

Thermal Properties of Side-Chain Phosphorus-Containing Epoxide Cured with Amine

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ABSTRACT: Glycidyoxy diphenylphosphine oxide (GDPPPO), a side-chain phosphorus-containing monoepoxide, was prepared. The compound, GDPPPO, was mixed with 4,4'-diglycidylether of bisphenol A-type epoxy resin, DER 331. The reaction kinetics of the mixture, GDPPPO–DER 331, cured with diethyltriamine (DETA), and the thermal decomposition properties of the thermosets were studied. For the GDPPPO–DER 331–DETA curing systems, it was found that the activation energy of the curing reaction is 45.0 kJ/mol for the GDPPPO–DETA system, and it decreases with the content of GDPPPO. According to the method of Ozawa, the average apparent thermal decomposition activation energies of the thermosets with phosphorus-containing monoepoxide are from 138.5 to 178.1 kJ/mol, which are higher than that of the DER 331–DETA system (95.8 kJ/mol). However, the lower crosslinking density and gel fraction of the system with the phosphorus-containing monoepoxide, GDPPPO, result in poor protection of the intumescent char during thermal decomposition; thus, the char yield and limiting oxygen index (LOI) of the cured specimens decrease with increasing GDPPPO. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2741–2748, 2002; DOI 10.1002/app.10161

Key words: flame-retardance; thermosets; epoxy resins; degradation

INTRODUCTION

Epoxy thermosets are used in many industrial applications, such as in coatings, adhesives, composites, and encapsulation of microelectronic devices, due to their great versatility, low shrinkage, good chemical resistance, outstanding adhe-

sion, and excellent electrical insulation.^{1–7} Many halogen-containing compounds are commonly applied as flame-retardants in epoxy resins by blending or chemical modification to improve the flame resistance. For example, tetrabromobisphenol A epoxy resins were successfully used as a flame-retardant in printed circuit boards and in encapsulation of IC packages.

However, epoxides with halogenated compounds will format noxious and corrosive fumes during thermal decomposition. Many phosphorus-containing epoxy resins and curing agents have been synthesized as alternate materials.^{8–20}

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Buckingham et al. synthesized phosphorylated flame-retardant curatives for epoxy resins.¹² Derouet et al. modified epoxy resins by reacting 4,4'-diglycidylether of bisphenol A (DGEBA) with dialkyl (or aryl) phosphates.¹³ Liu et al. synthesized a phosphorus-containing epoxide, bis-glycidyloxy phenylphosphate (BGPP), and confirmed its flame-retardant properties.^{18–20} Wang et al. prepared a reactive heterocyclic phosphorus-containing diol to modify a DGEBA-type epoxide and showed that the flame retardancy, thermal stability, and glass transition temperature are improved by the rigid structure and pendant phosphorous group on the backbone.³

For increasing the mechanical properties and reducing the cost, the phosphorus-containing epoxy resins can also be blended with commercial epoxy resins. However, the effects of various compositions on the thermal properties of the thermosets are seldom reported. In previous work, we synthesized a main-chain phosphorus-containing epoxide, BGPP, then blended the product with various contents of a DGEBA-type epoxide and cured it with diethyltriamine (DETA). It was found that the BGPP–DETA system shows a relatively higher char yield and a limiting oxygen

index (LOI) value of 29–31.²¹ Furthermore, in this study, we prepared side-chain phosphorus-containing formulations by mixing glycidyloxy diphenylphosphine oxide (GDPPPO) with different contents of DER 331. The curing reactions of the side-chain phosphorus-containing blended epoxy resins with DETA and the thermal properties of these cured specimens were investigated and compared to the system with the main-chain phosphorus-containing epoxide, BGPP.

EXPERIMENTAL

Synthesis of Side-chain Phosphorus-containing Epoxy Resin (GDPPPO)

Glycidol (0.169 mol, ACROS, USA) was mixed with triethylamine (0.169 mol, ACROS) in 40 mL THF. This solution was cooled to 0°C; then, 0.3 g Cu₂Cl₂ was added. Diphenylphosphonic chloride (0.169 mol, ACROS) in 60 mL THF was added into the solution in dropwise for 30-min period, and the solution was reacted for 2 h at 0°C, then kept at room temperature for 2 days. The reaction can be shown as follows:



After being filtrated and stirred with an ice-cold NaOH solution (2 wt %), the reacted solution was extracted with ethyl acetate (Aldrich, USA) and dried on MgSO₄. Finally, the solution was filtered and the ethyl acetate removed and then purified by an LC column with EA/*n*-hexane (1/1) as the eluant.

Characterization of GDPPPO

Infrared Spectroscopy

Infrared spectra for the compound, GDPPPO, were observed by a Fourier transform infrared spectrophotometer (FTIR, Bio-Rad FTS-40).

NMR Spectroscopy

¹H-NMR and ³¹P-NMR spectra for diphenylphosphonic chloride and GDPPPO were recorded with a Bruker DMX-400 SB FT-NMR.

Epoxide Equivalent Weight

The epoxy equivalent weight (EEW) of GDPPPO was determined by the pyridinium chloride method described in the literature.²²

Thermal Analysis

Differential Scanning Calorimeter (DSC)

The blended resins, GDPPPO with various contents of DER 331, were mixed with a curing agent, DETA, at a stoichiometric ratio. The heat of the mixture released during the cure was measured by a DSC (Perkin–Elmer, DSC-7) under various conditions.

Thermogravimetric Analysis (TGA)

The mixtures of the blended resin and the curing agent prepared as mentioned above were cured

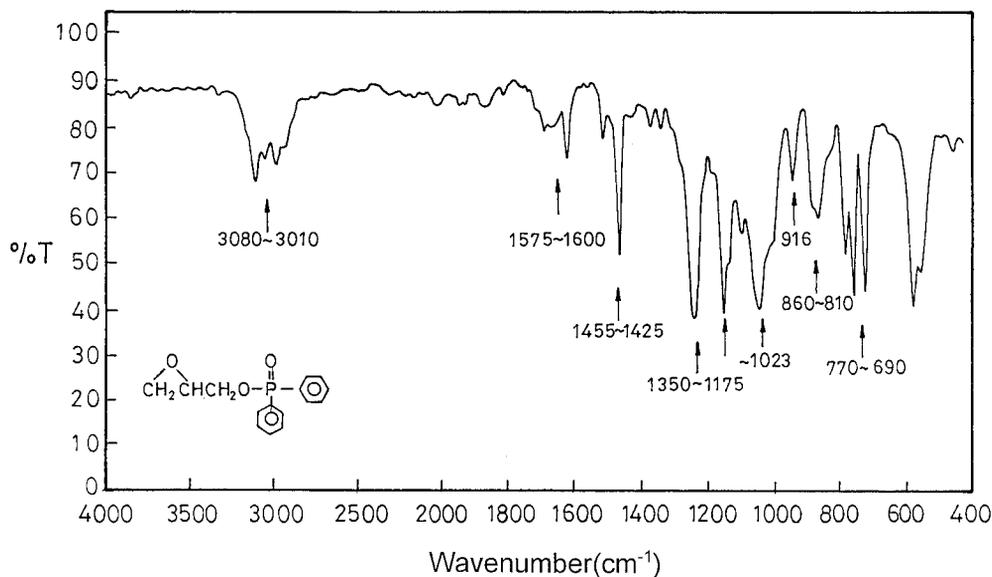


Figure 1 IR spectrum of GDPPO.

first, then analyzed by TGA (Perkin-Elmer, TGA-7) under a nitrogen atmosphere.

LOI

The relative flammability of the cured specimen was determined by an LOI tester (Custom Scientific Instruments Inc., CS-178). The values of the LOI were correspondent to the minimum ratio of oxygen in the mixture of oxygen and nitrogen that will support flaming of the samples for 30 s.

Gel Fraction

The gel fraction of the cured epoxy resin was determined by solvent extraction. The ground

sample was extracted with THF under reflux for 48 h at 100°C. The unextracted portion was assigned to the gel fraction by weight.

RESULTS AND DISCUSSION

Characterization of Side-chain Phosphorus-containing Monoepoxide, GDPPO

The FTIR spectra for the compound GDPPO are shown in Figure 1. The absorption peak at about 1023 cm^{-1} indicates the $\sim\text{P}-\text{O}-\text{CH}_2\sim$ group formed by the coupling reaction of glycidol with diphenylphosphonic chloride (DPPC), and the

Table I Infrared Absorbency of GDPPO

Functional Group	Wavenumber (cm^{-1})	Intensity	Type
P=O	1350-1175, 1250-1150	Very strong	Stretching vibration
P-O	1080-1100	Weak	Stretching vibration
P-Ar.	1455-1425	Medium-strong	Ar. ring stretching vibration
Ar.	3080-3010	Medium	C-H vibration
	1575-1600	Strong	-C=C-
	770-690	Strong	Ring deformation
	860-810	Strong	Bending vibration
Oxirane ring	~ 916	Strong	Ring vibration

Ar.: aromatic group.

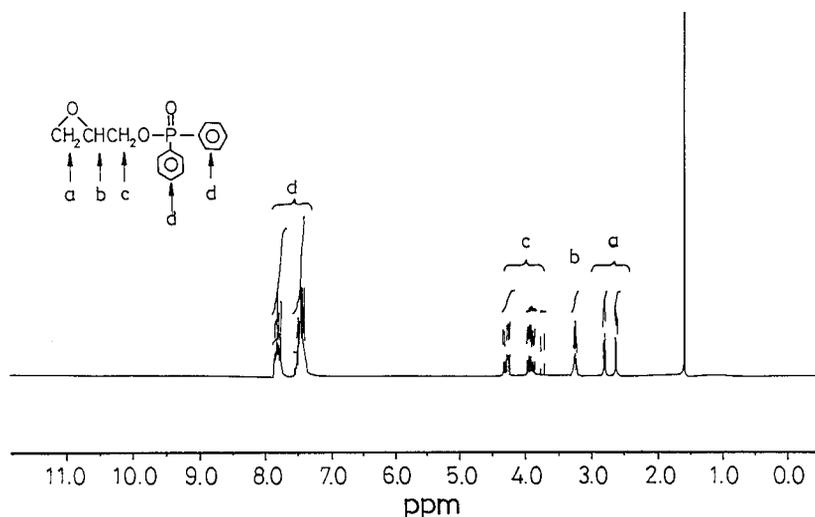


Figure 2 $^1\text{H-NMR}$ spectrum of GDPPO.

other absorption peaks corresponding to different groups of the GDPPO are listed in Table I.

Figure 2 indicates the NMR spectrum for GDPPO. The characterization data by $^1\text{H-NMR}$ are as follows:

- $\delta = 2.60\text{--}3.11$ ppm (oxiane-ring protons);
- $\delta = 3.90\text{--}4.31$ ppm ($\sim\text{P-O-CH}_2\sim$); and
- $\delta = 7.35\text{--}7.70$ ppm (aromatic protons).

A single peak, $\delta = 30.2$ ppm from the $^{31}\text{P-NMR}$ spectrum, was found for GDPPO. However, the peak of the reactant, DPPC, is at 36.8 ppm. It is believed that the shifting of the phosphorus atom

resulted from the replacement of the electron-withdrawing chloride on the reactant, DPPC, by the group $\sim\text{O-CH}_2$. The chemical structure of GDPPO can be confirmed by those spectrum data. The EEW of GDPPO is 281, analyzed by titration.²²

Curing Kinetics

Figure 3 shows the IR spectrum of the GDPPO-DETA curing systems at the heating rate of $10^\circ\text{C}/\text{min}$. The epoxy group (916 cm^{-1}) decreases with the temperature (time) and is consumed at about 150°C owing to the reaction between the monoep-

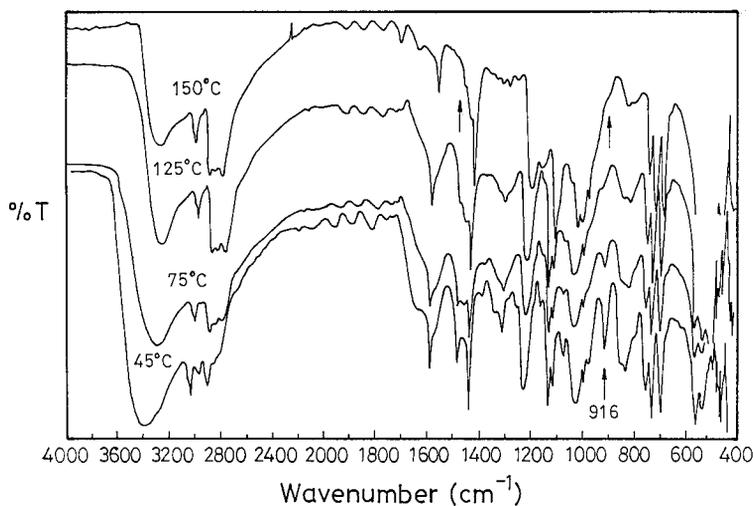


Figure 3 IR spectrum of GDPPO-DETA curing system.

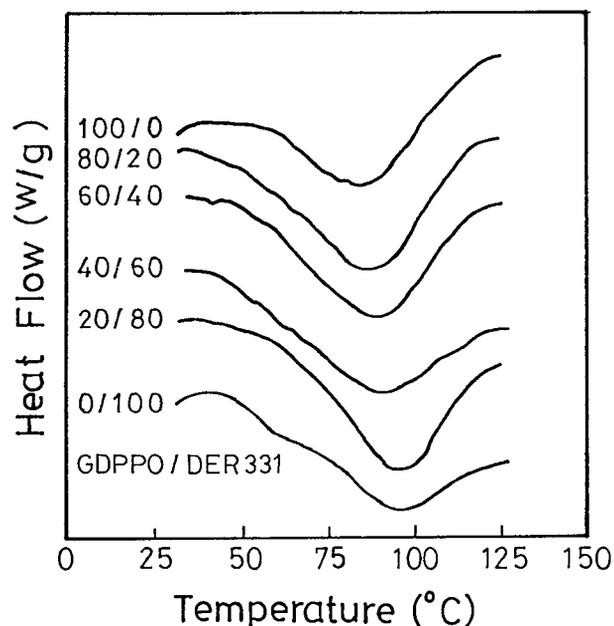


Figure 4 DSC thermograms of GDPPO-DER 331-DETA curing systems at a heating rate of 10°C/min.

oxide, GDPPO, and DETA. Furthermore, the blended resins, GDPPO with various contents of DER 331, were cured with DETA at a stoichiometric ratio, and the DSC thermograms of the GDPPO-DER 331-DETA curing systems are shown in Figure 4. It was found that the temperature, T_{\max} , at which the heat flow reaches the maximum value decreases with increasing of GDPPO as indicated in Table II, which indicates that GDPPO reacts with DETA more quickly than with DER 331.

The rate law of the curing reaction can be described as follows:

$$d\alpha/dt = k(1 - \alpha)^n \quad (2)$$

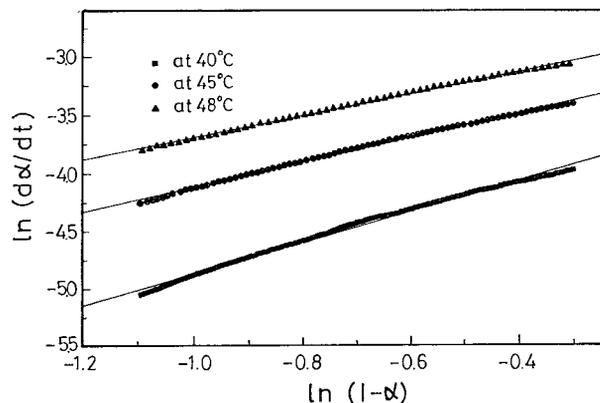


Figure 5 Plot of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$ for GDPPO-DER 331-DETA curing system (GDPPO/DER 331 = 40/60).

where k is the reaction rate constant; n , the reaction order; and $\alpha(EP)$, the epoxy conversion, which could be measured by the heat generation. Furthermore, the kinetic parameters, k and n , can be determined by plots of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$, such as in Figure 5.

Figure 6 shows the activation energy, E_a , for different curing systems. The activation energy is 45.0 kJ/mol for the GDPPO-DETA system, and this value is lower than that of the DER 331-DETA system (73.2 kJ/mol) and the main-chain phosphorus-containing diepoxide, BGPP, curing system (51.2 kJ/mol).²¹ For the GDPPO-DER 331-DETA curing system, as shown in Figure 6, the activation energy decreases with more GDPPO. It is believed that the mobility and reactivity of GDPPO are higher than those of BGPP or DER 331 due to GDPPO having a small molecular size and a flexible group, $\sim\text{P}-\text{O}-\text{CH}_2\sim$.

Glass Transition Temperature

The glass transition temperatures of the thermosets determined by DSC are shown in Table II.

Table II Characteristics of Various Curing Systems

Characteristics	GDPPO/DER 331 Molar Ratio				
	0/100	40/60	60/40	80/20	100/0
T_{\max} (°C) of curing by the DSC at 10°C/min	93	89	86	82	80
Reaction order of eq. (3)	1.1	1.1	1.1	1.0	1.0
T_g (°C) of thermoset by the DSC at 10°C/min	108	54	67	52	64
Gel fraction of the cured polymer (wt %)	93	79	72	54	0
LOI of thermoset	19-22	21-22	20-21	18-19	17-19

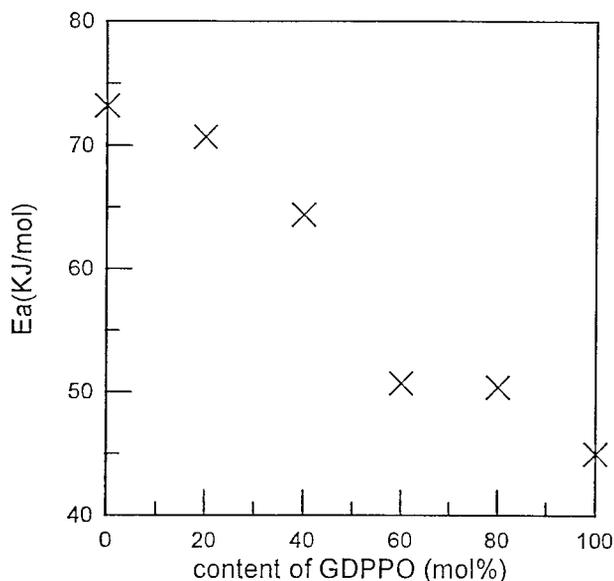


Figure 6 Activation energy for various curing systems (GDPPO–DER 331–DETA).

The thermoset with GDPPO shows a decrease in the T_g . It may be caused by the flexible group, $\sim\text{P}-\text{O}-\text{CH}_2\sim$, on GDPPO and the lower crosslinking density and gel fraction resulting from the monofunctional epoxide, GDPPO (see Table II).

TGA

The cured samples were analyzed by TGA at various heating rates under a nitrogen atmosphere. The DER 331–DETA thermoset exhibited a 5% weight loss at 345°C and decomposed at about 360°C as indicated in Figure 7 and Table III.

In the previous study for the main-chain phosphorus-containing diepoxide curing system, BGP–P–DETA, it was found that the char yield at 550°C is higher than that of the system without a phosphorus component, DER 331–DETA. On the contrary, for the GDPPO–DER 331–DETA system, the char yield decreases with an increasing content of the side-chain phosphorus-containing monoepoxide as shown in Table III.

This is perhaps because the lower crosslinking density and gel fraction of the system with the monoepoxide, GDPPO, result in poor protection of the intumescent char during thermal degradation. Figure 8 gives evidence for this explanation. Because the crosslinking density and gel fraction

of the DER 331–DETA thermoset with a stoichiometric ratio of the curing agent are higher than those with a lower content of DETA, the char yield of the stoichiometric system is higher.

Decomposition Kinetics

According to the method of Ozawa,²³ the apparent thermal decomposition activation energy, E_d , can be determined from the TGA thermograms under various heating rates, such as in Figure 9, and the following equation:

$$E_d = -\frac{R}{b} \left[\frac{d \log \beta}{d(1/T)} \right] \quad (3)$$

where R is the gas constant; b , a constant (0.4567); and β , the heating rate (°C/min).

The decomposition activation energies for different compositions are shown in Figure 10. Because of the formation of intumescent char resulted from the pyrolysis of the phosphorus/nitrogen-containing thermosets, the average activation energies of the GDPPO–DER 331–DETA system are from 138.5 to 178.1 kJ/mol, which are higher than that of the DER 331–DETA thermoset (95.8 kJ/mol).

LOI

For the main-chain phosphorus-containing epoxy thermoset, the polymer with the higher phosphorus content results in a higher LOI.²¹ On the contrary, because the lower crosslinking density

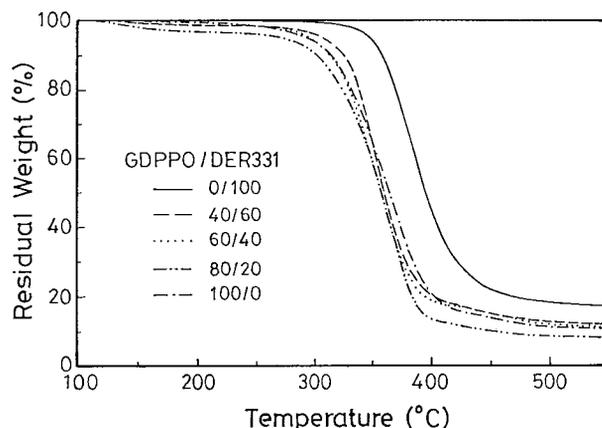


Figure 7 TGA thermograms of GDPPO–DER 331–DETA thermosets.

Table III Weight-loss Characteristics Measured by TGA at 10°C/min Under Nitrogen Atmosphere

Characteristics	GDPPPO/DER 331 Molar Ratio				
	0/100	40/60	60/40	80/20	100/0
Temperature at 5% weight loss	345	305	293	290	270
Residual weight (%) at 550°C	16.9	12.0	11.3	10.6	8.13

Characteristics	BGPP/DER 331 Molar Ratio				
	0/100	40/60	60/40	80/20	100/0
Temperature at 5% weight loss	345	285	279	259	221
Residual weight (%) at 550°C	16.9	21.2	22.8	26.2	26.2

and gel fraction of the system with the monoepoxide, GDPPPO, result in poor protection of intumescent char during thermal decomposition, the LOI of the thermoset decreases with increasing GDPPPO, although the phosphorus content increases (see Table II).

CONCLUSIONS

The activation energy decreases with increasing GDPPPO for the GDPPPO-DER 331-DETA curing system. Since the formation of intumescent char resulted from the pyrolysis of the thermosets with

phosphorous/nitrogen components, the average activation energies of the GDPPPO-DER 331-DETA system are from 138.5 to 178.1 kJ/mol, which are higher than that of the DER 331-DETA thermoset (95.8 kJ/mol). But the lower crosslinking density and gel fraction of the system with the monoepoxide, GDPPPO, result in a decrease in the T_g , and the poor protection of intumescent char during thermal decomposition, the char yield, and the LOI decreases with increasing content of GDPPPO.

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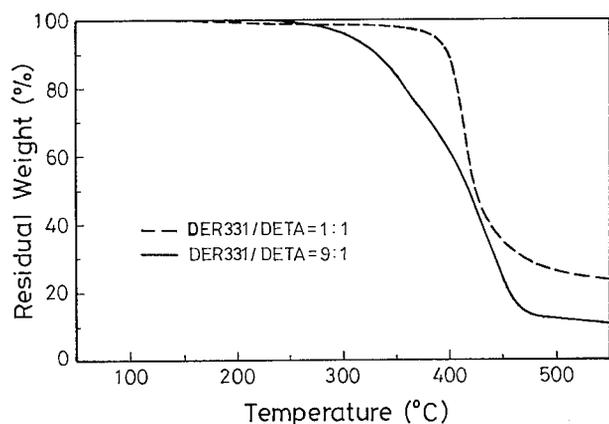


Figure 8 TGA thermograms of DER 331-DETA thermosets for various contents of the curing agent.

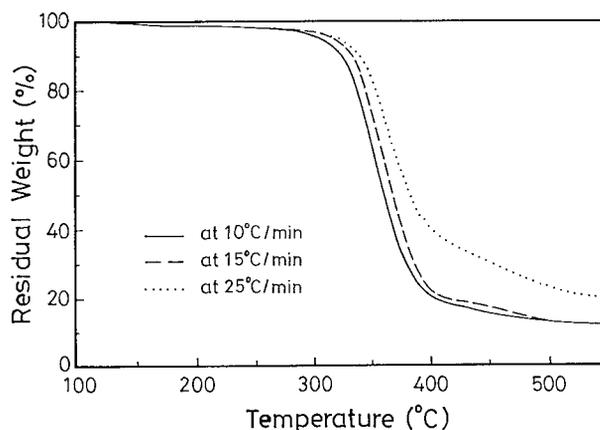


Figure 9 TGA thermograms of thermosets at various heating rates (GDPPPO/DER 331 = 40/60).

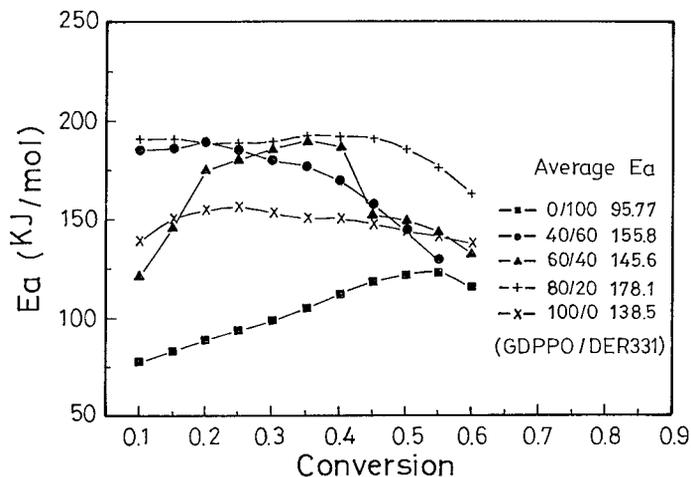


Figure 10 Apparent decomposition activation energies versus the decomposition conversion.

REFERENCES

- May, C. A. *Epoxy Resins—Chemistry and Technology*, 2nd ed.; Marcel Dekker: New York, 1988.
- Lee, H.; Neville, K. *Hand Book of Epoxy Resin*; McGraw-Hill: New York, 1967.
- Wang, C. S.; Shieh, J. Y. *Polymer* 1998, 39, 5819.
- Wang, C. S.; Fritz, D. B.; Mendoza, A. *Polym Mater Sci Eng* 1988, 59, 763.
- Wong, C. P. *Adv Polym Sci* 1988, 84, 63.
- Cheng, K. C.; Lai, K. C.; Chiu, W. Y. *J Appl Polym Sci* 1999, 71, 721.
- Cheng, K. C. *J Polym Sci Polym Phys Ed* 1998, 36, 2339.
- Fischer, R. G.; Calbick, C. J. U.S. Patent 5 084 546, 1992.
- Yamazaki, K.; Ryoshi, H.; Hori, T. U.S. Patent 5 096 980, 1992.
- Gamino, G.; Costa, L.; Martinasso, G. *Polym Deg Stab* 1989, 23, 359.
- Maiti, S.; Banerjee, S.; Palit, S. K. *Prog Polym Sci* 1993, 18, 227.
- Buckingham, M. R.; Lindsay, A. J.; Stevenson, D. E.; Muller, G.; Morel, E.; Costes, B.; Henry, Y. *Polym Deg Stab* 1996, 54, 311.
- Derouet, D.; Morvan, F.; Brosse, J. C. *J Appl Polym Sci* 1996, 62, 1855.
- Mikroyannidis, J. A.; Kourtidis, D. A. *J Appl Polym Sci* 1984, 29, 197.
- Mikroyannidis, J. A.; Kourtidis, D. A. *Adv Chem Ser* 1984, 208, 351.
- Chin, W. K.; Shau, M. D.; Tsai, W. C. *J Polym Sci Polym Chem Ed* 1995, 33, 373.
- Wang, T. S.; Yeh, J. F.; Shau, M. D. *J Appl Polym Sci* 1996, 59, 215.
- Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S.; Jeng, R. J.; Perng, L. H. *J Appl Polym Sci* 1996, 61, 613.
- Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S.; Jeng, R. J. *J Appl Polym Sci* 1996, 61, 1789.
- Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S. *J Polym Sci Polym Chem Ed* 1997, 35, 565.
- Cheng, K. C.; Yu, S. Y.; Chiu, W. Y., for publication in *J Appl Polym Sci*.
- Smith, I. T. *Polymer* 1961, 2, 95.
- Ozawa, T. *Bull Chem Soc Jpn* 1968, 38, 1881.