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Maleimide-epoxy resins: preparation, thermal properties, and flame retardance

Chuan-Shao Wu[a], Ying-Ling Liu[b,c,*], Keh-Ying Hsu[b]

[a]*Department of Textile Engineering, Nan Ya Institute of Technology, 320, Chungli, Taoyuan 32023, Taiwan, ROC*
[b]*Department of Chemical Engineering, Chung Yuan Christian University, 22, Pu-Jen, Chungli, Taoyuan 32023, Taiwan, ROC*
[c]*R&D Center for Membrane Technology, Chung Yuan Christian University, 22, Pu-Jen, Chungli, Taoyuan 32023, Taiwan, ROC*

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Abstract

Maleimide modified epoxy compounds were prepared through reacting *N*-(4-hydroxylphenyl)maleimide (HPM) with diglycidylether of bisphenol-A. Triphenylphosphine and methylethylketone were utilized in the reactions as a catalyst and a solvent, respectively. The resulting compounds possessed both oxirane ring and maleimide group. The kinetics of the curing reactions of the maleimide-epoxy compounds and amine curing agents, 4,4-diaminodipheylmethane (DDM) and dicyandiamide (DICY), were studied. Incorporation of maleimide groups into epoxy resins provided cyclic imide structure and high cross-linking density to the cured resins, to bring high glass transition temperatures (179 °C) and good thermal stability (above 380 °C) to the cured resins. High char yields in the thermogravimetric analysis and high limited oxygen index values (25.5–29.5) were also observed for the cured resins to impy their good flame retardance.

Keywords: Epoxy resin; Maleimide; Thermal properties

1. Introduction

Epoxy resins are widely used in industrial applications owing to their many attractive properties, such as excellent chemical and solvent resistance, good thermal and electrical properties, high strength and modulus, good adhesion property, and good processability [1]. Up to now, research efforts on improving epoxy resins' properties are still attractive for advanced applications. For example, epoxy resins with superior thermal stability are expected for using as molding compounds and encapsulation materials in advanced electronic components. Generally, modifying epoxy resins with polyimides or imido compounds [2–13] provided a convenient approach of enhancing the thermal stability of epoxy resins. Therefore, epoxy resins were cured with reactive polyimide [2–4], polyamic acid [5], and imido-modified curing agents [6] to introduce imide structures into epoxy resin. The thermal stability of the above-mentioned imide-epoxy resins was significantly leveled up both in the initial decomposition temperature (IDT) and the integral procedural decomposition temperature (IPDT) [7]. On the other hand, epoxy resins modified with maleimide compounds also received attractive attentions, due to the similar curing conditions and processing properties of the epoxy resins and maleimides. [8–12] Maleimide-epoxy resins usually showed appropriate properties between epoxy and maleimide resins [13]. Thus, both the intercrossed and the interpenetrating systems (IPN) based on bismaleimides and epoxy resins were prepared and exhibited good thermal and mechanical properties [8–12]. Additionally, since imide groups could provide char formation in the condensed phase to improve polymers flame retardant properties, epoxy resins modified with imide compounds through chemical reactions or physical blending have been reported to show good flame retardant properties [14].

In this work, a maleimide compound with hydroxyl group was first synthesized. Maleimide-epoxy compounds were consequently obtained through a simple addition reaction between the oxirane ring of epoxy compound and hydroxyl group of maleimide. The resulting maleimide-epoxy compounds possessed both oxirane ring and

* Corresponding author. Address: Department of Chemical Engineering, Chung Yuan Christian University, 22, Pu-Jen, Chungli, Taoyuan 32023, Taiwan, ROC. Tel.: +886-3-2654130; fax: +886-3-2654199.
E-mail address: ylliu@cycu.edu.tw (Y.L. Liu).

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maleimide reactive groups. Each of the reactive groups might form crosslinking networks under thermal curing reaction to bring about high crosslinking density. The synthesis, characterization, and curing reaction of the maleimide-epoxy compounds as well as the properties of the cured resins were investigated. As mentioned previously, the developed resins in this study were expected to show good thermal properties and flame retardance.

2. Experimental section

2.1. Materials

Maleic anhydride and 4-aminophenol were purchased from Aldrich Chemical Co. Diglycidylether of bisphenol-A (epoxy equivalent weight EEW = 188) was supplied from Chang Chun Plastics Co. (CCP, Taiwan) with its commercial code of BE188. Dicyandiamide (DICY), 4,4′-diaminodiphenylmethane (DDM), and triphenylphosphine (TPP) were from Tokyo Kasei Kogyo Co. Ltd (Japan). Dimethylformamide (DMF) and toluene received from Fisher Co. were dried with the standard procedures prior to use.

2.2. Synthesis of N-(4-hydroxyphenyl)maleamic acid (HPMAc, 2) [15–17]

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 (d, 1H), 6.47–6.51 (d, 1H), 6.76–6.79 (d, 2H), 7.45–7.48 (d, 2H), 9.43 (s, 1H), 10.53 (s, 1H). Elemental analysis found % (Calcd %) C: 57.93 (57.97), H: 4.40 (4.35), N: 6.78 (6.76).

2.3. Synthesis of N-(4-hydroxyphenyl)maleimide (HPM, 3) [15–17]

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, washed with 5 wt% sodium bicarbonate solution, and with water. The crude product was recrystallized from a mixed solvent of water–isopropanol (1:1 v/v) to give an orange 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 (d, 2H), 7.12–7. 17 (m, 4H). Elemental analysis found % (Calcd %) C: 63.54 (63.49), H: 3.68 (3.70), N: 7.44 (7.41).

2.4. Synthesis of maleimide-epoxy compounds (MIE, 4)

MIE was prepared through reacting BE188 and HPM with various feeding ratios. The preparation of MIE-40 was taken as an example. HPM (0.027 mol, 3.74 g) and BE188 (12.53 g) dissolved in 20 ml of methylethylketone (MEK) was charged into a 150 ml round-bottom flask. Triphenylphosphine (TPP, 0.05 g) was added to the solution as a reaction promoter. The reaction solution was then heated to reflux (at about 130–140 °C) for 4 h, and then cooled to room temperature. The solvent was removed out with a rotary evaporator. The product was then heated at 70 °C under vacuum for 6 h to give a solid product (yield: 100%). Characterization on MIE-40: softening point 112 °C; epoxy equivalent weight = 451 (calculated value: 439). IR (KBr, cm^{-1}): 716 (C=O bending), 915 (oxirane ring), 1388 (C–N stretching), 1711 (C=O symmetrical stretching), 1778 (C=O asymmetrical stretching), 3471 (–OH). ^{1}H NMR (ppm, in DMSO-d_6): 1.54 (s, 6H), 2.64–2.66 (t, 1.2H), 2.77–2.81 (t, 1.2H), 3.25–3.28 (m, 1.2H), 3.43 (m, 0.8H), 3.71–3.77 (m, 1.2H), 3.95 (b, 3.2H), 4.20–4.25 (m, 1.2H), 5.39 (b, 0.8H), 6.71–7.29 (m, 12.8H). Elemental analysis found % (Calcd %) C: 69.21 (69.87), H: 5.80 (5.72), N: 2.88 (2.96).

2.5. Preparation of cured epoxy resins

The cured epoxy resins were obtained from thermally curing MIE with amine compounds, DDM and DICY, as curing agents. Certain amounts of MIE and curing agent were mixed together in methylethylketone solution and cured in oven. The conditions of curing reaction for MIE/DDM and MIE/DICY compositions were 80 °C (1 h), 140 °C (1.5 h), 230 °C (2 h), and 80 °C (1 h), 180 °C (1.5 h), 230 °C (2 h), respectively.

2.6. Measurements

Infrared spectra (FT-IR) were obtained from a Perkin–Elmer 2000 FT-IR. ^{1}H NMR spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer with DMSO-d_6 as a solvent. Gel permeation chromatography was measured with a Lab Alliance Series III GPC with a Polymer Laboratories column of PLRP-S elueting with tetrahydrofuran as a solvent at a flow rate of 1.0 ml/min and at 30 °C. Differential scanning calorimetry (DSC) thermograms were recorded with a Perkin–Elmer DSC 7

at a heating rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a Perkin–Elmer TGA 7 Thermogravimetric Analyzer at a heating rate of 10 °C/min under nitrogen or air atmosphere. IPDT proposed by Doyle [18] was calculated by using Eq. (1) [19–20]:

$$\text{IPDT (°C)} = A^*K^*(T_f - T_i) + T_i \quad (1)$$

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. The activation energies (E_a) of decomposition reaction of the cured epoxy resins were calculated from TGA thermogram buy means of the integral method basing on the Horwitz–Metzger's equation (Eq. (2)) [20–21]:

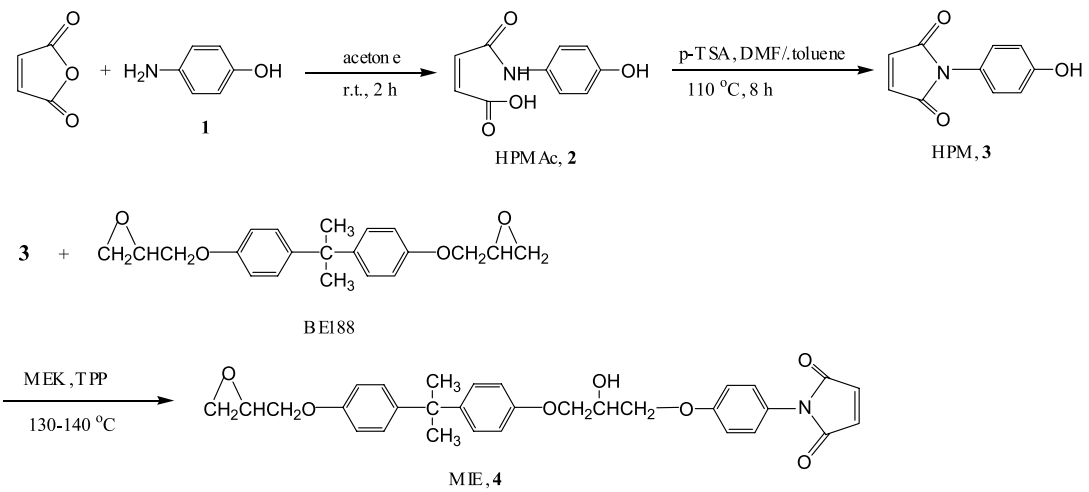
$$\ln\{\ln(1-\alpha) - 1\} = E_a\theta/RT^2\text{max} \quad (2)$$

where α is the decomposition ratio, θ the difference between T and T_{max}, T_{max} the temperature of maximum rate of weight loss, and R the ideal gas constant. The activation energy was given by the straight line corresponding to the plot of $\ln\{\ln(1-\alpha)^{-1}\}$ versus θ. 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.

3. Results and discussion

3.1. Preparation of MIE epoxy compounds

The preparation of the maleimide-epoxy compounds (MIE) was performed through reacting HPM with a diglycidylether of bisphenol-A (BE188) via addition reactions between the phenol group and the oxirane group (Scheme 1). Owing to the high viscosity of the resulting products, a solution process was carried out for the above-mentioned reactions with 500 ppm of triphenylphosphine as a catalyst and methylethylketone as a solvent. The A1 catalyst (ethyltriphenylphosphonium acetate/acetic acid complex), which was commonly used as a catalyst for the reaction between phenol derivatives and epoxy compounds [22], was not proper for the reaction between HPM and BE188 owing to resulting in gel-like products. The reaction compositions and the properties of the obtained compounds were listed in Table 1. The EEW values of the maleimide-epoxy compounds calculated from reaction compositions were coincident with the values measured from titration experiments. This result implies the high conversions of the reactions between phenol groups and oxirane rings. The occurrence of the above-mentioned reaction was monitored by FTIR (Fig. 1). The decrease in the intensity of the absorption peak of oxirane ring at 915 cm^{-1} was observed, to reveal the decrease of oxirane ring's concentration alone with the performance of the reaction. The chemical structure of the resulting maleimide-epoxy compounds was demonstrated with the absorption peaks at 1388 cm^{-1} (C–N), 1711, 1778, and 716 cm^{-1} (imide group), and 1603 cm^{-1} (C=C). Moreover, ^{1}H NMR analysis on the MIE compounds also demonstrated their chemical structure (Fig. 2). The appearance of the absorption peaks at about 3.95 ppm (ring opened oxirane ring, $-OCH_2CH(OH)-$) and 5.39 ppm ($-COH$) demonstrated the performance of the addition reaction between HPM and BE188. The peaks at about 2.64, 2.77, 3.25, 3.75, and 4.24 ppm showed the typical oxirane absorptions, and the peak at 1.54 ppm exhibited the absorption of the isopropyl group. Moreover, the HPM/BE188 unit ratios were directly calculated from the peak area ratios of the absorption at 6.71–7.29 ppm (aromatic proton and $CH{=}CH$) over the absorption at 1.54 ppm (isoprypyl group), and the results were coincident with the feeding ratios of HPM/BE188 for every MIE compounds. Additionally, the chemical structures of MIE compounds



Scheme 1. Preparation of *N*-(4-hydroxyphenyl)maleimide (HPM) and maleimide-modified epoxy compounds (MIE).

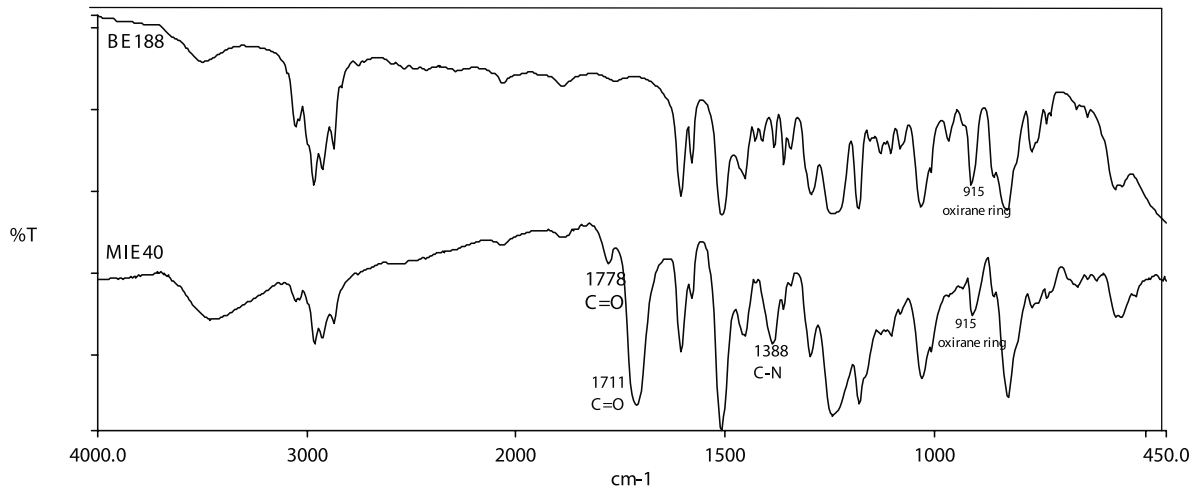


Fig. 1. FTIR spectra of epoxy compounds before (BE188) and after (MIE-40) reacting with HPM.

were also confirmed with the experimental results of elemental analysis (Table 1).

The MIE compounds are solid rather than viscous liquid, due to incorporation of the heterocyclic hard imido-phenyl groups and increase of molecular weight. The softening points of the MIE compounds increased with increasing their maleimide contents. On the other hand, Fig. 3 showed the GPC chromatography of the BE188 epoxy resin and the maleimide-modified resin MIE-40. Two major peaks at retention time of about 3.608 and 3.217 min were observed for BE188. For MIE-40, another peak at about 2.525 min was observed. This integration of peak area of this peak increased with HPM content increasing, to imply the incorporation of HPM onto BE188. Moreover, no peak was observed at the region of short retention time to denote that there was few epoxy resins of two-end modification of HPM. Furthermore, The MIE compounds showed good solubility in acetone and methylethylketone, both are commonly used as solvents for processing epoxy resins. The good solubility of MIE compounds suggested they could be processed with the commercial epoxy resins under the present processing equipments and conditions for epoxy resins.

3.2. Curing reactions of MIE

It is well known that both the oxirane group and maleimide group reacted with amine groups through addition reactions [23–24]. Moreover, the maleimide groups might crosslink through self-addition reaction

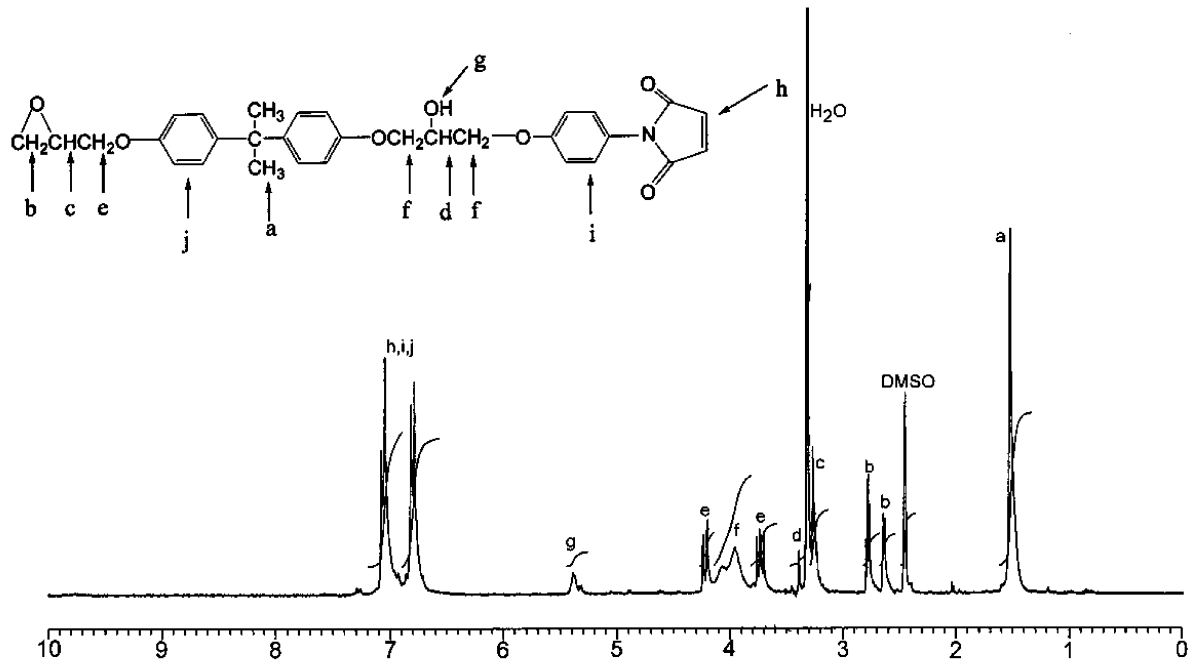


Fig. 2. ^{1}H NMR spectrum of MIE-40.

Table 1
Synthesis of maleimide-modified epoxy compounds

Epoxy compound	Feeding ratio[a]		EEW (g/mol)		Softening point (°C)	Elemental analysis		
	BE188	HPM	Calculated	Measured		C (%) found (calcd)	H (%) found (calcd)	N (%) found (calcd)
MIE-10	1.0	0.1	230	241	40	73.12(73.07)	7.01(7.03)	0.66(0.68)
MIE-20	1.0	0.2	282	281	78	71.99(72.27)	6.66(6.75)	1.28(1.24)
MIE-30	1.0	0.3	350	355	91	71.62(71.59)	6.47(6.51)	1.66(1.72)
MIE-40	1.0	0.4	439	451	112	71.05(71.01)	6.26(6.31)	2.10(2.12)
MIE-50	1.0	0.5	565	578	128	70.44(70.50)	6.11(6.14)	2.51(2.48)

[a] In equivalent molar ratios.

under heating [24]. Therefore, while curing MIEs with amine agents, all the three above-mentioned reactions might occur. In this work, the curing compositions were taken with the same stoichiometric amounts of the amine curing agent and oxirane groups. Therefore, most of the amine groups are expected to react with oxirane groups at low temperature region. Since almost no amino group was left to react with maleimide group, only self-addition reaction occurred for maleimide groups in the curing reaction. The resulting products were, therefore, possessing high crosslinking densities. The reactions were directly observed with DSC monitoring on the curing composition (Fig. 4). The endothermic peak was from the melting behavior of DDM. At higher temperature region, two exothermic peaks were observed. From the reaction temperature Peak I might arise from the epoxy-amine reaction. Moreover, Peak I was observed to shift to low temperature region with using a MIE compound having high maleimide content in the curing composition. The peak shift implies that incorporation of maleimide groups might increase the reactivity of the oxirane group toward amine group. The enhanced reactivity of the oxirane ring could be interpreted with the electron effect [25]. Maleimide group served as an electron-withdrawing group to decrease the electron density of the oxirane ring, consequently to increase its electrophilicity. On the other hand, the integrated peak area of Peak II (the reaction enthalpies) increased with increasing the maleimide group contents of MIE compounds. This result revealed that Peak II should involve with reactions of maleimide. With the above tactic the cured resins were expected to possess high degree of crosslinked density. Therefore, high glass

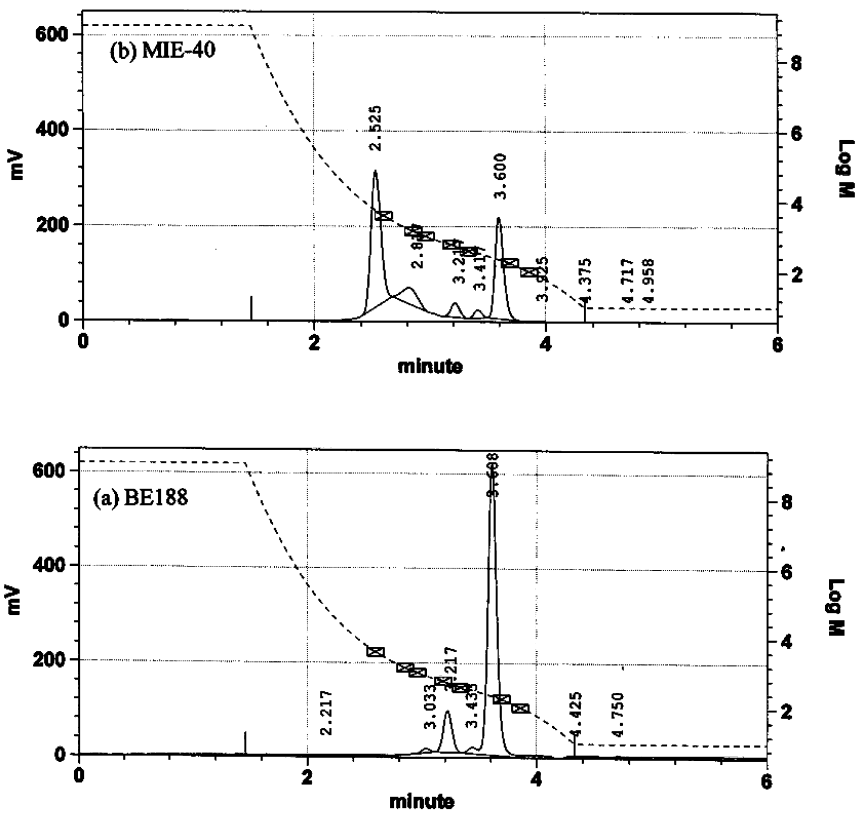


Fig. 3. GPC chromatography of (a) BE188 and (b) MIE-40.

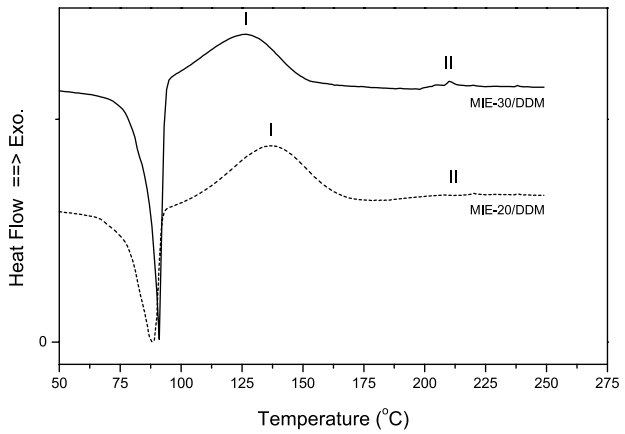


Fig. 4. DSC thermograms monitoring on the curing reactions of MIE compounds with DDM.

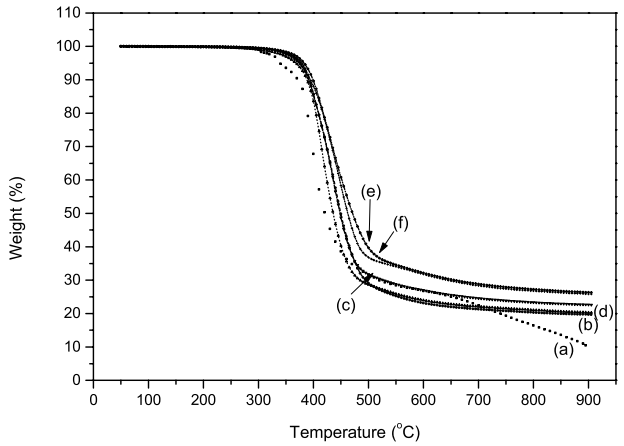


Fig. 5. TGA thermograms of cured resins in nitrogen atmosphere: (a) BE188-DDM; (b) MIE10-DDM; (c) MIE20-DDM; (d) MIE30-DDM; (e) MIE40-DDM; and (f) MIE50-DDM.

transition temperatures were observed for the cured resins (Table 2).

The activation energies of the curing reactions were calculated from DSC experimental data by means of Ozawa's [26–28] and Kinssinger's [27,28] methods (Table 2). The activation energies of curing reactions of oxirane groups with DDM and DICY (peak I) were about 47 and 106 kJ/mol, respectively. Both of the values were comparable with the activation energies of other epoxy compounds curing with DDM and DICY [29–33]. The activation energies of Peak II reactions ranged between 137 and 156 kJ/mol, increasing with increasing the maleimide contents of MIE compounds. The high activation energy of this reaction further demonstrated that the maleimide self-addition reaction contributed to the exothermic Peak II of the DSC thermogram.

3.3. Thermal properties of the cured epoxy resins

The glass transition temperatures of the cured resins were measured by DSC scans at a heating rate of 20 °C/min (Table 2). The T_g of the cured resins increased with increasing the maleimide contents of MIE compounds. The enhancement on the glass transition temperatures of the cured resins should arise from both of the rigidity of maleimide groups and high crosslinking density of the cured resins. It was noteworthy that MIE-50 based resins exhibited high glass transition temperatures above 170 °C. The high T_g of the resins suggested themselves being potentially applied for FR-5 copper clad laminates and IC substrates [34].

The thermal stability of the cured maleimide-epoxy resins was investigated with thermogravimetric analysis (TGA). Figs. 5 and 6 showed some TGA curves of the cured resins in nitrogen and in air atmosphere, respectively. The analyzing data was collected in Tables 3 and 4. From the TGA thermograms of the cured maleimide-epoxy resins, it was clearly observed the thermal stability of the cured resins

Table 2
The compositions and curing reaction data of the maleimide-epoxy resins

Cured resin sample	Curing composition		Activation energy of curing reaction (kJ/mol)				T_g of the cured resins (°C)
	MIE	Curing agents	Ozawa's methods		Kissinger's method		
			1st stage	2nd stage	1st stage	2nd stage	
MIE10-DDM	MIE-10	DDM	45.2	–[a]	43.9	–[a]	142
MIE20-DDM	MIE-20	DDM	44.1	138.9	41.8	133.2	155
MIE30-DDM	MIE-30	DDM	48.6	141.1	44.4	138.5	159
MIE40-DDM	MIE-40	DDM	47.7	149.3	43.6	147.5	162
MIE50-DDM	MIE-50	DDM	48.3	155.3	44.4	152.3	179
MIE10-DICY	MIE-10	DICY	111.1	–[a]	110.3	–[a]	141
MIE20-DICY	MIE-20	DICY	107.7	137.8	105.7	133.5	143
MIE30-DICY	MIE-30	DICY	114.6	140.3	111.8	138.9	150
MIE40-DICY	MIE-40	DICY	106.3	154.5	104.3	150.1	168
MIE50-DICY	MIE-50	DICY	104.8	156.2	103.1	155.6	172
BE188/HPM40/DDM	BE188/HPM[b]	DDM	45.5	150.2	42.3	146.5	157

[a] No obvious exothermic peak observed in the DSC thermograms.
[b] Mixture of BE188 and HPM with a 0.4 equivalent mole of HPM.

Table 3
Thermal analysis data of the cured epoxy resins: evaluation with TGA under nitrogen atmosphere

Epoxy resin	Thermal stability data				Char ratios (%)		Activation energy of decomposition	
	A^*	K^*	IDT (°C)	IPDT (°C)	700 °C	800 °C	T_{max} (°C)	E_a (kJ/mol)
BE188-DDM	0.5760	1.3070	369	652	22.1	16.0	398	145.1
MIE10-DDM	0.5354	1.4872	382	687	21.2	21.0	431	145.9
MIE20-DDM	0.5248	1.5116	383	684	22.0	21.0	433	133.0
MIE30-DDM	0.5520	1.5923	381	753	24.4	23.2	433	143.8
MIE40-DDM	0.5680	1.6843	386	815	28.1	26.2	429	143.8
MIE50-DDM	0.5771	1.7121	384	841	28.7	27.3	445	132.9
MIE10-DICY	0.5017	1.3359	379	586	15.3	14.4	443	133.0
MIE20-DICY	0.5220	1.4420	380	652	19.5	18.4	438	141.2
MIE30-DICY	0.5217	1.4658	377	661	20.4	19.2	436	152.1
MIE40-DICY	0.5499	1.5019	380	710	22.0	20.8	450	136.5
MIE50-DICY	0.5529	1.6292	380	770	25.1	24.0	444	132.9
BE188/HPM40/DDM	0.5808	1.6354	370	810	24.5	22.3	405	142.2

was improved with the incorporation of maleimide groups. The reliable degradation temperature and kinetic parameters, such as the IDT, the temperature of maximum rate of weight loss (T_{max}), the IPDT, and the activation energy of thermal decomposition (E_a), were utilized to assess the thermal stability of the epoxy resins [12] (Tables 3 and 4). With incorporation of maleimide group, the IPD of epoxy resin was raised from 369 to about 381–386 °C. The enhancement of incorporation maleimide groups on the thermal stability of epoxy resins was thus demonstrated. On the other hand, the IPDT also systematically increased with increasing the contents of the maleimide groups. The high IPDTs of the maleimide-modified epoxy resins indicated that high amounts of resins' residual with good anti-volatile characteristics were yielded at high temperature region. The relatively low IPDT of the DICY cured epoxy resins was reasonably understood with the high volatile compositions of DICY. From Tables 3 and 4 it was read that the char yields of the epoxy resins were increased with incorporation of maleimide groups. Moreover, in spite the Tmax of the maleimide-modified epoxy resins moved to higher temperature region, the activation energy of decomposition reaction (E_a) of the cured resins did not show significant variation. The similar activation energies of decomposition of the maleimide-modified and non-modified epoxy resins revealed the maleimide groups did not play important roles in the resins' decomposition at temperatures around 400–450 °C. On the other hand, while heated in air, the maleimide-modified epoxy resins showed relatively low activation energies of decomposition than did BE188-DDM (Table 4). This result might be due to the incorporation of thermally stable groups decreasing the temperature-sensitivity of the resins' decompositions. Similar results were also observed with other modified epoxy resins [21].

3.4. Flame retardance

From the above discussion, incorporating maleimide groups into epoxy resins resulted in improvements on the thermal stability of the resins. The retardation on the

Table 4
Thermal analysis data of the cured epoxy resins: evaluation with TGA under air atmosphere

Epoxy resin	Thermal stability data				Char ratios (%)		Activation energy of decomposition			
	A^*	K^*	IDT (°C)	IPDT (°C)	700 °C	800 °C	$T_{max}{}^a$ (°C)	$E_a{}^a$ (kJ/mol)	T_{max} (°C)	E_a (kJ/mol)
BE188-DDM	0.5345	1.0000	366	477	0.0	0.0	438	157.5	634	77.6
MIE10-DDM	0.5361	1.0000	383	479	7.4	0.0	425	122.7	673	72.2
MIE20-DDM	0.5446	1.0000	383	485	7.5	0.0	444	102.2	674	80.5
MIE30-DDM	0.5463	1.0000	395	487	8.0	0.0	424	121.6	670	85.0
MIE40-DDM	0.5495	1.0000	395	484	8.2	0.0	435	92.9	670	90.9
MIE50-DDM	0.5426	1.0000	396	489	9.0	0.0	435	93.8	670	90.9
MIE10-DICY	0.5177	1.0000	374	464	4.4	0.0	443	106.6	658	74.9
MIE20-DICY	0.5225	1.0000	375	468	5.5	0.0	455	85.9	647	83.7
MIE30-DICY	0.5261	1.0000	381	471	6.3	0.0	453	86.8	645	76.4
MIE40-DICY	0.5331	1.0000	386	476	8.2	0.0	423	98.7	655	78.0
MIE50-DICY	0.5397	1.0000	386	482	9.5	0.0	458	97.7	677	78.0
BE188/HPM40/DDM	0.5184	1.0000	358	481	0.0	0.0	407	121.3	604	78.6

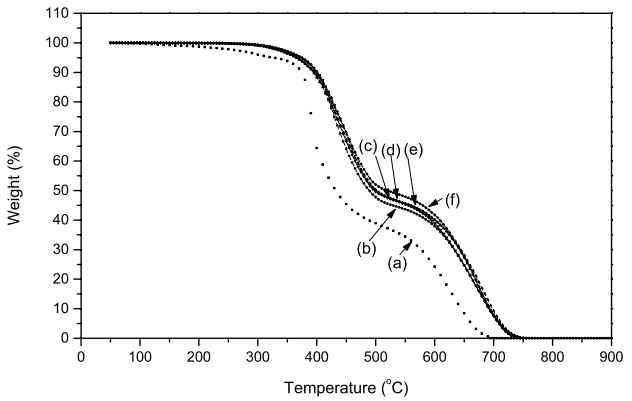


Fig. 6. TGA thermograms of cured resins in air atmosphere: (a) BE188-DDM; (b) MIE10-DDM; (c) MIE20-DDM; (d) MIE30-DDM; (e) MIE40-DDM; and (f) MIE50-DDM.

thermal degradation rates of the resins at high temperature region was observed. Therefore, the cured maleimide-epoxy resins exhibited very high char yields. 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 limit the resins' flammability. A polymer forming high char yields leading to high flame retardance has been demonstrated [35,36]. Therefore, good flame retardance was expected for the cured maleimide-epoxy resins, and was probed with measuring their LOI values (Table 5). The LOI values of the epoxy resins were found to linearly increase with increasing the maleimide groups' contents (Fig. 7). Moreover, the measured LOI values were found to be coincident with the values calculated from Krevelen's equation of

$$\mathrm{LOI} = 17.5 + 0.4\sigma \tag{3}$$

where σ is polymer's char ratio (Fig. 7). It could be concluded that the developed maleimide-epoxy resins might be considered as a halogen-free and phosphorus-free flame retardant materials with good thermal properties, and be

Table 5
The LOI values of the epoxy resins

Epoxy resin	LOI values	
	Calculated[a]	Measured
BE188-DDM	23.9	23.0
MIE10-DDM	25.9	25.5
MIE20-DDM	25.9	26.0
MIE30-DDM	26.8	27.0
MIE40-DDM	28.0	28.5
MIE50-DDM	28.4	29.5
MIE10-DICY	23.3	25.0
MIE20-DICY	24.9	25.5
MIE30-DICY	25.2	26.0
MIE40-DICY	25.8	27.0
MIE50-DICY	27.1	28.5
BE188/HPM40/DDM	26.4	25.0

[a] Calculated from Krevelen's equation [33,34].

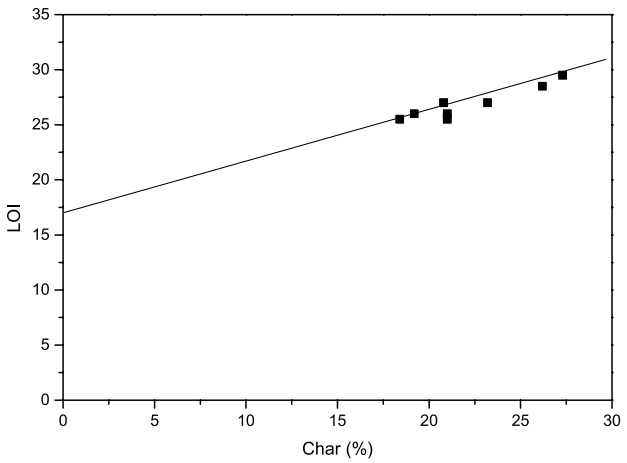


Fig. 7. The plot of the epoxy resins' char yields versus LOI values. The straight line represent the Krevelen's equation: LOI = 17.4 + 0.4(char × yield).

applicable in the environment friendly 'green' products of advanced electronics.

3.5. The blending system of BE188/HPM/DDM

The curing system of BE188/HPM/DDM blending was also investigated as a control experiment. The BE188/HPM mixture containing 40% HPM (equipment mol%) was cured with DDM to give an example (BE188/HPM40/DDM) for comparing with MIE40-DDM, which contains the same maleimide content with the blending of BE188/HPM40/DDM. The exothermic behavior of the BE188/HPM40/DDM curing system was similar with that of the MIE-DDM systems. However, both of the exothermic peaks shifted to high temperature region. On the other hand, for the cured samples, BE188/HPM40/DDM showed its T_g at about 157 °C, which a little lower than the T_g of MIE40-DDM (162 °C). Moreover, the thermal stability of BE188/HPM40/DDM was not as good as that of MIE40-DDM (Fig. 8). Moreover, the char yields and LOI values of BE188/HPM40/DDM were also smaller that those values of

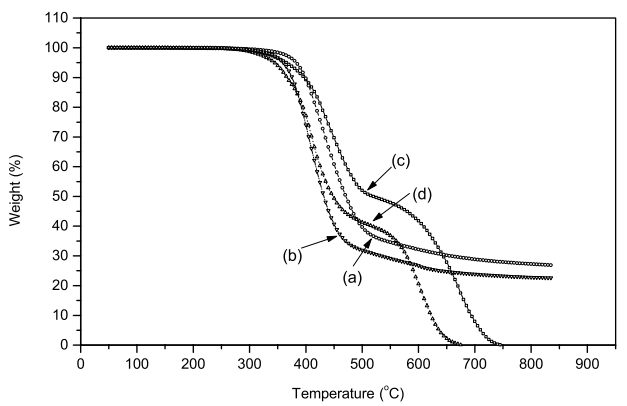


Fig. 8. TGA thermograms of maleimide-epoxy resins: (a) MIE40-DDM in N_2; (b) BE188/HPM40/DDM in N_2; (c) MIE40-DDM in air; (d) BE188/HPM40/DDM in air.

MIE40-DDM. The above results demonstrate that incorporation of maleimide groups into epoxy resins with covalent bonding might provide miscibility between maleimide and epoxy resins to give significant enhancement on the thermal and flame retardant properties of the cured resins.

4. Conclusions

Phenylmaleimido group was successfully incorporated into bisphenol-A type epoxy to result in compounds possessing both oxirane ring and maleimide reactive groups. Thermally curing the maleimide-epoxy compounds with DDM and DICY, cured resins with high glass transition temperatures and excellently thermal stability were obtained. With measuring the resins' char ratios and LOI values, the resulted resins also exhibited improved flame retardant property. The prepared resins' outstanding properties make them be potentially applied in the modern electrical and electronic industries, especially for the environment friendly 'green' products.

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