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Curing of Epoxy Resins with 1-[Di(2-Chloroethoxyphosphinyl)Methyl]-2,4- and -2,6-Diaminobenzene

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Synopsis

Fire-resistant compositions were prepared using 1-[di(2-chloroethoxyphosphinyl)methyl]-2,4- and -2,6-diaminobenzene (DCEPD) as a curing agent for typical epoxy resins such as EPON 828 (Shell), XD 7342 (Dow), and MY 720 (Ciba Geigy). In addition, compositions of these three epoxy resins with common curing agents such as *m*-phenylenediamine (MPD) or 4,4'-diaminodiphenylsulfone (DDS) were studied to compare their reactions with those of DCEPD. The reactivity of the three curing agents toward the epoxy resins, measured by differential scanning calorimetry (DSC), was of the order MPD > DCEPD > DDS. The relatively lower reactivity of DCEPD toward epoxy resins was attributed to electronic effects. It was shown that the heat of polymerization (ΔH_{pol}) increases with increasing epoxy functionality of the resin. The polymers obtained were characterized by DSC, thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and Fourier-transform infrared (FT-IR). The polymers of DCEPD showed a relatively lower polymer decomposition temperature (PDT) and a higher char yield than the polymers of the common curing agents. Furthermore, it was shown that the thermal characteristics of the compositions were dependent upon the ratio of the reactants. The fire resistance of the polymers was evaluated by determining their limiting oxygen index (LOI) value. The DCEPD polymers, especially those with polyfunctional epoxy resins, showed a significantly higher fire resistance as compared with those polymers of common curing agents.

INTRODUCTION

Epoxy resins are widely used in coating, adhesive, flooring, laminating, and casting applications.¹ The flammability of epoxy resins, however, is a major hazard. Many techniques have been utilized to impact flame retardancy into epoxy resins. Ammonium phosphate, phosphorus-halogen mixtures, organophosphorus compounds, and compositions of organophosphorus compounds containing chlorine and bromine all impart flame resistance to epoxy resins. Approximately 5–6% phosphorus is required to attain significant flame retardation. A variety of phosphorus-halogen compositions containing about 2% phosphorus and 6% chlorine produce self-extinguishing epoxy resins.²

A convenient way to reduce the flammability of epoxy-resin compositions is the utilization of a fire-resistant crosslinking agent. Several investigations concerning flame retardation of epoxy resins by this method have been recently reported. Brominated poly(*p*-vinylphenol),³ hydroxy alkylphosphines,⁴ phosphate and pyrophosphates esters,⁵ organic phosphonates,⁶ and complex

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compounds of boron trifluoride with phosphines⁷ have been proposed as curing agents for epoxy resins.

The objective of this investigation is to reduce the flammability of epoxy-resin compositions using a phosphorus-containing curing agent. Specifically, the polymerization of some commercially available epoxy resins with DCEPD was studied. The latter compound has been prepared by nitration and subsequent hydrogenation of di(2-chloroethoxyphosphinyl)methyl benzene (J. A. Mikroyannidis, private communication). This preparation is of interest, since according to the literature,⁸⁻¹⁰ the Michaelis-Arbuzov reaction gives unsatisfactory results with nitro-substituted halides. DCEPD has been obtained in a satisfactory yield from relatively inexpensive and readily available starting materials by using the preparation mentioned by Mikroyannidis.

EXPERIMENTAL

Instrumentation

IR spectra were recorded using a Nicolet MX-1 FT-IR spectrometer with KBr pellets. TGA and DSC were performed on a DuPont 1090 Thermal Analyzer System. A heating rate of 20°C/min was used in both nitrogen and air atmospheres with a flow rate of 80 cm³/min. A DuPont 980 DMA connected with a 1090 Thermoanalyzer was used to evaluate glass-transition temperatures of the compositions. The DMA measurements were made at a heating rate of 5°C/min.

The LOI of the compositions was determined with a Stanton Redcroft flammability unit (ASTM D 2863-74). The LOI specimens measuring 70 × 6.5 mm were formed by the curing of the epoxy resin-curing agent mixtures into a mold. The mixture of nitrogen and oxygen passed upward through the chimney at a flow rate of 18 L/min. LOI, which is the quantity of oxygen (by volume) in a mixture of oxygen and nitrogen that supports burning, was then evaluated as

$$\text{LOI} = \frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$$

Materials

Curing Agents. The DCEPD has been prepared and characterized by elemental analysis, IR, and ¹H NMR spectroscopy. It has been shown by IR and ¹H NMR spectroscopy that the product obtained by nitration of the di(2-chloroethoxyphosphinyl)methyl benzene and subsequent hydrogenation consisted of about 90% 2,4-diamino and 10% 2,6-diamino isomer. The analytical sample of DCEPD had mp 116–119°C. This chemical structure is shown below.

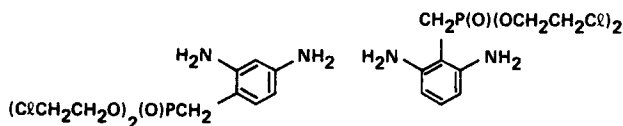


TABLE I
Chemical Structure of Epoxy Resins

EPOXY RESIN	EEW	STRUCTURE
EPON 828	185-192	
XD 7342	162	
MY 720	105.5	

Polymerization of epoxy resins with DCEPD was compared with that of common commercial grade curing agents such as *m*-phenylenediamine (MPD) and 4,4'-diaminodiphenylsulfone (DDS).

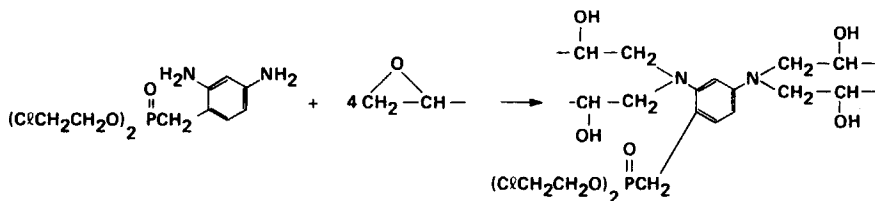
Epoxy Resins. The chemical structure and the epoxy equivalent weight (EEW) of typical epoxy resins with different epoxy functionalities such as EPON 828 (Shell) based on diglycidyl ether of bisphenol A, XD 7342 (Dow) based on triglycidyl ether of tris(hydroxymethyl)methane, and MY 720 (Ciba Geigy) based on tetraglycidyl ether of 4,4'-diaminodiphenylmethane are given in Table I.

Sample Preparation. The epoxy resins and curing agents were dissolved in acetone at a low temperature to obtain a homogeneous mixture of the reactants. The solvent was stripped off in a vacuum, and the resinous residue obtained was directly used for DSC measurements.

RESULTS AND DISCUSSION

The synthesis of DCEPD and its applications as a fire-retardant material were undertaken because of its promising structural features. From observing its structure, it is seen that DCEPD carries a di(2-chlorethoxyphosphinyl)methyl group bound to *m*-phenylenediamine, which is widely used as a curing agent for epoxy resins. The DCEPD therefore combines the characteristics of a curing agent for epoxy resins with those of an efficient phosphorus-containing fire retardant.

Three typical epoxy resins containing a different number of epoxy groups per molecule were utilized for polymerization with curing agents (Table I). To obtain a highly crosslinked polymer with good thermal stability, a 1-epoxy equivalent weight of the epoxy resins was polymerized with 0.25 mol of curing agent. For such a ratio of reactants, 1-amine proton corresponds to each epoxy group. The reaction of 1-[di(2-chloroethoxyphosphinyl)methyl]-2,4-diaminobenzene, which is the predominant isomer in the synthesized product of DCEPD with an epoxy resin may be shown as follows:



Furthermore, compositions of the epoxy resins with common curing agents such as MPD and DDS were studied for comparative purposes.

The polymerization reactions were studied using DSC. Typical DSC curves of the polymerizing agents utilized are shown in Figure 1. The first endotherm peak appeared in the DSC curve of DCEPD and corresponds to its melting point (110–113°C). The corresponding DSC peaks show that the melting and boiling points of MPD and DDS are in good agreement with literature values.

In the DSC study of polymerization reactions, great care was taken to obtain homogenous mixtures of the epoxy resins and the curing agents. For this purpose, the reactants were dissolved in acetone, and a sample from the mixture obtained after removal of the solvent under reduced pressure was immediately scanned to preclude prepolymerization. Figures 2 and 3 show typical DSC thermograms of the epoxy resin–curing agent compositions, both uncured and cured. Some thermal characteristics of these systems are shown in Table II. Specifically, the onset temperature (T_1) calculated by the intersection of the tangent to the front side of the exotherm curve with the base line, the exotherm peak temperature (T_2), and the evolved heat of polymerization or pyrolysis (ΔH_{pol} or ΔH_{pyr}) are given in Table III. Figure 3 also shows the DSC thermograms of the three epoxy resins without the curing agent, indicating exotherm peaks in the region of 300–400°C. This particular exotherm peak is believed

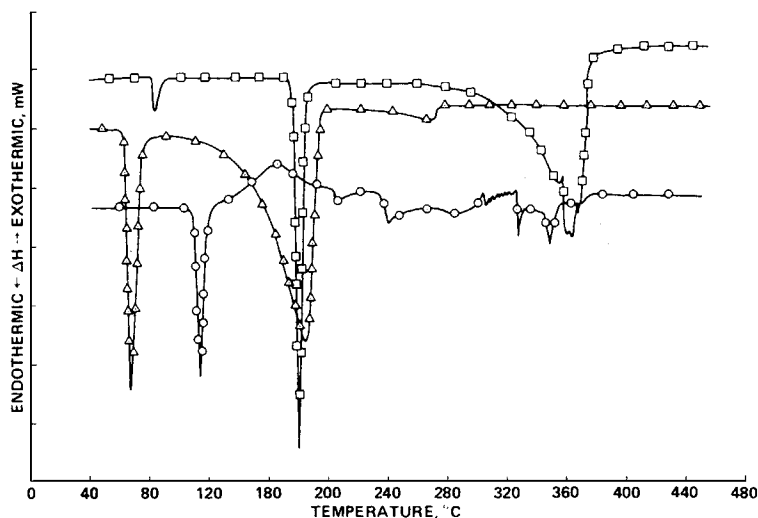


Fig. 1. DSC thermograms of curing agents in N_2 : (O) of DCEPD; (Δ) of MPD; (\square) of DDS; heating rate = 20°C/min.

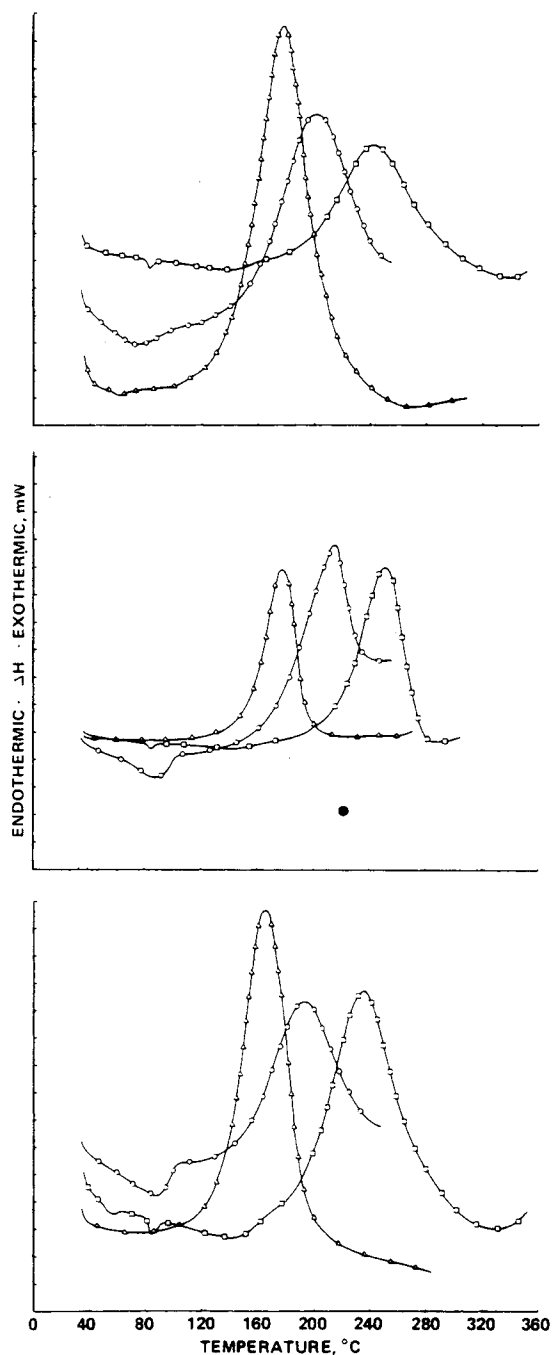


Fig. 2. DSC thermograms of the epoxy resin-curing agent compositions (0.25 mol of curing agent/EEW) uncured in N_2 ; heating rate = $20^\circ\text{C}/\text{min}$. Top: (O) EPON 828-DCEPD; (Δ) EPON 828-MPD; (\square) EPON 828-DDS. Middle: (O) XD 7342-DCEPD; (Δ) XD 7342-MPD; (\square) XD 7342-DDS. Bottom: (O) MY 720-DCEPD; (Δ) MY 720-MPD; (\square) MY 720-DDS.

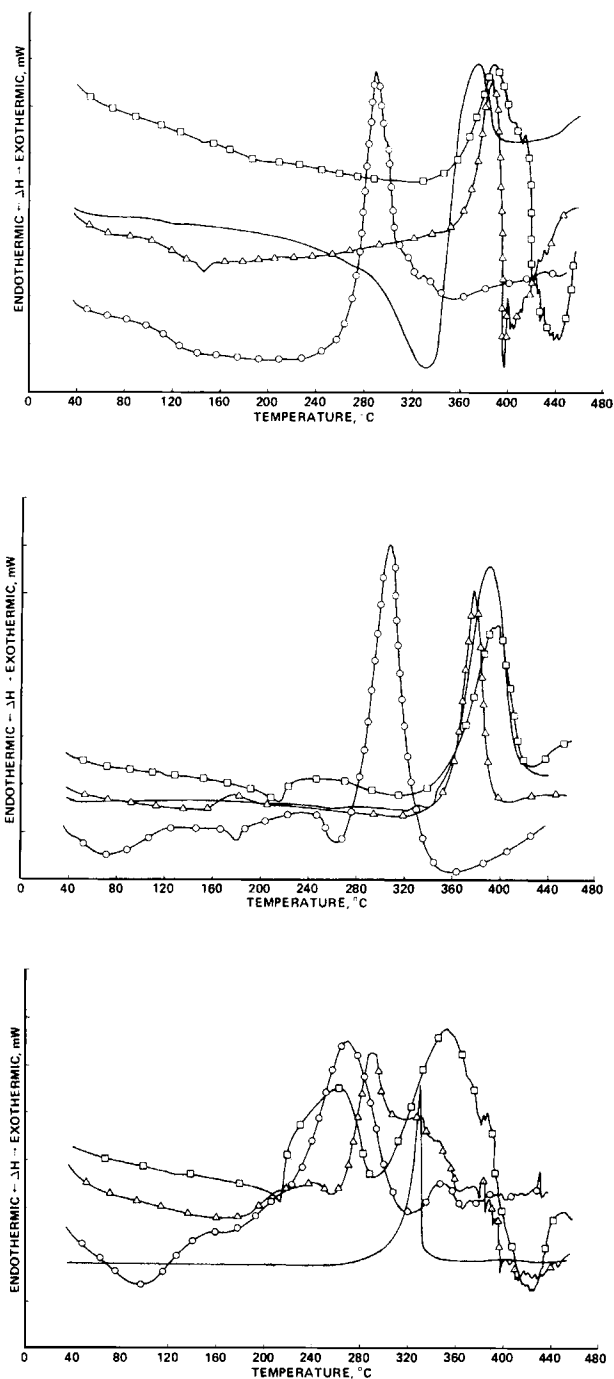


Fig. 3. DSC thermograms of the epoxy resin-curing agent compositions (0.25 mol of curing agent/EEW) cured and of epoxy resins without curing agent in N_2 ; heating rate = $20^\circ\text{C}/\text{min}$. Symbols are the same as in Figure 2; (—) EPON 828, XD7342, and MY 720 in the top, middle, and bottom, respectively.

TABLE II
Thermal Characteristics of Epoxy Resin-Curing Agent Compositions^a

Epoxy resin	Curing agent	Compositions ^a Polymerization			Pyrolysis		
		T_1 (°C)	T_2 (°C)	ΔH_{pol} (J/g)	T_1 (°C)	T_2 (°C)	ΔH_{pyr} (J/g)
EPON 828	DCEPD	156.9	201.0	145	270.1	288.9	94
EPON 828	MPD	140.4	177.3	308	364.0	386.6	70
EPON 828	DDS	191.8	243.7	224	352.5	389.0	102
XD 7342	DCEPD	151.4	190.7	172	278.2	307.1	210
XD 7342	MPD	133.7	165.3	320	360.0	378.1	121
XD 7342	DDS	186.9	233.8	276	359.9	395.9	97
MY 720	DCEPD	174.7	213.7	208	221.7	169.1	214
MY 720	MPD	153.2	177.8	356	268.6	291.0	85
MY 720	DDS	216.3	249.7	331	304.8	352.7	100

^a 0.25 mol of curing agent/EEW.

to be due mainly to isomerization of the epoxy groups to carbonyl groups and to thermal polymerization of the epoxy groups.¹¹ It has been reported¹²⁻¹⁴ that when ethylene oxide was heated to 380°C or above, it rearranged to acetaldehyde with an evolution of a quantity of heat of about 100 kJ/mol of ethylene oxide. Since the epoxides are derivatives of ethylene oxide, it is reasonable to assume that they behave in a similar manner.

The appearance of vapors in this temperature range indicated that volatilization and decomposition occur simultaneously with isomerization and polymerization. In the case of EPON 828, which was the less viscous resin utilized, an endotherm peak (-79 J/g) appears in the range of 287-334°C due to volatilization and decomposition. A smaller exotherm peak (+39 J/g) that follows at 352-372°C corresponds to its isomerization and polymerization.

Figure 2 shows that these systems (DSC thermograms of the uncured epoxy resin-curing agent compositions) start to release heat at about 133-216°C. No exotherms can be detected in the DSC thermograms of the epoxy resins without a curing agent or completely cured epoxy resins in the same temperature range, thus indicating that the peaks are attributed to the exothermic curing reactions. The influence of the chemical reactivity of the curing agents on cure behavior is apparent (Fig. 2). In all cases of epoxy resins utilized, the exotherm starting temperature increases according to the order: MPD < DCEPD < DDS. A curing agent which shows a lower exotherm starting temperature under the same set of curing conditions is more reactive toward the epoxy resin utilized.^{11,15} It is therefore reasonable to propose that the chemical reactivity of the three different curing agents toward the epoxy resins increases as follows: MPD > DCEPD > DDS. The lower reactivity of DCEPD toward epoxy resins as compared with that of MPD should be attributed to electronic effects. It is believed¹⁶ that the polymerization of epoxy resins with an amine occurs via a nucleophilic attack of the amine nitrogen to the methylene carbon atom of the epoxy group. In the case of DCEPD, the electron-withdrawing phosphinyl group reduces the electron density of the amine nitrogens and therefore impedes their nucleophilic attack on the methylene carbon atom of the epoxy group. The DDS shows the lowest

reactivity toward epoxy resins and this should be attributed to lower basicity and nucleophilicity of its amine nitrogens.

Furthermore, the heat of polymerization (ΔH_{pol}) of the same curing agent with the three epoxy resins follows the trend: EPON 828 < XD 7342 < MY 720. It is apparent that ΔH_{pol} increases with increasing epoxy group number per resin molecule. Comparison of ΔH_{pol} of the same epoxy resin with the three curing agents shows that ΔH_{pol} is higher in the case of MPD and lower in that of DCEPD.

Before scanning the DSC thermograms (Fig. 3), the epoxy resin-curing agent compositions were cured for a sufficient time (4 h) at a temperature at which the first curing heat was released (MPD, 120°C; DCEPD, 160°C; and DDS, 190°C). The DSC thermograms of DCEPD compositions do not show residual exotherms present in the curing temperature range. This process reveals that the heating was sufficient to complete the cure. However, the thermograms of some of the common curing-agent compositions show an incomplete cure for a residual exotherm heat in the curing temperature range. From the residual exotherm heat of these systems, and the heat of polymerization (ΔH_{pol}) of the same uncured samples, the percentage cure attained under these experimental conditions was calculated as follows: XD 7342-MPD, 98%; XD 7342-DDS, 92%; MY 720-MPD, 97%; and MY 720-DDS, 82%. It should be noted that a desirable property for a curing agent is one where the complete polymerization of DCEPD with various epoxy resins is achieved under relatively mild heating.

The large exotherm peaks that appear in the DSC thermograms of Figure 3 are attributed to pyrolysis of the polymers. It can be seen that the DCEPD polymers show a comparatively lower pyrolysis temperature. This behavior of DCEPD polymers is confirmed by TGA data.

The position of the polymerization or pyrolysis exotherm peaks in the DSC thermograms is significantly dependent upon the ratio of the reactants. A number of epoxy resins-DCEPD compositions in which 1-epoxy equivalent weight reacted with 0.50 mol of diamine were also studied. The results obtained from the DSC thermograms of these compositions are given in Table III. Both the polymerization and the pyrolysis peaks of the compositions are shifted to a lower temperature in the DSC thermograms as the curing agent concentration is increased (Table III). Since a less crosslinked polymer is obtained in the latter case, it is reasonable to expect the pyrolysis temperature of this polymer to be lower.

TABLE III
Thermal Characteristics of Epoxy Resin-DCEPD Compositions under Various Reactants Ratios

Epoxy resin	Polymerization			Pyrolysis		
	T_1 (°C)	T_2 (°C)	ΔH_{pol} (J/g)	T_1 (°C)	T_2 (°C)	ΔH_{pyr} (J/g)
0.50 mol of DCEPD/epoxy equivalent weight						
EPON 828	146.3	185.0	186	240.1	273.6	102
XD 7342	143.9	176.9	129	228.0	278.7	73
MY 720	161.0	189.9	185	220.9	246.0	66
0.25 mol of DCEPD/epoxy equivalent weight						
EPON 828	156.9	201.0	145	270.1	288.9	94
XD 7342	151.4	190.7	172	278.2	307.1	210
MY 720	174.7	213.7	208	221.7	269.1	214

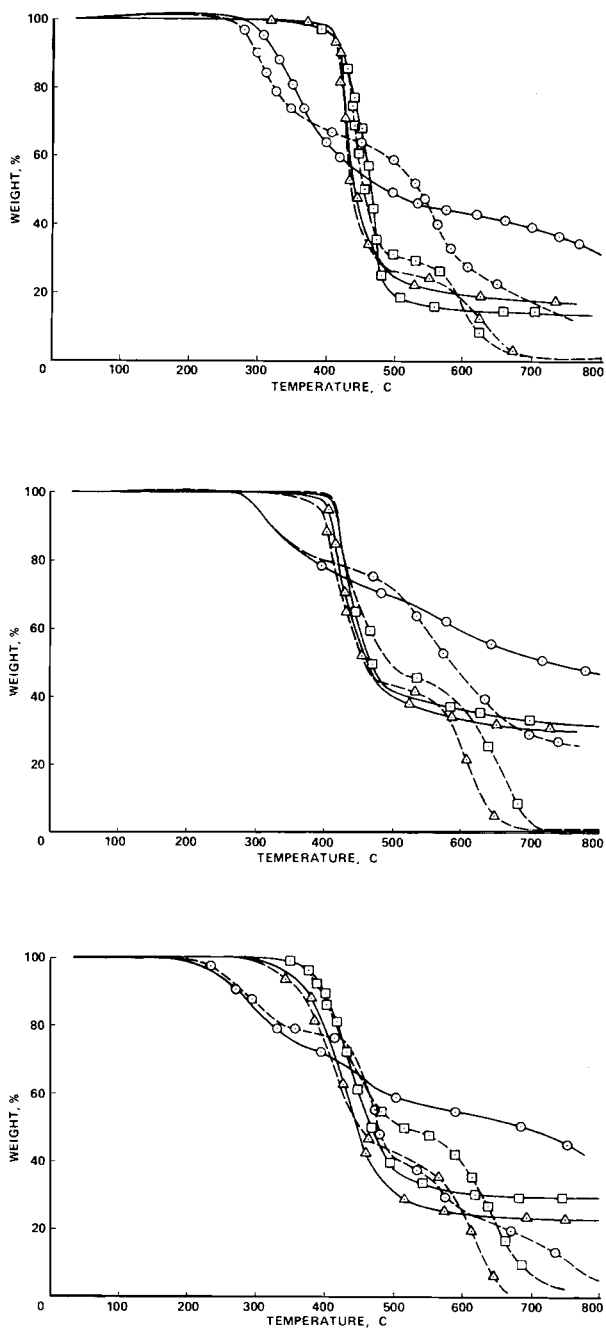


Fig. 4. TGA thermograms of the epoxy resin-curing agent compositions (0.25 mol of curing agent/EEW) cured (—) in N_2 and (---) in air; heating rate $20^\circ\text{C}/\text{min}$. Symbols are the same as in Figure 2.

Thermogravimetric analytical data in nitrogen and air of the cured epoxy resin-curing agent compositions (0.25 mol of curing agent/EEW) are presented in Figure 4. The PDT, the maximum polymer decomposition temperature

TABLE IV
Thermal Stability of Epoxy Resin-Curing Agent Compositions^a

Epoxy resin	Curing agent	In nitrogen			In air			PDT _{air} /PDT _{N₂}		
		PDT (°C)	PDT _{max} (°C)	TCP (°C)	Char yield (%; 650°C)	PDT (°C)	PDT _{max} (°C)		TCP (°C)	Char yield (%; 650°C)
EPON 828	DCEPD	287.0	351.6	500.0	42.0	261.5	309.1	550.0	23.0	0.91
EPON 828	MPD	399.2	436.3	476.9	18.5	388.1	431.9	495.4	8.0	0.97
EPON 828	DDS	416.7	459.1	503.3	15.0	403.9	447.3	511.5	4.5	0.97
XD 7342	DCEPD	265.0	317.7	550.0	56.0	265.0	315.0	615.0	38.0	1.00
XD 7342	MPD	388.0	431.5	483.3	31.5	376.5	425.0	533.5	5.0	0.97
XD 7342	DDS	401.7	443.3	491.0	35.0	399.2	439.5	562.0	23.5	0.99
MY 720	DCEPD	235.0	297.7	550.0	53.0	235.0	295.0	650.0	22.0	1.00
MY 720	MPD	361.4	424.7	492.9	23.5	345.4	409.5	545.6	5.0	0.96
MY 720	DDS	381.7	439.2	502.7	29.5	363.9	425.1	603.2	22.5	0.95

^a 0.25 mol of curing agent/EEW.

(PDT_{max}), the temperature of complete pyrolysis (TCP), and the char yield in percent at 650°C are shown in Table IV. The PDT and the TCP were determined by the intersection of the tangent to the steepest portion of the TGA curve with the strain-line part of the curve before and after the polymer degradation, respectively. The PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred.

It can be seen that the DCEPD compositions show lower PDT (235–287°C) and higher char yield (42–56% in nitrogen and 22–38% in air at 650°C) than the other compositions. Flame-retardant treatments lower the temperature of initial decomposition, reduce the activation energy of the decomposition reaction, and increase the char yield. Char formation is important to the prediction of flammability. A linear relationship between the oxygen index and the char residue on pyrolysis for halogen-free polymer has been proposed.¹⁷ Increased char formation can usually limit the production of combustible carbon-containing gases, decrease the exothermicity due to pyrolysis reactions, and decrease the thermal conductivity of the surface of a burning material.¹⁸ The DCEPD compositions form a significantly higher char yield than the nonphosphorylated compositions do, a fact indicative of the superiority of DCEPD compositions with respect to flammability. It should be noted that the DCEPD compositions with the trifunctional epoxy resin, XD 7342, gave the highest char yield obtained (56% in nitrogen and 38% in air at 650°C). The ratio of the polymer decomposition temperature in air to that in nitrogen atmosphere (PDT_{air}/PDT_{N_2}) varies from 0.91 to 1.00. This suggests that decomposition is not seriously affected by the presence of oxygen.

The glass transition temperature (T_g) of some compositions (0.25 mol of curing agent/EEW) was evaluated by DMA. The results are summarized as follows: XD 7342-DCEPD, 160°C; XD 7342-DDS, 211°C; MY 720-DCEPD, 167°C; and MY 720-DDS, 263°C. It can be seen that the DCEPD compositions show a lower glass transition temperature than do the corresponding DDS compositions.

The incorporation of phosphorus into the polymers was confirmed by their IR Spectra. The polymers of DCEPD with the three epoxy resins show the characteristic absorption band of P—O—C linkage¹⁹ at about 960 cm^{-1} (Ref. 19).

The fire resistance of the compositions of DCEPD as well as of the common curing agents was evaluated by determining their LOI value. For this purpose,

TABLE V
LOI Values of the Epoxy Resin-Curing Agent Compositions^a

Epoxy resin	Curing agent	P %	CL %	N %	LOI
EPON 828	DCEPD	2.87	5.64	2.59	28.1
EPON 828	MPD	0	0	3.25	27.2
EPON 828	DDS	0	0	2.79	22.9
XD 7342	DCEPD	3.18	6.26	2.87	29.6
XD 7342	MPD	0	0	3.70	28.0
XD 7342	DDS	0	0	3.12	25.3
MY 720	DCEPD	4.14	8.14	7.47	59.3
MY 720	MPD	0	0	10.57	30.8
MY 720	DDS	0	0	8.36	29.0

^a 0.25 mol of curing agent/EEW.

homogenous mixtures of the curing agents with the epoxy resins (0.25 mol of curing agent/EEW) were prepared by melting, and the LOI values of the specimens were determined by forming them into a mold using the curing process (Table V). The estimated phosphorus, chlorine, and nitrogen content of the compositions is also given in Table V. The compositions of DCEPD show a seriously higher fire resistance compared with the compositions of common curing agents because of the phosphorus-chlorine-nitrogen synergism. Since the content of the compositions in these three elements increases with increasing epoxy functionality of the resin, the degree of fire resistance follows the same trend. All DCEPD compositions should be self-extinguishing because compositions containing approximately 2% phosphorus and 6% chlorine are known to produce self-extinguishing epoxy resins.² The MY 720-DCEPD composition shows an excellent fire resistance due to the relatively higher content in phosphorus, chlorine, and nitrogen. It is reasonable that if a higher concentration of DCEPD is used for the composition preparation, the polymers obtained will show a higher fire resistance, although in this case the PDT will be lower.

CONCLUSION

It was demonstrated that fire-resistant compositions of various epoxy resins can be prepared using DCEPD as a curing agent. The lower reactivity of DCEPD toward epoxy resins compared with that of MPD was attributed to the presence of the electron-withdrawing phosphinyl group in the DCEPD molecule. It was shown that the heat of polymerization increases with increasing epoxy functionality of the resins. The thermal characteristics of the compositions were dependent upon the ratio of the reactants. The polymers of DCEPD exhibited a lower polymer-decomposition temperature and a higher char yield than did the corresponding polymers of common curing agents.

References

1. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.
2. M. Lewin, S. M. Atlas, and E. M. Pearce, *Flame-Retardant Polymeric Materials*, Plenum, New York and London, 1975, p. 362.
3. Asao Takahasi and Masaru Shimizu, *Fire Retard.*, *Proc. Int. Symp. Flammability Fire Retard.*, 212 (1979).
4. V. E. Lyapichev and O. I. Tuzhikov, *Funkts. Org. Soedin. Polim.*, 57 (1972).
5. Minoru Hosoda and Eiichi Kashiwagi, *Japan Kokai* 73 56,229 (1973); *Chem. Abstr.*, **79**, 116421y (1973).
6. F. W. David Cross, *Ger. Offen.* 2,212,390 (1972); *Chem. Abstr.*, **78**, 30806v (1973).
7. E. M. Sadykova, Z. B. Chelnokova, I. D. Kolli, R. A. Rodionov, and V. I. Spitsyn, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (4), 786 (1972).
8. G. M. Kosolapoff, *Organophosphorus Compounds*, 1st ed., Wiley, New York, 1950, p. 122.
9. J. I. G. Catogan, *Quart. Rev.*, **22**, 222 (1968).
10. R. J. Sundberg, *J. Org. Chem.*, **30**, 3604 (1965).
11. H. C. Anderson, *Anal. Chem.*, **32**, 1592 (1960).
12. E. Peytral, *Bull. Soc. Chim.*, **39**, 306 (1926).
13. W. W. Heckert and E. Mark, Jr., *J. Am. Chem. Soc.*, **51**, 2706 (1929).
14. R. E. Parker and N. S. Issacs, *Chem. Rev.*, **59**, 737 (1959).
15. S. C. Lin and E. M. Pearce, *J. Polym. Sci.*, **17**, 3095 (1979).
16. K. J. Saunders, *Organic Polymer Chemistry*, Halsted, New York, 1973, p. 378.

17. D. W. Van Krevelen, *Polymer*, **16**, 615 (1975).
18. E. M. Pearce and R. Liepins, *Environ. Health Perspectives*, **11**, 69 (1975).
19. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1975, p. 352.

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