

Thermal stability of some naphthalene- and phenyl-based epoxy resins

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Dedicated to Professor Kwan-Ting Liu on the occasion of his 65th birthday.

Abstract

Six epoxy monomers were synthesized and cured using 4,4'-methylenedianiline (DDM). The glass transition temperatures (T_g) of naphthalene- and phenyl-based epoxy resins were in the ranges 175–213 °C and 128–200 °C, respectively. Naphthalene-based epoxy resins 1,5-bis(2,3-epoxypropoxy)naphthalene (**A**) and 2,7-bis(2,3-epoxypropoxy)naphthalene (**B**) have almost equal LOIs, implying that the effects of the position of the substituent on LOI was very weak. 4,4'-Bis(2,3-epoxypropoxy)benzylideneaniline (**D**) has the lowest LOI. The same trend was exhibited when some of the epoxy monomers were cured using the curing agent, sulfanilamide (SAA). The order of the LOIs of the epoxy resins was (**B**) = (**F**) > (**A**) > (**E**) > (**C**) > (**D**), when cured using 4,4'-methylenedianiline (DDM). Degradation proceeds in a single stage in an atmosphere of nitrogen and in two stages in air. At 800 °C, the epoxy polymer (**D**) has the highest char yield of all the epoxy resins.
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Keywords: Glass transition temperature (T_g); Differential scanning calorimetry (DSC); Thermogravimetric analysis (TGA); Limited oxygen index (LOI) tester

1. Introduction

Most flame-retardant materials contain halogens. Toxic, corrosive gases and large amounts of smoke are produced when they burn [1]. For environmental reasons, flame-retardant materials that do not contain halogens, such as phosphorus-containing materials, have been developed [2]. Basic facts concerning the flame resistance of polymeric materials have been published [3]. Aromatic rigid rod moiety epoxy polymers have been studied because of their thermal stability [4]. The degree of flammability of a polymeric material can be predicted from its chemical structure. In other words, there must be

some kind of relationship between thermal stability of aromatic epoxy polymers and their structure.

Naphthalene and phenyl rings have planar structures and can thus be easily packed. Such 'hard' structures increase the curing temperature and T_g of bismaleimide [5,6]. Naphthalene and phenyl tri-functional epoxy resins [7] have been reported to yield a high T_g and a high thermal stability [8,9]. The T_g increases as the functionality (di-, tetra-, pentafunctionality) of the epoxy increases. The phenyl-based epoxy resins [10–13] also exhibit the same phenomenon but their T_g was lower than those of naphthalene-based epoxy resins.

The combustion and burning of a polymer is a very complex process. In general, thermogravimetric analysis (TGA), the oxygen index (OI) and a cone calorimeter are used to determine factors, which influence the thermal stability of a polymer. In this study, naphthalene- and

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phenyl-based epoxies were synthesized and completely cured with DDM. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and limiting oxygen index (LOI) tester were used to examine the thermal stability of these systems. The synthetic procedures of epoxy monomer (A–F) are outlined in Fig. 1. The structures of epoxy monomers (A–F) are shown in Table 1. The curing processes of epoxy monomers (A–F) cured with 4,4'-methylenedianiline (DDM) are presented in Fig. 2.

2. Experimental

1,5-Dihydroxynaphthalene and 4,4'-dihydroxybiphenyl were purchased from Tokyo Chemical Co. 2,7-Dihydroxynaphthalene, 2,2'-dihydroxybiphenyl, 4,4'-methylenedianiline (DDM), sulfanilamide (SAA) and 1,1'-bi-2-naphthol were obtained from ACROS Chemical Co. 4-Aminophenol and 4-hydroxybenzaldehyde were purchased from Riedel-de Haën Chemical Co. Tetramethyl biphenol epoxy (TMBP) was supplied by Shell Chemical Co. with a trade name of RSS1407 and an epoxy equivalent of 185. The bisphenol A epoxy (DGEBA) was supplied by Dow Chemical Co. with a trade name of DER 331 and an epoxy equivalent of 186. Solvents and reagents were reagent-grade and used as received without further purification.

The thermal decomposition of epoxy resins were thermogravimetrically analysed using TGA, Du Pont 951 instrument coupled to a Thermal Analyst 2000 in flowing (60 ml/min) air or nitrogen. Samples of 9–12 mg were used. Four different heating rates were examined: 2.5, 5, 10 and 15 °C/min from 50 °C to 800 °C.

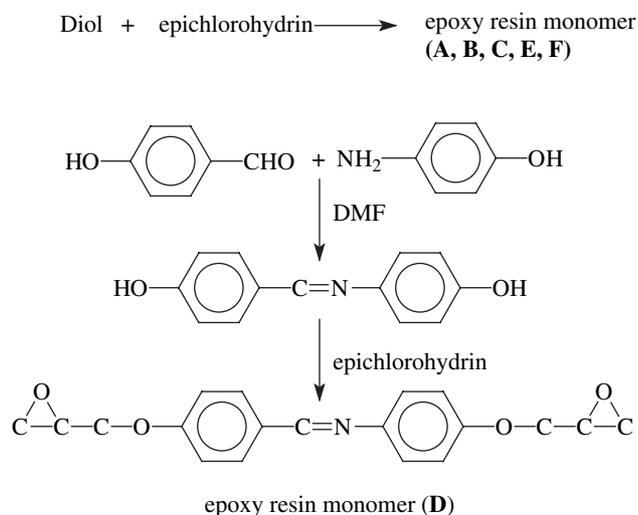


Fig. 1. The synthesis procedure of epoxy monomer (A–F).

The glass transition temperature was measured by a differential scanning calorimeter (Du Pont DSC 10). Dry nitrogen was used as a purge gas. Samples of approximately 5 mg were enclosed in aluminium DSC capsules. Dynamic heating experiments were performed with a nitrogen flow of 60 ml/min, and five different heating rates were considered: 2.5, 5, 10, 15 and 20 °C/min from 30 °C to 300 °C.

The LOI was determined with a Suga ON-1 instrument following the ASTM D 2863-95 procedure.

¹H NMR spectra were measured using a BRUKER AV-300 MHz FT-NMR spectrometer. IR spectra were recorded on a Perkin–Elmer (SPECTRUM 2000) FT-IR spectrometer.

3. Synthesis

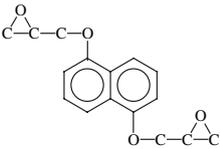
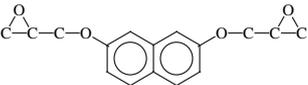
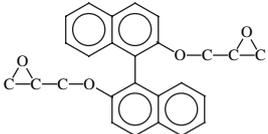
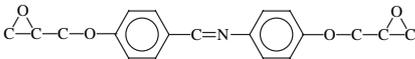
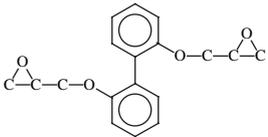
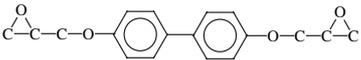
3.1. 1,5-Di(2,3-epoxypropoxy)naphthalene (A)

Compounds A, B, C, E and F were prepared according to the following procedure. A mixture of 20 g of 1,5-dihydroxynaphthalene, 195 ml of epichlorohydrin, and a trace amount of benzyl trimethyl ammonium chloride (BTEA) in a 500 ml three-neck round-bottom flask fitted with a condenser was refluxed until all the reactants were dissolved. The temperature of the mixture was maintained at 60 °C, then 40% sodium hydroxide aqueous solution was added slowly over a period of 3 h. The reaction mixture was stirred at room temperature for another 2 h. The unreacted epichlorohydrin was separated by a vacuum system. The solid mixture was washed with 20 ml of ether and 100 ml of water. The solid was recrystallised using a methanol ether mixture.

3.2. 4,4'-Bis(2,3-epoxypropoxy)benzylideneaniline (D)

A mixture of 24.4 g of 4-aminophenol, 21.8 g of 4-hydroxybenzaldehyde and 180 ml of DMF was placed in a 500 ml three-neck round-bottom flask fitted with a condenser under nitrogen. The reaction mixture was stirred for 30 min and then the temperature increased to 65 °C for another 8 h. The reaction temperature was reduced and DMF was separated using a vacuum system; then 270 ml of epichlorohydrin, and a trace amount of benzyl trimethyl ammonium chloride (BTEA) were added. The temperature of the mixture was maintained at 60 °C, then 40% sodium hydroxide aqueous solution was added slowly over a period of 3 h. The reaction mixture was stirred at 60 °C overnight. The unreacted epichlorohydrin was separated by a vacuum system. The solid mixture was washed with 20 ml of ether and 100 ml of water. The solid was recrystallised using methanol and ether mixture.

Table 1
Names and structures of epoxy monomers (A–F)

epoxy structure	Name(symbol)
	1,5- bis(2,3-epoxypropoxy) naphthalene (A)
	2,7- bis(2,3-epoxypropoxy) naphthalene (B)
	2,2'- bis(2,3-epoxypropoxy) binaphthalene (C)
	4,4'-bis(2,3-epoxypropoxy) benzylideneaniline (D)
	2,2'-bis(2,3-epoxypropoxy) biphenyl (E)
	4,4'-bis(2,3-epoxypropoxy) biphenyl (F)

3.3. Curing

The curing conditions of epoxy monomers (A–F) using the curing agent (DDM) were checked by the results of differential scanning calorimetry (DSC), over the temperature range 30–300 °C, at a heating rate of 10 °C/min. The epoxy monomer was used in the powder state, except that monomer (E) was a liquid.

4. Results and discussion

4.1. Differential scanning calorimetry (DSC)

In this study, polymers (A–C) are naphthalene-based epoxy polymers and (D–F) are phenyl-based polymers. Table 2 presents the glass transition temperatures (T_g) of the cured epoxy polymers.

Polymer (C) ($T_g = 204$ °C) has higher T_g than that of polymer (E) ($T_g = 128$ °C). Epoxy polymer (C) is naphthalene-based and polymer (E) is phenyl-based.

T_g of polymer (A) ($T_g = 213$ °C) is the highest of all the studied polymers. The naphthalene-based epoxy resin in polymer (A) (1,5-di-substituted) has a more symmetric structure than that in polymer (B) (2,7-di-substituted) of which T_g is 175 °C. Polymer (F) ($T_g = 177$ °C) is also more symmetrical and has a higher T_g than polymer (E) ($T_g = 128$ °C). It seems that the more symmetric structure causes the higher T_g . The other reason for the lower T_g of polymer (E) than that of polymer (F) could be the steric hindrance. Polymer (E) is strongly hindered in comparison with polymer (F). They are biphenyl-based structures where polymer (E) is 2,2'-di-substituted and polymer (F) is 4,4'-di-substituted; the biphenyl is more twisted in structure (E).

4.2. Thermogravimetric analysis (TGA)

The TGA measurements have been done under atmospheres of nitrogen and air. Figs. 3 and 4 show the TGA curves for epoxy polymers in nitrogen and air, respectively, at a 10 °C/min heating rate.

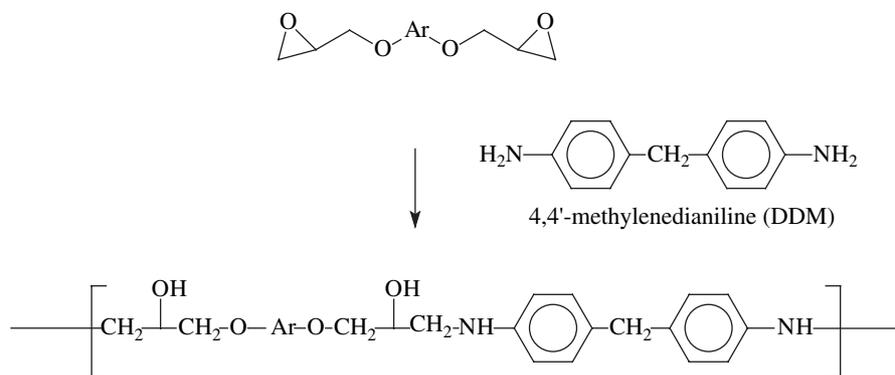


Fig. 2. The curing reaction of epoxy polymer (A–F).

Table 3 presents the results of thermogravimetric analysis (TGA) and weight loss during degradation in an atmosphere of nitrogen or air.

From 350 to 450 °C, epoxy polymers (B), (C) and (E) degrade more quickly than the others. At 800 °C, epoxy polymer (D) has a higher char yield than all the other polymers. The degradation is more complex for all epoxy polymers when TGA is measured in an atmosphere of air. Degradation is a single-stage process in an atmosphere of nitrogen and a two-stage process in air. Therefore, the degradation mechanism is different under each degradation condition. The residual weight in air (1–3%) is lower than that in nitrogen (12–48%) at 800 °C.

4.3. Limiting oxygen index (LOI)

The relative flammability of epoxy resins (A)–(F) was examined using the limiting oxygen index (LOI). Table 4 lists the results. The decreasing order of the LOIs of epoxy resins is (B) = (F) > (A) > (E) > (C) > (D). The polymer (D) is the easiest to burn.

Another experiment also yields the same result. Two monomers, 4,4'-bis(2,3-epoxypropoxy)benzylideneaniline and 4,4'-bis(2,3-epoxypropoxy)biphenyl, are cured using curing agent sulfanilamide (SAA), forming the polymers (G) and (H), respectively. Fig. 5 depicts the structures of the cured polymers.

Table 5 presents the thermogravimetric analysis (TGA) in an atmosphere of nitrogen or air and the LOIs of polymers (G) and (H).

Polymers (D) and (G) used the same starting monomer but different curing agents. The char yield of

polymer (G) is higher than that of polymer (H). The LOIs of polymer (G) and polymer (H) are 26.5 and 31.5, respectively. Polymer (G) is more flammable than polymer (H). The LOI of polymer (D) is lower than that of polymer (G) and that of polymer (F) is lower than that of polymer (H). The major difference between the structures of (A) and (B) is the position of the substituent. The position of the substituent of epoxy

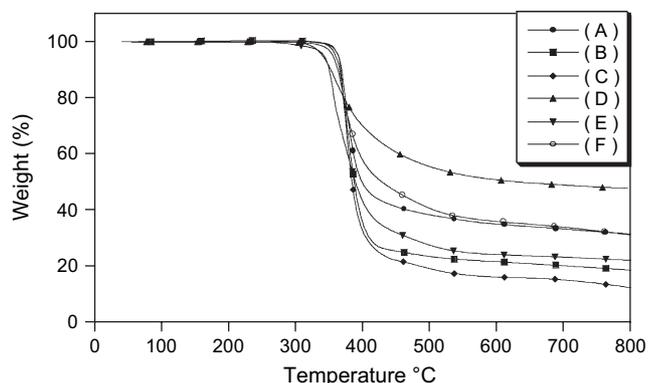


Fig. 3. The TGA curves of epoxy polymers in nitrogen at 10 °C/min heating rate.

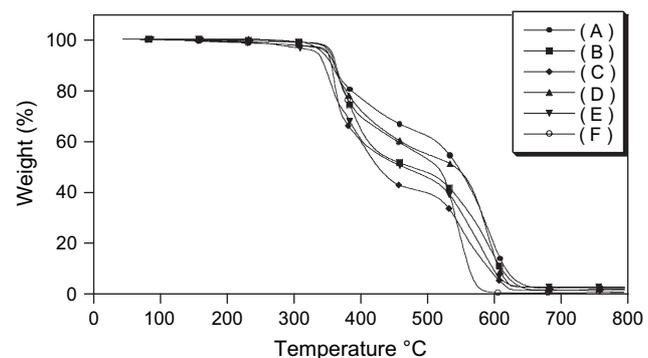


Fig. 4. The TGA curves of epoxy polymers in air at 10 °C/min heating rate.

Table 2
Glass transition temperatures (T_g) of epoxy polymers (A–F)

Polymer	T_g (°C)	Polymer	T_g (°C)
A	213	D	200
B	175	E	128
C	204	F	177

Table 3
Results of thermal degradation of epoxy resins (A–F) cured with DDM measured by TGA in nitrogen and air atmosphere at 10 °C/min heating rate

	Epoxy	5% Weight loss T (°C)	Maximum break T (°C)	Residual weight (%)			
				350 °C	450 °C	800 °C	
N ₂	A	364	374	99	41	32	
	B	360	377	98	26	19	
	C	364	372	99	22	12	
	D	341	360	91	61	48	
	E	343	355	90	32	22	
	F	356	370	97	47	31	
Air			Stage 1	Stage 2			
	A	356	362	591	97	68	3
	B	353	359	591	96	52	2
	C	352	360	548	96	44	2
	D	342	362	588	93	62	3
	E	333	351	590	87	52	2
	F	348	366	541	95	61	2

Table 4
Limiting oxygen index (LOI) of epoxy polymer (A–F)

Polymer	LOI	Polymer	LOI
A	29.5	D	26.0
B	30.0	E	28.5
C	27.0	F	30.0

monomers (**A**) and (**B**) are 1,5- and 2,7-, respectively. They have almost the same LOI. In Table 4, the LOI of polymer (**B**) is slightly higher than that of polymer (**A**). Therefore, the position of the substituent does not affect LOI in this case.

4.4. Activation energy (E_a)

The activation energy for degradation of these epoxy polymers was calculated by Ozawa's method [14]. Four different heating rates were applied—2.5, 5, 10 and 15 °C/min—from 50 to 800 °C/min. Tables 6 and 7 present the activation energies of degradation calculated by Ozawa's methods and measured in nitrogen and air, respectively.

The order of the average activation energies of degradation follows (D) > (A) > (F) > (B) > (C) > (E) in nitrogen. In Table 6, the order of average activation energies of degradation of stage 1 is (D) > (A) > (F) > (C) > (B) > (E). Table 7 reveals small difference in the average activation energies of degradation between stage 1 and stage 2. The epoxy polymer (**D**) has a long conjugated double bond in which two phenyl groups are connected by a C=N double bond, such that the structure is more stable than the other polymers.

5. Conclusions

The six epoxy resins can be divided into two different groups. One is naphthalene-based and the other is of the phenyl type. The colour of the epoxy polymer, formed by curing epoxy monomers (A–F) with DDM, is deep brown. In some cases, curing is performed under reduced pressure to prevent air bubbles from forming. Based on the results in this study, we concluded the following.

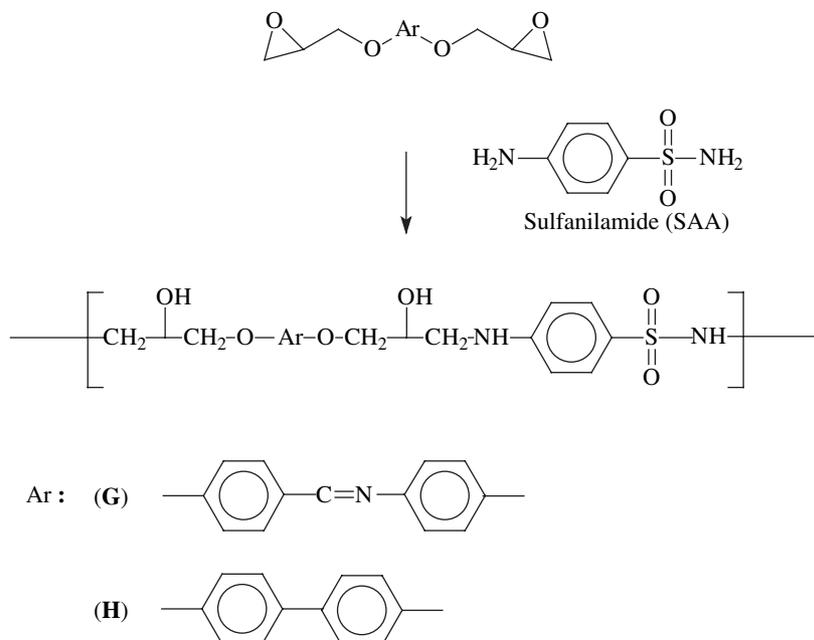


Fig. 5. The curing reaction of epoxy monomer (G–H).

Table 5

Results of thermal degradation and LOI of epoxy resins (G–H) cured with SAA measured by TGA in nitrogen or air atmosphere at 10 °C/min heating rate

	Epoxy	5% Weight loss T (°C)	Maximum break T (°C)		Residual weight (%)			LOI
					350 °C	450 °C	800 °C	
N ₂	G	332	346		81.9	62.5	48.8	26.5
	H	336	356		82.9	43.3	31.9	31.5
Air			Stage 1	Stage 2				
	G	324	346	570	82.9	64.6	5.7	–
	H	334	351	541	82.3	53.7	1.1	–

1. Degradation is more complex for all epoxy polymers when TGA is measured in an atmosphere of air. Degradation proceeds in a single stage in nitrogen and in two stages in air.
2. At 800 °C, epoxy polymer (D) that comes from 4,4'-bis(2,3-epoxypropoxy)benzylideneaniline cured with DDM gives the highest char yield of all the epoxy resins.

3. The degradation activation energy of these epoxy resins was determined by Ozawa's method. Epoxy polymer (D) has the greatest degradation activation energy of all the epoxy resins considered here, regardless of whether they are in nitrogen or air.
4. The order of the LOIs of the epoxy resins studied in this article is (B) = (F) > (A) > (E) > (C) > (D), when cured using 4,4'-methylenedianiline (DDM).
5. Naphthalene-based epoxy resins (A) and (B) have almost the same LOIs, indicating that the position of the substituent only weakly affects the LOI.
6. Epoxy resin (D) has the lowest LOI. The same trend is followed when this monomer was cured using sulfanilamide (SAA).

Table 6

The degradation energy (kJ/mol) calculated with Ozawa method in nitrogen atmosphere

Fractional weight loss (%)	Activation energy, E (kJ/mol) ^a					
	A	B	C	D	E	F
5	174	126	149	193	113	137
10	185	130	150	204	134	150
20	184	139	150	232	139	167
30	181	153	149		149	
40	187	160	148		165	
50		169	148			
60		191	150			
Average E	185	153	150	208	139	160

^a The E_a value was calculated using four different temperatures in each fractional weight loss. The R -value was in the range 0.988–0.953, and the S.D. was 0.010–0.007.

Table 7

The degradation energy (kJ/mol) calculated with Ozawa method in air atmosphere

Fractional weight loss (%)	Activation energy, E (kJ/mol) ^a					
	A	B	C	D	E	F
5	196	137	178	188		141
10	198	156	175	236	138	171
20		192	192	317	167	272
Average E_1	212	168	184	238	156	209
50	136			193		152
60	118	186		150	204	140
70	108	142		137	140	137
80	101	124	142	126	120	123
90	95		116	118	117	121
Average E_2	110	142	140	141	138	133

^a The E_a value was calculated using four different temperatures in each fractional weight loss. The R -value was in the range 0.987–0.955, and the S.D. was 0.01–0.006.

Acknowledgements

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