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ORIGINAL CONTRIBUTION

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Curing and pyrolysis of epoxy resins containing 2-(6-oxido-6*H*-dibenz(*c*,*e*)(1,2)oxaphosphorin-6-yl)-1,4-naphthalenediol or bisphenol S

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Abstract This work examines the curing kinetics, thermal properties, and decomposition kinetics of diglycidyl ether of bisphenol A (DGEBA) epoxies with three different curing agents, 2-(6-oxido-6*H*-dibenz(*c*,*e*)(1,2)oxaphosphorin-6-yl)-1,4-naphthalenediol (ODOPN), bisphenol A (BPA), and bisphenol S (BPS). The differential scanning calorimetry curing study reveals that the curing kinetics of the DGEBA/ODOPN epoxy is first order, independent of the scan rate. The ODOPN-containing epoxy, unlike the conventional BPA one, includes a phosphorus-containing bulky pendant aromatic group and results in an increase in the glass-transition temperature of 83 K, the char yield increases by a factor of 3, and the limiting oxygen index values increase from 23 to 27. For the BPS system, the glass-transition temperature increased slightly, and both the char yield and the limiting oxygen index value increased insignificantly when the test was conducted in air. Finally, the thermogravimetric analysis decomposition study in N_2 from Ozawa's analysis demonstrates that the DGEBA/BPS epoxy has the highest activation energy, followed by the regular DGEBA/BPA system, and lastly the DGEBA/ODOPN has the lowest activation energy. The low activation energy for the ODOPN system is attributed to the initial decomposition of the phosphorus compound in the formation of an insulating layer.

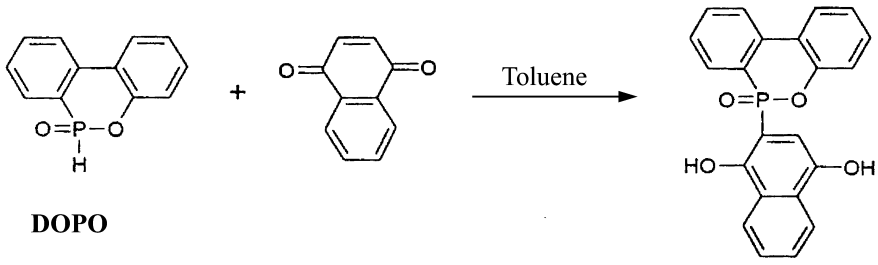
Keywords Curing kinetics · Flame retardancy · Thermal degradation · 2-(6-Oxido-6*H*-dibenz(*c*,*e*)(1,2) oxaphosphorin-6-yl)-1,4-naphthalenediol · Bisphenol A and bisphenol S

Introduction

Epoxy, one of the most important thermosetting resins in the electric, electronic, aerospace, or civil industries, has excellent characteristics, such as moisture resistance, low shrinkage, super mechanical properties, and low electric conductivity. Consequently, epoxy has become the most widely applied high-performance polymer in the world. However, the flammability of epoxy resin is a major limitation of applications that require high flame resistance. Epoxy compounds including some halogen atoms to retard flames have therefore become commonly used over the last decade. Unfortunately, halogen-containing materials release corrosive and toxic hydrogenated or aromatic halogens on combustion [1, 2]. This concern has motivated the search for nonhalogenic flame retardants. Organophosphorus compounds, which exhibit high flame resistance but generate little toxicity during combustion, have recently attracted much attention and are becoming increasingly popular [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29].

There has been extensive research on modifying epoxy by incorporating the O=P-O bond into the

Scheme 1



DOPO **ODOPN**

epoxy backbone [3, 4, 5, 6, 7, 8, 9, 10, 11]. Banks et al. [12] studied how covalently bound phosphorus affects the flame retardancy of polystyrene, poly(methyl methacrylate), polyacrylonitrile, and polyacrylamide. Furthermore, Kannan et al. [13] developed flame-retardant phosphorus-containing polyester amide. Even when the required flame retardancy was achieved, the polymers were found to degrade rapidly during heating owing to the cleavage of O=P-O bonds in the main chain. Many scholars have thus searched for epoxy systems that contain pendent phosphorus groups to increase the degradation temperature while maintaining flame retardancy [14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29].

Since a cyclic organic phosphorus compound, 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO), was developed in the 1970s, a series of compounds derived from the aryl phosphinate have been synthesized and used as flame-retardant curing agents or additives. Among them, a unique compound, 2-(6-oxido-6*H*-dibenz(*c*,*e*)(1,2)oxaphosphorin- 6-yl)-1,4-benzenediol (ODOPB), derived from DOPO, was synthesized and characterized by Wang and Lin [15]. ODOPB exhibits excellent flame retardancy and curing activity. Wang and Lin showed that ODOPB was a good flame-retardant curing agent that can be applied to an epoxy system, such as diglycidyl ether of bisphenol A (DGEBA), as well as to some polyester systems. The rigid structure of ODOPB and the pendant P group are responsible for the resulting phosphorus-containing epoxy resin having better flame retardancy, a higher glass-transition temperature, and greater thermal stability than the regular halogen-containing epoxy resin. Notably, a phosphorus content in the polymeric matrix of 2% was reported to increase significantly the flame retardancy.

In this study, following the investigation of Wang and Lin, a new compound resembling ODOPB, namely 2-(6-oxido-6*H*-dibenz(*c*,*e*)(1,2)oxaphosphorin-6-yl)-1,4-naphthalenediol (ODOPN), was synthesized and characterized. A series of DGEBA epoxies, with various phosphorus contents, were derived from ODOPN. The effect of the functionality of ODOPN on the flame retardancy and the glass-transition temperature was investigated. Additionally, a sulfur-containing epoxy–bisphenol S (BPS) cured with DGEBA was also prepared to compare the effect of phosphorus to that of sulfur on flame resistance. The properties of all the cured resins were evaluated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and determination of the limiting oxygen index (LOI). All the data were then compared to those for the neat DGEBA system and DGEBA cured with bisphenol A (BPA).

Experimental

Synthesis of ODOPN

DOPO (from TCI), 1,4-naphthaquinone (from TCI), 3-nitrobenoyl chloride, 4-nitrobenzoyl chloride (from Fluka), and 10% Pd/C (from Lancaster) were used without further purification. Based on the modified method of Endo et al. [30] and Wang and Lin [18], the ODOPN was synthesized by the addition of DOPO to 1,4-naphthaquinone (Scheme 1). Details regarding the synthesis and characterization of ODOPN was reported by Liou and Hsiao [31].

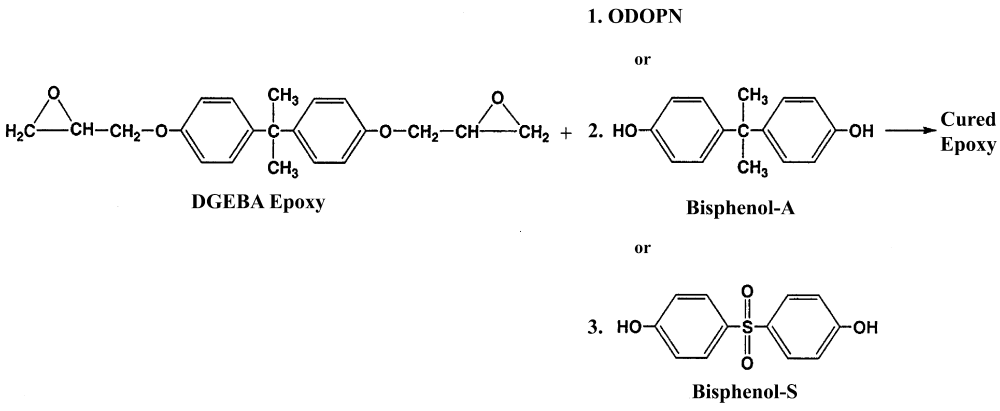
Curing reagent

ODOPN was used as a flame-retardant curing agent. The epoxy used was DGEBA with an epoxy equivalent weight of 190 g/Eq, which was kindly provided by Chang Chun Petrochemical (Taiwan). Two other curing agents, BPA and BPS, were purchased from Acros. The catalyst system, triphenylphosphine, was purchased from Acros and used as a curing accelerator. All the reagents (Scheme 2) were reagent grade and were used without further purification.

Curing procedure

The weight ratios of epoxy to the curing agent were 1.06 g/g for ODOPN, 1.52 g/g for BPS, and 1.67 g/g for BPA to maintain the molecular equivalence ratio at 1/1. Additionally, various amounts of ODOPN or BPS were added to BPA as an agent for curing DGEBA epoxy resin to determine the effect of phosphorus on flame retardancy. The curing agents consisted of ODOPN/BPA or BPS/BPA in different weight ratios (0/100, 25/75, 50/50, 75/25, 100/0). In this study, following the procedure of Barton et al. [32] and Hsieh and Su [33], a "dynamic curing process" was performed using the DSC instrument (PerkinElmer 7e). The samples were thermally cured and scanned under nitrogen (30cm^3/min) in the calorimeter at a heating rate of 20, 10, 5, or 2.5 K/min from 303 to 573 K. No postcuring was required since the curing was rapidly completed when the DSC pan reached a relatively high temperature for such a tiny quantity of sample (about 10 mg). As well as

Scheme 2



dynamic curing, isothermal curing was also performed in an oven at 433 K for 60 min. The samples were then subjected to DSC and DMA measurements, respectively, to determine their T_g values.

Characterization

The LOI is a common indicator to evaluate the flame retardancy of a material. It is defined as the minimum fraction of oxygen in an oxygen/nitrogen mixture that can just sustain the combustion of a specimen after ignition. In this study, the LOI was measured using a Santon Redcroft flame meter, modified by the method reported by Nair et al. [34]. Powdered samples (500 mg) were placed in a ceramic cup (diameter 40 mm, height 4 mm) placed in the middle of an Atlas cylindrical chamber (diameter 80 mm, height 200 mm) and a flame was applied from the top of the chamber for 10 s. A flow rate of 12 l/min was maintained in various ratios of N_2/O_2. The percentage of oxygen in the mixture just sufficient to sustain the flame for 30 s was taken as the LOI. The advantage of this method for measuring the LOI is that up to nine tenths of the testing material that would be consumed by regular ASTM measurement can be saved. The deviation of the LOI was reported to be approximately 5%.

TGA measurements were taken using a TA Instruments TGA 2950 at a heating rate of 10 K/min in a nitrogen or air atmosphere. DMA was performed using a PerkinElmer DMA 7e. The storage modulus, G', and tanδ against the scanning temperature were obtained at a heating rate of 3 K/min from ambient temperature to 493 K, at a frequency of 1 Hz and an amplitude of 4 μm. A sample of 12-mm length, 10-mm width, and 2-mm thickness was used. The test was performed in the three-point bending mode, at a tension ratio of 110%.

Results and discussion

Curing kinetics for the DGEBA/ODOPN system

DGEBA cured with ODOPN is a newly developed system, and it is quite important to understand its curing mechanism and hence this is our primary concern. DSC thermograms obtained at various heating rates are displayed in Fig. 1. The data were analyzed according to Ozawa's [35, 36] (or Prime's [37]) method. The governing equation is shown as follows.

$$E_a = -2.19R\left[\mathrm{d}\log q/\mathrm{d}\left(1/T_p\right)\right], \quad (1)$$

where E_a is the activation energy, q is the heating rate, R is the ideal gas constant, and T_p is the peak temperature

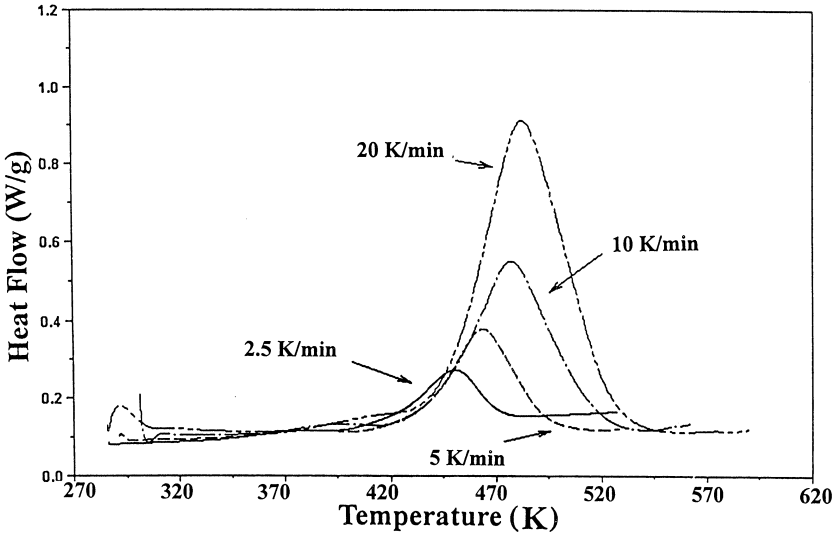


Fig. 1 Differential scanning calorimetry (*DSC*) thermograms for the diglycidyl ether of bisphenol A (*DGEBA*)/ 2-(6-oxido-6*H*-dibenz(*c*,*e*)(1,2)oxaphosphorin-6-yl)-1,4-naphthalenediol (*ODOPN*) epoxy system curing at various heating rates

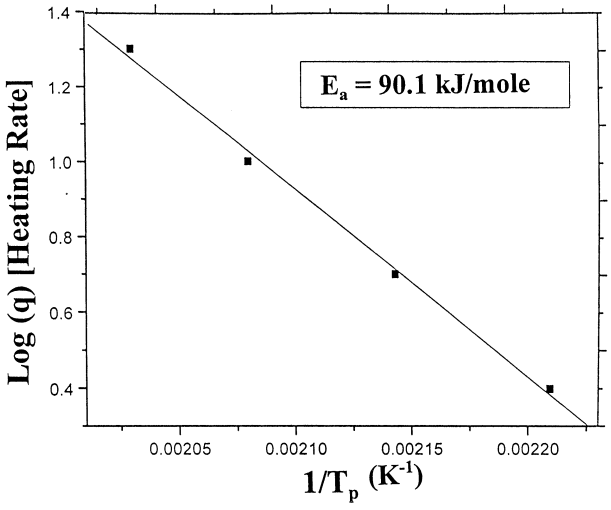


Fig. 2 Activation energy of curing through the treatment of Fig. 1 by Ozawa's method from Eq. (1)

of the DSC thermogram. Thus, a plot of log$q$ versus T_p^{-1} should be a straight line with a slope of $0.457E_a/R$ (Fig. 2). The activation energies calculated from Eq. (1) for DGEBA/ODOPN, DGEBA/BPA, and DGEBA/BPS are 90.1, 86.6, and 80.1 kJ/mol, respectively. They fall in the range from 80 to 90 kJ/mol. No significant difference was observed since all the reactions are associated with the cross-linking between diol and DGEBA within the same catalytic environment.

Figure 1 can be further converted into Fig. 3 by integrating the DSC thermopeak to obtain the reaction conversion as the ratio of the partial area up to a particular temperature to the total area. Friedman [38] suggested the following relationship to simulate the conversion trace:

$$\ln(d\alpha/dt) = \ln Z - (E_a/RT) + n\ln(1-\alpha), \quad (2)$$

Table 1 Values of n and ln$Z$ for treatment of Fig. 1 using Eqs. (1) and (2)

Heating rate (K/min)	n	ln$Z$
2.5	1.01	22.41
5	1.16	22.20
10	1.16	21.86
20	1.17	22.26

where E_a is the apparent activation energy calculated from Eq. (1) and is treated as a constant, n is the order of reaction, Z is the intercept of the plot, t is the curing time, and α is the conversion at a given temperature (Fig. 3). According to Eq. (2), the order of the reaction, n, was determined by plotting $\ln(d\alpha/dt)$ as a function of $\ln(1-\alpha)$. The results are summarized in Table 1 and indicate that the order of the cross-linking reaction (n) is approximately 1, independent of the scan rate. The conversion at a given temperature was then calculated by integrating Eq. (2) (n, as referred to in Table 1). The results are summarized in Fig. 3 for a convenient comparison with the experimental data obtained here. Although discrepancies become more apparent at the lowest heating rate, Fig. 3 generally agrees well with the prediction from the first-order Friedman equation.

Thermal stability analyses and flame retardancy measurements

T_g values measured for DGEBA/ODOPN obtained using DSC and DMA, respectively, are shown in Figs. 4 and 5. The T_g values were observed to be 10–15 K higher when obtained by DMA than by DSC. This result is normal and may be due to the different principles of the instrumental designs. However, the T_g values obtained by both measurements were found to increase with ODOPN content. This indicates that incorporating

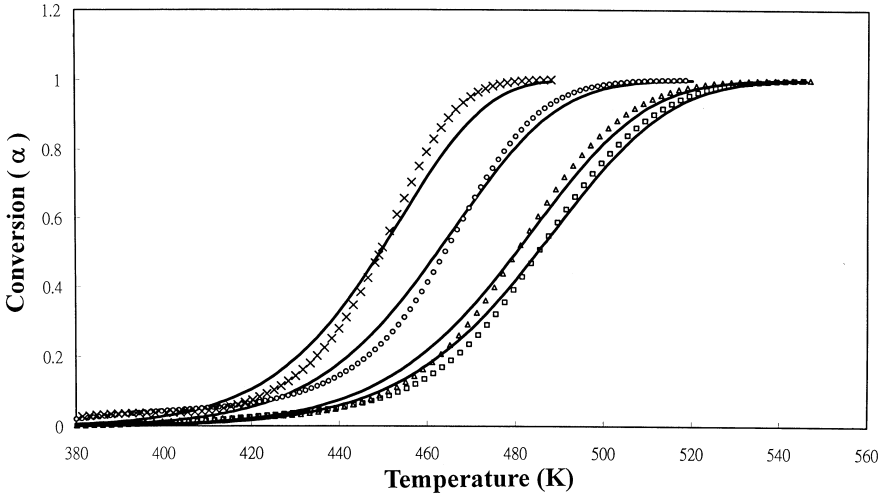


Fig. 3 Conversion curves from Fig. 1 at different heating rates: 2.5 K/min (*crosses*), 5 K/min (*circles*), 10 K/min (*triangles*), 20 K/min (*squares*). The corresponding *solid curves* were predicted using Eq. (2)

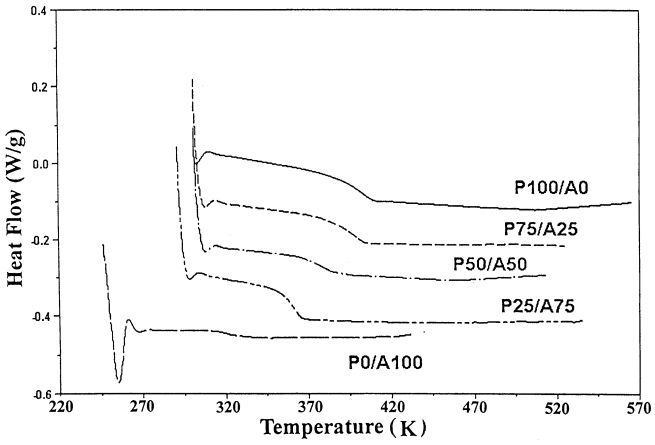


Fig. 4 The determination of T_g by DSC for cured DGEBA epoxy with a curing agent mixture consisting of ODOPN/bisphenol A (*BPA*) in different weight ratios

Table 2 T_g values of diglycidyl ether of bisphenol A (*DGEBA*) epoxy cured with different curing agents determined by differential scanning calorimetry (DSC) and dynamic mechanical analysis (*DMA*). 2-(6-Oxido-6*H*-dibenz(*c*,*e*)(1,2)oxaphosphorin-6-yl)-1,4-naphthalenediol (*ODOPN*), bisphenol A (*BPA*), bisphenol S (*BPS*)

Composition	T_g by DSC (K)	T_g by DMA (K)
BPA	321.9	333.1
ODOPN25/BPA75	362.9	374.3
ODOPN50/BPA50	386.1	393.9
ODOPN75/BPA25	397.2	411.8
ODOPN	405.2	421.1
BPS25/BPA75	326.2	337.1
BPS50/BPA50	352.7	364.5
BPS75/BPA25	356.8	367.9
BPS	363.6	376.6

ODOPN, a bulky rigid aromatic group, increases the rotational barrier. The barrier may suppress the molecular mobility and consequently increase the T_g. The modulus determined by the DMA test (Fig. 5) is also proportional to the ODOPN weight percent perhaps because the higher number of aromatic rings in ODOPN increases the polymer rigidity, and thus increases its modulus. The DSC and DMA results for the DGEBA/ODOPN system are given in Table 2 together with the results of the T_g measurement for the DGEBA/BPS system. Table 2 shows that the T_g of the BPS system, even lower than that of the ODOPN system, is higher than that of the BPA system. Liaw and Shen, Shim et al. [39], and Acitelli et al. [40] also obtained a similar result pertaining to viscosity. A reasonable explanation is that strong intermolecular attraction among DGEBA chains is formed by the presence of sulfur in BPS.

TGA is the conventional means of evaluating the thermal stability of epoxy resins. Typical TGA thermograms at various heating rates in nitrogen, and their first derivatives, for DGEBA epoxies cured with ODOPN, BPS, and BPA respectively, are shown in Fig. 6a–c. Details of the results with additional TGA work on the mixtures of the curing agents, ODOPN/BPA, and BPS/BPA are presented in Table 3. Figure 6a–c reveals that the ODOPN system has the lowest temperature of maximum degradation rate, T_{dmax}, but the highest char yield. Furthermore, Table 3 shows that T_{dmax} declined as the phosphorus content increased. The char yields, however, increased with phosphorus content. Both results are attributable to the initial decomposition of the phosphorus compound. In the early decomposition, dehydration of phosphorus-containing polymer is initiated, producing a layer composed of

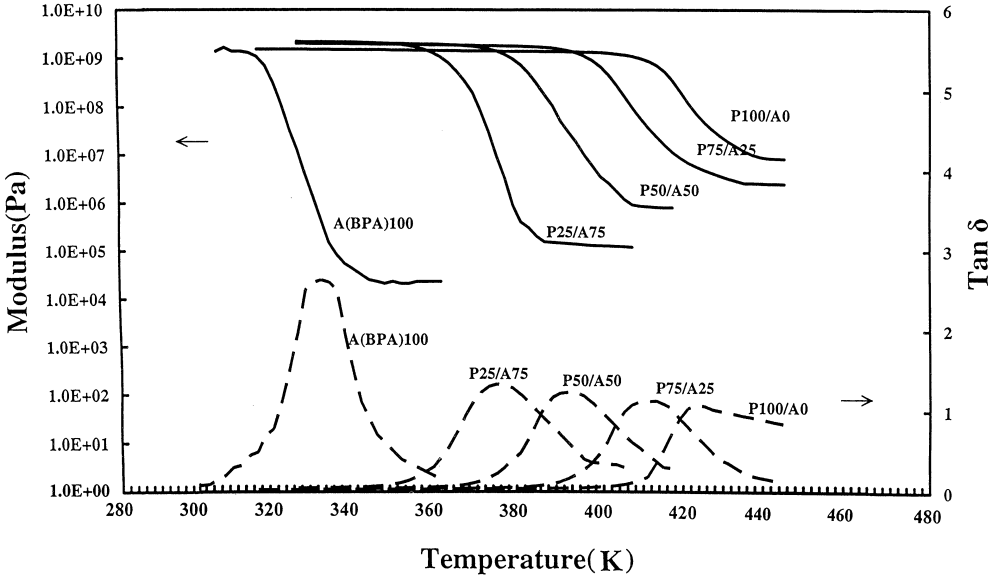


Fig. 5 The determination of T_g by dynamic mechanical analysis (*DMA*) for cured DGEBA epoxy with a curing agent mixture consisting of ODOPN/BPA in different weight ratios

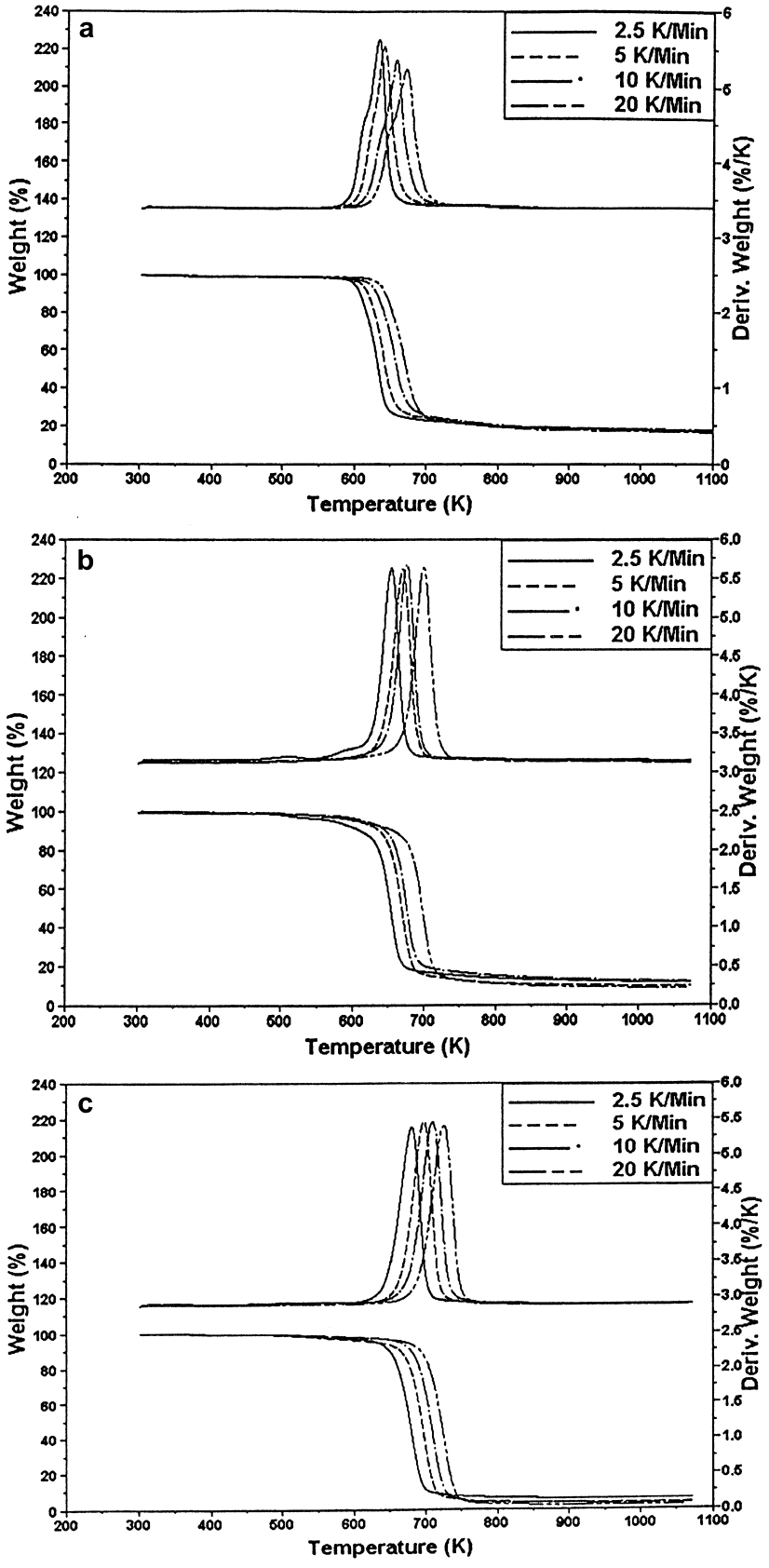


Fig. 6a–c Typical thermograms at various heating rates in N_2, and their first derivatives, for DGEBA epoxies cured with ODOPN, bisphenol S, and BPA, respectively

Table 3 Thermal properties of DGEBA epoxy cured with different curing agents

Curing agent composition	P (%)	S (%)	T_{dmax} (K)	973 K char yield in N_2 (%)	973 K char yield in air (%)
BPA	0.15		710	3.6	0.2
ODOPN25/BPA75	1.34		688	13.1	
ODOPN50/BPA50	2.40		669	16.0	
ODOPN75/BPA25	3.36		664	17.1	
ODOPN	4.22		658	19.3	18.4
BPS25/BPA75		1.32	699	5.7	
BPS50/BPA50		2.56	695	7.7	
BPS75/BPA25		3.80	684	9.4	
BPS		5.02	676	12.8	0.5

phosphate groups on the polymer's surface that insulates the underlying polymer from heat and oxygen. Furthermore, the vapor from dehydration may dilute the flammable gases and quench the flame. Thus, the decomposition temperature decreased as the phosphorus content increased. Notably, the T_{dmax} of ODOPN, although lower than that of BPA, is much higher than that of other linear or cyclic phosphorus systems [41, 42, 43]. Sato and Yokoyama [44, 45, 46, 47, 48] reported that polymers with a high aromatic content exhibited fire retardancy and thermal stability. Accordingly, the high T_{dmax} of the ODOPN system is attributable to the four benzene rings attached to the unit structure of the ODOPN molecule.

TGA measurements performed in air can provide information that more closely pertains to real combustion behavior than those performed in nitrogen. However, the presence of oxygen complicates the decomposition of the resins. The char yield from DGEBA/ODOPN is compared in Table 3 with that from DGEBA /BPA in different atmospheres. The ODOPN system yields 19.3% in N_2 and 15.2% in air at 973 K, while for BPA at the same temperature the char residue is only 3.6% in N_2 and nearly zero in air. This result demonstrates that the oxygen in the air slightly affects the flame retardancy of a phosphorus-containing epoxy. Similar results have been reported by Liu et al. [41] and Wang and coworkers [14, 15].

Table 3 also indicates that the BPS system gives a lower T_{dmax} but a higher char yield in N_2 than the BPA system. Restated, the BPS system shows similar tendencies, but lower flame retardancy and thermal stability in N_2 than does ODOPN. Liaw and Shen [49] reported that an epoxy resin, based on BPS, exhibits the advantages of resistance to deformation by heat and thermal stability in N_2. The results obtained here agree with those of Liaw and Shen. However, the char yield dropped dramatically to nearly zero when BPS was exposed to air at 973 K. This implies that a sulfur-containing group can increase the flame retardancy of epoxy resins in N_2 but not in air. Similar results were found in the LOI measurement and further discussion is made later.

Van Krevelen [50] has thoroughly examined the relationship between char yields and flame retardancy and concluded that the char residue after pyrolysis is linearly proportional to the LOI. Increasing char yield can reduce the generation of combustion gases, limit the exothermicity of the pyrolysis reaction, decrease the solid conductivity of heat, and thus suppress the flammability of materials. In this study, the cured epoxies DGEBA/BPA, DGEBA/ODOPN, and DGEBA/BPS were examined further by measuring their LOI; the results are shown in Table 4. The table demonstrates that the LOI value of the phosphorus-containing system significantly exceeds that of the neat system [51]; however, the sulfur-containing system shows no flame resistance. These results are consistent with the results of TGA measurement in air. The flame retardancy of ODOPN epoxy might be attributed to its high aromatic content and the effect of phosphorus, while the sulfur content has only a small effect on flame retardancy in air.

Degradation kinetics

The activation energy of degradation for a given TGA weight fraction (weight percent) can be determined by Ozawa's method, described earlier. The only difference is that the peak temperature obtained here is from the TGA scan for degradation, instead of from the DCS scan for curing. This practical approach to investigating decomposition has been frequently applied to a variety of aromatic polymers [52], such as polyimides, poly (ether sulfone), poly(*p*-xylylene), and epoxy-containing ODOPB [18]. As shown in Fig. 7, a good linear rela-

Table 4 Activation energy and limiting oxygen index (*LOI*) values for DGEBA epoxy cured with different curing agents

DGEBA epoxy cured with different curing agents	Average activation energy of degradation (kJ/mol)	LOI
ODOPN	177.1	27
BPS	221.3	24
BPA	190.8	23

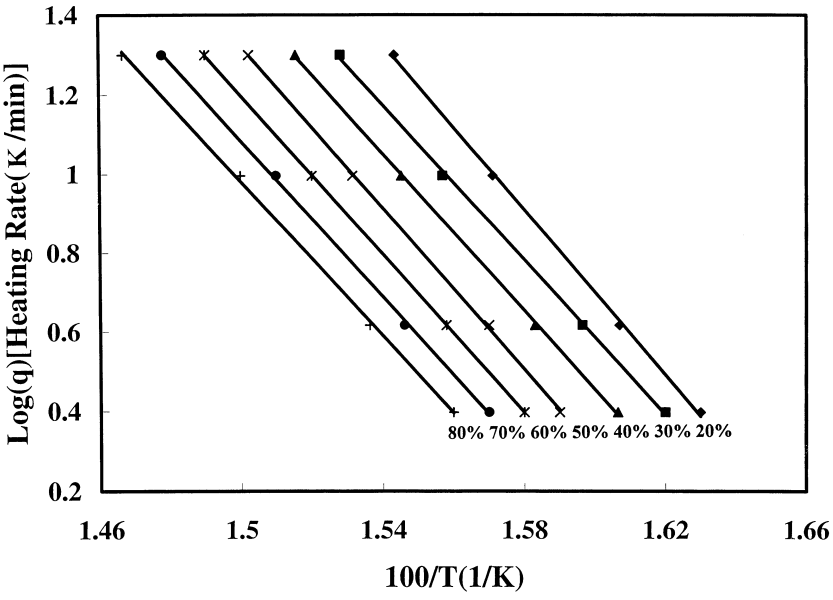


Fig. 7 The treatment of thermogravimetric analysis traces for DGEBA/ODOPN (Fig. 6a) by Ozawa's method to obtain the activation energy of degradation at various conversion ratios The E_a values for 80%, 70%, 60%, 50%, 40% 30%, and 20% are 165.2, 165.6, 169.0, 174.1, 181.5 191.0, and 193.2 kJ/mol, respectively

tionship between log$q$ and the reciprocal peak temperature is observed for the DGEBA/ODOPN system. This result indicates the thermal decomposition of the epoxy, DGEBA/ODOPN, in N_2 was controlled by a single activation energy. The average activation energy could be calculated by averaging out the E_a values obtained from Eq. (1) for each conversion ratio. Similarly, the average E_a values for the degradation of DGEBA/BPS and DGEBA/BPA were determined and the results are summarized in Table 4. Table 4 reveals that the DGEBA/BPS epoxy exhibits the highest activation energy, followed by the regular DGEBA/BPA system, and the DGEBA/ODOPN has the lowest activation energy. The low E_a for DGEBA/ODOPN is attributable to the initial decomposition of the phosphorus compound in the formation of an insulating layer. A similar explanation was given in the previous T_{dmax} discussion. Moreover, Table 4 is consistent with the report of Liaw and Shen on the sulfur-containing epoxy. The irrotational double bonds of the O=S=O group in BPS might retard the molecular mobility and consequently hinder pyrolysis.

Conclusion

Cured DGEBA epoxies were prepared with three different curing agents, BPA, ODOPN, and BPS. Introducing a phosphorus-containing bulky pendant group, like ODOPN, into the epoxy increases the thermal stability, the glass-transition temperature, the char yield, and the LOI values compared to those of the conventional BPA system. For the BPS system, the glass-transition temperature increased slightly, but an insignificant improvement was observed in the thermal stability, the char yield, and the LOI value when testing was performed in air. The DSC curing study indicates that the curing kinetics of the ODOPN/DGEBA epoxy is first order, independent of the scan rate. Finally, the TGA decomposition study in N_2 using Ozawa's method demonstrates that the DGEBA/BPS epoxy has the highest activation energy, followed by the regular DGEBA/BPA system, and lastly the DGEBA/ODOPN system has the lowest activation energy. The low activation energy for the ODOPN system is attributed to the initial decomposition of the phosphorus compound in the formation of an insulating layer. In regard to the sulfur-containing epoxy, the inflexible double bonds of the O=S=O group in BPS might retard the molecular mobility and consequently hinder pyrolysis.

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