

Synthesis, Thermal Behavior, and Cone Calorimetry of Organophosphorus Epoxy Materials

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ABSTRACT: An organophosphorus epoxy resin with diglycidyl ether of bisphenol A (DGEBA), which has improved fire performance, was synthesized from the reaction of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and DGEBA. The epoxy resin was then cured with an isomeric mixture of 3,5-diethyltoluene-2,4-diamine and 3,5-diethyltoluene-2,6-diamine. The reaction kinetics were measured by Fourier transform IR, ¹H-NMR, and differential scanning calorimetry. The effect of the incorporation of a phosphorus species into the epoxy network structures was also measured using

thermogravimetric, thermal conductivity, and dynamic mechanical thermal analyses. The fire performance was measured using cone calorimetry, which showed that a significant improvement was achieved by the addition of only 1–4% phosphorus into the epoxy backbone. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3696–3707, 2003

Key words: resins; flame retardance; thermal properties; cone calorimetry

INTRODUCTION

Epoxy resins have been used commercially in many industries because of their many attractive properties such as good mechanical behavior, electrical properties, adhesive strength and chemical resistance, ease of processing, and low cost. This has led to a wide range of applications in surface coatings; semiconductor and insulating materials for electrical devices; and structural reinforced composites for aerospace, marine vehicles, and automobiles.^{1–3} New materials are required in order to use epoxy materials in applications where excellent fire performance is critical to save the infrastructure and preserve human life. A burning polymer constitutes a highly complex system. Chemical reactions may take place in three independent regions: within the condensed phase, at the interface between the condensed phase and the gas phase, and the gas phase. Burning begins with an initial energy transfer to the surface of the materials at ambient temperatures and continues through to a self-sustaining and propagating fire. The process begins by thermally degrading the polymer, resulting in the evolution, ignition, and continued combustion of flammable gases. An effective fire retardant requires the ability to suppress one or more of these stages either chemically or physically. The thermal decomposition mecha-

nisms of polymers have been reported in detail over many years.⁴

The fire performance of epoxy materials can be improved by the addition of various fillers such as antimony trioxide, magnesium hydroxide, compounds based on silicon and boron, and phosphorus-containing compounds, which are particularly important. Depending on the nature of the filler, the thermal conductivity (TC) and heat capacity of the polymer may change and increase the fire retardant behavior. The addition of specific fire retardant fillers is known to increase the fire resistant behavior of epoxies. Large amounts of these additives are usually required, often at least 30 wt % polymer. Moreover, the addition of any particular fire retardant filler to a polymer can significantly influence its combustion behavior, such as reducing the ignition time; however, this often leads to an increase in toxic gases, which causes a substantial reduction in processing ability and deleterious effects on the mechanical properties.⁵

Phosphorus-containing compounds are being increasingly used recently as materials for flame retardants by incorporating them into the reacting polymer backbone. This strategy leads to an improvement in thermal and fire resistance⁶ and the use of less phosphorus overall. The reaction of diglycidyl ether of bisphenol A (DGEBA) with diallyl or aryl phosphate, followed by curing with 4,4'-diamino phenyl sulfone (DDS), results in a polymer with good thermal stability and flame retardant behavior.⁷ Phosphorus-containing hardeners such as bis(4-nitrophenoxy)phenyl phosphine oxide and bis(4-aminophenoxy)phenyl

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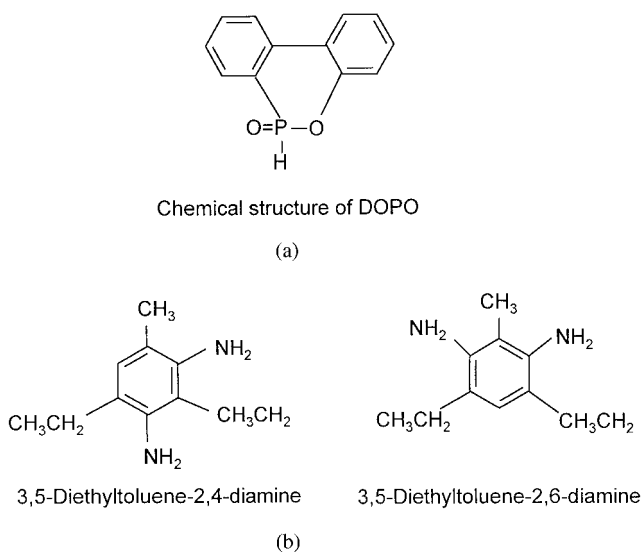


Figure 1 The chemical structures of (a) DOPO and (b) curing agent.

phosphine oxide are also used by researchers for curing with DGEBA, and the subsequent thermal stability and fire resistance behavior of the polymer is substantially improved.^{8–10}

The main objective of this study focuses on the reaction of DGEBA with a phosphorus-containing compound 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its curing with a mixture of 3,5-diethyltoluene-2,4-diamine and 3,5-diethyltoluene-2,6-diamine (Ethacure-100) in order to improve the thermal and flame resistance of the epoxy polymer. A similar system cured with DDS instead was previously reported,¹¹ but the flame properties as measured by cone calorimetry were neither described nor reported. Moreover, the details of the synthesis and characterization of phosphorus modified DGEBA has not been reported. The Ethacure-100 curative is easy to blend with epoxy resins even at room temperature and the resulting mixture has a longer pot life and better mechanical properties than other known systems.

EXPERIMENTAL

Materials

The epoxy resin used in the study was DGEBA (DER-331 Dow Chemical Company). The organophosphorus compound DOPO was obtained from Tokyo Kasei Kogyo Co., Ltd. The curing agent used in this experiment was a mixture of 3,5-diethyltoluene-2,4-diamine and Ethacure-100 (Albemarle Corporation). Figure 1(a,b) shows the chemical structure of DOPO and the curing agent used in this work.

Synthesis

The DGEBA epoxy resin (250 g) was placed into a three-necked round-bottom flask and heated to 130°C

in an oil bath connected to a temperature controller. The DOPO (66 g) was then added and mixed with a mechanical stirrer while keeping the temperature at 130°C until a clear solution was obtained.¹¹ The temperature was then raised to 180°C and stirring was continued for a further 5 h until a transparent solution of 3% phosphorus-DGEBA epoxy was obtained. The amount of DOPO was varied to produce P-DGEBA epoxy materials with 1, 2, 3, and 4% phosphorus content. The epoxy equivalent weight (EEW) was determined by following the method described elsewhere.¹²

Curing procedure of epoxy resin

The mixture was cooled to 60°C under continuous stirring. A stoichiometric amount of the curing agent was added to the phosphorus-containing epoxy resin with vigorous stirring for 1 h. This mixture was then placed into Teflon coated molds and cured at 120°C for 4 h and postcured at 200°C for 2 h. The prepared sample was then cut to the desired sample size for physical, mechanical, and thermal analyses.

Characterization of samples

A ¹H-NMR spectrum was obtained on a Bruker 500-MHz ¹H-NMR spectrometer. Fourier transform IR (FTIR) was recorded on a Perkin-Elmer FTIR spectrometer. The wavenumbers were recorded from 400 to 4000 cm⁻¹ for mid-IR and 4000 to 8000 cm⁻¹ for near IR (NIR). Differential scanning calorimetry (DSC) temperature scans were carried out on a Perkin-Elmer DSC-7 in a nitrogen atmosphere. The DSC-7 was calibrated with indium and zinc standards. Samples of 7–10 mg were sealed in aluminum pans and heated from 50 to 300°C at a scanning rate of 10 K/min. The loss tangent (tan δ) of the cured samples was determined on a Rheometric Scientific dynamic mechanical thermal analysis (DMTA) instrument (DMTA IV). The cured samples were clamped in a medium frame using a small center clamp in dual cantilever mode. Frequency sweep scans were performed from 80 to 260°C at 2°C/min using a frequency of 1 Hz and a strain of 1%.

Thermogravimetric analysis (TGA) was performed on the cured samples using a TG-92 Setaram thermal analyzer. The thermographs were obtained at a heating rate of 10°C/min using 10–15 g of the powdered sample. The experiments were made in a static air atmosphere. Nondestructive TC of the samples was carried out at room temperature using a Perkin-Elmer Pyris TC probe. Samples (10 × 70 × 0.5 cm) were made and placed on the TC probe to measure the TC (W/m k) at room temperature (26.0°C).

Fire performance tests including time to ignition (TTI), rate of heat release (RHR), time to reach maximum RHR, smoke density, carbon monoxide and car-

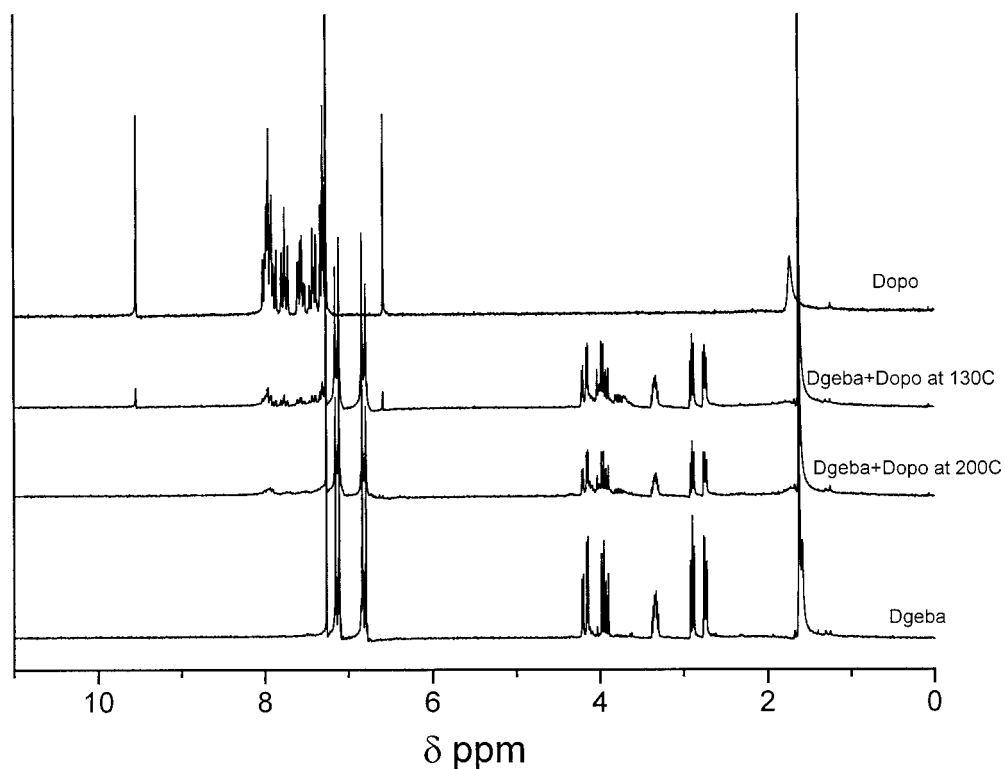


Figure 2 $^1\text{H-NMR}$ spectra of DGEBA, DOPO, and DOPO-DGEBA at 130 and 200°C.

bon dioxide evolution, and sample mass loss were determined by cone calorimetry in accordance with the procedure described in an ASTM standard method.¹³

The heat flux produced was 50 kW/m² on the specimen, which had an exposed surface of 100 × 100 mm. The testing equipment consists of a radiant electric

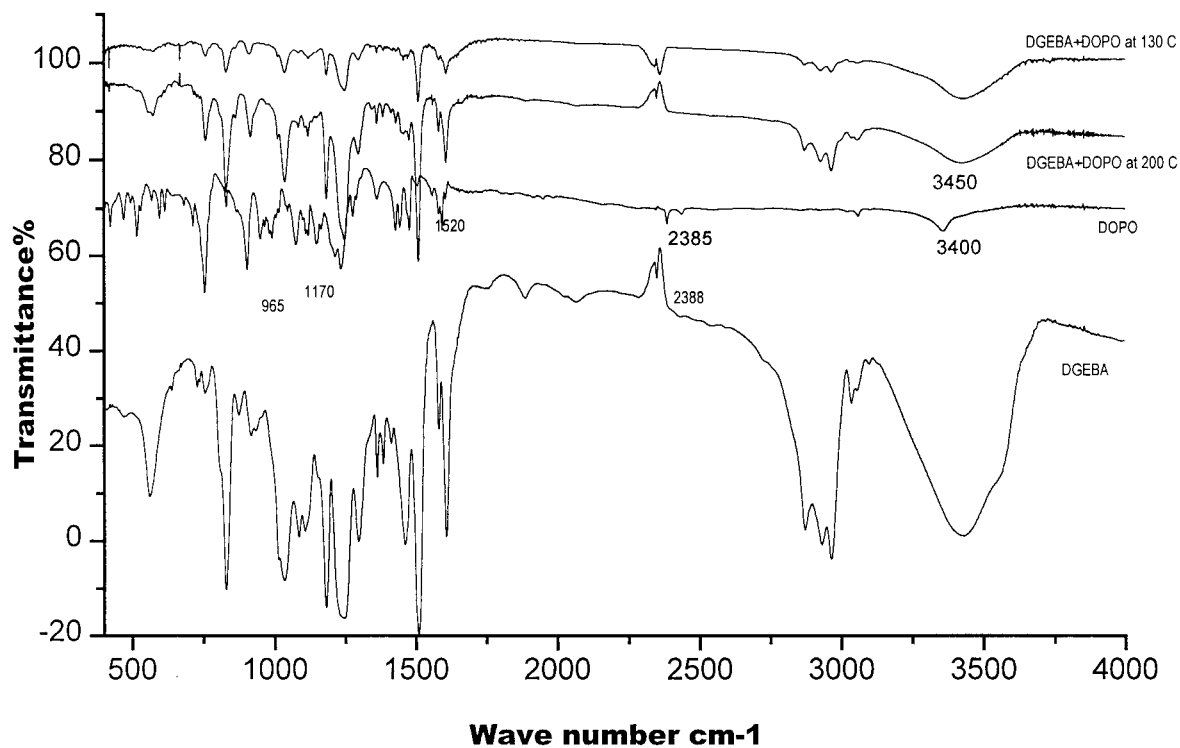


Figure 3 FTIR spectra of DOPO, DGEBA, and a mixture of DOPO and DGEBA at 130 and 200°C.

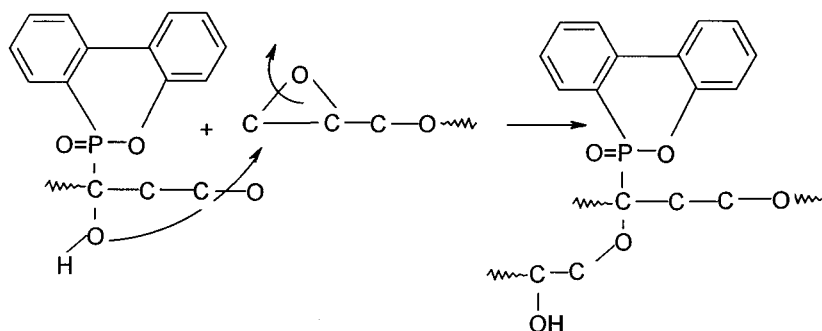


Figure 4 The proposed etherification reaction between DOPO and DGEBA.

heater in a trunk-conic shape, an exhaust gas system with oxygen monitoring and an instrument to measure the gas flux, an electric spark for ignition, and a load cell to measure the weight loss. The test was terminated after 500 s of exposure. The TTI measures the time to achieve sustained flaming combustion at a particular cone irradiance. The smoke density is measured by the decrease in transmitted light intensity of a helium-neon laser beam photometer, and it is expressed in terms of the specific extinction area (SEA, m^2/kg). The maximum value, the average to 180 s after ignition, and the overall average values are determined for the RHR. The total mass after the desired test time was calculated as a percentage of the initial sample mass.

RESULTS AND DISCUSSION

Characterization of structure

Wide ranges of organophosphorus epoxy materials containing 1–4% phosphorus were prepared and characterized by $^1\text{H-NMR}$, FTIR, and DSC analysis. Figure 2 shows the $^1\text{H-NMR}$ of pure DOPO, virgin DGEBA, the reaction of DOPO and DGEBA at 130°C , and the reaction of DOPO and DGEBA at 200°C . The $^1\text{H-NMR}$ data suggest that, at higher temperatures (200°C), DOPO completely reacts with the epoxy backbone by adding to the epoxide group via an etherification mechanism, creating a phosphorus-containing epoxy material as proposed by Lin and Wang.¹⁴

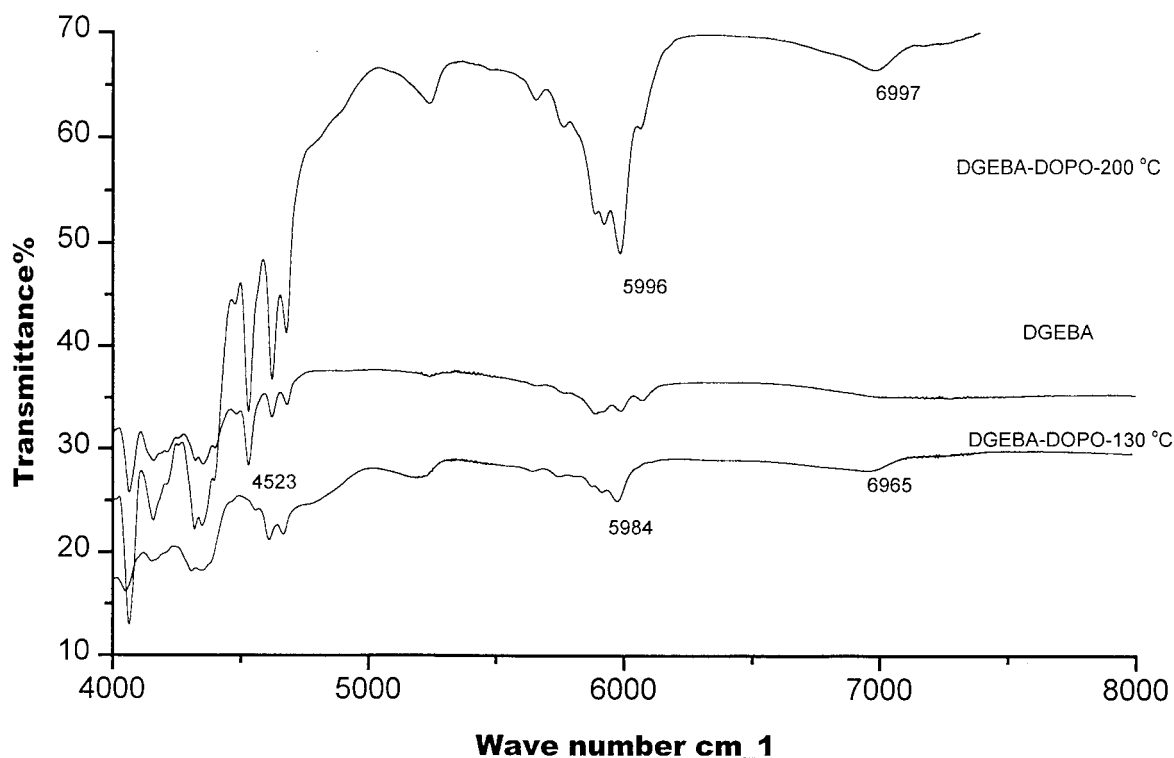


Figure 5 The near IR of DGEBA and DOPO mixes at 130 and 200°C .

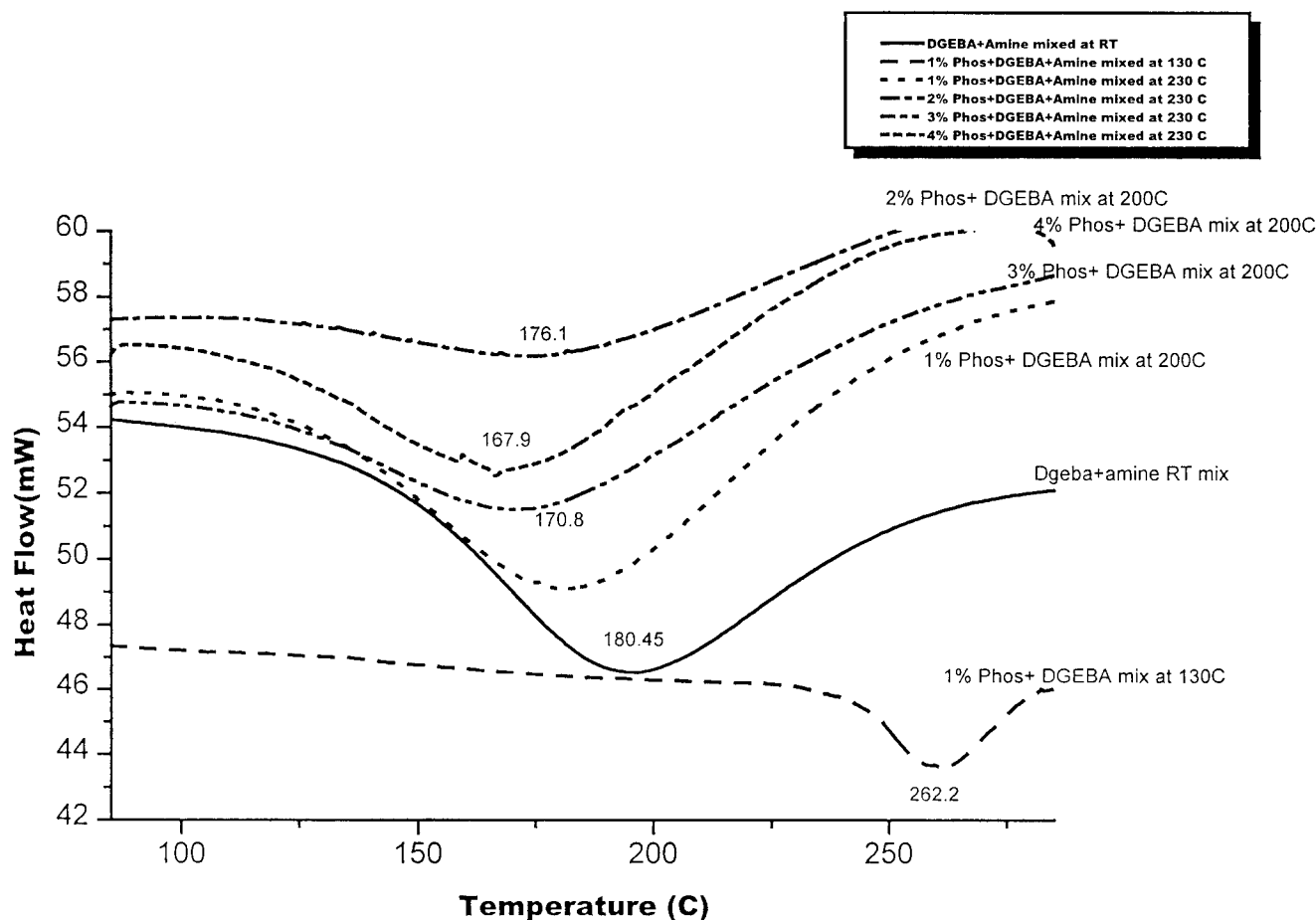


Figure 6 DSC thermographs of organophosphorus-DGEBA cured with amine.

The presence of DOPO in the DGEBA backbone was further confirmed by FTIR analysis, as shown in Figure 3. A strong P—H absorption at 2385 cm^{-1} was observed for DOPO, and an OH absorption around 3450 cm^{-1} was observed for the DOPO and DGEBA mixture. The disappearance of P—H stretching is due to the addition of an epoxide group and the subsequent etherification reaction between the hydroxyl that is formed and the epoxy group. The multiple absorption peaks of methylene groups at $2800\text{--}3000\text{ cm}^{-1}$ suggest the structure proposed in Figure 4. Furthermore, the P=Ph stretching frequency of DOPO at 965 and 1170 cm^{-1} was found to be shifted to 1145 cm^{-1} and the P=O frequency of DOPO at 1195 cm^{-1} was broadened. A strong, sharp peak at 1025 cm^{-1} was due to P—O—C (aromatic) stretching, which is characteristic of the presence of an organophosphorus moiety in the DGEBA network.¹⁵

Figure 5 shows the typical NIR spectrum of the mixture of DGEBA and DOPO at 130 and 200°C . Small bands at 5996 and 6997 cm^{-1} in the mixture at 130°C are from the presence of P—H stretching of DOPO and O—H stretching, respectively. However, these peaks became sharper and clearer when the mixture was heated at 230°C . This NIR spectrum suggests the

formation of an addition product between DGEBA and DOPO at 130°C .¹⁶ However, when the mixture was heated at 230°C , these peaks became sharper and clearer with the appearance of a new epoxide peak at around 4523 cm^{-1} . This result clearly suggests that DOPO is now a part of the DGEBA backbone and supports the formation of the structure in Figure 4.

DSC was used to study the curing reactions of the organophosphorus epoxy with the amine curing agent. Typical DSC thermographs of various amounts of phosphorus-containing epoxy with the amine curing agent are shown in Figure 6. These thermographs provide valuable information for determining the environment of the curing reaction. When DOPO (1% P) was mixed with DGEBA at 130°C and cured with the amine hardener, an exothermic peak was observed at 262.2°C , which is much higher than the exothermic peak of DGEBA cured with amine alone (195.0°C). The higher exothermic peak of 1% organophosphorus at 130°C can be explained by the fact that no reaction between the epoxy resin and the amine takes place at that temperature, which is due to the electron withdrawing group (—P=O) reducing the electron density of the electron-donating amine groups. Moreover, the bulk structure of unreacted DOPO hinders the reaction between the ep-

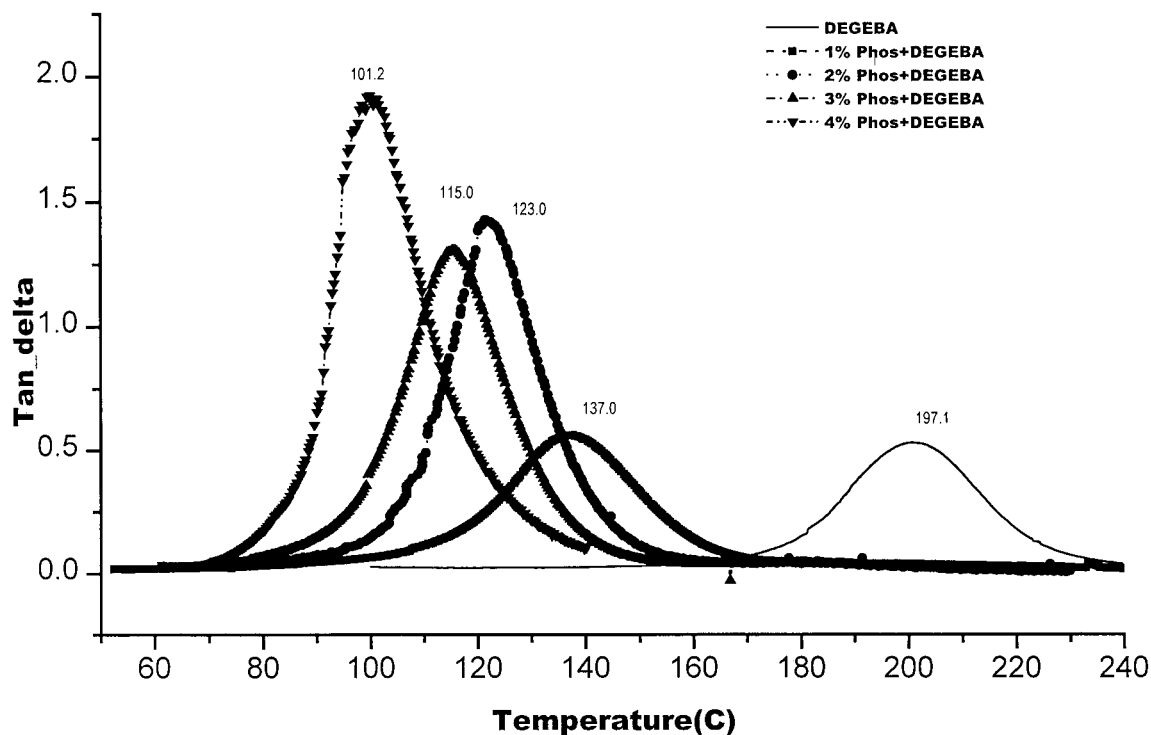


Figure 7 Dynamic mechanical analysis of DGEBA and cured organophosphorus-DGEBA.

oxy and amine, resulting in a delay of the curing. However, the exothermic peak of completely reacted organophosphorus epoxy cured with amine shows a lower value compared to DGEBA cured with amine alone. It is clearly seen that the peak temperature decreases as the amount of phosphorus is increased in the epoxy. Thus, as shown by the DSC thermographs, the curing temperature decreases but the change in enthalpy varies because of the epoxy etherification reaction with phosphorus and the increase in phosphorus content.

Thermal and flame retardant properties of cured epoxy resins

DMTA study

Figure 7 shows the $\tan \delta$ spectra from dynamic mechanical analyses of the cured organophosphorus epoxy materials. As can be seen, increasing the phospho-

rus content caused a substantial decrease in the temperature of the peak in the $\tan \delta$ spectra. Table I shows the changes in the glass-transition temperature (T_g) and storage modulus at 100°C and at T_g plus 30°C. Also listed are the EEWs of the epoxy resins, which clearly show a relationship between a decrease in the T_g and an increase in the EEW. The increasing height of the $\tan \delta$ peak and T_g with increasing phosphorus content can be ascribed to a greater range of molecular interactions available in the cured network. Wang observed similar results and proposed that the higher EEW of organophosphorus epoxy reduces the crosslink density, subsequently decreasing the glass-transition temperature.¹⁴ It is interesting that the storage modulus was found to increase relative to the unmodified epoxy amine network. The lower crosslink density is confirmed by the greater height of

TABLE I
DMTA Results of Cured Epoxy Resins

Sample	EEQ (g/eq)	T_g (°C)	Height of $\tan \delta$	Modulus at 100°C	Modulus at $T_g + 30^\circ\text{C}$
DGEBA + amine	189.7	202.2	0.60×10^9	7.19×10^8	8.9×10^5
DGEBA + 1% P + amine	215.0	137.0	0.68×10^9	7.74×10^8	1.9×10^7
DGEBA + 2% P + amine	252.0	123.1	1.42×10^9	1.30×10^9	3.8×10^6
DGEBA + 3% P + amine	308.0	119.0	1.35×10^9	1.34×10^9	3.9×10^6
DGEBA + 4% P + amine	485.0	101.2	1.93×10^9	1.19×10^7	8.3×10^5

EEQ, epoxy equivalent weight.

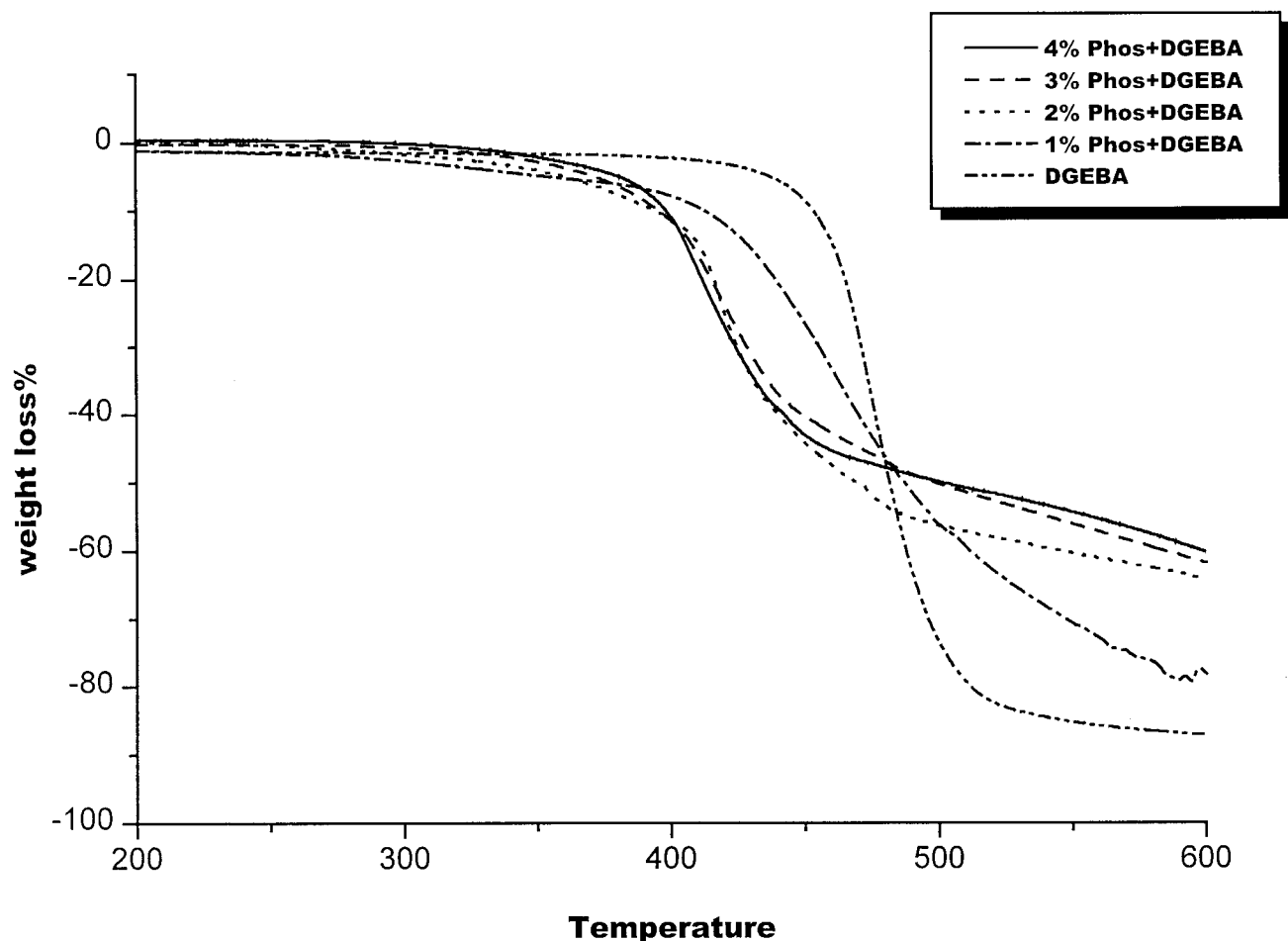


Figure 8 TGA thermographs of DGEBA and cured organophosphorus-DGEBA.

the δ relaxation observed in Figure 7, which is indicative of greater relaxation strength. The detailed DMTA results listed in Table I demonstrate that how the glass-transition temperature and EEW vary with the phosphorus content.

TGA study

In order to examine the effect of the DOPO structure on the thermal stability of cured DGEBA resins, the TGA data were determined and analyzed. Figure 8 shows the weight loss with the temperature for the range of phosphorus modified epoxy resins we prepared. As can be seen, the onset of degradation temperatures of the organophosphorus epoxy resins are lower (375–400°C) than those of the phosphorus free epoxy, which is around 440–460°C. The decrease in the degradation onset temperature also increases with greater phosphorus content in the epoxy and is likely due to the decomposition of P—O—C bonds.^{17,18} However, the weight losses of the organophosphorus epoxy resins at higher temperatures were found to be much less than that of the phosphorus-free epoxy

resin. A linear dependence of the char yield on the phosphorus content of the epoxy resin was observed, as shown in Figure 9. The mechanism of improved fire performance via phosphorus modification can now be seen. Whereas the phosphorus species decreases the thermal stability, the increasing char content with phosphorus prevents the transfer of combustible gases to the surface of the material, thereby decreasing the pyrolysis reaction and improving the fire resistance. Furthermore, the phosphorus groups are consumed at an early stage of degradation and form an insulating protection layer, which increases the thermal stability at higher temperatures. This phenomenon has also been described as fire resistance via the condensed phase.^{19,20} Other than the decomposition temperature and the weight loss in TGA, the char yield at high temperature reveals another aspect of the thermal properties of the materials. As shown in Figure 9, all the phosphorus-containing epoxy resin creates higher char yield and the char yields are directly proportional to the content of phosphorus in the epoxy backbone. As described earlier, the char yields result from the

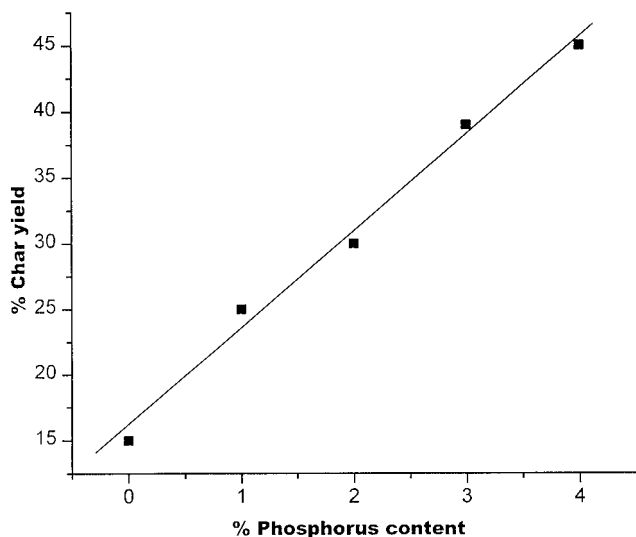


Figure 9 The char yields as a function of the phosphorus content in DGEBA.

decomposition of phosphorus groups and the formation of phosphorus-rich insulating layers.

The flame retardant properties of a polymer can be predicted from the char yields and the limited oxygen index (LOI), which is a measure of the flammability of the materials. The LOI is the minimum concentration of oxygen in an oxygen/nitrogen mixture that will just support combustion. It has been reported that high char yield and larger LOI values are indicative of better flame retardant properties for polymers.^{21,22} It has been reported that the LOI value of an organophosphorus epoxy resin can be calculated as follows¹⁹:

$$\text{LOI} = 3.0(\text{temp. of 50\% wt loss}/10)^{1/3} \times (\text{P content})^{1/2} \quad (1)$$

The LOI is also calculated from the char yield (CR) using the following equation^{23,24}:

$$\text{LOI} = 17.5 + 0.4\text{CR} \quad (2)$$

A significant increase in the LOI was observed when the data were plotted as a function of the char yield as shown in Figure 10. This indicates that the presence of phosphorus in the epoxy backbone had a great effect on reinforcing the flame retardancy of the epoxies. It is also noteworthy that the LOI values increase with an increase in the phosphorus contents of the epoxy. A strong linear relationship between the LOI and char yield is shown in Figure 10. When the linear line is extrapolated, the char yield of DGEBA accurately coincides with the LOI value of DGEBA at 18.8. The LOI value of a phosphorus–novolac system was found to be similar.²⁵ This result implies that the presence of phosphorus groups has a great influence

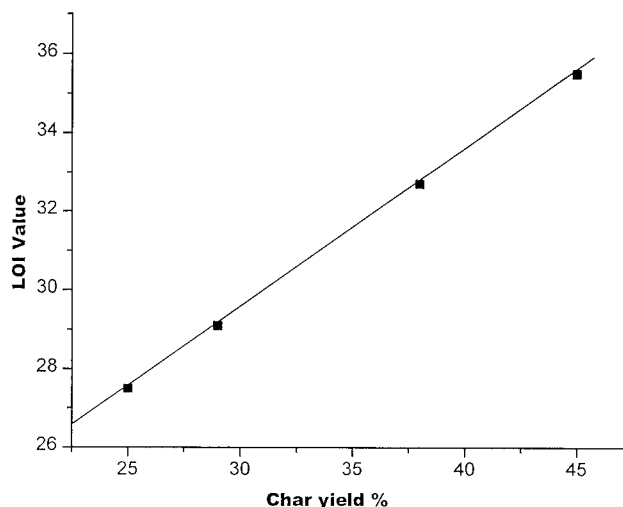


Figure 10 The limited oxygen index as a function of the char that is formed.

on the thermal stability and flame retardant properties of epoxy materials.

TC analysis

In order to provide a TC analysis, thermally conductive fillers are required to disperse in the polymer matrix. It is well known that the flow of heat in non-metals like polymers occurs by phonons or lattice vibration. In order to minimize the TC, the phonon scattering process must be maximized. Figure 11 shows the measured TC of the cured epoxy materials as a function of the phosphorus content at 26.4°C. We observed that the TC decreases with increasing phosphorus content because the DOPO molecule is thermally nonconductive. Further, the presence of DOPO in the epoxy resin backbone decreases the conductive pathway. This result clearly supports the influence of

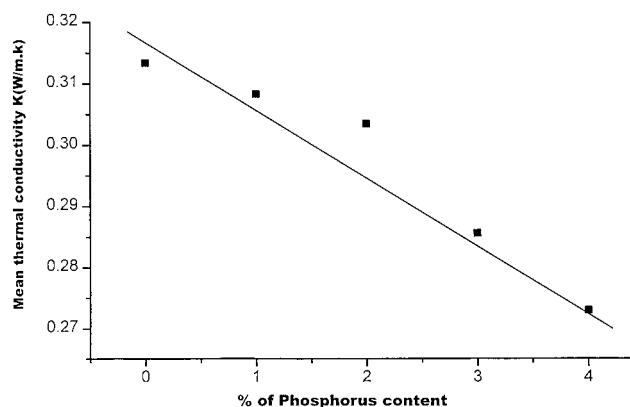


Figure 11 The thermal conductivity as a function of the phosphorus content in DGEBA.

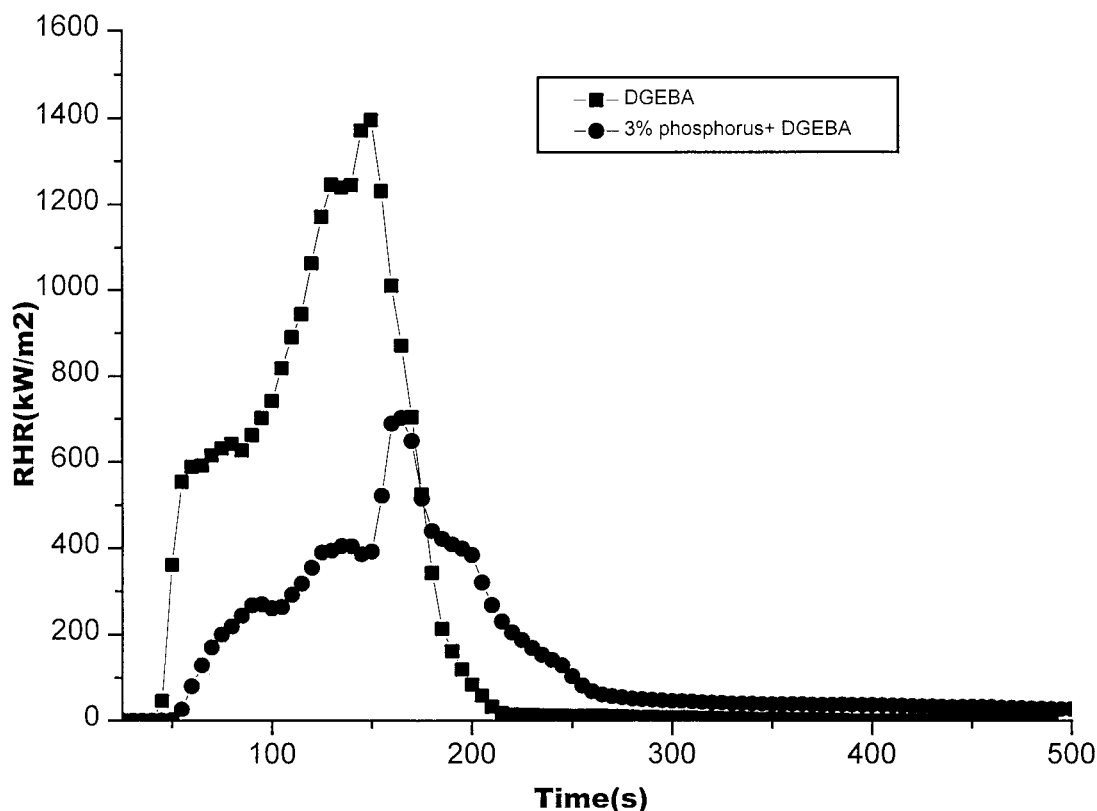


Figure 12 The rate of heat release as a function of time.

phosphorus content on the thermal and flame properties of epoxies at higher temperatures.

Cone calorimetry analysis

Figure 12 shows the RHR variation with time at a heat flux of 50 kW/m^2 . The RHR is a measure of the heat release per unit surface area of burning materials. Cone calorimetry characterizes the fire retardant behavior of the materials with respect to the peak and average RHR, SEA, and smoke production rates (CO_2 and CO). The maximum RHR of DGEBA was observed after burning for 150 s; however, much improvement was observed when 3% phosphorus was added to DGEBA. The sudden decrease in the rate of RHR with time is attributable to the formation of a char layer, which acts as a thermal insulator. In the case of DGEBA, the char yield is less than that of phosphorus-containing resins and thus shows a higher RHR. This result suggests that the presence of an organophosphorus group enhances char formation and acts as a flame retardant barrier on the surface of epoxy resins. A higher percentage of mass residue or char indicates a condensed-phased flame retardant mechanism, which is described elsewhere.²⁶ The effect of phosphorus on the flame test by cone calorimetry has been summarized in Table II.

Figure 13 shows the effective heat of combustion (EHC). The EHC can be defined as the quantity of heat produced by combustion of a unit amount of materials. The EHC for DGEBA and P-DGEBA remained constant until approximately 220 s of burning, thereafter decreasing for DGEBA but increasing for the P-DGEBA material. The change in EHC with time indicates the compositional changes of the samples with time. In the case of DGEBA, the sharp fall in the EHC after 220 s is probably due to the degradation of the epoxy materials. In the P-DGEBA, the increase in the EHC is due to the increase in char formation. Scudamore et al.²⁷ also observed similar types of

TABLE II
Cone Calorimetry Data of DGEBA and Organophosphorus-DGEBA

Fire properties	DGEBA	3% P-DGEBA
Time to ignition(s)	65.00	55.00
Max. rate of heat release (kW/m^2)	1402.50	702.30
Ave. rate of heat release (kW/m^2)	389.80	291.10
Time to max. RHR (s)	155.00	165.00
Ave. effective heat of combustion (MJ/kg)	21.20	15.80
Ave. carbon dioxide yield (kg/kg)	1.48	1.07
Total heat evolved (MJ/m^2)	117.30	64.05

RHR, rate of heat release.

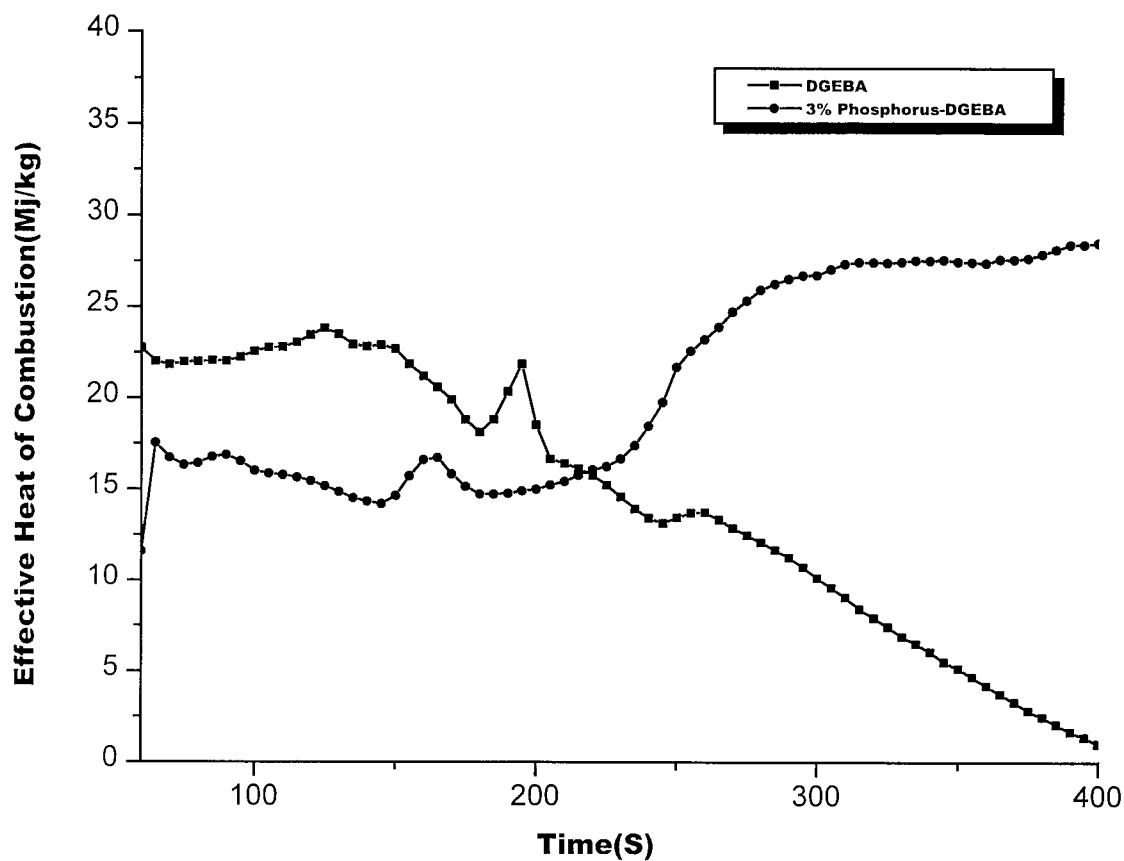


Figure 13 The effective heat of combustion as a function of time.

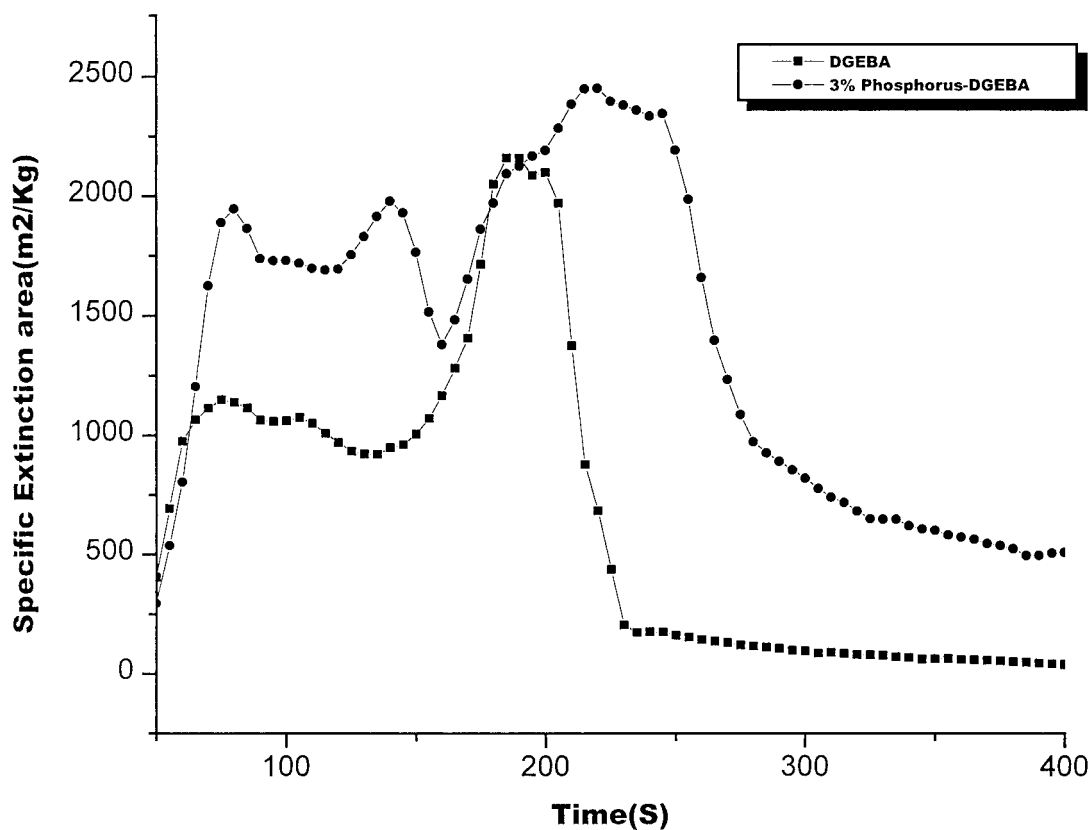


Figure 14 The specific extinction area as a function of time.

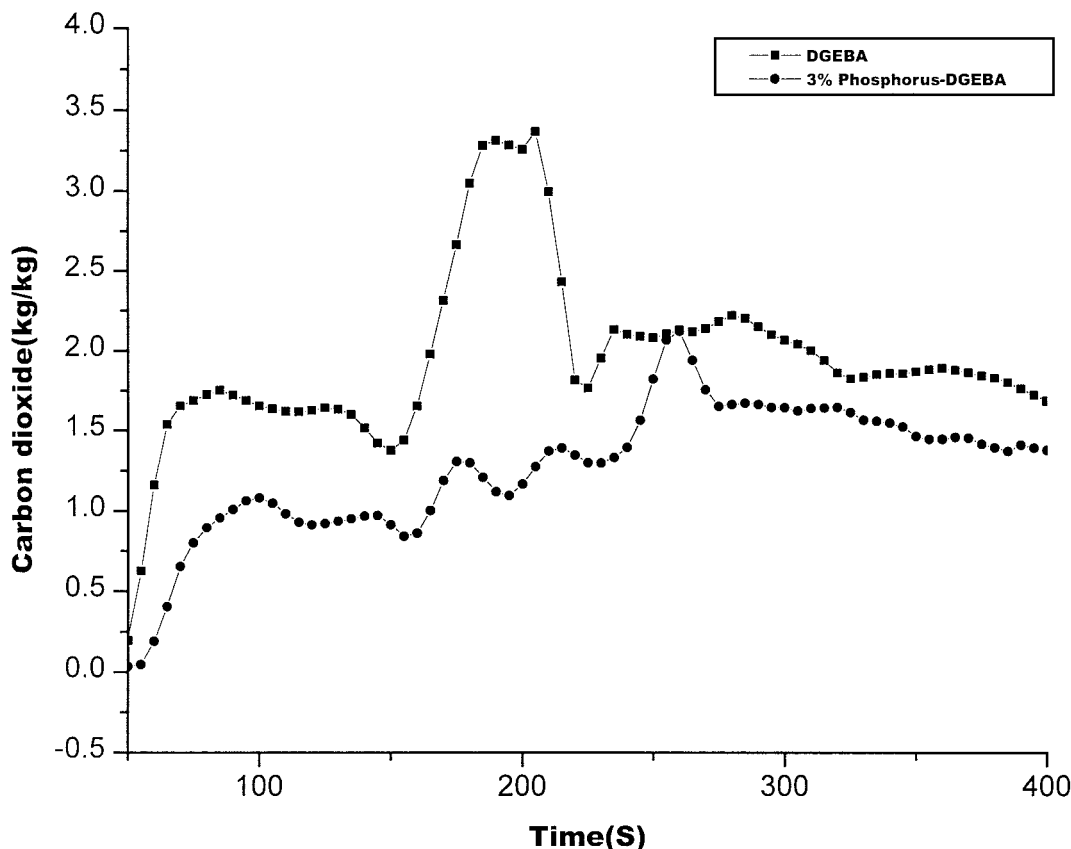


Figure 15 The emission of carbon dioxide as a function of time.

changes in the EHC during combustion of a glass reinforced polymer and explained them in terms of the formation of charring.

An important characteristic in the evaluation of the fire performance of epoxy resins is the smoke generation (SEA) and generation of CO and CO₂. Smoke generation is generally defined as

$$SEA = (dA/dt)/(dm/dt) \quad (3)$$

where A is the extinction area of the sample and dm/dt is the mass velocity of smoke production.²⁸ Figure 14 shows the SEA of DGEBA and P-DGEBA as a function of time. The SEA value of P-DGEBA was found to be higher and occurred for a longer time compared to DGEBA. This can be explained by the fact that P-DGEBA converts into smoke more easily when it burns; however, it but does so over a longer period of time. In Figure 15 the CO₂ emission during burning shows that the CO₂ rate is always higher for DGEBA compared to organophosphorus epoxy resins. Higher levels of CO₂ production during fire create a large indication of a potential hazard for human health. Phosphorus species incorporated into the DGEBA backbone have more potential as candidates to be considered as good fire retardant composite materials.

CONCLUSION

Phosphorus-containing epoxies were successfully synthesized and cured with amines. These materials were characterized in detail using FTIR, ¹H-NMR, and DSC. The thermal properties were studied in detail by DMTA, TMA, and TC. The flame retardancy properties were investigated by cone calorimetry. Introduction of organophosphorus groups into the epoxy resins leads to a decrease in the onset temperature of degradation but significantly increases the char yield with increasing phosphorus content. Thus, by controlling the amount of phosphorus content in the epoxy resin, it is possible to regulate the thermal and flame retardant behavior of the epoxy resins.

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