

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

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ABSTRACT: A main-chain phosphorus-containing diepoxide, bis-glycidyl ether phenylphosphate (BGPP), was synthesized, then blended with various contents of a 4,4'-diglycidylether of bisphenol A (DGEBA)-type epoxy resin, DER 331. The curing reactions of the blended resins with diethyltriamine (DETA) and the thermal properties of the cured specimens were investigated with an infrared spectrophotometer, a differential scanning calorimeter, and a thermogravimetry analyzer. The activation energy is 51.2 kJ/mol for the BGPP–DETA curing system, and it increases with the content of DER 331 for the BGPP–DER 331–DETA systems. The average apparent decomposition activation energies of the thermosets with phosphorus-containing epoxide are from 147.3 to 165.1 kJ/mol, which are higher than that of the DER 331–DETA system (95.8 kJ/mol). The BGPP–DETA system shows a relatively higher char yield and limiting oxygen index (LOI) value, 29–31, but the thermoset with BGPP results in a decrease in the T_g . © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2733–2740, 2002; DOI 10.1002/app.10160

Key words: flame-retardance; thermosets; curing of polymers; glass transition; epoxy resins

INTRODUCTION

Because of their great versatility, low shrinkage, good chemical resistance, outstanding adhesion, and high-grade electrical insulation, epoxy thermosets are used in many industrial applica-

tions.^{1–3} For the requirement of flame resistance, bromine compounds are widely used as flame retardants for polymers by blending or chemical modification. However, the products with halogen compounds will generate toxic and corrosive smoke during combustion; thus, a number of nonhalogen-based systems, such as phosphorus-containing compounds, have been investigated as replacements for the halogen flame retardants.^{4–16}

For example, Derouet et al.⁹ modified epoxy resins by reacting 4,4'-diglycidylether of bisphe-

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nol A (DGEBA) with dialkyl (or aryl) phosphates, then cured those epoxy resins with 4,4'-diaminodiphenylsulfone (DDS) and showed that the flame-retardant property is improved by chemically bonding diphenylphosphate grafts onto the backbone. Liu et al.¹⁴⁻¹⁶ synthesized a phosphorus-containing epoxide, bis-glycidyloxy phenylphosphate (BGPP), then cured it with various amines. They found that the products with a high phosphorus content of 11.5% by weight resulted in high char yields and high limiting oxygen index (LOI) values, which confirmed the flame-retardant behavior of the BGPP thermosets. The phosphorus-containing epoxy resin can also be blended with commercial nonphosphorus-containing epoxides, such as DGEBA, to increase the mechanical properties and to reduce the cost. However, the relation between the thermal properties of the phosphorus-containing epoxy thermosets and compositions has not been discussed.

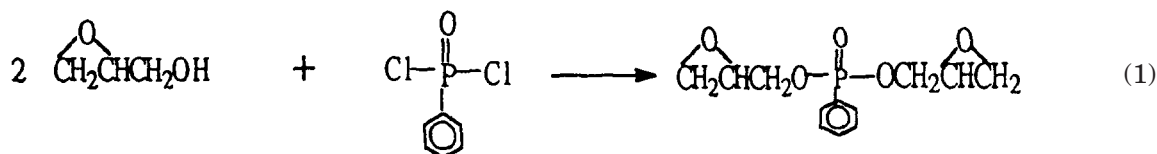
A series of studies was made in our laboratory for several types of phosphorus-containing epoxy thermosets: (1) main-chain phosphorus-containing epoxide blended with DGEBA; (2) side-chain phosphorus-containing epoxide blended with DGEBA; and (3) DGEBA cured with phosphorus-containing amine. In this work, we synthe-

sized the main-chain phosphorus-containing epoxide, BGPP, then blended the product with various contents of a DGEBA-type epoxide, DER 331. The curing reactions of the blended resins with diethyltriamine (DETA) and the thermal properties of the cured specimens were investigated. The kinetics of curing, the glass transition temperature (T_g), the thermal degradation, and the flame-retardation property dependent on the different compositions are discussed.

EXPERIMENTAL

Synthesis of Main-chain Phosphorus-containing Epoxy Resin (BGPP)¹⁶

Glycidol (0.169 mol, ACROS, USA) was dissolved in 40 ml THF, then mixed with triethylamine (0.169 mol, ACROS). This solution was cooled to 0°C in an ice bath; then, 0.3 g Cu_2Cl_2 was added. Phenylphosphonic dichloride (PPDC, 0.077 mol, ACROS) in 60 ml THF was added into the solution dropwise during a 30-min period, and the solution was reacted for 2 h at 0°C and kept at room temperature for 48 h. 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 MgSO_4 . Finally, the solution was filtered and the ethyl acetate removed and then purified using an LC column with EA/*n*-hexane (1/1) as the eluant. The final product, BGPP, is a light yellow thick liquid.

Characterization of BGPP

Infrared Spectroscopy

Infrared spectra for the product, BGPP, were obtained using a Bio-Rad FTS-40 Fourier transform infrared (FTIR) spectrophotometer.

NMR Spectroscopy

¹H-NMR and ³¹P-NMR spectra for PPDC and BGPP were recorded with a Bruker DMX-400 SB FT-NMR.

Epoxide Equivalent Weight

The epoxy equivalent weight (EEW) of BGPP was determined by the pyridinium chloride method described in the literature.¹⁷

Thermal Analysis

Differential Scanning Calorimetry (DSC)

The synthesized phosphorus-containing diepoxide was mixed with various contents of a DGEBA-type epoxide, DER 331. The blended

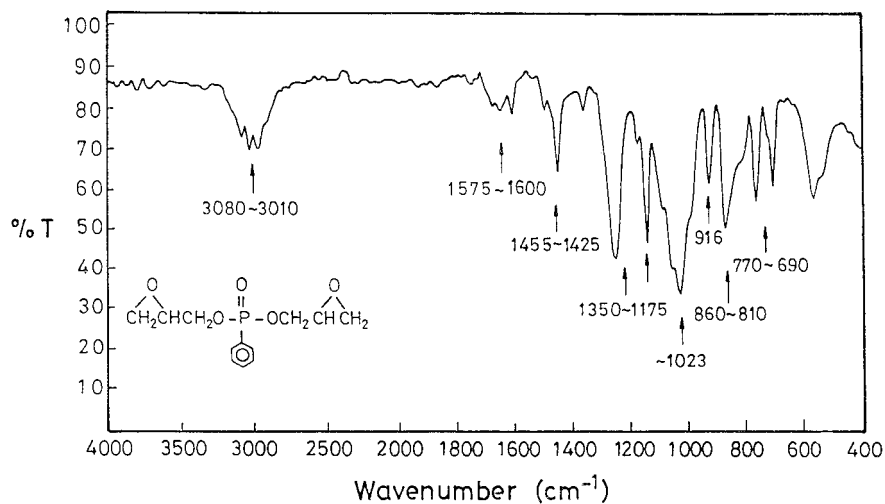


Figure 1 IR spectrum of BGPP.

resin and curing agent, DETA, were mixed at a stoichiometric ratio, then sealed in aluminum pans. The sealed samples were quenched in a liquid nitrogen bath. The heat released during cure was determined by DSC (Perkin-Elmer, DSC-7) under either isothermal or nonisothermal conditions.

Thermogravimetric Analysis (TGA)

The mixtures of the blended resin and curing agent prepared as mentioned above were cured first under different curing cycles, then analyzed by TGA (Perkin-Elmer, TGA-7) at various heating rates 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.

RESULTS AND DISCUSSION

Characterization of Main-chain Phosphorus-containing Diepoxide (BGPP)

The product, BGPP, was analyzed by FTIR and NMR. The results are shown in Figures 1 and 2.

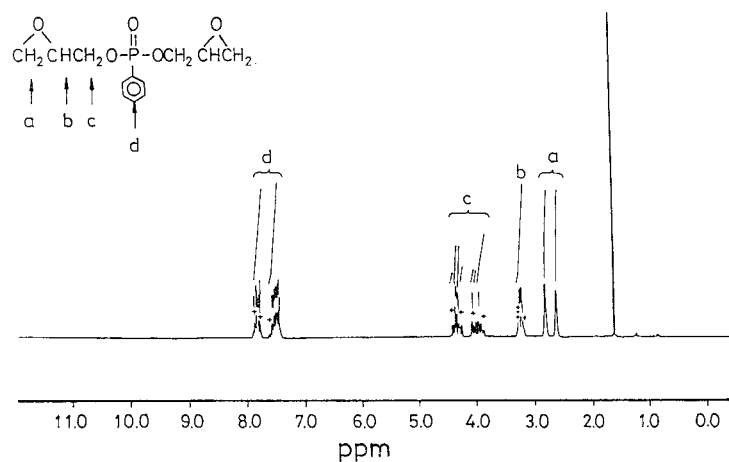


Figure 2 ¹H-NMR spectrum of BGPP.

Table I Infrared Absorbency of BGPP

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.

The absorption peak at about 1023 cm⁻¹ indicates the P—O—CH₂ group formed by the coupling reaction of glycidol with PPDC. The other absorption peaks of the FTIR are shown in Table I.

Figure 2 indicates the NMR spectrum for BGPP. The characterization data by ¹H-NMR are as follows:

$\delta = 2.60\text{--}3.11$ ppm (oxiane-ring protons);

$\delta = 3.90\text{--}4.31$ ppm (P—O—CH₂); and

$\delta = 7.35\text{--}7.70$ ppm (aromatic protons).

Furthermore, a single peak, $\delta = 20.6$ ppm from the ³¹P-NMR spectrum, was found for BGPP. However, the peak of the reactant, PPDC, is at 37.3 ppm. The shifting on the phosphorus atom may have resulted from the replacement of the electron-withdrawing chloride on the reactant, PPDC, by the —O—CH₂ group. Those spectrum data confirm the chemical structures of BGPP. The EEW of the products, BGPP, was determined to be 142 by titration.¹⁷

Curing Kinetics

The synthesized phosphorus-containing diepoxide, BGPP, was mixed with various contents of the DGEBA-type epoxide, DER 331, then cured with DETA at a stoichiometric ratio. The curing kinetics was studied by DSC and FTIR. Figure 3 shows DSC scanning of the curing systems for different compositions. The temperature, T_{\max} , at which reaction rate reaches the maximum value decreases with an increasing content of BGPP (see Table II). This phenomenon indicates that the synthesized product, BGPP, is cured with DETA more quickly than with DER 331. The IR

spectrum of the BGPP–DETA curing systems at 10°C/min is shown in Figure 4. The epoxy group (916 cm⁻¹) decreases with temperature (time) and is consumed at about 150°C.

The extent of the reaction, epoxy conversion $\alpha(\text{EP})$, could be calculated by the heat generation up to time t , $\Delta H(t)$, measured by DSC, and the total heat of the reaction, ΔH_T , by the following equation²:

$$\alpha(\text{EP}) = \frac{\Delta H(t)}{\Delta H_T} \quad (2)$$

The curing rate can be described as follows:

$$d\alpha/dt = k(1 - \alpha)^n \quad (3)$$

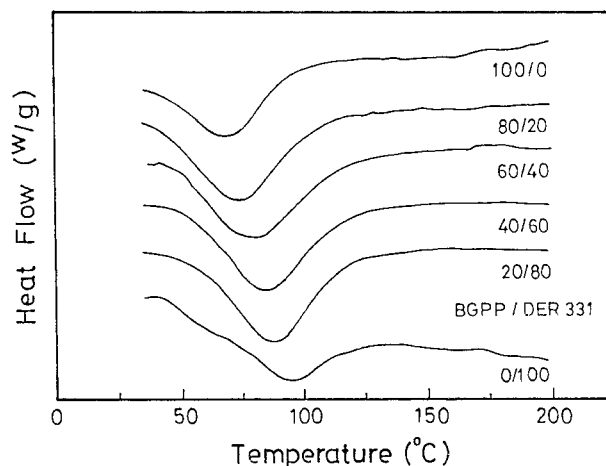


Figure 3 DSC thermograms of BGPP–DER 331–DETA curing systems at a heating rate of 10°C.

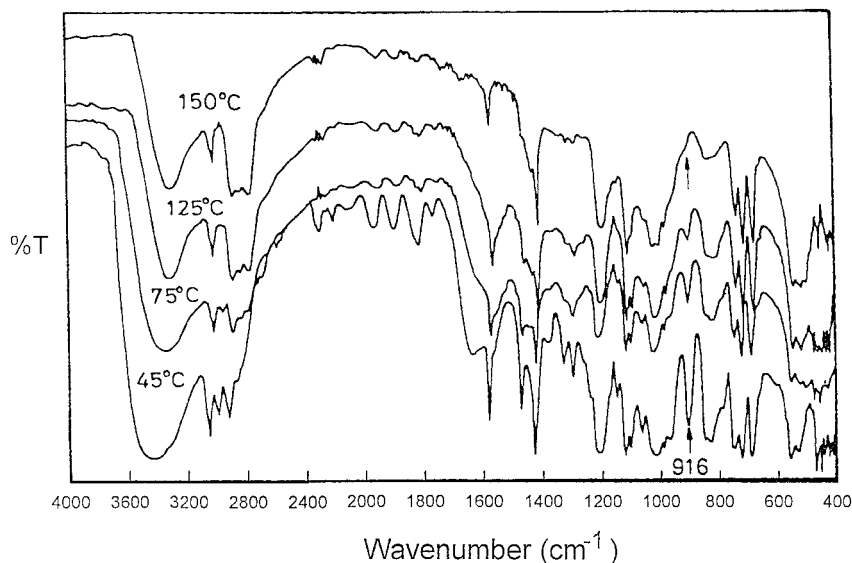


Figure 4 IR spectrum of BGPP-DETA curing system.

where k is the reaction rate constant, and n , the reaction order, which can be determined by plots of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$, such as in Figure 5.

The reaction order and activation energy, E_a , for various curing systems are shown in Table II and Figure 6, respectively. The activation energy is 51.2 kJ/mol for the BGPP-DETA system, and this value is lower than that of the DER 331-DETA system (73.2 kJ/mol). Furthermore, the activation energy decreases with BGPP for the three-component systems. This could be due to the small molecular size and flexible group, P—O—CH₂, of BGPP in comparison with DER

331, and the mobility and reactivity of BGPP are higher than those of DER 331.

Glass Transition Temperature

The samples were cured first, then analyzed by DSC at a heating rate of 10°C/min. The glass transition temperatures of the thermosets determined by DSC are shown in Table II. The thermoset with BGPP shows a decrease in the T_g , which may be caused by the flexible group, P—O—CH₂, on the main chain of BGPP.

TGA

The samples were cured first, then analyzed by TGA at various heating rates under a nitrogen atmosphere. As shown in Figure 7 and Table II, the DER 331-DETA thermoset exhibited a 5% weight loss at 345°C and decomposed at about 360°C. For the BGPP-DETA system, which contains 9.53 wt % phosphorus, the curve indicates that the decomposition temperature and the slope of decomposition are lower than those of the DER 331-DETA system.

For the BGPP-DER 331-DETA thermosets, it was found that the decomposition temperature decreases with an increasing phosphorus-containing epoxy resin, BGPP. Furthermore, the IR spectrum indicates that the phosphorus-containing groups (about 1300–1000 cm⁻¹) remained in

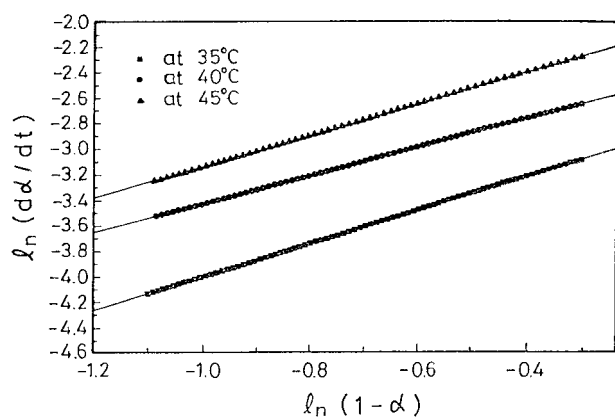


Figure 5 Plot of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$ for BGP-DER 331-DETA curing system (BGPP/DER 331 = 40/60).

Table II Characteristics for Various Curing Systems

Characteristics	BGPP/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	79	73	68	63
T_g (°C) of thermoset by the DSC at 10°C/min	108	58	63	62	59
Reaction order of eq. (3)	1.1	1.0	1.0	1.0	1.1
Temperature at 5% weight loss by the TGA at 10°C/min under nitrogen atmosphere	345	285	279	259	221
Residual weight (%) at 550°C by the TGA at 10°C/min under nitrogen atmosphere	16.9	21.2	22.8	26.2	26.2
Phosphorus content (P wt %)	0	3.24	5.12	7.20	9.53
Nitrogen content (N wt %)	3.99	4.39	4.62	4.88	5.17
LOI	19–22	23–26	24–26	27–29	29–31

the char at 550°C as shown in Figure 8. The decomposition temperatures of the thermosets with BGPP lower than that of DER 331–DETA is characteristic of the intumescent char formation that resulted from the pyrolysis of the phosphorus/nitrogen-containing polymers. This intumescent char would retard further thermal degradation of the polymer; thus, with a higher content of phosphorus-containing epoxide, the char yield at 550°C increased (see Table II).

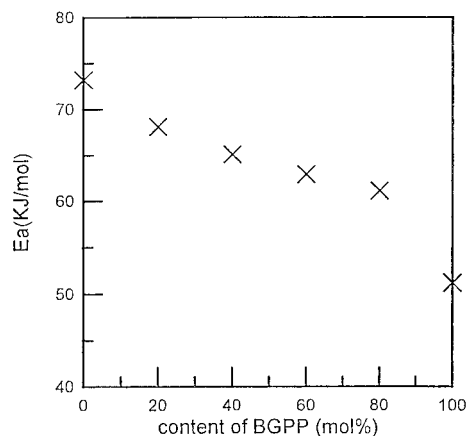
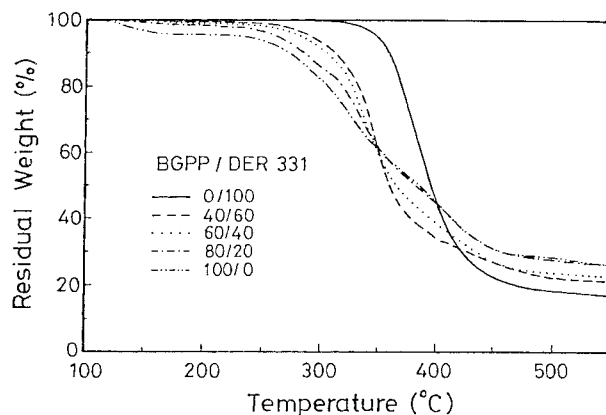
Decomposition Kinetics

Figure 9 shows TGA thermograms for different compositions at 10, 15, and 25°C/min. By the method of Ozawa,¹⁸ the apparent decomposition activation energy, E_d , can be determined by the following equation:

$$E_d = -\frac{R}{b} \left[\frac{d \log \beta}{d(1/T)} \right] \quad (4)$$

where R is the gas constant; b , a constant (0.4567); and β , the heating rate (°C/min). The decomposition activation energy was calculated by the slope, $d \log \beta/d(1/T)$, and the results are shown in Figure 10.

The average activation energies of the phosphorus-containing thermosets are from 147.3 to 165.1 kJ/mol, which are higher than that of the DER 331–DETA system (95.8 kJ/mol). The intumescent char formed from the pyrolysis of the phosphorus/nitrogen-containing polymers would retard the thermal degradation of the polymer; thus, the decomposition activation energy increases.

**Figure 6** Activation energy for various curing systems (BGPP–DER 331–DETA).**Figure 7** TGA thermograms of BGPP–DER 331–DETA thermosets.

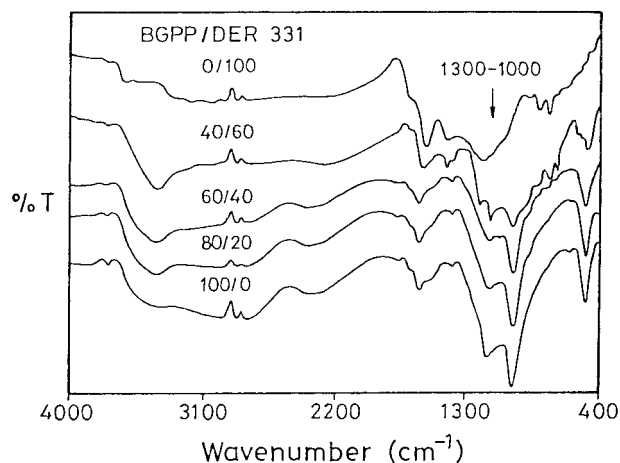


Figure 8 IR spectrum of the char remaining at 550°C for BGPP-DER 331-DETA thermosets.

LOI

The LOI of the polymer increased with the phosphorus content of the samples, as shown in Table II and Figure 11. The BGPP-DETA system shows a relatively higher char yield and LOI value, 29–31, while the thermoset without phosphorus, DER 331-DETA, exhibited a lower LOI value, 19–22. Furthermore, the LOI values for various phosphorus contents of the polymers can be expressed by an empirical relationship as follows (see Fig. 11)¹⁹:

$$\text{LOI} = 20.40 + 102.1 \text{ P } \%$$

where P % is the weight percentage of phosphorus.

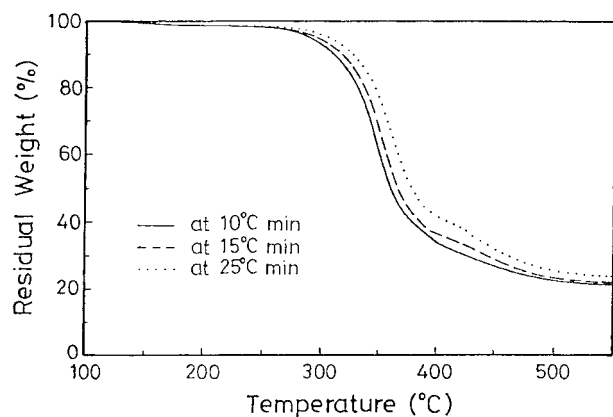


Figure 9 TGA thermograms of thermosets at various heating rates (BGPP/DER 331 = 40/60).

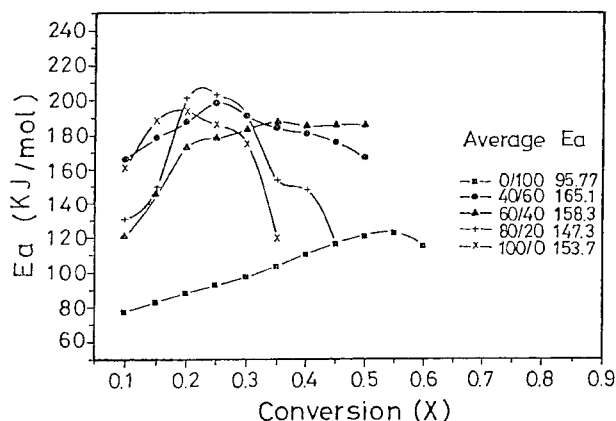


Figure 10 Apparent decomposition activation energies versus the decomposition conversion X .

CONCLUSIONS

The activation energy for the BGPP-DETA curing system was 51.2 kJ/mol, and this value is lower than that of the DER 331-DETA system, 73.2 kJ/mol. The average apparent decomposition activation energies of the thermosets with phosphorus-containing epoxide are from 147.3 to 165.1 kJ/mol, which are higher than that of the DER 331-DETA system (95.8 kJ/mol). The BGPP-DETA system shows a relatively higher char yield and LOI value, 29–31, but the thermoset with BGPP shows a decrease in the T_g .

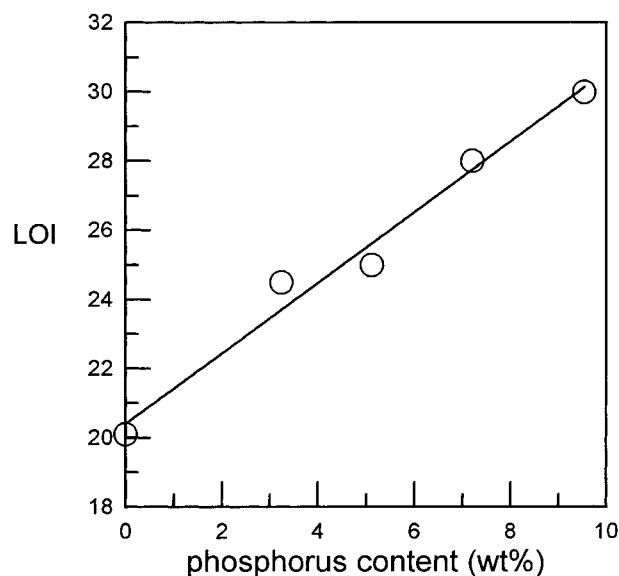


Figure 11 Plot of LOI versus phosphorus content.

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