C group in the cyclohexenyl ring, the peaks at 1211 and 1289  $\text{cm}^{-1}$  were due to the absorptions of P=O bond in -CH<sub>2</sub>-O-P=O and -Ar-O-P=O moieties, respectively, whereas the peaks at 1023 and 919 cm<sup>-1</sup> were attributed to the stretching vibration of -C-O-P in -CH2-O-P and -Ar-O-P moieties, respectively, and the absorption of benzene ring was found at 1589 and 1490 cm<sup>-1</sup>. Similar characteristic peaks could be observed in the FTIR spectrum of Olefin II except for the absence of absorptions of benzene ring, P=O in -Ar-O-P=O and -C-O-P in -Ar-O-P. After epoxidation reactions of Olefin I and II, the previous C=C absorptions disappeared completely, and new characteristic peak of epoxy ring at about 825 and 785 cm<sup>-1</sup> appeared, indicating that the C=C bonds in the cyclohexenyl rings were converted into epoxy groups (Figs. 1S-4S, Supporting information).

Fig. 1 shows the <sup>1</sup>H NMR spectra of Epoxide I and its precursor Olefin I. For Olefin I, the signals at 7.19–7.39 ppm could be assigned to the protons on benzene ring, the peaks at 5.66 and 3.93 ppm were due to the protons on CH—CH of the cyclohexenyl rings and CH<sub>2</sub>–O, respectively, and signals at 1.33–2.18 ppm were corresponded to the protons of other cycloaliphatic CH<sub>2</sub> groups. After epoxidation, the signals at 5.66 and 5.70 ppm due to the protons of



Fig. 3. Variation of viscosity as a function of temperature of epoxides.



Fig. 4. DMA spectra of cured epoxides.

CH=CH disappeared completely, whereas the new signals at 3.17 and 3.15 ppm corresponding to the protons of epoxy rings appeared, demonstrating that the epoxidation reactions were complete. Similar signals were assigned in the <sup>1</sup>H NMR spectra of Olefin II and Epoxide II (Fig. 2). Moreover, in the <sup>31</sup>P NMR spectra of Epoxide I and II (Figs. 5S and 6S, Supporting Information), only one single peak at -6.03 ppm and -3.54 ppm was observed, respectively, further confirming the designed structure as depicted in Scheme 1.

### 3.2. General physical properties

The synthesized Epoxide I and II are liquid at room temperature and have viscosities at 25 °C of 990 and 2210 mPa s, respectively, which are higher than that of ERL-4221 due to their multifunctionality, bulky molecular structure or the presence of aromatic benzene ring. However, it was found that their viscosity values rapidly decreased with temperature (Fig. 3). For Epoxide II, upon raising temperature to 35 °C, its viscosity rapidly decreased to 625 mPa s. Moreover, at 85 °C, Epoxide II had even the similar viscosity value to ERL-4221. This excellent temperature thixotropic property is especially favorable for encapsulating of chip on board and optoelectronic device. In this case, the encapsulants are required to have low viscosity at increased temperature to enable convenient operation, and meanwhile, when the temperature is decreased to room temperature, the high viscosity makes that the desirable packaging shapes can be maintained. In addition, for flip chip packaging process, the operation is usually conducted in the temperature range of 80–90 °C to shorten the underfilling time. At this temperature, Epoxide I and II have the comparable low viscosities and flow abilities to the commercially used ERL-4221.

Fig. 4 illustrates the spectra of dynamic mechanical analysis (DMA) of cured Epoxide I, II and ERL-4221 as a function of temperature at a heating rate of  $2 \, ^{\circ}C$ /min and a frequency of 1 Hz.

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DMA and DSC results of cured epoxides.

	Storage Modulus						
Sample	Glassy region <sup>a</sup> (GPa)	Rubber region <sup>b</sup> (MPa)	ρ (10 <sup>-3</sup> mol/cm <sup>3</sup> )	T <sub>g</sub> -DSC (°C)	T <sub>g</sub> -DMA (°C)		
Epoxide I	2.5	7.1	0.66	113	130		
Epoxide II	2.6	28	1.72	199	227		
ERL-4221	2.3	17	0.94	175	191		

<sup>a</sup> Storage modulus at 30 °C.

<sup>b</sup> Storage modulus at  $T_{g}$ -DMA + 30 °C.



Fig. 5. TGA and DTG plots the cured epoxides: (A) in Nitrogen and (B) in Air.

The data of  $T_{\rm g}$  values obtained from tan  $\delta$  and the storage modulus at both glassy region and rubbery region are summarized in Table 2. In principle, according to the theory of rubber elasticity, the crosslinking density ( $\rho$ ) of a cured epoxy network is proportional to its storage modulus in the rubbery region as shown in the equation  $\rho = E/3RT$ , where *E* the storage modulus at  $T_{\rm g}$  + 30 °C, *R* the gas constant and *T* the absolute temperature at  $T_{\rm g}$  + 30 °C [32,33]. As can be seen from Table 2, the crosslinking density of cured trifunctional Epoxide II was higher by 294% and 64.7% than that of Epoxide I and ERL-4221, respectively.

The analysis of the height and width of the tan  $\delta$  peak could also provide information about the crosslinking density and network homogeneity of cured epoxides. The tan  $\delta$  peak is the maximum ratio of viscous component to elastic component. Since the increase of segmental mobility in cured epoxy is favorable for viscous component, it can be assumed that the larger height value of tan  $\delta$  peak implies a looser network. As illustrated in Fig. 4, the variation of height of tan  $\delta$  peak for the three cured samples exhibited the same trend as that of *E* value, which further supported the fact that the cured Epoxide II had the denser crosslinking network, whereas the network of Epoxide I is looser than the others. On the other hand, considering that tan  $\delta$  peak is indicative of the occurrence of glass transition and at this temperature the polymer segments starts to gain mobility, the width of tan  $\delta$  peak can reflect the distribution of segmental length between two crosslinking points

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TGA data of cured epoxides.

Sample	Phosphorus	TGA (N <sub>2</sub> Atmosphere)			TGA (Air Atmosphere)		
	content (wt%)	IDT <sup>a</sup> (°C)	$T_{\max}^{b}$ (°C)	Yield <sup>c</sup> (%)	IDT <sup>a</sup> (°C)	T <sub>max</sub> <sup>b</sup> (°C)	Yield <sup>c</sup> (%)
Epoxide I	4.6	222	259	10.9	224	265	11.9
Epoxide II	3.7	257	279	10.0	260	274	8.6
ERL-4221	0	316	368	1.3	320	363	0

<sup>a</sup> IDT is the initial decomposition temperature of cured epoxide.

<sup>b</sup> Temperature of the maximum weight loss rate.

<sup>c</sup> Char yield at 800 °C.

in network. The half-peak width in Fig. 4 showed that, relative to Epoxide I and ERL-4221, the cured product based on Epoxide II had an obviously narrow tan  $\delta$  peak, indicating a dense and uniform network. The reason could be attributed to its highly symmetric trifunctional structure.

In addition, the cured Epoxide I and II had much higher storage modulus (about 2.5 GPa) in glassy regions than ERL-4221 (2.3 GPa) because of the respective contribution of rigid benzene ring in Epoxide I and trifunctional structure of Epoxide II. The enhanced modulus values are advantageous for them in electronic packaging applications.

The glass transition temperatures for the three cured epoxies were obtained from DMA and DSC methods. Similar to other polymer systems [6,20,33], in this study, the glass transition temperatures from DMA ( $T_g$ -DMA) are higher than the corresponding values from DSC curves ( $T_g$ -DSC), and the  $T_g$  values of



Fig. 6. Isothermal TGA plots at 260 °C under air atmosphere for the cured epoxides.

 Table 4

 Isothermal TGA data (260 °C) of cured epoxides.

Sample	Weight lo	Weight loss (%)						
	1 min	3 min	5 min	8 min	12 min			
Epoxide I	3.2	67.3	84.3	87.2	88.8			
Epoxide II	2.2	14.9	57.7	66.4	68.1			

the three cured samples followed the order: Epoxide II > ERL-4221 > Epoxide I, which trend was consistent with that of crosslinking density. The rigid cycloaliphatic structure and the dense crosslinking network resulted into the cured trifunctional epoxide II significantly high  $T_g$  (199 °C for  $T_g$ -DSC and 227 °C for  $T_g$ -DMA), which, to our knowledge, is among the highest glass transition temperature for liquid aliphatic epoxies (cured with HMPA) reported previously in the literature.

### 3.3. Thermal degradation property and mechanism

To investigate the thermal decomposition behaviors of cured epoxides, the TGA and derivative (DTG) curves as a function of temperature were recorded and presented in Fig. 5, and the thermogravimetric data are summarized in Table 3. As expected, the phosphate-containing epoxides degraded at the lower temperature and exhibited higher degradation rate than ERL-4221. In nitrogen atmosphere, the cured Epoxide I, Epoxide II and ERL-4221 started to degrade at about 231 °C, 260 °C, and 320 °C, and the temperatures of the maximum weight loss were 259 °C, 279 °C and 368 °C, respectively. The decomposition behaviors in air atmosphere are similar except for a slight change in char yield, meaning that the oxidative atmosphere had no significant effects on the degradation of cured epoxides. Moreover, the residual chars of cured Epoxide I and II at 800 °C (8-12 wt%) were much higher than that of ERL-4221 (about 0 wt%), which were similar to the previous reports that the phosphorus-containing polymers usually had the higher char yield [28].

The cured Epoxide I and II were thermally stable up to 230 °C, offering sufficient reliability and resistance to heat shock generated during the working of integrated circuit or optoelectronic device. However, once the decomposition temperature was reached, the degradation process was very quick. The steep and sharp TGA curves indicated that the thermal decomposition of Epoxide I and II networks occurred in a narrow temperature range, i.e., their decomposition processes were very sensitive to temperature. To further investigate the degradation rate of cured phosphate-containing epoxides, isothermal TGA curves were measured at 260 °C under air atmosphere (Fig. 6), and the results are summarized in Table 4. It was seen that the samples based on Epoxide I and II lost nearly 70% weights within only 3 min and 8 min, respectively, which phenomena were rarely observed for the previous thermally reworkable epoxy resins [15–20].

The data in Tables 3 and 4 showed that, relative to Epoxide II, the cured Epoxide I displayed an obviously lower initial decomposition



**Fig. 7.** Optimized geometries and bond lengths of C–O bond by computational modeling for (A) phosphate group and (B) primary carbon–ester group.



Fig. 8. FTIR spectra of pyrolysis products of cured Epoxide II under air atmosphere: (a) 0 min/260 °C, (b) 2 min/260 °C, (c) 10 min/260 °C, (d) 20 min/320 °C, (e) 20 min/360 °C.

temperature and, given the same time, the sample based on Epoxide I had the more weight loss. For example, after degradation at 260 °C for 3 min, the cured Epoxide I lost weight of 67.3%, whereas it was only 14.9% for Epoxide II. The reason could be attributed to two factors. On the one hand, the phosphorus content of cured Epoxide I (4.6 wt%) was higher than that in Epoxide II (3.7 wt%), indicative of a higher density of weak phosphate bond in Epoxide I network. On the other hand, the looser crosslinking network in cured Epoxide I was advantageous for the diffusion of phosphorus acid generated in network to catalyze the pyrolysis of other phosphate bonds. These two factors could account for Epoxide I the lower degradation temperature and higher degradation rate than Epoxide II.

As a comparison, ERL-4221 had the decomposition temperature of the maximum weight loss rate of 368 °C, which was far higher than Epoxide I and II, implying that the primary carbon—ester bond was more thermally stable than the phosphate bond. The evidence from the Hartree-Fock computational calculation using Gaussian 03W program package supported the above experimental results.



**Fig. 9.** FTIR spectra of the condensate of volatilized pyrolysis products at 260  $^{\circ}$ C with increasing degradation time: (a) collected at 2 min; (b) collected at 10 min.



Fig. 10. Removal test of cured Epoxide II on a glass slide: (A) transparent cured Epoxide II, (B) heat-treated under air atmosphere at 260 °C for 4 min, (C) wiping with acetone; (D) a clean slide after wiping.

The optimized geometries and bond lengths of C–O bond in phosphate and primary carbon–ester are illustrated in Fig. 7. The bond length of O–C in phosphate was 1.420 Å while that in primary carbon–ester bond was 1.415 Å, demonstrating that the bond of O–C in phosphate is weaker than that in primary carbon–ester.

For the cured Epoxide II, its isothermally degraded process under air atmosphere with different time at 260 °C, 320 °C and 360 °C, respectively, was followed using FTIR method, and the obtained spectra are shown in Fig. 8. The comparison between spectra a, b and c revealed that, after pyrolysis of 2 min at 260 °C, a wide absorption in the range from 2100 to 3200  $\text{cm}^{-1}$  appeared, and its intensity became more pronounced after the time was prolonged to 10 min. A similar evolution trend was also displayed for the absorption at about 1648 cm<sup>-1</sup>. These peaks were attributed to the characteristic absorption of the stretching vibration of OH and O=P groups in organic phosphorous acid, produced from the cleavage of O–C bond of phosphate ester moiety in the network. Moreover, at high temperature, the organic phosphorous acid was liable to react to form pyrophosphates [34], as confirmed by the increased intensity of P-O-P-O absorption bands lying at  $900-1100 \text{ cm}^{-1}$  and  $1300-1250 \text{ cm}^{-1}$ . As revealed by the isothermal TGA results above, after 10 min of degradation at 260 °C, more than 60% weight had lost, we believed that, with the collapse of network, large amount of cycloaliphatic fragments from HMPA and Epoxide II moieties had volatilized, reflecting in the greatly decreased peak intensities of absorptions at 2933, 2871 and 1458 cm<sup>-1</sup> (CH<sub>2</sub>), and 1734 cm<sup>-1</sup> (COO). After the temperature was further increased to 320 °C and 360 °C, the characteristic peaks of phosphorous groups such as P=O, P-O-P-O bonds remained similar except that the intensity of aliphatic C–H (2938 and 2854 cm<sup>-1</sup>) and ester group (1734 cm<sup>-1</sup>) further decreased, indicating that the thermal pyrolysis process was almost complete after 10 min under air atmosphere at 260 °C.

In order to further elucidate the degradation mechanism, for the cured Epoxide II, the volatilized components with different time of thermal decomposition at 260 °C were collected and analyzed by FTIR spectra. As shown in Fig. 9, in the initial 2 min, the FTIR spectra of the condensate displayed strong characteristic absorptions of cycloaliphatic moieties at 2929 and 2857 cm<sup>-1</sup>, carboxylic group at 1701 and 2665  $\text{cm}^{-1}$  and the ester group at 1732  $\text{cm}^{-1}$ . As the degradation time was increased to 10 min, the shoulder peak of ester bond at 1732  $\text{cm}^{-1}$  disappeared completely, and the new absorptions at 1857 and 1773 cm<sup>-1</sup> belonging to acid anhydride group appeared. In this study, since hexahydro-4-methylphthalic anhydride (HMPA) was used as curing agent to react with epoxides to form ester bond, and its content in cured network was more than 48 wt%, the results in the above FTIR spectra revealed that, in the initial thermal pyrolysis stage, the break of phosphate bonds and small amount of ester bonds made the volatilized components mainly consist of large molecular fragments of cycloaliphatic acids or cycloaliphatic esters with HMPA skeleton. With the increase of pyrolysis time, the nearly complete break of ester bonds produced hexahydro-4-methylphthalic acid, and some of them dehydrated to vield HMPA in the end.

Based on the FTIR spectra and TGA analyses as well as the molecular modeling results, the mechanism of thermal

degradation of this series of phosphor-containing epoxides could be proposed: at the decomposition temperature, the thermallylabile phosphate groups firstly pyrolyze to yield strong organic phosphoric acid, and which then catalyze the cleavage of other adjacent phosphate or ester bonds, leading to the collapse of network. The synergistic influence of two factors, i.e., the presence of weak phosphate bond evenly distributed within the three-dimensional crosslinking network on the molecular level and the in-situ catalyzing of organic phosphoric acid on the decomposition of phosphate or carbon-ester groups, was responsible for the suitably low cleavage temperature and rapid degradation rate.

### 3.4. Removal test

For the practical application of a reworkable epoxy resin, it is desired that its cured product can provide enough adhesion strength on the substrate and sufficient reliability up to 220 °C equivalent to conventional epoxy packaging material, and meanwhile, in the event of necessity, the epoxy crosslinking network can collapse rapidly within several minutes in the temperature range of 220–280 °C to allow the faulty chip to be removed. Moreover, the residue attached on the substrate should be cleaned easily with some common noncorrosive solvents such as acetone, chloroform and dichloromethane so that the subsequent surface grinding and polishing processes are unnecessary.

To evaluate the reworkable property of the epoxies synthesized, in this study, about 1 g of mixture of trifunctional Epoxide II and HMPA with the molar ratio of 1:0.8 was cured on a glass slide using 2-ethyl-4methylimidazole as catalyst under the same curing condition as the sample for TGA and DMA measurements. The cured film sample was transparent with area of about  $50 \times 50 \text{ mm}^2$  (Fig. 10A). The temperature of a muffle furnace was pre-determined at 260 °C, in which the cured sample was heat-treated for 4 min. The black residue on the glass slide could be wiped off easily with acetone and a very clean glass slide was obtained (Fig. 10B–D). The test above demonstrated that the quick degradation at the desired temperature and easy cleaning process of substrate could be realized using the present epoxides.

### 3.5. Flame retardant property

The flame retardant properties of these two epoxy resins were examined by the LOI measurement method. The LOI values of samples based on Epoxide I and II were 23.9 and 22.7, respectively, exhibiting the obvious increase in LOI by 31% and 25% compared to that of ERL-4221 (18.2), respectively. As revealed by the FTIR result, at high temperature, the pyrolysis residues for Epoxide I and II were mainly the condensed phosphorus-containing solids, which served as a fire protection layer to retard the further combustion of polymers. Considering the high flammability of current commercial cycloaliphatic epoxy resins due to their aliphatic structures, the significant improvement in flame retardant property for the present two phosphorus-containing epoxides was of significance as environment-friendly halogen-free electronic packaging materials.

### 4. Conclusions

We have designed and synthesized two liquid, di- and trifunctional cycloaliphatic epoxides containing thermally cleavable phosphate group. The cured polymer based on the trifunctional epoxide had the  $T_{\rm g}$  value of 227 °C, which is among the highest  $T_{\rm g}$ for liquid epoxies (cured with HMPA) reported previously in the literature. Compared to the commercial cycloaliphatic epoxide ERL-4221, the two cured epoxides started to decompose at obviously low temperature of 225 and 260 °C, respectively, which fell in the desirable rework temperature range of 200-300 °C. The low degradation temperature and rapid degradation rate are attributed to that the weak phosphate bonds evenly distributed in the network and the auto-accelerated effect on the cleavages of adjacent phosphate and ester bonds by the organic phosphoric acids generated during thermal decomposition, as demonstrated by the results of computational calculation and the isothermal FTIR spectra of solid pyrolysis products and volatized components.

The reworkable test showed that, after heat-treatment for only 4 min at 260 °C, the residue of cured trifunctional epoxide on a glass slide could be easily wiped off using acetone to obtain a very clean substrate so that additional grinding and polishing processes are not necessary. Moreover, the introduction of phosphate group into the epoxy network led to the cured epoxides apparently enhanced flame retardant property. Therefore, the combination of several favorable characteristics such as reworkability, halogen-free flame retardancy, high glass transition temperature and mechanical modulus endow the epoxides synthesized promising application potential as environment-friendly electronic packaging materials.

### Acknowledgments

The support from the Program for New Century Excellent Talents in University of China (Grant No. NCET-06-0280) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (Grant No. 2005-546), is gratefully acknowledged.

#### Appendix. Supporting information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2010.08.039.

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