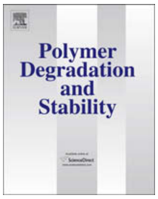
Polymer Degradation and Stability 93 (2008) 2077–2083

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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



Thermal and physical properties of flame-retardant epoxy resins containing 2-(6-oxido-6*H*-dibenz⟨*c*,*e*⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-naphthalenediol and cured with dicyanate ester

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ARTICLE INFO

Article history:
Received 23 June 2008
Received in revised form 2 September 2008
Accepted 5 September 2008
Available online 25 September 2008

Keywords:
Dicyanate ester
Flame retardancy
Phosphorus-containing epoxy resin
Thermal property

ABSTRACT

2-(6-oxido-6*H*-dibenz(*c*,*e*)(1,2)oxaphosphorin-6-yl)-1,4-naphthalenediol (DOPONQ) was prepared by the addition reaction of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) with 1,4-naphthoquinone. The phosphorus-containing diol (DOPONQ) was used as a reactive flame retardant by an advancement reaction with the diglycidyl ether of bisphenol-A epoxy (DGEBA) resin at various stoichiometric ratios. DOPONQ-containing advanced epoxy was separately cured with various dicyanate esters to form flame-retardant epoxy/cyanate ester systems. The effect of the phosphorus content and dicyanate ester structure on the curing characteristic, glass transition temperature, dimensional stability, thermal stability, flame retardancy, and dielectric property was studied and compared with that of the control advanced bisphenol-A epoxy system. The DOPONQ-containing epoxy/cyanate ester systems exhibited higher glass transition temperatures as well as better thermal dimensional and thermal degradation stabilities. The flame retardancy of the phosphorus-containing epoxy/dicyanate ester system increased with the phosphorus content, and a UL-94 V-0 rating could be achieved with a phosphorus content as low as 2.1%.

1. Introduction

Epoxy resins are widely used as matrix resins for structural composites and electronic parts because of their ease of handling and processability, low shrinkage on cure, superior electrical and mechanical properties, and good adhesion to many substrates. However, their flammability and the limitation on their upper use temperature restrict their application. Consequently, many techniques have been developed to modify the epoxy backbone in an effort to improve the thermal and flame retardancy characteristics of epoxy polymers. Tetrabromobisphenol-A is a typical example of the aromatic bromine compounds used as flame retardants for epoxy resins [1–3]. The halogenated compounds, however, are known to generate toxic smoke and corrosive fumes during combustion. Organo-phosphorus compounds incorporated into resins are found to generate less toxic gases and corrosive smoke than do halogen-containing compounds, and they also exhibit high flame retardancy [4–6]. They are, therefore, the materials of choice among the halogen-free flame retardants.

Several approaches for improving the flame retardancy of epoxy polymers based on 2-(6-oxido-6*H*-dibenz(*c*,*e*)(1,2)oxaphosphorin-6-yl)hydroquinone (DOPOBQ), a phosphorus-diol derived from the addition reaction of DOPO with *p*-benzoquinone, were reported by Wang and Shieh [7,8]. These studies mainly involved the application of a DOPOBQ-containing epoxy resin [9–17] and a DOPO-modified curing agent [18–24]. Nevertheless, few articles incorporated a phosphorus element into the advanced epoxy resin by chain extension with a reactive DOPONQ-containing reagent.

Dicyanate esters possess many excellent properties, such as high glass transition temperatures, good thermal stability, low moisture absorption, low dielectric constants over a wide range of frequency and temperature, and epoxy-like processing in that they can be cured at low temperatures. The ability to improve the glass transition temperature and enhance the thermal stability of an epoxy by copolymerization is an attractive feature [25–28].

In this paper, continuing our research on the flame-retardant epoxy [7,8,18,19,22,29], a phosphorus and naphthalene-containing novolac (DOPONQ) was synthesized and characterized. Advanced DOPONQ-containing epoxy resins were prepared by a chain extension of DGEBA with DOPONQ and then cured with a dicyanate ester. The effects of the cyanate ester structures and DOPONQ

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0141-3910/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2008.09.002

contents on the thermal, flame-retardant, dielectric, and moisture resistance properties of the crosslinked DOPONQ-based epoxy/cyanate ester resins were investigated in order to understand the structure–properties relationship. The properties of the resulting copolymer have been compared with those of the control bisphenol-A epoxy (DGEBA) system.

2. Experimental

2.1. Materials

Bisphenol-A (BPA), 1,4-naphthoquinone (NQ), 4,4′-biphenol (BIP), 4,4′-oxydiphenol (ODP), and 2-ethoxyethanol were purchased from Acros, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) from TCI, the cyanogen bromide from Fluka, and bisphenol-A dicyanate (BADCy) and tetramethyl bisphenol F dicyanate (TBFDCy) from Ciba Co. All of these materials were used as-received. The biphenol dicyanate (BIDCy) and oxydiphenol dicyanate (ODDCy) were synthesized according to a previously reported method [30]. The diglycidyl ether of bisphenol-A (DGEBA) with an epoxy equivalent weight (EEW) of 188 g was kindly obtained from the Chang Chun Plastic Co. The A-1 catalyst is an ethyltriphenyl phosphonium acetate acetic acid complex, which is commonly used as an advancement catalyst that serves to extend the chain of the epoxy resin in order to increase its molecular weight. All other solvents (LC grade) were obtained from various commercial sources and used without further purification.

2.2. Monomer synthesis

2.2.1. Preparation of phosphorus-containing reagents (DOPONQ)

DOPONQ was prepared by modification of the method described in our previous report [31,32]. A 1 L four-inlet flask was filled with 54 g (0.25 mol) of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and 100 mL of 2-ethoxyethanol. The mixture was heated to 90 °C under a nitrogen atmosphere, and the stirring was continued until DOPO dissolved completely. Subsequently, 35.55 g (0.225 mol) of 1,4-naphthoquinone (NQ) was slowly added to this solution, and the temperature was then increased to 125 °C, where it remained for 4 h. The mixture was filtered and further recrystallized from 2-ethoxyethanol to produce solid crystals of 2-(6-oxido-6*H*-dibenz⟨*c*,*e*⟩⟨1,2⟩-oxaphosphorin-6-yl)-1,4-naphthalenediol (DOPONQ). Yield, 93%. IR (KBr): 1592 cm^{-1} (P–Ph), 1240–1190 cm^{-1} (P═O), 938, 748 cm^{-1} (P–O–Ph), 3500–3200 cm^{-1} (Ph–OH). The shift and splitting pattern of the ^{1}H NMR spectrum were 6.55 (d, 1H), 7.36 (m, 2H), 7.50 (m, 5H), 7.82 (t, 1H), 8.10 (d, 1H), 8.20 (d, 1H), 8.33 (m, 2H), 9.78 (s, 1H), 10.72 (s, 1H). ^{31}P NMR: a singlet peak at $\delta = 31.70$ ppm. Elemental analyses calcd. for $C_{22}H_{15}O_4P$: C, 70.59%; H, 4.01%; O, 17.11%; P, 8.29%. Found: C, 70.54%; H, 4.06%; O, 17.47%; P, 8.25%. Mass spectrometry (MS: *m*/*z*): 375 (100, $M + 1^+$).

2.2.2. Advancement of the epoxy resin with DOPONQ

An epoxy resin (DGEBA) was added to a four-neck round-bottomed flask, equipped with a vacuum outlet, stirrer, temperature controller, and a Dean–Stark trap with a reflux condenser. It was heated under full vacuum at 100 °C for approximately 1 h in order to drive off the residual water; subsequently, various stoichiometric amounts of DOPONQ were added. The molar ratio and weight of DGEBA and DOPONQ are listed in Table 1. The mixture reacted at 160 °C for 90 min in the presence of 500 ppm of the A-1 catalyst. The EEW and designated abbreviations of the final products are listed in Table 1, and the reaction equation is shown in Scheme 1.

Table 1
Sample formulations and EEW value of DGEBA reacted with BPA or DOPONQ

Epoxy code	DGEBA:BPA[a]	Weight of DGEBA (g)	Weight of BPA (g)	EEW (Cal.)	EEW (Exp.)
Control	2.03:1	100	29.87	481	490
Epoxy code	DGEBA:DOPONQ[a]	Weight of DGEBA (g)	Weight of DOPONQ (g)	EEW (Cal.)	EEW (Exp.)
DN-1	4.08:1	100	24.38	309	314
DN-2	2.14:1	100	46.48	517	522

[a] Equivalent ratio (epoxide:OH).

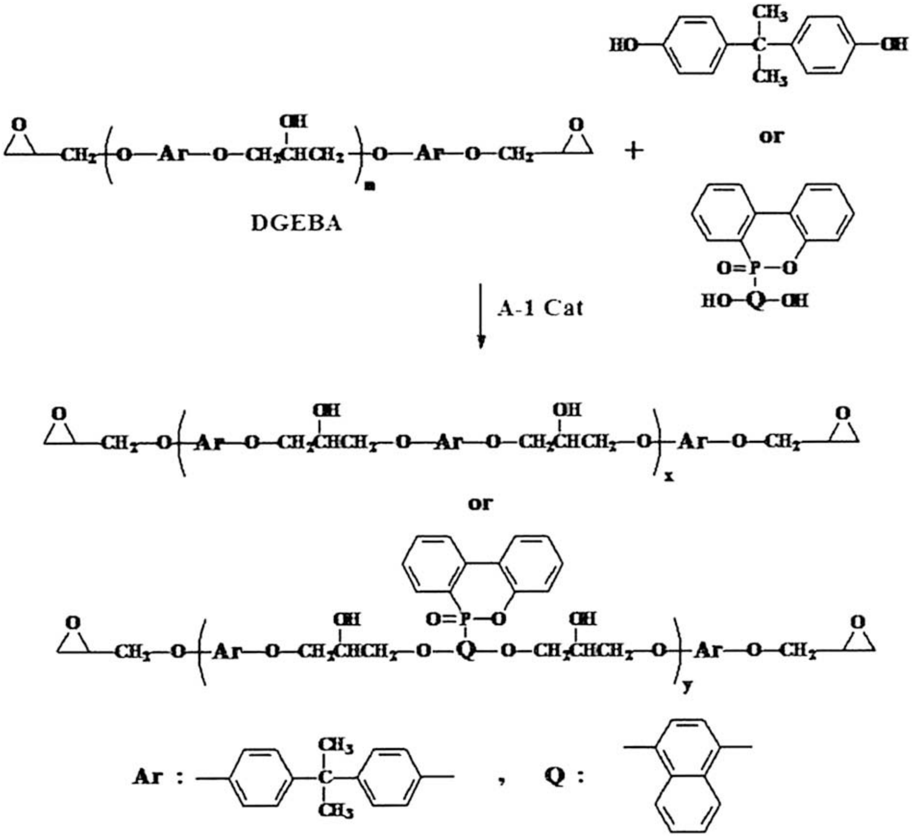
2.3. Curing procedure of the epoxy/dicyanate ester resins

Phosphorus-containing DOPONQ-epoxy and the control BPA-epoxy were separately cured with BADCy, TBFDCy, BIDCy, and ODDCy, respectively, in a stoichiometric equivalent ratio. The structures of dicyanate esters are listed in Scheme 2. The mixture was heated on a hot plate with continuous stirring until a homogenous solution was obtained. The mixture was cured in an oven at 180 °C for 2 h, 210 °C for 3 h, and then 240 °C for 2 h.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer 16 PC type spectrometer with KBr pellets. Spectra in the optical range of 400–4000 cm^{-1} were obtained by averaging 16 scans at a resolution of 4 cm^{-1}. ^{1}H NMR spectra were registered using a Varian UNITY INOVA-500. Mass spectrometry analyses were performed on a Bruker APEX II, while elemental analysis was performed using a Heraus CHN-Rapid elemental analyzer. A Perkin–Elmer DSC 7 was used to obtain DSC scans from samples of about 5–10 mg in a nitrogen atmosphere (20 cm^3/min) using a heating rate of 10 °C/min. DMA was carried out with a Perkin–Elmer DMA 7. The storage modulus E' and $\tan\delta$ were determined as the sample was subjected to temperature scan mode at a programmed heating rate of 10 °C/min from room temperature to 300 °C. The coefficient of thermal expansion was measured with the TMA mode of a Perkin–Elmer DMA 7 at a heating rate of 5 °C/min. Thermal gravimetric analyses (TGA) were performed with a Perkin–Elmer TGA 7 using a heating rate of 20 °C min^{-1} in a nitrogen atmosphere (20 cm^3/min) from 100 °C to 700 °C using a platinum boat. An Agilent 4291B measurement system at a temperature of 30 °C using the two parallel plate mode at 1 GHz was used to obtain dielectric measurements. The EEW of the epoxy resin was determined by the $HClO_4$/potentiometric titration method. The procedure involved the titration of a solution of epoxy resin, which was dissolved in methylene chloride containing tetraethylammonium bromide and a crystal violet indicator, with a standardized solution of perchloric acid in glacial acetic acid. When the epoxy groups were completely consumed, the free hydrogen bromide caused a color change in the crystal violet indicator. The epoxy EEW [33] of the resins was calculated using the following formula: $\text{EEW} = 100W/AN$, where W is the mass of the epoxy resin sample (g), A is the volume of the perchloric acid solution used for the titration (mL), and N is the normality of the perchloric acid solution.

The UL-94 vertical test was performed according to the testing procedure with a test specimen bar 127 mm long, 12.7 mm wide, and approximately 1.27 mm thick. During the test, the polymer specimen was subjected to two 10-s ignitions. After the first ignition, the flame was removed and the time for the polymer to self-extinguish (t_1) was recorded. Cotton ignition would be noted if polymer dripping occurred during the test. After cooling, a second



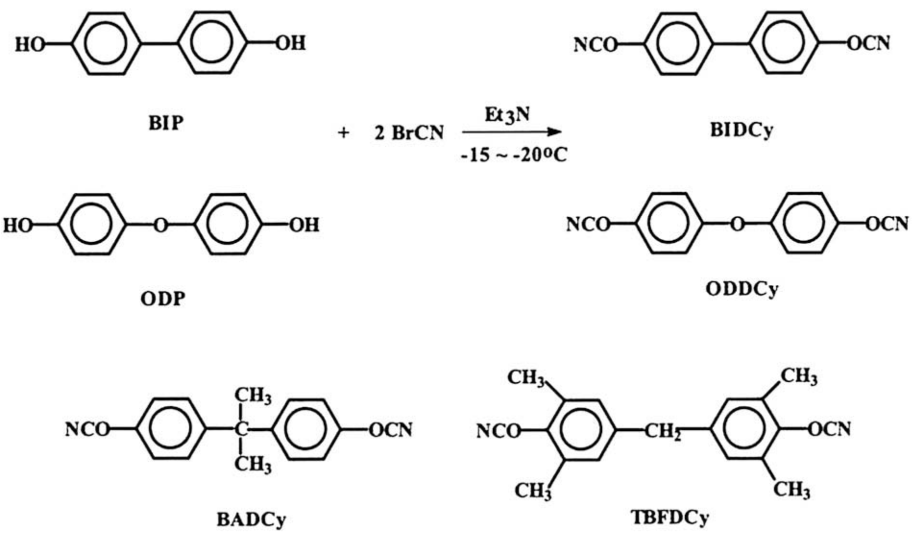
Scheme 1. The advancement of DGEBA epoxy with DOPONQ or Bisphenol-A.

ignition was performed on the same sample, and the self-extinguishing time (t_2) and dripping characteristics were recorded. If the sum $t_1 + t_2$ was less than 10 s with no dripping, the sample would be considered a V-0 material. Moisture absorption was tested as follows: 1×1 cm^2 samples with 0.1 cm thickness were dried under vacuum at 120 °C until moisture had been expelled. After being cooled down to room temperature, the sample was weighed and then placed into 100 °C water for 24 h and then re-weighed. The moisture absorption was calculated as the percent weight gain $= (W/W_0 - 1) \times 100\%$, where W is the weight of sample after placing it into 100 °C water for 24 h and W_0 is the weight of the sample prior to placing it into the water.

3. Results and discussion

3.1. Characterization of DOPONQ and advanced epoxy resin

DOPONQ with phenolic OH groups was synthesized by the addition of DOPO to 1,4-naphthoquinone in a quantitative yield. As the reaction proceeded, the distinctive absorption at 2440–2275 cm^{-1}



Scheme 2. Dicyanate ester monomers used in the study.

for P–H stretching in the DOPO disappeared, while a broad absorption at approximately 3500–3200 cm^{-1} for phenolic OH appeared in DOPONQ. The conversion of DOPO to DOPONQ was also confirmed by the ^1H NMR spectra. Furthermore, the ^{31}P NMR spectrum of the DOPONQ exhibited a single peak at $\delta = 31.70$ ppm. Epoxy resins with various phosphorus contents were prepared by applying the advancement of bisphenol-A epoxy (DGEBA) with DOPONQ. The reaction scheme is shown in Scheme 1. In order to compare the thermal, mechanical, and flame-retardant effects of DOPONQ versus the control, the advancements of epoxy resins with bisphenol-A (BPA) were also performed. The epoxy group was determined by back-titration using a perchloric acid crystal violet indicator [11,34]. The EEW values (Table 1) of the synthesized DOPONQ-epoxy were 314 and 522, which were close to the theoretical EEW of 309 and 517, respectively.

3.2. DSC curing behavior

The typical DSC analysis of the thermal polymerization behavior of a DOPONQ-containing epoxy/BADCy dicyanate ester at a scanning rate of 10 °C/min was investigated, and the results are shown in Fig. 1. The curing reactivity of the DOPONQ-epoxy/dicyanate ester could be judged by the maximum temperature of the polymerization exotherm (T_p) as listed in Table 2. The DNTB (epoxy/TBFDCy) system had the highest initial (T_i) and maximum (T_p) temperatures for the curing reaction among all the epoxy/dicyanate esters. This was attributed to TBFDCy having four bulky *ortho*-methyl substituents, which shield and sterically hinder the reactive groups and thus delay the exothermic temperature. The exothermic temperatures (T_p and T_f) were shifted to a lower temperature as the amount of the DOPONQ groups in the epoxy increased. From Table 2, the higher the phosphorus content in the DOPONQ group in the epoxy resins, the lower the exothermic heat (ΔH) of reaction; this is due to the increase of the EEW, in other words, the reactive epoxy ring is reduced [29].

Fig. 1 reveals two slightly distinct exothermic peaks similar to the phenomenon reported by Shimp and Wentworth [35] and Lin [36]. The curing reactions between the difunctional glycidyl ether and the dicyanate ester have been well studied [13,35–37]. It has been confirmed that the epoxide does react with cyanurate and converts the triazine ester into isocyanurate and oxazolidinone. The structure of the cured products depends on the rate of each reaction and the initial equivalent ratio of the dicyanate ester and glycidyl ether. In this study, the equivalent ratio of the epoxy group/cyanate ester group was fixed to a constant value 1/1, and the curing conditions were set in the same order to simplify the scope of the discussion.

Table 2
Sample formulation and DSC data of various DOPONQ-containing epoxy/dicyanate ester resins

Epoxy/dicyanate ester sample code	Epoxy	Curing agent[a]	T_i[b] (°C)	T_p[c] (°C)	T_f[d] (°C)	ΔH (J/g)
BADCy	–	BADCy	206	292	321	413
DNBA-1	DN-1		150	224	248	328
DNBA-2	DN-2		146	213	237	221
TBFDCy	–	TBFDCy	223	288	321	113
DNTB-1	DN-1		191	270	295	302
DNTB-2	DN-2		192	244	271	121
BIDCy	–	BIDCy	192	256	301	604
DNBI-1	DN-1		160	228	262	521
DNBI-2	DN-2		145	216	239	291
ODDCy	–	ODDCy	189	247	286	583
DNOD-1	DN-1		150	224	259	428
DNOD-2	DN-2		151	212	239	237

[a] Equivalent ratio (epoxide:OCN = 1:1).
[b] The initial temperature of the reaction peak.
[c] The peak temperature of the reaction peak.
[d] The final temperature of the reaction peak.

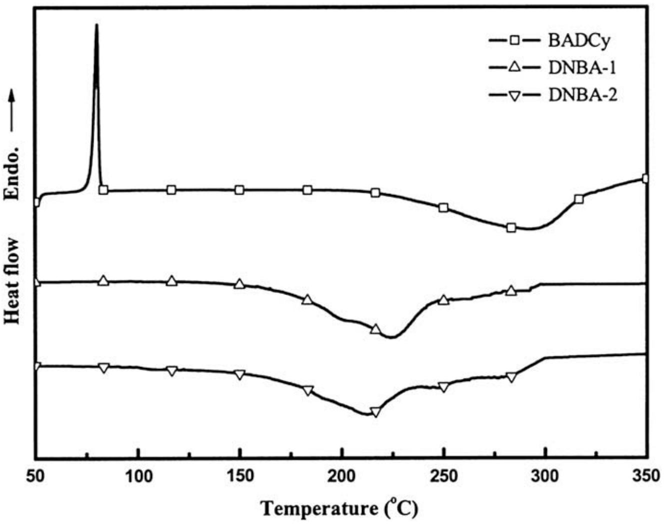


Fig. 1. Typical DSC thermograms of BADCy, DNBA-1, and DNBA-2 at a heating rate of 10 °C/min.

3.3. DMA analysis

The modulus and glass transition temperatures (T_gs) of the cured resins are illustrated in Fig. 2, and the results are listed in Table 3. The DN-2 series with a higher DOPONQ content in the advanced epoxy resins possessed lower glass transition temperatures than those of the corresponding DN-1 cured resins. This might be attributed to the DN-2 advanced epoxy resin with a higher EEW than that of the DN-1 system, which led to an increase in the size of the bridging group between two crosslinked points and, subsequently, to a decrease in the glass transition temperature. As would be expected, in these DOPONQ-advanced epoxy systems (both the DN-1 and DN-2 series), the incorporation of the bulky rigid DOPONQ structure, which increases rigidity and acts as a motion barrier, led to a higher T_g (approximately 25–45 °C) and modulus than those of the control advanced BPA-epoxy systems. The glass transition temperatures of the advanced epoxy resins were in the order of BIDCy > BADCy > ODDCy > TBFDCy, which is in agreement with the increasing flexibility of the chain rotation

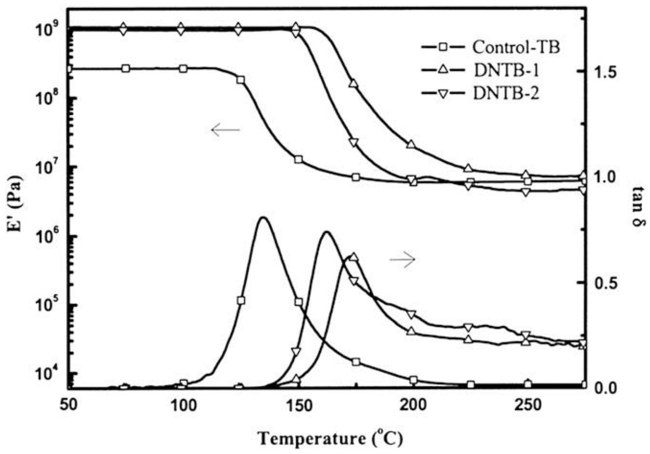


Fig. 2. Typical dynamic mechanical analysis of Control-TB, DNTB-1, and DNTB-2 at a heating rate of 10 °C/min.

Table 3
DMA data of advanced epoxy/dicyanate ester systems

Epoxy/dicyanate ester sample code	Epoxy	Curing agent[a]	T_g[b] (°C)	E' (GPa)		
				E' at 50 °C	E' at T_g	E' at 275 °C
Control-BA	Control	BADCy	148	0.338	0.073	0.009
DNBA-1	DN-1		186	0.695	0.157	0.007
DNBA-2	DN-2		174	1.040	0.120	0.005
Control-TB	Control	TBFDCy	135	0.265	0.047	0.006
DNTB-1	DN-1		175	1.080	0.141	0.007
DNTB-2	DN-2		162	0.985	0.136	0.004
Control-BI	Control	BIDCy	159	0.668	0.135	0.013
DNBI-1	DN-1		207	0.907	0.133	0.012
DNBI-2	DN-2		183	0.852	0.157	0.005
Control-OD	Control	ODDCy	146	0.247	0.047	0.006
DNOD-1	DN-1		184	0.871	0.182	0.012
DNOD-2	DN-2		171	1.520	0.283	0.010

[a] Equivalent ratio (epoxide:OCN = 1:1).
[b] Peak temperature of tan δ curve.

Table 4
TMA data of advanced epoxy/dicyanate ester systems

Sample code	T_g[a] (°C)	CTE[b] (10^{-5}/°C)	
		$<T_g$	$>T_g$
Control-BA	121	70	200
DNBA-1	168	62	150
DNBA-2	149	65	173
Control-TB	105	67	255
DNTB-1	155	61	200
DNTB-2	134	63	216
Control-BI	133	66	178
DNBI-1	180	61	153
DNBI-2	162	62	166
Control-OD	118	66	185
DNOD-1	160	60	159
DNOD-2	143	64	170

[a] Onset temperature for glass transition.
[b] Coefficient of thermal expansion determined by TMA.

except for the TBFDCy system. As discussed above, the epoxy/TBFDCy system with the bulky methyl group *ortho* to the –OCN functionality increased steric hindrance and had a relatively lower T_g than that of the other dicyanate esters.

No matter which dicyanate ester was used to cure the DOPONQ-advanced epoxy system, they all possessed a higher T_g (162–207 °C) than those of the DOPO-containing epoxies cured with methylene dianiline (MDA) ($T_g \sim 161$ °C) [7] or 4,4′-diamodiphenylsulfone (DDS, $T_g \sim 164$ °C) [6] that were previously reported. This result may be attributed to the fact that the cured DOPONQ-containing/dicyanate ester systems contain rigid naphthalene groups in addition to a triazine and oxazolidone structure, which comes from the trimerization of the dicyanate ester and the reaction of the dicyanate ester with the epoxy group, respectively.

3.4. TMA analysis

Thermally induced dimensional changes of these cured resins were investigated by a thermo-mechanical analyzer. The typical TMA traces of Control-BI, DNBI-1, and DNBI-2 at a heating rate of 5 °C/min are shown in Fig. 3. According to the results listed in Table 4, the coefficient of thermal expansion (below T_g) of the epoxy/dicyanate ester systems was approximately 6.0–7.0 × 10^{-5}/°C. No matter which dicyanate ester was used, the coefficients of thermal expansion (CTE) of the DN-2 systems were slightly higher than those of the DN-1 systems, which was due to the increased EEW. It is noteworthy that both phosphorus-containing systems possessed a lower CTE than that of the control bisphenol-A system, especially for temperatures beyond the T_g. In the DOPONQ-containing systems (DN-1 and DN-2), the EEW of the DN-1 system was much lower than that of the control and the DN-2 system. This resulted in the lowest CTE. On the other hand, although the DN-2 system possessed a slightly higher EEW than the control, the presence of its planar naphthalene structure contributed to its lower CTE [38,39]. The glass transition temperature decreased with increasing EEW in the phosphorus-containing systems and was higher than that of the control system.

3.5. TGA analysis

The typical thermogravimetric traces for DOPONQ-containing epoxy/BIDCy (DNBI systems) were performed under nitrogen as shown in Fig. 4. The other epoxy/dicyanate esters show similar thermal degradation behavior in N_2 (not shown here for brevity); it exhibited a major mass loss via a single large decrease of approximately 70% from 360 °C to 450 °C, and then the rate of mass loss decreased substantially.

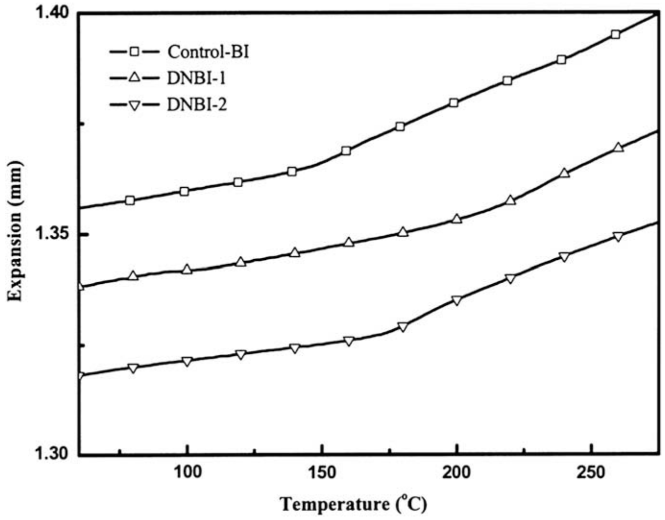


Fig. 3. Typical TMA traces of Control-BI, DNBI-1, and DNBI-2 at a heating rate of 5 °C/min.

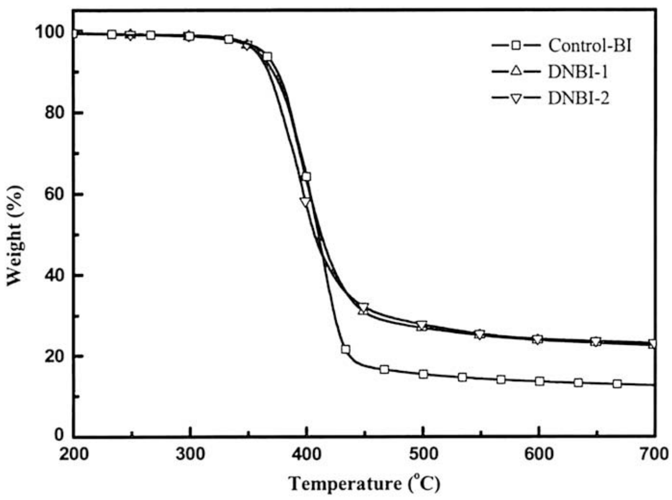


Fig. 4. Typical TGA thermograms of Control-BI, DNBI-1, and DNBI-2 in N_2 at a heating rate of 20 °C/min.

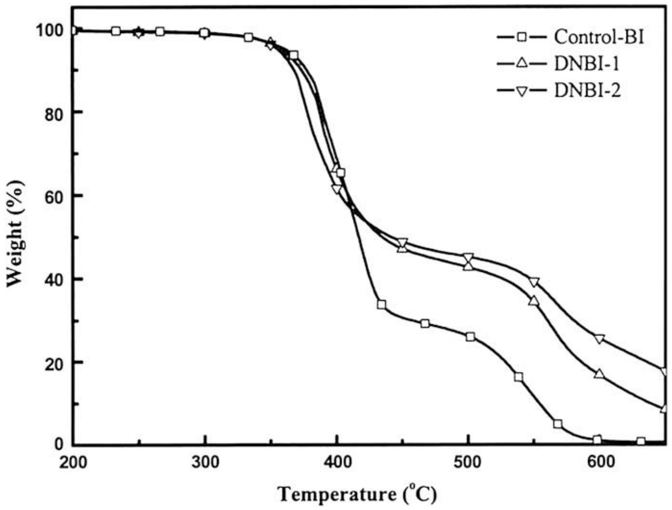


Fig. 5. Typical TGA thermograms of Control-BI, DNBI-1, and DNBI-2 in air at a heating rate of 20 °C/min.

In an air/oxidation environment, the thermal degradation showed a more complicated behavior as shown in Fig. 5 for the typical DOPONQ-containing epoxy/BIDCy. The onset temperature of degradation began at approximately 360 °C, followed by a major weight loss (a decrease of approximately 55%) from about 360 °C to 450 °C, and then the mass continued to decrease at a reduced rate from about 450 °C to 500 °C. The region of intermediate thermal stability reflects the thermal stability of the char layer formed during oxidative degradation. The increased rate of mass loss beyond 500 °C illustrates the continued degradation of the char layer, and the variations in rate and final yields at 650 °C point to the effect of an increased phosphorus addition upon the network.

From Tables 5 and 6, in both nitrogen and air atmosphere, the DN-2 system with a high phosphorus content showed a slightly lower $T_{d,5\%}$, $T_{d,10\%}$ and T_{max} than the corresponding DN-1 system. This is because the system with a higher phosphorus content has less thermostability at the beginning of thermodegradation due to the O=P–O bond being less stable than the –C–C– bond [11]. In this retarded-degradation phenomenon, the phosphorus-containing systems are consumed at an early stage of degradation and form an insulating protective layer, which prevents the transfer of combustible gases to the surface of the materials [7,18,19]. As a result, the DN-2 epoxy resin has better thermal stability at high temperature (step II) and a higher char yield (fire resistance) in comparison with DN-1 and the control systems. This is consistent with the UL-94 measurement discussed below.

Table 5
TGA data of advanced epoxy/dicyanate ester systems in N_2 at a heating rate of 20 °C/min

Sample code	$T_{d,5\%}$ (°C)	$T_{d,10\%}$ (°C)	Temp. of rapid weight loss T_{max} (°C)		Char yield at 700 °C (Y_c, %)
			Step I	Step II	
Control-BA	360	374	405	–	9.5
DNBA-1	357	369	403	–	15.4
DNBA-2	354	365	397	–	18.1
Control-TB	342	363	396	–	12.3
DNTB-1	353	366	393	–	17.8
DNTB-2	346	357	386	–	18.1
Control-BI	362	375	403	–	12.6
DNBI-1	357	371	402	–	22.5
DNBI-2	356	367	398	–	23.1
Control-OD	357	370	398	–	13.1
DNOD-1	356	368	396	–	20.8
DNOD-2	353	365	390	–	21.9

Table 6
TGA data of advanced epoxy/dicyanate ester systems in air at a heating rate of 20 °C/min

Sample code	$T_{d,5\%}$ (°C)	$T_{d,10\%}$ (°C)	Temp. of rapid weight loss (°C)		Char yield at 650 °C (%)
			Step I	Step II	
Control-BA	357	375	406	543	0
DNBA-1	358	372	399	569	8.5
DNBA-2	353	365	386	572	18.7
Control-TB	344	367	401	548	0
DNTB-1	358	369	390	569	9.8
DNTB-2	348	357	377	571	18.2
Control-BI	360	377	405	545	0
DNBI-1	357	373	396	564	9.2
DNBI-2	355	368	384	568	18.7
Control-OD	356	370	400	550	0
DNOD-1	356	370	392	560	8.8
DNOD-2	353	366	384	571	18.5

3.6. UL-94 measurements

UL-94 is an industry standard for flame retardancy. As shown in Table 7, the UL-94 rating increases from the V-2 grade for the control to V-0 for the DOPONQ-containing epoxy/dicyanate esters series. The flame retardancy of the cured DOPONQ-containing systems increases with phosphorus content, which was in good agreement with the results from the char yield. The burning time of the phosphorus-containing epoxy was clearly lower than that of the control bisphenol-A system. In addition, the cured DOPONQ-containing systems produced much less fume and no dripping; thus, the flame retardancy could be enhanced remarkably by raising the content of phosphorus in the advanced epoxy resins.

3.7. Dielectric properties and water absorption

From Table 8, the dielectric constants and dissipation factors increased in the order DNTB < DNBA < DNBI < DNOD system, which is consistent with the water absorption. The DNTB system contained TBFDCy with four hydrophobic methyl groups, which significantly affected the dielectric constant, dissipation factor, and water absorption. In addition, the DN-2 series with higher DOPONQ content in the formulation showed a higher dielectric constant, dissipation factor, and water absorption than those of the cured DN-1 systems. This was attributed to an increase in high polar sites

Table 7
Results of UL-94 flame retardancy test of cured advanced epoxy/dicyanate ester resins

Sample code	P Content (wt%)	Fume[a]	Drip	t_1	t_2	UL-94[b]
Control-BA	0	++	No	>30	–	V-2
DNBA-1	1.14	+	No	5.25	5.45	V-1
DNBA-2	2.07	+	No	1.35	2.56	V-0
Control-TB	0	++	No	>30	–	V-2
DNTB-1	1.10	+	No	4.24	6.29	V-1
DNTB-2	2.03	+	No	2.12	2.57	V-0
Control-BI	0	++	No	>30	–	V-2
DNBI-1	1.19	+	No	5.53	5.52	V-1
DNBI-2	2.14	+	No	1.22	1.95	V-0
Control-OD	0	++	No	>30	–	V-2
DNOD-1	1.17	+	No	5.49	6.27	V-1
DNOD-2	2.11	+	No	1.87	2.78	V-0

[a] +++: heavy; ++: medium; +: slight.
[b] V-0: $t_1 + t_2 < 10$ s; V-1: $t_1 + t_2 < 30$ s; V-2: $t_1 + t_2 > 30$ s.

Table 8
Dielectric properties and moisture absorption of advanced epoxy/dicyanate ester systems

Sample code	D_k at 1 GHz	D_f at 1 GHz	Moisture absorption (%)
Control-BA	3.05	0.007	0.99
DNBA-1	3.10	0.009	1.12
DNBA-2	3.20	0.011	1.26
Control-TB	2.90	0.005	0.88
DNTB-1	2.96	0.006	1.02
DNTB-2	3.18	0.009	1.20
Control-BI	3.19	0.009	1.13
DNBI-1	3.02	0.008	1.13
DNBI-2	3.26	0.010	1.30
Control-OD	3.25	0.010	1.16
DNOD-1	3.13	0.008	1.20
DNOD-2	3.30	0.012	1.37

of the O═P–O groups of the cured resins (DOPO systems); the increase, however, was quite limited. No matter which dicyanate ester was incorporated into the advanced epoxy, the dielectric constant and dissipation factor of the advanced epoxy/dicyanate ester systems were lower than those of the neat epoxy system (for the DGEBA/DDM system, $D_k = 3.70$ and $D_f = 0.0204$ at 1 GHz) [40]. This result may be attributed to the cyanate groups undergoing trimerization to form a triazine ring, which provided the excellent electrical properties of the cured network.

4. Conclusion

A phosphorus and naphthalene-containing diol (DOPONQ) was synthesized. A series of flame-retardant epoxy/cyanate ester resins were prepared from the advanced DOPONQ-containing epoxy and dicyanate esters. The DOPONQ-containing advanced epoxy provided a better flame retardancy, higher T_g, and lower CTE than those of the control bisphenol-A resins. In addition, the char yield and flame retardancy of the cured DOPONQ systems increased with phosphorus content. Besides the fact that a V-0 rating can be achieved with as low as 2% phosphorus in the DOPONQ-containing epoxy/dicyanate ester resins, the cured phosphorus-containing epoxy systems produced much less fumes than the cured bisphenol-A epoxy systems during combustion. These properties should make this DOPONQ-containing epoxy/cyanate ester resin attractive for practical applications such as flame-retardant laminates.

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