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Polymer 44 (2003) 6465–6473
polymer
www.elsevier.com/locate/polymer

Novel thermosetting resins based on 4-(*N*-maleimidophenyl)glycidylether
I. Preparation and characterization of monomer and cured resins

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Received 6 May 2003; received in revised form 6 August 2003; accepted 7 August 2003

Abstract

A hybrid monomer of 4-(*N*-maleimidophenyl)glycidylether (MPGE), which possesses both oxirane ring and maleimide curable groups, was first synthesized from *N*-(4-hydroxyphenyl)maleimide and epichlorohydrin by using benzyltrimethylammonium chloride as a catalyst. MPGE was then cured with amine compounds (DDM and DICY) and diethylphosphite (DEP) to result in crosslinking networks. The curing kinetics and mechanisms were studied. High glass transition temperature, good thermal stability, and attractive flame retardance were observed for the prepared resins. These thermal and flame retardant properties of the cured resins were further enhanced by using DEP as the curing agent, which incorporated phosphorus into the cured resins.

Keywords: Thermosets; Maleimide; Epoxy resin

1. Introduction

Thermosetting resins are extensively used as the structural adhesives in composites for aircrafts. In the modern electronic and electrical industrials, laminates and molding compounds based on thermosetting resins are also applied for printed circuit boards and semiconductor encapsulations [1]. Epoxy resins and polyimides are the most popular thermosetting polymers for above-mentioned applications. Generally, epoxy resins are known as having high tensile strength and modulus, low shrinkage in cure, high adhesion properties, and good chemical and corrosive resistance. The ease of chemical modification and convenience of processing operations also spread the application of epoxy resins. However, the developed surface mounting technology, lead-free soldering process, and other advanced electronic packaging techniques require materials being able to sustain high processing temperatures and providing superlative thermal and mechanical properties [2,3]. In the above-mentioned fields as well as aircraft applications, epoxy resins are under limit owing to their insufficient thermal stability and mechanical properties. Polyimides and polybismaleimides, owing to their high performance, are therefore, utilized for applications in advanced electronics and aerospace [4]. On the other hand, polyimide materials are usually accompanied with the drawbacks of poor processibility, brittleness, and high cost. Therefore, modifications on epoxy resins and polyimides are widely investigated for providing materials with moderate cost and satisfied properties.

For combining the versatility of epoxy resins with the high-temperature properties of imide compounds, considerable studies have been reported [5–23]. The approaches included forming epoxy resin–polybismaleimides interpenetrating network (IPN) [5–9], curing epoxy resins with agents containing imide groups [10–13], and blending epoxy resins with thermoplastic polyimides or functional polyimides [14–16]. One of the main drawbacks of these three approaches was the imperfect miscibility between epoxy resins and imide compounds, to bring about poor processibility and limits on resin formulation. On the other hand, introduction of imido groups into the backbones of epoxy compounds attracted considerable work to result in imide–epoxy resins [17–23]. However, the reported approaches encountered decrease in crosslinking density and glass transition temperatures of the resulting resins.

We have devoted to develop maleimide–epoxy compounds to bring new thermosetting resins possessing good processibility, thermal stability, and flame retardance [24].

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0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.08.006

In this work, a hybrid monomer containing both oxirane ring and maleimide groups was synthesized from *N*-(4-hydroxyphenyl)maleimide and epichlorohydrin. The hybrid monomer was then cured with conventional amine curing agents (4,4′-diaminodiphneylmethane (DDM) and dicyanodiamide (DICY)) and a thermal latent curing agent of diethylphosphite (DEP) [25]. Both of the oxirane and maleimide group involved the curing reactions to form highly crosslinking network. The kinetics of the curing reaction and the thermal characterization of the prepared resins were discussed. The thermal stabilities and flame retardance [16,24] of the cured resins were obviously enhanced by he incorporation of the maleimide structures. Moreover, extremely high flame retardance was observed with the resins cured with DEP owing to the incorporation of phosphorus element.

2. Experimental

2.1. Materials

4-Aminophenol, maleic anhydride, diethylphosphite (DEP), *p*-toluenesulfonic acid (*p*-TSA), and benzyltrimethylammonium chloride (BTAC) from Aldrich Co. were used as received. 4,4-Diaminodiphenylmethane (DDM) and dicyanodiamide (DICY) were industrial products. Epichlorohydrin (ECH) was purchased from Lancaster Synthesis Co.

2.2. Equipment

Infrared spectra (FTIR) were obtained with a Perkin–Elmer 2000 FTIR. ^{1}H NMR spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer. Elemental analysis was performed with a Heraeus CHN–O rapid elementary analyzer with benzoic acid or 4-nitroaniline as a standard. DSC thermograms were recorded with a Thermal Analysis (TA) DSC-2900 in nitrogen. Thermogravimetric analysis (TGA) was performed by a TA TGA-2050 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen or air atmosphere. Limited oxygen index (LOI) values were measured on a Stanton Redcraft flame meter. The percentage in the O_2–N_2 mixture, deemed sufficient to sustain the flame was taken as the LOI value.

2.3. Synthesis of N-(4-hydroxyphenyl)maleamic acid (HPMAc, 2)

In a 1 l 3-necked flask, equipped with a mechanical stirrer and a reflux condenser, maleic anhydride (0.88 mol, 86.4 g) dissolved in 700 ml acetone was charged. The solution was stirred at ambient temperature, and 4-aminophenol (0.80 mol, 87.2 g) was added in portions over 30 min. The reaction solution turned into a yellow slurry. After stirring for 1.5 h the slurry was filtered. The solid was washed with acetone, then dried at 50 °C under vacuum to give a yellow powder product (yield: 94%). IR (KBr, cm^{-1}): 2900–3200 (–COOH), 3354 (N–H), 1627 (C=O), 1603 (C=C), 1522 (–Ph). ^{1}H NMR (ppm, in DMSO-d_6): 6.31–6.35 (1H, –C*H*=), 6.47–6.51 (1H, –C*H*=), 6.76–6.79 (2H, aromatic protons), 7.45–7.48 (2H, aromatic protons), 9.43 (1H, –N*H*–), 10.53 (1H, –COO*H*). Elemental analysis found % (calcd %) C: 57.93 (57.97), H: 4.40 (4.35), N: 6.78 (6.76).

2.4. Synthesis of N-(4-hydroxyphenyl)maleimide (HPM, 3)

In a 1 l 3-necked flask, equipped with a mechanical stirrer, a water segregator, and a reflux condenser, HPMAc (0.6 mol, 123.2 g), *p*-toluenesulfonic acid (0.05 mol, 8.75 g), dimethylformamide (60 ml) and toluene (700 ml) were charged. The mixture was heated to reflux for about 8 h until the slurry turned into a clear solution and the stoichiometric amount of water was segregated. After removing toluene, the residue was poured into a large amount of water. The precipitate was collected with filtration and then washed with a sodium bicarbonate solution (5 wt%) and with water. The crude product was recrystallized from a mixed solvent of water–isopropanol (1:1 v/v) to give an orange yellow crystalline needle product (yield: 64%). IR (KBr, cm^{-1}): 3482 (Ph–OH), 1778 (C=O asymmetrical stretching), 1705 (C=O symmetrical stretching), 1388 (C–N stretching), 717 (C=O bending), ^{1}H NMR (ppm, in DMSO-d_6): 6.87–6.90 (2H, –C*H*=C*H*–), 7.12–7.17 (4H, aromatic protons). Elemental analysis found % (calcd %) C: 63.54 (63.49), H: 3.68 (3.70), N: 7.44 (7.41).

2.5. Synthesis of 4-(N-maleimidophenyl)glycidylether (MPGE, 4)

HPM (0.1 mol, 18.7 g) was mixed with 100 g of epichlorohydrin (ECH) in a 500 ml 3-necked flask equipped with a stirrer, condenser, and a nitrogen inlet. After adding BTAC (1.8 g, 0.01 mol) to the solution, the mixture was stirred under nitrogen for 24 h at 60 °C. Excess ECH was removed under reduced pressure and the solid residue was dissolved in ethylene acetate, washed with water and dried over $MgSO_4$. The product was purified by chromatography using a silica column and ethyl acetate/toluene (1:1 in vol.) to give MPGE product (yield 55%; melting point, 45–50 °C; epoxy equivalent weight = 254). IR (KBr, cm^{-1}): 715 (C=O bending), 912 (oxirane-ring), 1248, 1037 (Ph–O–CH_2), 1375 (C–N stretching), 1609 (C=C), 1715 (C=O symmetric stretching), 1781 (C=O asymmetric stretching), 3070 (C–H of imide group). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 2.72 and 2.87 (2H, –(O)CH_2); 3.68 (1H, –CH_2C*H*(O)–); 4.13–4.26 (2H, –Ph–OCH_2–); 6.87 (2H, –C*H*=C*H*–); 7.03–7.54 (4H, aromatic protons).

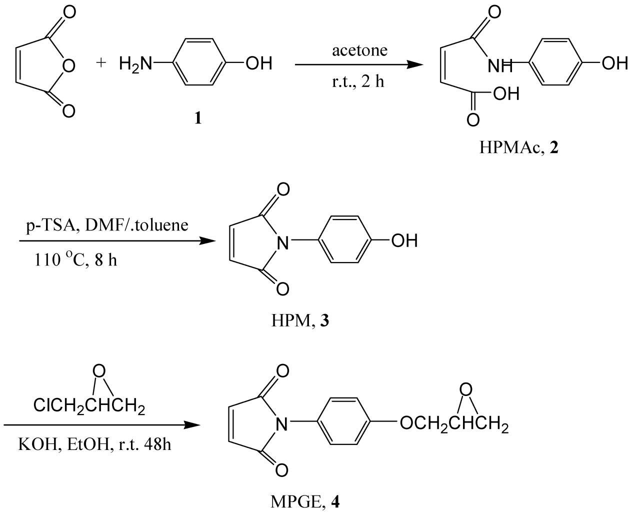
2.6. Preparation of cured resins

MPGE and curing agent (DDM, DICY, or DEP) were dissolved in methylethylketone to form a homogeneous solution. After evaporating the solvent at ambient temperature the mixture was cured with specific curing condition to result in cured resins. The curing compositions and conditions for preparing the cured resins were listed in Table 1.

3. Results and discussion

3.1. Preparation and characterization of hybrid monomer

4-(*N*-maleimidophenyl)glycidylether (MPGE) was prepared from reacting epichlorohydrin with *N*-(4-hydroxyphenyl)maleimide (HPM), which was synthesized according to the reported method [24,26] (Scheme 1). The first attempt of synthesizing MPGE was performed under basic condition with employing KOH as a catalyst. The crude product was analyzed with thin film chromatography and showed complicated compositions containing various byproducts. Pure MPGE was obtained by means of column chromatography with a low yield less than 25%. The strong basic condition of the reaction might cause the hydrolysis of the imide groups of HPM and MPGE, therefore, to result in mixed byproducts. To compensate this flaw benzyltrimethylammonium chloride (BTAC), which was reported being useful in the synthesis of glycidyl phosphinate compounds without causing hydrolysis of the phosphinate compounds [27], was utilized in the synthesis of MPGE. The product yield was significantly raised to about 55%. The chemical structure of the obtained MPGE compound was characterized with FTIR and ^{1}H NMR. The absorption peak at around 913 cm^{-1} was observed in the FTIR spectrum of MPGE (Fig. 1) to demonstrate the formation of oxirane groups. The absorption peaks deriving from the cyclic maleimide group were also observed at 1781 (C=O asymmetric stretching), 1718 (C=O symmetric stretching), 1375 (C–N stretching), and 1610 (C=C) cm^{-1}. Other specific absorption bands at 3070 (C=C–H), 1245 and 1037 (Ph–O–CH$_2$), and 1513 cm^{-1} (phenyl) gave more evidence to the obtained compound having the expected chemical structure. Further characterization was performed with ^{1}H NMR (Fig. 2). The specific absorption peaks were observed at 2.72 and 2.87 (2H, $-(O)CH_2$); 3.68 (1H, $-CH_2CH(O)-$); 4.13–4.26 (2H, $-Ph-OCH_2-$); 6.87 (2H, $-CH{=}CH-$); 7.03–7.54 (4H, aromatic protons). The chemical shifts of the absorption peaks and the area ratios of the peak integration were found to be coincident with the expected chemical structure. Moreover, the experimental results of titration of epoxy equivalent weight also demonstrated the success of synthesizing of MPGE compound. MPGE was solvable in most of the industrial-using solvents, such as acetone, methylethylketone, tetrahydrofuran, *N*,*N*-dimethylacetamide, dimethylsulfoxide, ethylene acetate, methanol, ethanol, 1-methyl-2-pyrrolidone, and dimethylformamide. The good organo-solubility of MPGE suggested its good processibility associating with the current industrial processes.



Scheme 1. Synthesis of MPGE.

Table 1
Preparation of cured resins based on MPGE

Sample code	Curing composition in equivalent ratio MPGE	DDM	DICY	DEP	Curing conditions	T_g (°C)
DDM08-L	1	0.8	–	–	125 °C (1 h), 170 °C(2 h), 195 °C (2 h)	119
DDM18-L	1	1.8	–	–	125 °C (1 h), 170 °C(2 h), 195 °C (2 h)	137
DICY08-L	1	–	0.8	–	125 °C (1 h), 170 °C(2 h), 220 °C (2 h)	118
DICY18-L	1	–	1.8	–	125 °C (1 h), 170 °C(2 h), 220 °C (2 h)	146
DEP08-L	1	–	–	0.8	125 °C (1 h), 170 °C(2 h), 220 °C (2 h)	91
DDM08-H	1	0.8	–	–	125 °C (1 h), 170 °C(2 h), 195 °C (2 h), 260 °C (2 h)	210
DDM18-H	1	1.8	–	–	125 °C (1 h), 170 °C(2 h), 195 °C (2 h), 260 °C (2 h)	202
DICY08-H	1	–	0.8	–	125 °C (1 h), 170 °C(2 h), 220 °C (2 h), 260 °C (2 h)	219
DICY18-H	1	–	1.8	–	125 °C (1 h), 170 °C(2 h), 220 °C (2 h), 260 °C (2 h)	219
DEP08-H	1	–	–	0.8	125 °C (1 h), 170 °C(2 h), 220 °C (2 h), 260 °C (2 h)	203

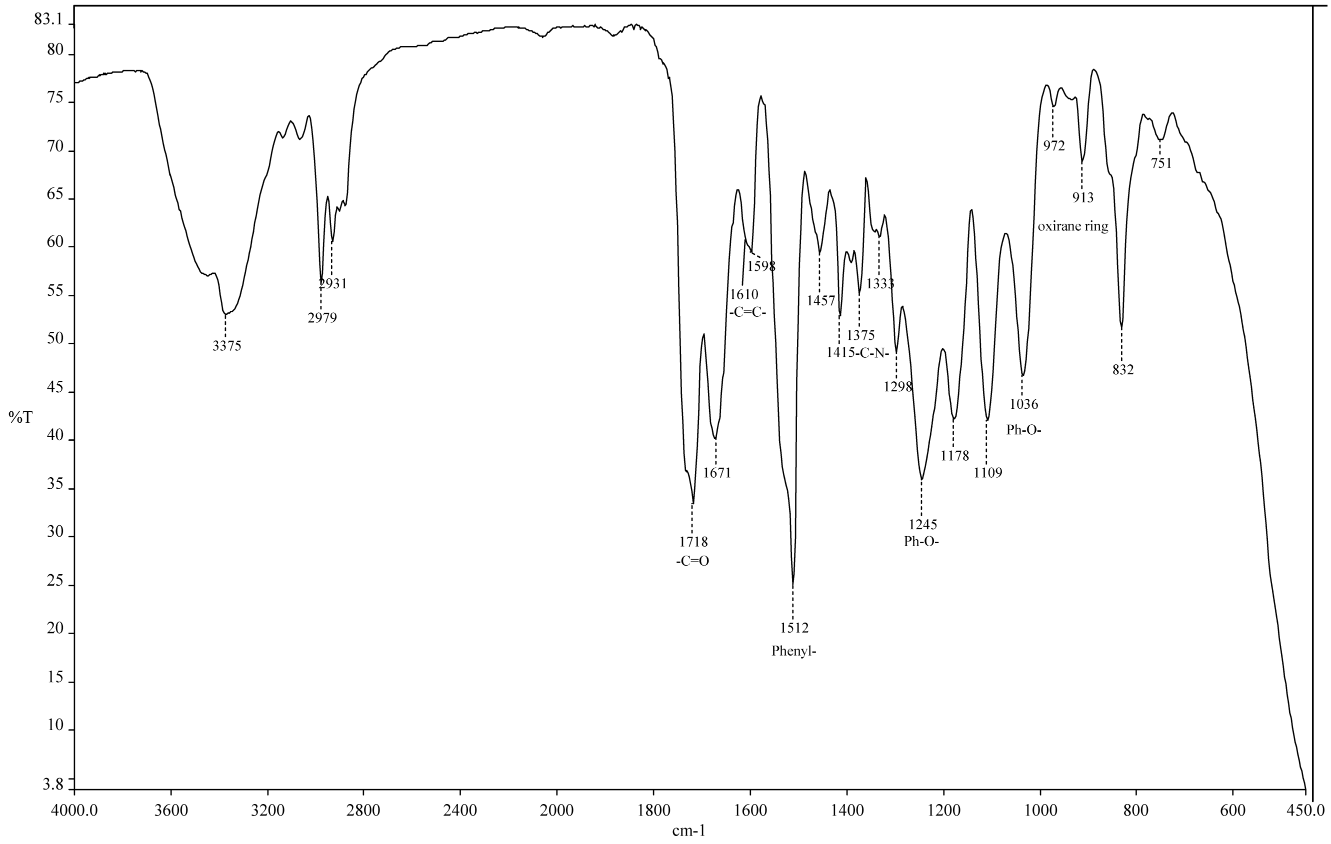


Fig. 1. FTIR spectrum of MPGE.

3.2. The curing reactions of MPGE

Two commonly used amine compounds, DDM and DICY, were first utilized as curing agents for MPGE, and the curing compositions were shown in Table 1. The reaction compositions of DDM-08 and DICY-08, in which the ratios of oxirane group of MPGE over the active hydrogen of the curing agent were 0.8, were performed to lead all of the amine hydrogens reacting with the oxirane groups and preventing the occurrence of the reaction between the maleimide groups and amine groups. The other reaction compositions (DDM-1.8 and DICY-1.8), which had excess amine curing agents to oxirane groups of MPGE, was preformed to examine the effect of the amine–maleimide addition reaction. The thermal behaviors of the MPGE curing reactions were monitored with DSC scanning experiments (Fig. 3). Two exothermic peaks were found for DDM curing reactions. The first peak might come from the reaction of the amine groups of DDM with the oxirane rings of MPGE, and the second peak from the self-addition reaction of the maleimide groups of MPGE. On the other hand, only one exothermic peak was observed for the DICY

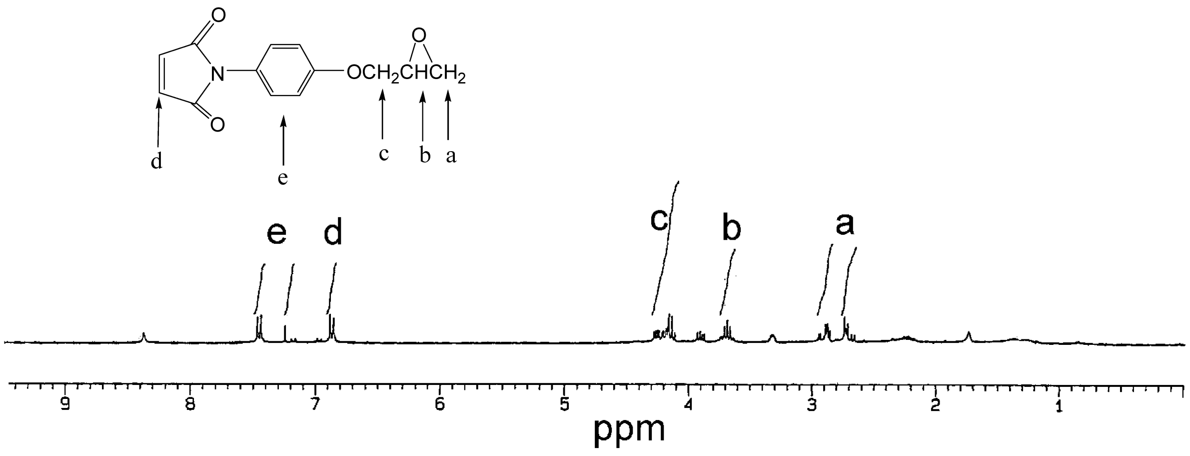


Fig. 2. ^{1}H NMR spectrum of MPGE.

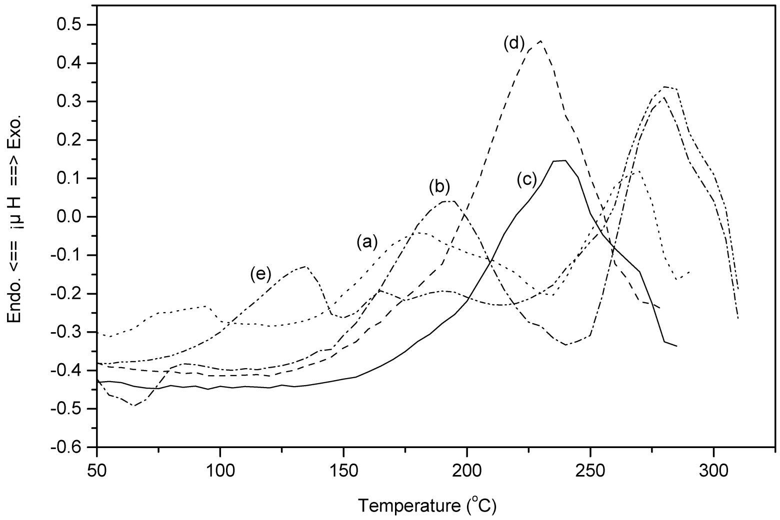
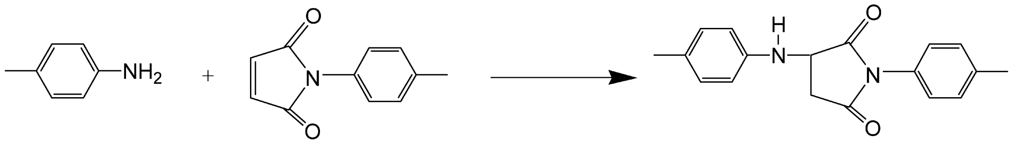


Fig. 3. DSC thermograms of MPGE curing reactions with (a) 0.8 equiv. amount of DDM, (b) 1.8 equiv. amount of DDM, (c) 0.8 equiv. amount of DICY, and (d) 1.8 equiv. amount of DICY, (e) 0.8 equiv. amount of DEP. The experiments were taken in nitrogen atmosphere at a heating rate of 10 °C/min.

curing compositions. Since epoxy compound/DICY compositions showed their reaction exothermic peaks above 160 °C [28–30], the one exothermic peak of MPGE/DICY curing reaction should be owing to the overlap of the DICY–oxirane group reaction and the maleimide self-addition reaction occurring at the temperature range of 160–250 °C. On the other hand, the second exothermic peak was observed to shift to low temperature region for reaction compositions having excess amine compounds. It was therefore, suggested that another reaction might take place at relatively low temperatures while the reaction compositions having excess amine groups. One reasonable inference was the occurrence of the reaction between amine groups and maleimide groups. This reaction was one of the Michael addition reactions and could form the aspartimide structure as shown below.



MPGE was also cured with a thermal latent curing agent DEP. The thermal latent characteristic of DEP for curing MPGE was also observed by DSC measurement (Fig. 3, curve e). Compared with the thermogram of MPGE/DDM curing compositions, an additional exothermic peak was observed at about 130 °C. This exothermic peak came from the following ethanol-elimination reaction of DEP to form the active P–OH group toward curing the epoxy resins. The thermal characteristics, reaction mechanisms and latent properties of DEP/epoxy curing reactions were demonstrated with GC/MS and ^{1}H NMR in the previous work [25]. Other exothermic peaks at about 180 and 277 °C were assigned to be from oxirane curing reaction with the formed P–OH groups and the self-addition reaction of maleimide group, respectively.

According to Kissinger's [31] and Ozawa's [32] methods, the activation energies of the exothermic reactions were obtained from various DSC thermograms measured at different heat rates. Two relationships among activation energy (E_a), heating rates (ϕ), and temperatures of exothermic peak (T_p) showing as

$$E_a = \frac{-R}{1.052}\frac{\Delta \ln \phi}{\Delta(1/T_p)} \tag{1}$$

and

$$-\ln(\phi/T_p^2) = \ln(E_a/R) - \ln(A^*n) - (n-1)\ln(1-x)P + E_a/(RT_p) \tag{2}$$

were utilized. The activation energies of the curing reactions were determined from the slopes of the plots of ln(heating rate) vs. $1/T_p$ (Eq. (1)) and $-\ln(\psi/T_p^2)$ vs. $(1/T_p)$ (Eq. (2)), respectively. The calculated activation energies of the MPGE curing reactions were listed in Table 2. The

Table 2
The activation energies of MPGE curing reactions (kJ/mol)

Curing samples[a]	Kissinger's method First reaction	Second reaction	Ozawa's method First reaction	Second reaction
DDM08	76.14	115.27	79.83	118.30
DDM18	69.60	94.00	73.41	98.01
DICY18	86.87	–	90.36	–
DICY08	88.62	–	92.07	–
DEP08[b]	75.32	166.21	78.23	166.54

[a] DDM08 indicating using DDM as the curing agent with an amount of 0.8 equiv. of MPGE.

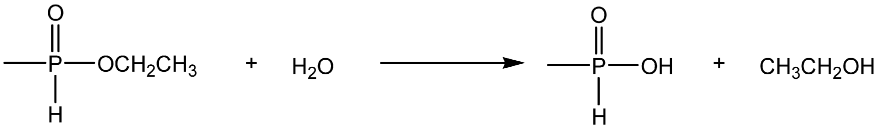
[b] The first exothermic reaction coming from the decomposition of DEP was not counted in.

activation energy for the first reaction peak of MPGE/DDM composition was 76.14 and 79.83 kJ/mol from Kissinger's and Ozawa's method, respectively. The values of the activation energies from the two methods were similar, and the values from Ozawa's method were a little larger than those from Kissinger's method [33]. As mentioned above, this exothermic peak arose from the reaction between oxirane ring and amino groups, and the value of the activation energy was comparable with other reported activation energy values of epoxy compounds/DDM curing reactions [29–30,33] The activation energy of the second exothermic reaction was 115.27 kJ/mol (Kissinger's method). However, this value was lower than the activation energy of maleimide self-addition reaction, to imply some Michael addition reaction between amino group and maleimide ring may also involve in the second exothermic peak region. While using excess DDM in the curing composition, the activation energy of the second exothermic reaction was significantly lowered. This result is reasonable owing to excess amine compound induced much occurrence of the Michael addition reaction between amine compound and maleimide. For the DICY cured compositions, only one exothermic peak was observed and its activation energy was about 86.87 from Kissinger's method (90.36 kJ/mol from Ozawa's method). The value was a little higher than those of DICY/epoxy curing reactions [29,30] and lower than the activation energy of maleimide self-addition reactions, to further demonstrate both of the curing reaction of DICY/epoxy and self-addition reaction of maleimide group contributing to the exothermic behavior. On the other hand, the high activation energy (about 166 kJ/mol) of the last exothermic peak of the DEP/MPGE curing reactions was noteworthy. Since there was no amino group in the DEP/MPGE composition, only the self-addition reaction of maleimide group contributed to the exothermic behavior at this temperature region.

The curing reactions of MPGE with the amine compounds could be considered involving several reactions, including oxirane ring/amine addition, amine/maleimide addition, maleimide self-addition, and oxirane ring/hydroxyl group esterification. The complicated reactions are therefore under detail studies with some model compounds (ex. glycidylphenylether, *N*-phenylmaleimide, and aniline) to dig out much about the mechanisms of the MPGE curing reactions.

3.3. Thermal analysis of the cured resins

Cured resins basing on various compositions and curing conditions were prepared for examining their thermal properties (Table 1). L series samples (cured at low temperature region) were taken as resins with only performing the epoxy curing reactions. H Series samples (cured at high temperature region) were taken as resins with fully performing the oxirane and maleimide curing reactions. The glass transition temperatures of the cured resins were examined with DSC measurements and the results were collected in Table 1. The relatively low glass transition temperatures for the L series samples were due to the low crosslinking densities of the resins. Excess curing agent resulted in a level up of the glass transition temperatures of the L series samples (DDM18-L and DICY18-L). Excess amine induced much occurrence of the amine–maleimide Michael addition reaction at about 195 °C to increase the crosslinking densities of the cured resins. While being fully cured, all the H series samples exhibited rather high glass transition temperatures above 200 °C. The sample of DICY18-H showed its T_g as even high as 219 °C. On the other hand, the relatively low glass transition temperatures of the DEP cured resins might be due to their possessing of the soft linkage of P–O bonding. The high glass transition temperatures of the prepared resins



$$-\overset{O}{\overset{\|}{\underset{H}{\underset{|}{P}}}}-OCH_2CH_3 + H_2O \longrightarrow -\overset{O}{\overset{\|}{\underset{H}{\underset{|}{P}}}}-OH + CH_3CH_2OH$$

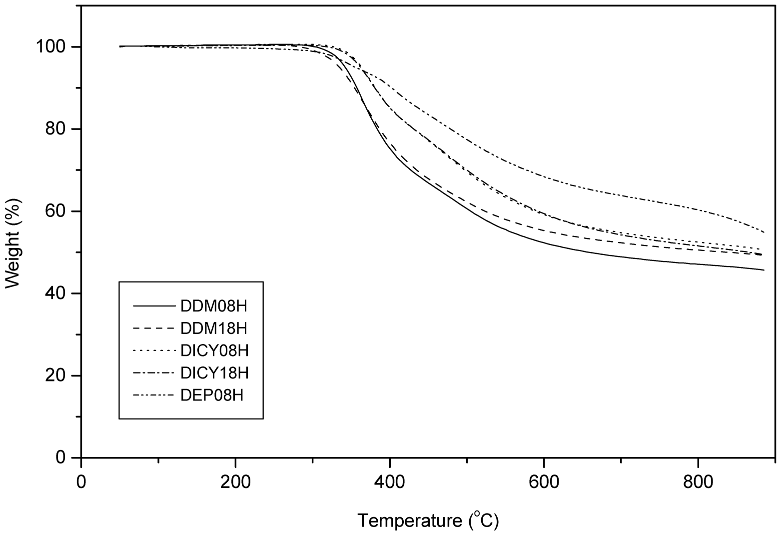


Fig. 4. TGA thermograms of cured resins in nitrogen atmosphere.

Table 3
Thermal stability data of the prepared resins

Samples	TGA analysis in N_2			TGA analysis in air			LOI
	T_d[a] (°C)	IPDT (°C)	Char yield at 800 °C (%)	T_d[a] (°C)	IPDT (°C)	Char yield at 800 °C (%)	
DDM08-H	342	1656	47.13	355	511	1.10	38.0
DDM18-H	334	1847	50.54	363	548	1.37	38.0
DICY08-H	363	1889	52.48	345	529	3.02	38.5
DICY18-H	361	1767	51.57	340	539	1.74	38.0
DEP08-H	355	2287	60.38	348	669	11.01	48.0

[a] The temperature at 5% weight loss.

were noteworthy for applying the resins as high performance structural materials in aerospace and electronic industrials.

The thermal stability of the cured resins were examined with TGA measurements (Figs. 4 and 5) and estimated with the degradation temperature (T_d, temperature at 5% weight loss) and integral procedural decomposition temperature (IPDT) [21,24,34]. IPDT proposed by Doyle [34] was

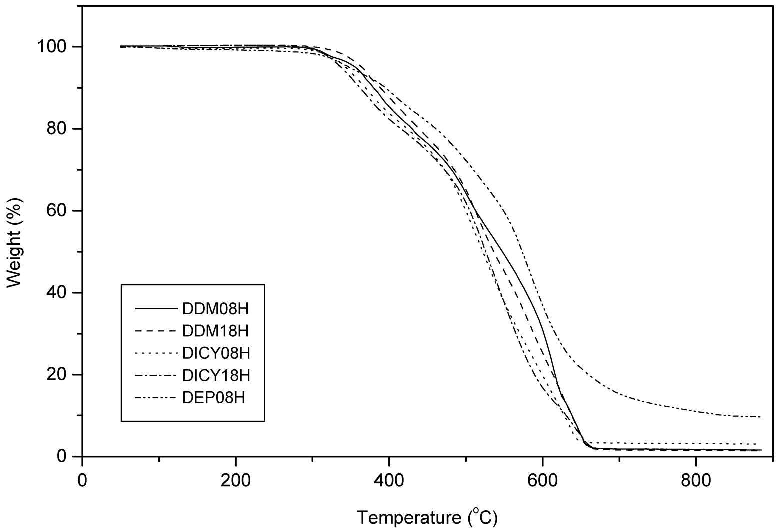


Fig. 5. TGA thermograms of cured resins in air atmosphere.

calculated by using Eq. (3) [21,24,34]:

$$\mathrm{IPDT}(^\circ\mathrm{C}) = A^* K^* (T_\mathrm{f} - T_\mathrm{i}) + T_\mathrm{i} \quad (3)$$

where A^* is the area ratio of total experimental curve decided by total TGA thermogram, K^* the coefficient of A^*, T_i the initial experimental temperature, and T_f the final experimental temperature. All of the analytical data of the TGA measurements were collected in Table 3. The degradation temperatures of the cured resin DDM08-H was 342 °C, and DICY08-H 363 °C, which were comparable with the commercial epoxy resins. The weight loss rate of the maleimide–epoxy resins at high temperature regions were significantly retarded, while being compared with the DGEBA cured epoxy resins. The enhancement of the thermal stability of epoxy-based resins with the incorporation of maleimide structure into the cured resins was demonstrated. The good thermal stability of the prepared resins was further verified with the IPDT evaluation. Extremely high IPDT from 1656 to 1888 °C were found for all of the prepared resins. Since DGEBA/DDM cured resin exhibited its IPDT of 652 °C, the developed resins exhibited superior thermal stability over the common epoxy resins.

3.4. Flame retardance of the MPGE based resins

The high char yields of the developed resins were also noteworthy. Increasing char formation could limit the production of combustible gases, decrease the exothermicity of the pyrolysis reactions, and decrease the thermal conductivity of the resins, consequently to reduce the flammability of the resins. A polymer with high char yield often leaded to good flame retardance [35–38]. Therefore, the flame retardance of the prepared resins was estimated with LOI measurement, and the results were collected in Table 3. High LOI values of about 38.0 were found for the resins to imply their excellent flame retardant properties. The self-extinguishing behavior was also observed for the resins. Moreover, the measured LOI values were also found to follow the Krevelen's equation of $\mathrm{LOI} = 17.5 + 0.4$ (polymer's char ratio) [35,36].

The weight loss rate of the DEP cured resins in thermogravimetric analysis was significantly depressed. The thermal stability and the flame retardance of the maleimide–epoxy resins, including IPDT, char yield, and LOI value, were further enhanced by using DEP as the curing agent. The above-mentioned results were owing to the incorporation of phosphorus into the resins. Organophosphorus groups promote the dehydration and char-forming reactions under heat to result in phosphorus-rich carboneous residual with good thermal-oxidative stability [39–41]. Therefore, the condensed phase mechanism of flame retardation acted with the phosphorus char to exhibit especially high LOI value deviating from the Krevelen's equation [39–41]. A phosphorus–nitrogen synergistic effect of flame retardance was read out from the DEP/MPGE cured resins, which exhibited a very high LOI value of 48.0.

4. Conclusions

Thermosetting epoxy–maleimide resins were obtained from a novel monomer possessing both oxirane ring and maleimide curable groups. Using amine compounds as curing agents, the resulted resins exhibited good thermal stability, high glass transition temperatures, extremely high integral procedural decomposition temperatures, and good flame retardant property. The above-mentioned properties of the maleimide–epoxy resins were further enhanced by using diethylphosphite as a curing agent. The developed resins were expected to be applicable in advanced structural materials for aerospace and electronic industrials, especially for the so called halogen-free 'green' products.

Acknowledgements

Financial support on this work from National Science Council, Taiwan, Republic of China is highly appreciated (Grant No. NSC-91-2216-E-033-003).

References

[1] Jones FR. In: Ellis B, editor. Chemistry and technology of epoxy resins. London: Chapman & Hall; 1994. p. 256–302. Chapter 8.

[2] Henningsen GC, Gause SA. In: Coombs CF Jr, editor. Printed circuits handbook. New York: McGraw-Hill; 1996. p. 1–31. Chapter 8.

[3] Alternatives to halogenated flame retardants in electronic and electrical products. IVF Research Publication 99824, Molndal, Sweden; 1999.

[4] Takekoshi T. In: Ghosh MK, Mittal KL, editors. Polyimides. New York: Marcel Dekker; 1996. p. 7.

[5] Kumar AA, Alagar M, Rao RMVGK. Polymer 2002;43:693.

[6] Musto P, Martuscelli E, Ragosta G, Russo P, Scarizni G. J Appl Polym Sci 1998;69:1029.

[7] Kumar AA, Alagar M, Rao RMVGK. J Appl Polym Sci 2001;81:2330.

[8] Han JL, Chern YC, Li KY, Hsieh KH. J Appl Polym Sci 1998;70:529.

[9] Kim WG, Nam TY. J Polym Sci Part A: Polym Chem 1996;34:957.

[10] Lee CJ. US Patent 4,487,894; 1984.

[11] Ichino T, Hasuda Y. J Appl Polym Sci 1987;34:1667.

[12] Agag T, Takeichi T. Polymer 1999;40:6557.

[13] Gaw K, Jikei M, Kakimoto M, Imai Y, Mochjizuki A. Polymer 1997;38:4413.

[14] Hodgin JH, Simon GP, Varley RJ. Polym Adv Technol 1998;9:3.

[15] Hay JN, Woodfine B, Dacies M. High Perform Polym 1996;8:35.

[16] Shiobara T, Okuse S, Aoki T, Kato H. US Patent 6,143,423; 2000.

[17] Matinez PA, Cadiz V, Mantecon A, Serra A. Angew Makromol Chem 1985;133:97.

[18] Mantecon A, Cadiz V, Serra A, Martinez PA. Angew Makromol Chem 1988;156:37.

[19] Adhinarayanan K, Packirisamy S, George RS, Rao VL, Ramaswamy R. J Appl Polym Sci 1991;43:783.

[20] Abraham G, Packirisamy S, Adhinarayanan K, Feby AG, Ramaswamy R. J Appl Polym Sci 2000;78:1729.

[21] Park SJ, Kim HC, Lee HI, Suh DH. Macromolecules 2001;34:7573.

[22] Yang NC, Jeong JK, Suh DH. Polym Prepr 2001;42:535.

[23] Abraham G, Packirisamy S, Vijayam TM, Ramaswamy R. J Appl Polym Sci 2003;88:1737.

[24] Wu CS, Liu YL, Hsu KY. Polymer 2003;44:565.

[25] Chiu YS, Liu YL, Wei WL, Chen WY. J Polym Sci Part A: Polym Chem 2003;41:432.

[26] Hao J, Jiang L, Cai X. Polymer 1996;37:3721.

[27] Alcon MJ, Espinosa MA, Galia M, Cadiz V. Macromol Rapid Commun 2001;22:1265.

[28] Ashcroft WR. In: Ellis B, editor. Chemistry and technology of epoxy resins. London: Chapman & Hall; 1994. p. 49. Chapter 2.

[29] Liu YL, Hsiue GH, Chiu YS, Jeng RJ, Perng LH. J Appl Polym Sci 1996;61:613.

[30] Liu YL, Hsiue GH, Chiu YS. J Polym Sci Part A: Polym Chem 1997; 35:565.

[31] Kissinger HE. Anal Chem 1957;29:1072.

[32] Ozawa TJ. Therm Anal 1970;2:301.

[33] Liu YL. J Polym Sci Part A: Polym Chem 2002;40:359.

[34] Doyle CD. Anal Chem 1961;33:77.

[35] Krevelen DW. Polymer 1975;16:615.

[36] Krevelen DW. Chimia 1974;28:504.

[37] Wu CS, Liu YL, Chiu YS. Polymer 2002;43:4277.

[38] Jeng RJ, Wang JR, Lin JJ, Liu YL, Chiu YS, Su WJ. J Appl Polym Sci 2001;82:3526.

[39] Banks M, Ebdon JR, Johnson M. Polymer 1994;35:3470.

[40] Liu YL, Hsiue GH, Chiu YS, Jeng RJ, Ma C. J Appl Polym Sci 1996; 59:1619.

[41] Hilado CJ. Flammability handbook for plastics. Lancaster: Technomic Punlishing; 1998. Chapter 5; p. 189–230.