

Chemical Modification of Epoxy Resins by Dialkyl(or Aryl) Phosphates: Evaluation of Fire Behavior and Thermal Stability

D. DEROUET,* F. MORVAN, and J. C. BROSSE

Laboratoire de Chimie et Physicochimie Macromoléculaire, Université du Maine, Avenue Olivier Messiaen, 72017 Le Mans, France

SYNOPSIS

The improvement of flame-retardation of thermosetted epoxy-amine resins was attempted by chemically incorporating phosphorus-containing reagents. By reacting 4,4'-diglycidylether of bisphenol A (DGEBA) with dialkyl(or aryl) phosphate, it was possible to chemically modify the epoxy resin and then cure it in the presence of 4,4'-diaminodiphenylsulfone (DDS) to obtain epoxy-amine resin with good flame-retardant and thermal stability behaviors. The quantitative aspect of the addition of dialkyl(or aryl) phosphate onto glycidyle oxiranes was evaluated by elemental analysis of the modified epoxy-amine resins. Flammability and thermal behaviors of modified DGEBA/DDS resins depend on the nature of phosphate groups (the best flame-retardation was observed on resins bearing phenyl phosphate groups) and their concentration in the material. In relation to DGEBA/DDS samples containing additives of the same structure [trialkyl(or aryl) phosphate], cured resins incorporating chemically bonded phosphate groups show a better flame-retardation. On the contrary to the nonmodified DGEBA/DDS [with or without trialkyl(or aryl) phosphate as additive], combustion of modified DGEBA/DDS resins is accompanied by formation of intumescent char. Chemical modification of DGEBA by dialkyl(or aryl) phosphates can be carried out *in situ* during the curing of epoxy resins without change in the fire behavior.

© 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic bromine compounds in conjunction with antimony oxide are widely used as flame-retardants for epoxy resins. Major problems encountered with these systems concern production of highly toxic and corrosive products during combustion.¹ These considerations have recently led to the reexamination in terms of overall fire hazards of halogen-based systems and the search of new fire-retardants. Among them, organophosphorus compounds have demonstrated good ability as flame-retardants for polymeric materials.² They develop on heating a foamed carbonaceous char, which protects the polymer surface from the flame action. This layer acts

as a physical barrier to heat transfer from the flame to the plastic material and to diffusion of combustible gases, which feed the combustion process.^{3,4}

The purpose of the present study was to investigate the ability of organophosphorus to inhibit the combustion of materials, notably when they are associated to polyols. It deals with the fire behavior of epoxy-amine resins [systems based on DGEBA (4,4'-diglycidylether of bisphenol A) with DDS (4,4'-diaminodiphenylsulfone) as a hardener chemically modified by dialkyl(or aryl) phosphates. The phosphorus compounds introduced as substances chemically bonded onto the organic network remain more effectively resistant to combustion during time because they don't diffuse towards the material surface.⁵

Organophosphorus groups were introduced on thermosetting epoxy resin by means of glycidylether functions, by using the P—OH group

* To whom correspondence should be addressed.

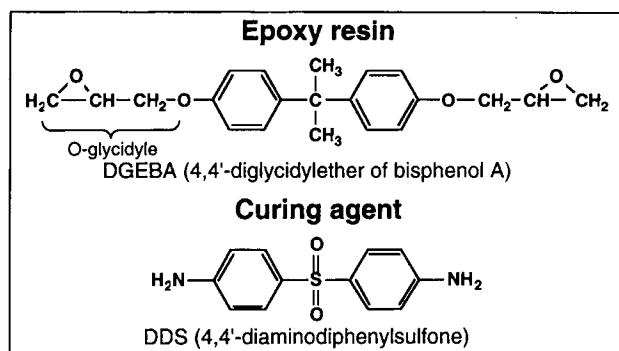
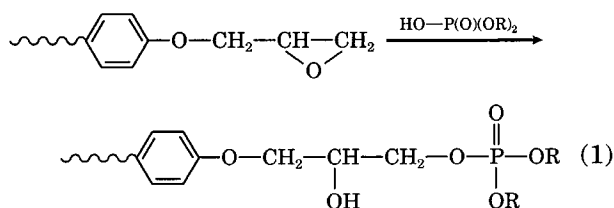


Figure 1 Molecular structure of the epoxy prepolymer and diamine used for synthesis of the epoxy networks.

reactivity of dialkyl(or aryl) phosphate type reagents $[\text{HO}-\text{P}(\text{O})(\text{OR})_2]$ towards the oxirane ring [eq. (1)].



R: Me, Et, Bu, Ph

Flammability and thermal behavior of specimens, including chemically bonded (alkyl or aryl) phosphate groups onto the epoxy-amine resin backbone, were compared respectively with those of specimens containing additives, such as a trialkyl(or aryl) phosphate.

EXPERIMENTAL

Raw Materials Used

Solvents and Gases

Solvents were commercial products. Acetone was dried and distilled on calcium sulfate, then kept on 3 Å molecular sieve. Toluene and dichloromethane (of 99.5% purity) were used as received. Gases used for thermal analysis were of 99.99% purity.

Reagents

DGEBA (4,4'-diglycidylether of bisphenol A) and DDS (4,4'-diaminodiphenylsulfone) were supplied by Aérospaciale (Suresnes, France). Figure 1 shows the structural formulae of both monomers. DGEBA (Dow Chemical product, referenced DER 332) was purified by recrystallization from acetone-methanol (m.p. 42°C). Its equivalent weight in epoxide was determined by ^1H NMR spectroscopic titration⁶ by using 1,1,2,2-tetrachloroethane as an internal standard. The measured value for purified DGEBA was 171, for a theoretical value of 170. DDS was purified by recrystallization from ethanol-water.

Dialkyl(or Aryl) Phosphates

Phosphoric acid (PA) (Janssen) was used as received. Dibutyl phosphate (DBP) (Fluka; purity > 97%) was distilled before use.

Synthesis of Diethyl Phosphate (DEP). The chloride derivative (diethyl chlorophosphate) was introduced onto an excess of distilled water, and the solution

Table I DGEBA Chemical Modification by Dialkyl(or Aryl) Phosphates

Dialkyl(or Aryl) Phosphate	DGEBA Oxirane Conversion (%)					
	Oxiranes Converted		Oxiranes Converted		Oxiranes Converted	
	Into Phosphorus Units ^a (%)	Oxiranes Really Consumed ^b (%)	Into Phosphorus Units ^a (%)	Oxiranes Really Consumed ^b (%)	Into Phosphorus Units ^a (%)	Oxiranes Really Consumed ^b (%)
DMP	5.0	5.3	10.0	11.6	20.0	23.5
DEP	5.0	5.9	10.0	12.7	20.0	23.2
DBP	5.0	5.4	10.0	12.8	20.0	23.5
DPP			10.0	10.4		
PA			10.0	10.0		

^a These agree with a modification of X% of the DGEBA oxiranes by dialkyl(or aryl) phosphate.

^b Determinated from ^1H NMR spectrum.

Table II DGEBA Chemical Modification by Phosphoric Acid Derivatives: Oxirane Transformation in Relation to the Dialkyl(or Aryl) Phosphate

Dialkyl(or Aryl) Phosphate	DGEBA Oxirane Conversion (%)	Oxirane Transformation ^a (%)		
		β -hydroxyphosphate	Dioxaphospholane	Ether
DMP	5.3	82.8	3.1	14.1
DMP	11.6	85.3	3.2	11.5
DMP	23.5	83.2	2.7	14.1
DEP	5.9	83.6	1.3	15.1
DEP	12.7	85.5	0.9	13.6
DEP	23.2	84.5	1.8	13.7
DBP	5.4	85.9	0.9	13.2
DBP	12.8	86.0	0.9	13.1
DBP	23.5	84.8	1.4	13.8
DPP	10.4	88.9	8.3	2.8

^a Determinated from ¹H NMR spectrum.

was stirred for 1 h. The aqueous phase was extracted with dichloromethane, then the organic solution was dried on anhydrous sodium sulfate. After filtration and removing the dichloromethane, diethyl phosphate was distilled under reduced pressure (b.p. at 0.3 mm Hg = 36–37°C).

Synthesis of Dimethyl Phosphate (DMP). The chloride derivative (dimethyl chlorophosphate), which was prepared by phosphorus oxychloride diesterification using methanol (slow addition of two moles of methanol on one of POCl₃ at 0°C; a dry air stream was passed through the solution to extract the formed HCl), was transformed into its acid derivative by using the same procedure as described above for the diethyl phosphate synthesis.

Synthesis of Diphenyl Phosphate (DPP). The chloride derivative (diphenyl chlorophosphate) was hydrolyzed for 12 h at room temperature into an excess of distilled water. The aqueous phase was extracted with dichloromethane, then the organic phase was dried on anhydrous sodium sulfate. After filtration and dichloromethane removing, the product was crystallized. The diphenyl phosphate acid was purified by recrystallization from hexane (m.p. = 59°C).

Partial Chemical Modification of DGEBA by Dialkyl(or Aryl) Phosphate

The chemical modification was carried out in relation to the organophosphorus reagent.

Table III Phosphorus Contents in Epoxy–Amine Resin Specimens Prepared From the Couple: DGEBA Chemically Modified by Dialkyl(or Aryl) Phosphate/DDS

Dialkyl(or Aryl) Phosphate	DGEBA Modification Yields (%/Oxirane Rings)					
	5.0		10.0		20.0	
	Theoretical Phosphorus Content (%)	Real Phosphorus Content ^a (%)	Theoretical Phosphorus Content (%)	Real Phosphorus Content ^a (%)	Theoretical Phosphorus Content (%)	Real Phosphorus Content ^a (%)
DMP	0.65	0.68	1.31	1.34	2.50	2.46
DEP	0.66	0.64	1.29	1.24	2.49	2.43
DBP	0.65	0.68	1.27	1.33	2.39	2.36
DPP			1.15	1.19		
PA			0.72	0.75		

^a Determinated by elemental analysis.

Table IV Phosphorus Contents in Epoxy–Amine Resin Specimens, Including Trialkyl(or Aryl) Phosphate, as Additives (10 mol % in Relation to DGEBA Diglycidyl Groups)

Trialkyl(or Aryl) Phosphate	TMP (%)	TEP (%)	TBP (%)	TPP (%)
Theoretical phosphorus content	1.26	1.23	1.20	1.17
Real phosphorus content ^a	1.28	1.24	1.17	1.22

^a Determinated by elemental analysis.

Dialkyl Phosphates

64.7 mmol (22 g) of DGEBA and the dialkyl phosphate (predetermined amount in relation to the wished percentage of modification → 5%, 6.5 mmol; 10%, 12.9 mmol; 20%, 25.9 mmol) were introduced into a screw-capped tube, and the mix was vigorously stirred for 5 h into an oil bath thermostated at 50°C. At the end, the product was controlled by ¹H and ³¹P NMR, in view to determine the real modification yield.

Diphenyl Phosphate

73.5 mmol (25 g) of DGEBA and 14.7 mmol (3.7 g) of diphenyl phosphate (theoretical percentage of modification: 10%) were placed into an Erlenmeyer flask and dissolved in 200 mL of acetone. The mix was stirred at room temperature for 20 h. Then, acetone was extracted by using a rotary evaporator, and modified DGEBA was finally dried at 60°C *in vacuo*. At the end, the product was analyzed by ¹H and ³¹P NMR, and the real modification yield was determined.

Phosphoric Acid (PA)

Because the reactivity of its third POH acid function is much lower than the two first ones, phosphoric acid was considered as a bifunctional reagent. So, according to this remark, the proportions used to prepare a 10% modified DGEBA resin were as follows: 73.5 ml (25 g) of DGEBA and 7.3 mmol (0.7

g) of PA. The reaction was carried out in acetone as above.

Preparation of Epoxy Resin Specimens

Resins First Modified by the Dialkyl(or Aryl) Phosphates

22 g of the dialkyl(or aryl) phosphate modified DGEBA were placed into an Erlenmeyer flask and magnetically stirred into an oil bath thermostated at 135°C. Then, DDS in quantity depending on the residual epoxides (one primary amine function for two residual oxirane functions from the modified DGEBA) was slowly added. Stirring was maintained until the mix became homogeneous. Then, the blend was casted into a TeflonTM mold so as to prepare specimens 126 × 6 × 5 mm (characteristics of specimen for LOI measures), and curing was achieved at 180°C for 3 h in an oven. Specimens were demolded when warm.

Resins Containing Trialkyl(or Aryl) Phosphates as Additives

The procedure was the same as above. 64.7 mmol (22 g) of DGEBA, 12.9 mmol of trialkyl(or aryl) phosphate, and 32.3 mmol (8 g) of DDS were initially used to prepare epoxy resin containing 10% of trialkyl(or aryl) phosphate.

Table V *T_g* Values for the Different DGEBA/DDS Resin Specimens

Sample	DGEBA/DDS Reference Sample	Organophosphate in the DGEBA/DDS Thermosetted Resin								
		Chemically Bonded							Additive	
		DMP 10%	DEP 10%	DBP			DPP 10%	PA 10%	TMP 10%	TPP 10%
				5%	10%	20%				
<i>T_g</i> (°C)	184	142	125	140	119	104	190	97	143	144

Table VI Values of LOI Measurements for the Different DGEBA/DDS Resin Specimens

Sample	DGEBA/DDS Reference Sample	Organophosphate in the Thermosetted Resin			
		Chemically Bonded			Additive
		DGEBA/ 10% DAP ^a /DDS	DGEBA/ 10% DPP/DDS	DGEBA/ 10% PA/DDS	DGEBA/ 10% TPP/DDS
LOI values	28	28	32	30	31

^a DAP = DMP, DEP, or DBP.

Characterisation of Products

NMR Spectroscopy

¹H NMR spectra were recorded on a Fourier transform spectrometer, Bruker AC 400, in CDCl₃ solution, using tetramethylsilane (TMS) as an internal standard. ³¹P NMR spectra were recorded on Bruker AC 400 Fourier transform spectrometer in CDCl₃ solution, using phosphoric acid as an external standard.

Glass Transition Temperatures

The glass transition temperatures T_g were determined using a Perkin-Elmer DCS 7 apparatus. All measurements were made in nitrogen at a heating rate of 20°C/min on samples weighing about 15 mg. T_g was taken at the inflexion point of the curve.

Thermogravimetric Analysis

The thermogravimetric analyses were performed in air using a TGA 7 Perkin-Elmer analyzer, at a heating rate of 20°C/min from 40 to 800°C. The air flow rate (compressed air) was 50 ml/min.

Limiting Oxygen Index

Oxygen index measurements were performed using a AIS apparatus with a magnetodynamic oxygen analyzer, according to the ASTM D-2863-70 specification. Both oxygen and nitrogen were connected to the equipment through pressure regulators (about 2 bars). Predetermined O₂/N₂ atmospheres were continuously sent through the combustion chamber. Test specimens (126 × 6 × 5 mm) were clamped in the holder vertically in the approximate center of the combustion column with the top of the specimen

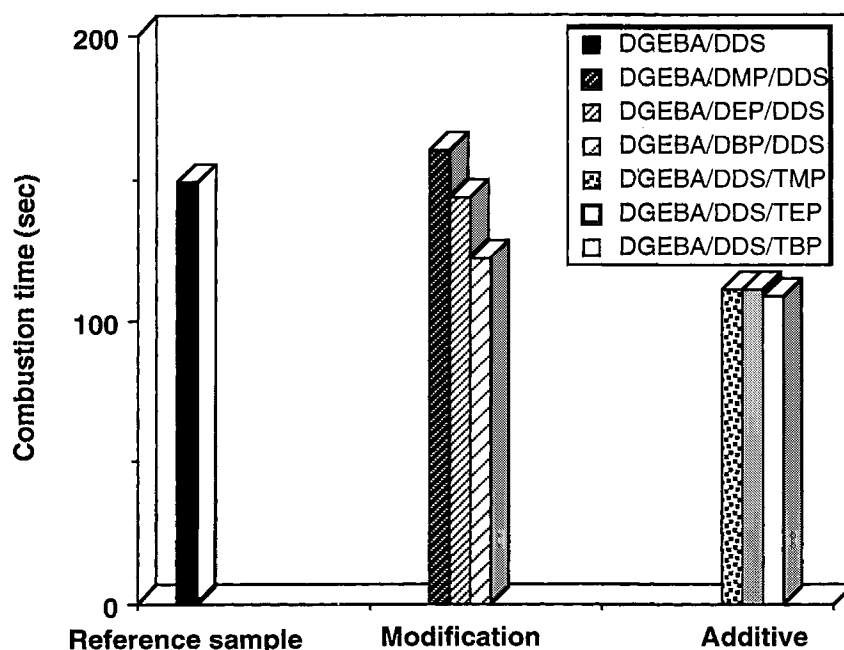


Figure 2 Specimen combustion times in a 28% oxygen atmosphere.

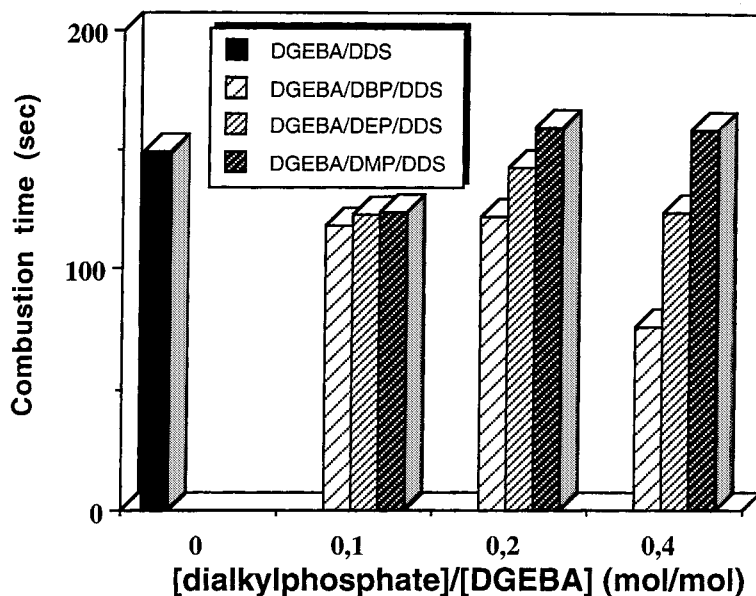


Figure 3 Influence of the concentration in dialkyl phosphate groups.

at least 40 mm below the open column. The top of the specimen was ignited using a butane gas burner so that the specimen was well lit and the entire top was burning.

In the LOI test, the relative flammability of the specimen was determined by measuring the minimum concentration of oxygen, in a flowing oxygen/nitrogen atmosphere (gas flow: 17 L/min), that will just support flaming combustion of the specimen: it corresponds to the minimum concentration of oxygen in the mixture just necessary so that the specimen burns during at least 3 min, or over a length of 50 mm.

To compare the flammability behaviors of the different samples, advancement of the flame downwards was also measured in seconds over a 3 cm length.

Elemental analyses were made by the Service Central d'Analyse of CNRS (Vernaison, France).

RESULTS AND DISCUSSION

Partial Chemical Modification of DGEBA by Dialkyl(or Aryl) Phosphate

The partial chemical modification of DGEBA by dialkyl(or aryl) phosphates was realized according to the optimized conditions selected previously.⁷ DGEBA, partially modified at 5, 10, and 20%, were prepared by reaction with the different dialkyl(or aryl) phosphates. The reagent molar ratios used

were, respectively, as follows [dialkyl(or aryl) phosphate]/[DGEBA] = 0.1, 0.2, and 0.4. Reactions were carried out in the melt (dialkyl phosphates) or in acetone (diphenyl phosphate and phosphoric acid), at 50°C for 5 h. Each modified DGEBA was controlled by ³¹P NMR to verify the completion of the reaction and by ¹H NMR to determine the real chemical modification yield by comparison of the aromatic hydrogen signal area with that of the signal corresponding to hydrogens from residual oxirane rings (Table I).

It is important to note that, during the partial modification process, the dialkyl(or aryl) phosphate reagent is completely consumed, leading to a modified DGEBA bearing practically two categories of functional groups: organophosphorus groups resulting from the addition of the dialkyl(or aryl) phosphate reagent onto oxirane rings (2 β -hydroxyphosphate regioisomers coming from 1 : 1 addition and a dioxaphospholane addend), and residual epoxides. The part of initial oxiranes, which is transformed into ether structures by reaction onto hydroxyle groups, is low (Table II). The quasi-absence of secondary reactions is important to allow to the network building by reaction of residual epoxides with the hardener.

Preparation of Epoxy-Amine Resin Specimens

Cross-linking of modified epoxy resins was achieved by thermal method using 4,4'-diaminodiphenylsul-

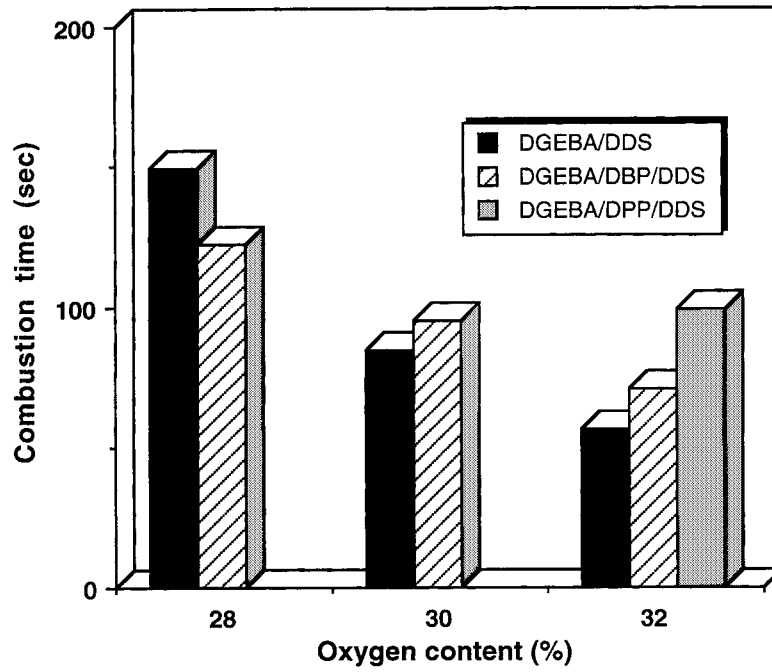


Figure 4 Evolution of combustion times of the specimen in function of the atmosphere composition.

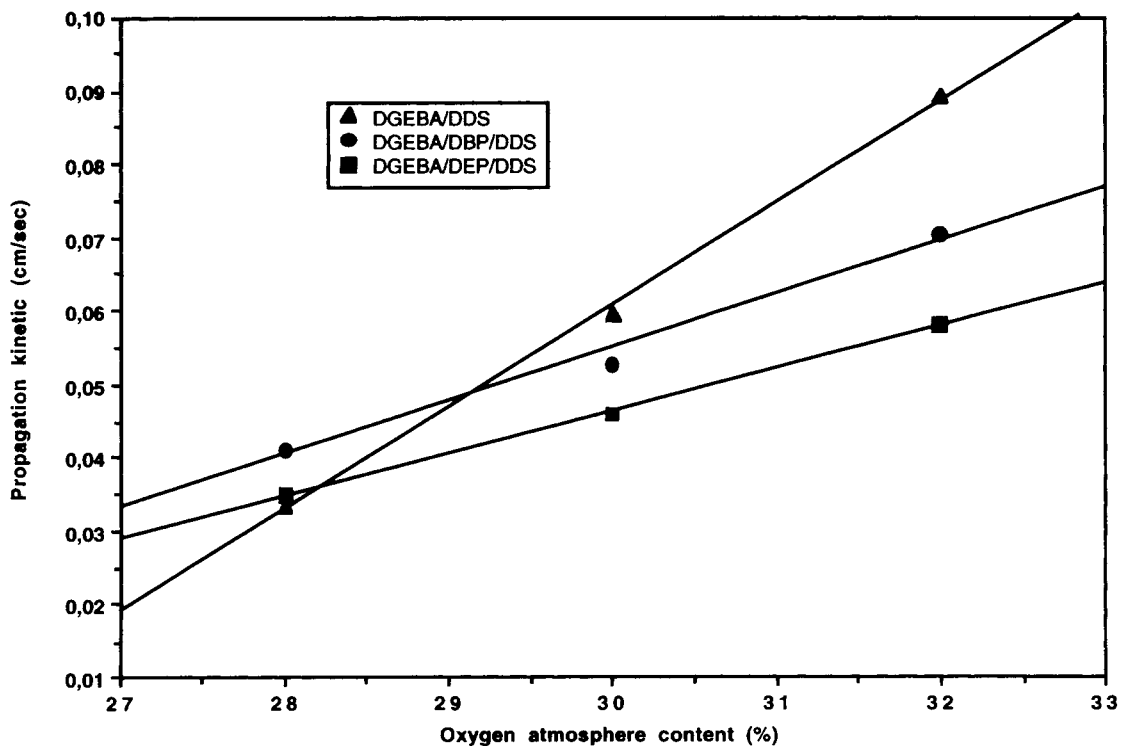


Figure 5 Flame propagation kinetics versus oxygen atmosphere concentration.

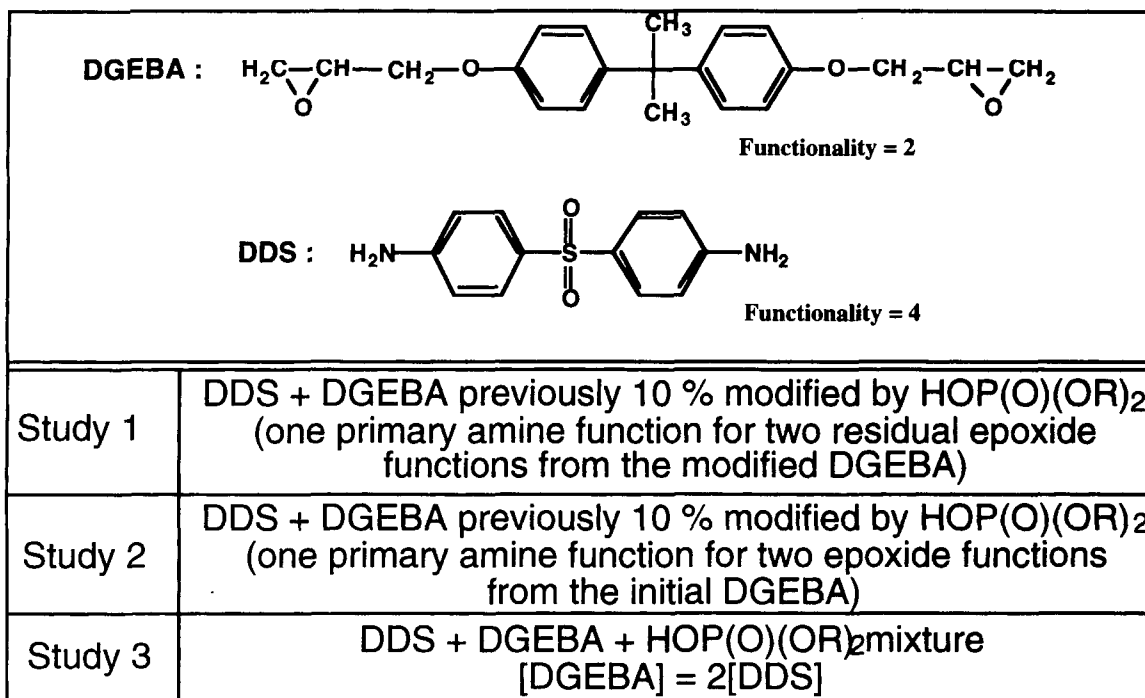


Figure 6 Formulations used to study the influence of DDS concentration (studies 1 and 2) and of the conditions of the chemical modification carrying out (realized before or during the curing; studies 2 and 3).

fone (DDS) as a hardener. Two sorts of specimens were prepared.

- Specimens containing phosphate compounds as additives: trimethyl phosphate (TMP), triethyl phosphate (TEP), tributyl phosphate (TBP), and triphenyl phosphate (TPP).
- Specimens including chemically bonded organophosphate groups onto the epoxy-amine resin backbone.

DGEBA-DDS resin specimens were also prepared as a reference sample for a further comparison of flammability and thermal behaviors.

Theoretical and real contents of phosphorus in the specimens are summarized in Tables III and IV. Phosphorus contents in the resultant modified epoxy-amine resins were approximately 0.7, 1.3, and 2.4 for epoxy-amine resins, respectively, prepared from epoxy resins modified at 5, 10, and 20% by dialkyl(or aryl) phosphate.

In order to examine the effects of organophosphate grafts on the DGEBA/DDS network, the glass transition temperatures (T_g) of DGEBA/DDS chemically modified by dialkyl(or aryl) phosphates were compared with those of DGEBA/DDS resins

containing trialkyl(or aryl) phosphates as additives (Table V).

Thermosetted epoxy-amine resins chemically modified by dialkyl phosphates bring out a decrease in T_g , which is all the more important, so the n -alkylester is long. By increasing the n -alkylester length, the free volume in the network is increased, and so its density decreases.⁸ Moreover, because of their great flexibility, n -alkylester substituents of phosphate grafts act also as a plasticizer, and, the longer their length, the higher the resultant plasticizing effect.

An opposite effect is noticed with the thermosetted resin bearing diphenyl phosphate grafts. Its T_g is higher than that of the reference sample. This result is probably explained by the rigidity brought out by the phenyl groups, but also by the weaker concentration of ether bonds in the network compared to the dialkyl phosphates modified resins, because it was previously shown that the presence of more flexible ether bonds tends to decrease the network density and the T_g .⁹

T_g value of thermosetted resin 10% modified by phosphoric acid is very low. Because the addition of phosphoric acid onto oxirane DGEBA is not accompanied by ether bond formation and because the phosphorus reagent is sufficiently small, this result

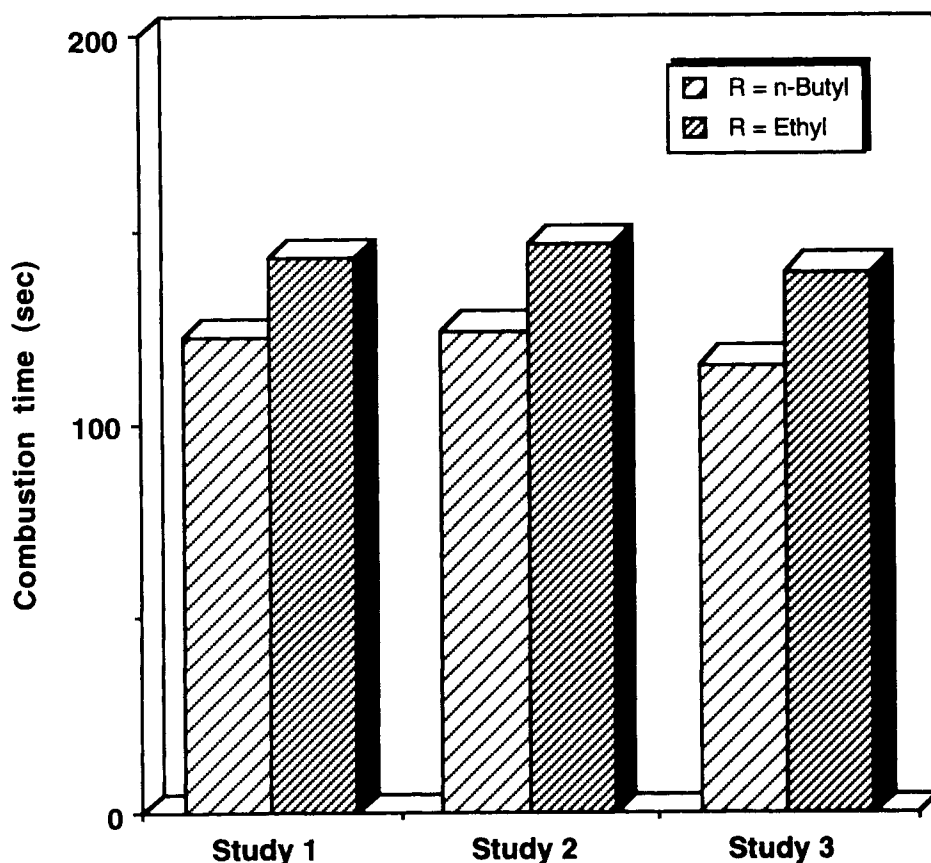


Figure 7 Influence of experimental conditions.

is surprising. Only the highest flexibility of phosphate bonds compared to that of amine bonds can explain this result.

Evolution of T_g in relation to concentration of phosphate grafts was also studied in the case of thermosetted resins modified by DBP. The higher the concentration in dibutyl phosphate grafts, the lower the T_g value (increase of the free volume). This result is in accordance with the plasticizing effect induced by the *n*-alkyl substituents of phosphate grafts.

The comparison of these T_g measures with those of thermosetted epoxy-amine resins containing additives of structure similar to the organophosphate grafts was realized only on two cases (Table V). In the case of methylphosphate derivatives, the same values of T_g were noticed, which proves that cross-link density does not effect the T_g . On the other hand, the important decrease of T_g value observed in the case of DGEBA/DDS incorporating triphenyl phosphate additive in relation to that of the DPP modified resin is difficult to understand.

Evaluation of Thermal and Flammability Behaviors of the Samples: Limiting Oxygen Index

Flammability behaviors of phosphorus modified DGEBA/DDS specimens were studied as described in experimental part. The first time, oxygen index measures were realized but, to best compare the inflammability behaviors of the different samples, the advancement of the flame downwards was also measured on a 3 cm length. In all cases, results were compared to a thermosetted DGEBA/DDS reference specimen.

LOI values were measured for specimens prepared from DGEBA 10% modified by dialkyl(or aryl) phosphates (Table VI). They show that fire-retardation of epoxyamine resins does not seem to be improved by chemical introduction of dialkyl phosphate grafts. On the other hand, phenyl phosphate derivatives lead to a good increase of their fire-retardation (LOI > 28): the comparison with the LOI value of a DGEBA/DDS specimen containing triphenyl phosphate as additive proves that the best fire behavior is achieved when phenyl phosphate

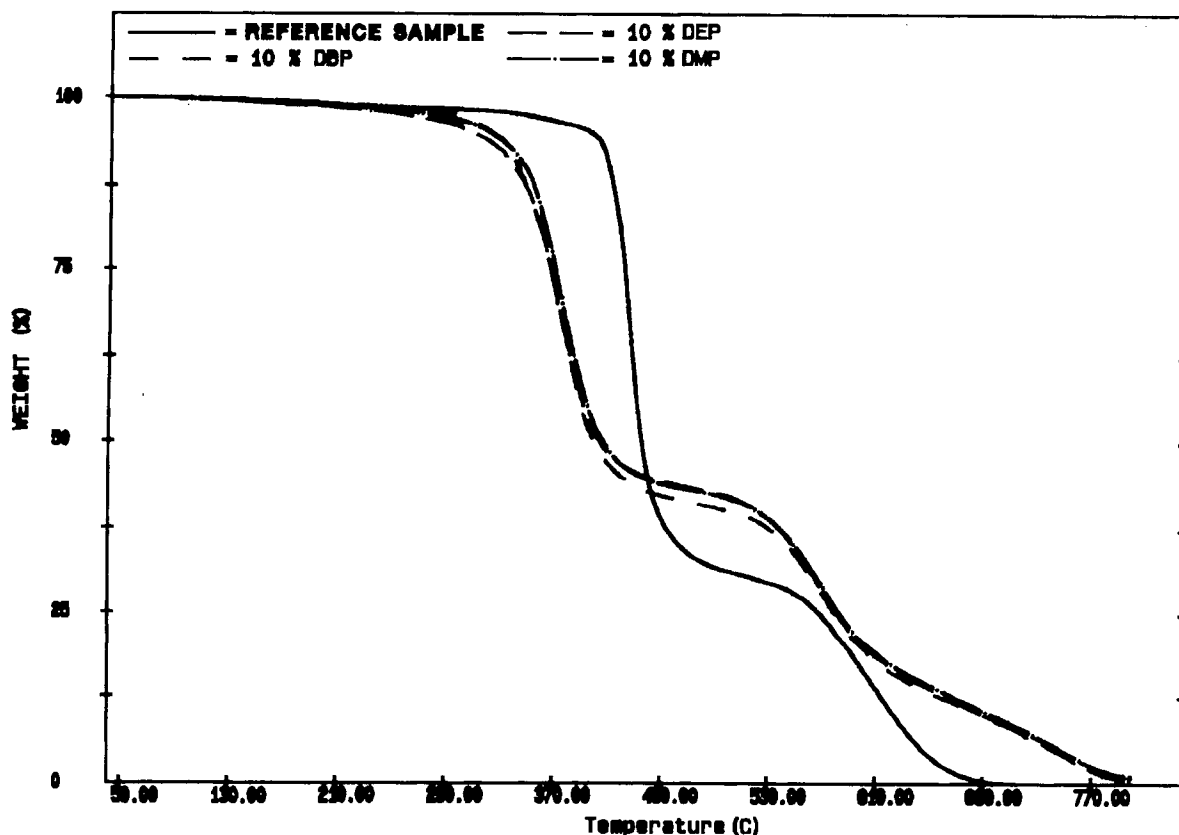


Figure 8 TGA curves of modified resins: influence of the nature of the dialkyl (or aryl) phosphate groups.

molecules are chemically bonded onto the resin backbone.

In order to get more details about the fire behavior of DGEBA/DDS resins modified by dialkyl phosphates, the combustion times of specimens prepared from DGEBA 10% modified by dialkyl phosphates were measured in a 28% oxygen atmosphere and respectively compared with those of corresponding specimens containing the same concentrations of trialkyl phosphate as additive (Table IV; Fig. 2). They show that the fire behavior of crosslinked DGEBA/DDS resins is not improved by chemical incorporation of dialkyl phosphate groups onto the epoxy resin backbone (except for the dimethyl phosphate derivative) but is always greater than those of the resins containing corresponding trialkyl phosphate additives. An increase of the *n*-alkyl chain length in dialkyl phosphate grafts reduces the combustion time, therefore it feeds the combustion and increases the volume of intumescent char. In all cases, combustion of DGEBA/DDS modified systems is accompanied by formation of intumescent char, whereas DGEBA/DDS reference sample and

specimens containing trialkyl phosphates burn without formation of intumescent char.

The fire behavior of the samples by measuring combustion times in relation to dialkyl phosphate graft concentrations is given in Figure 3. Results are surprising because increase of the concentration of the chemically bonded dialkyl phosphate groups onto the resin and increase of alkyl chain length feed the combustion and improve expansion of the intumescent char. However, at low concentration of dialkyl phosphate groups (molar ratio [DAP]/[DGEBA] = 0.1), the combustion times are the same whatever the length of the alkyl ester chains. Whatever the dialkyl phosphate graft may be, optimum fire-retardation is obtained with a specimen prepared from 10% modified DGEBA.

In relation with DGEBA/DDS reference sample, only specimens incorporating DGEBA modified more than 10% by DMP show a better fire behavior.

The fire-resistance behaviors of the samples by measuring combustion times in different atmospheres with varying oxygen content are given in Figure 4. In a 28% oxygen atmosphere content, the

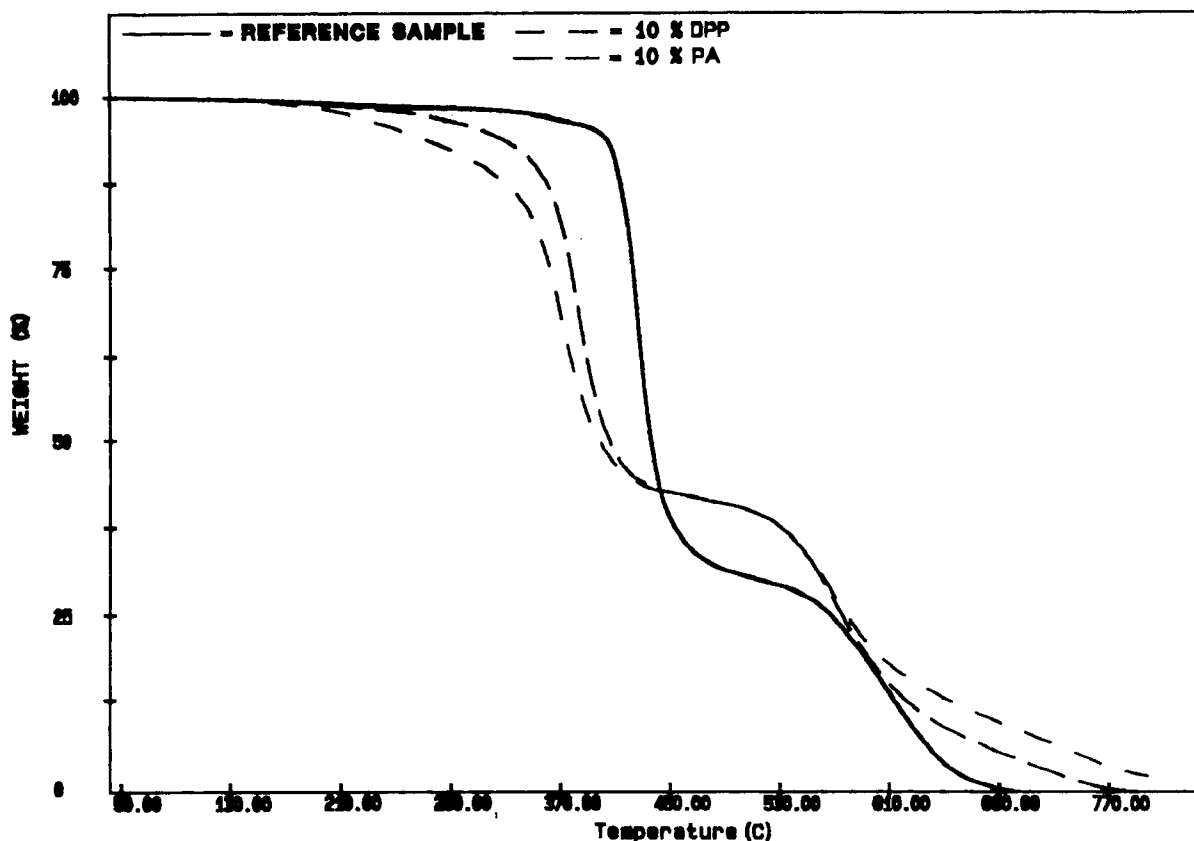


Figure 9 TGA curves of modified resins: influence of the nature of the dialkyl (or aryl) phosphate groups.

DGEBA/DDS reference sample burns easier than specimens prepared from DGEBA 10% modified by DBP or DEP, but with more difficulties than that bearing DMP. On the other hand, as soon as oxygen atmosphere content oversteps 30%, a surprising change is noticed because combustion times of specimens 10% modified by DBP or DEP become, as for DMP, longer than that of DGEBA/DDS reference specimen. With specimens 10% modified by DPP, an autoextinguishment is observed in lower oxygen atmosphere contents (<32%).

The representation of flame propagation kinetic (time taken by the flame front to burn a 5 cm specimen length) versus oxygen atmosphere content (Fig. 5) shows for each type of specimen a linear increase of the flame propagation kinetic in accordance with the oxygen atmosphere content. On the other hand, the straight line slope decreases according to the following: DGEBA/DDS reference sample > DGEBA/DBP/DDS > DGEBA/DEP/DDS. The phosphorus-modified DGEBA/DDS resins, from the burning point of view, are less sensitive to the atmosphere change than the reference sample because the foamed carbonaceous char formed onto the

polymer surface limits the heat transfer to the bulk and slows down the diffusion of volatile products.

Because the fire behavior measures were carried out on specimens, including DDS quantities determined in relation to the residual glycidyle oxirane of the phosphate grafted DGEBA resins (one primary amine function for two residual epoxide functions from the modified DGEBA), the DDS proportion in the DGEBA/DDS reference sample is not the same as in the modified ones. So it was important to verify the influence of DDS concentration on the DGEBA/DDS system fire-retardation. In this aim, specimens including DGEBA 10% modified by dialkyl phosphates were prepared by using a half molecular quantity of DDS in relation to initial DGEBA (studies 1 and 2; Fig. 6), and their combustion times were compared to those of the previous specimens. Results summarized in Figure 7 show that fire-retardation is not influenced by the DDS concentration in the resin.

A further study was realized to verify if the fire behavior of DGEBA/DDS chemically modified by dialkyl phosphates could be influenced by the chemical modification conditions (studies 2 and 3; Fig.

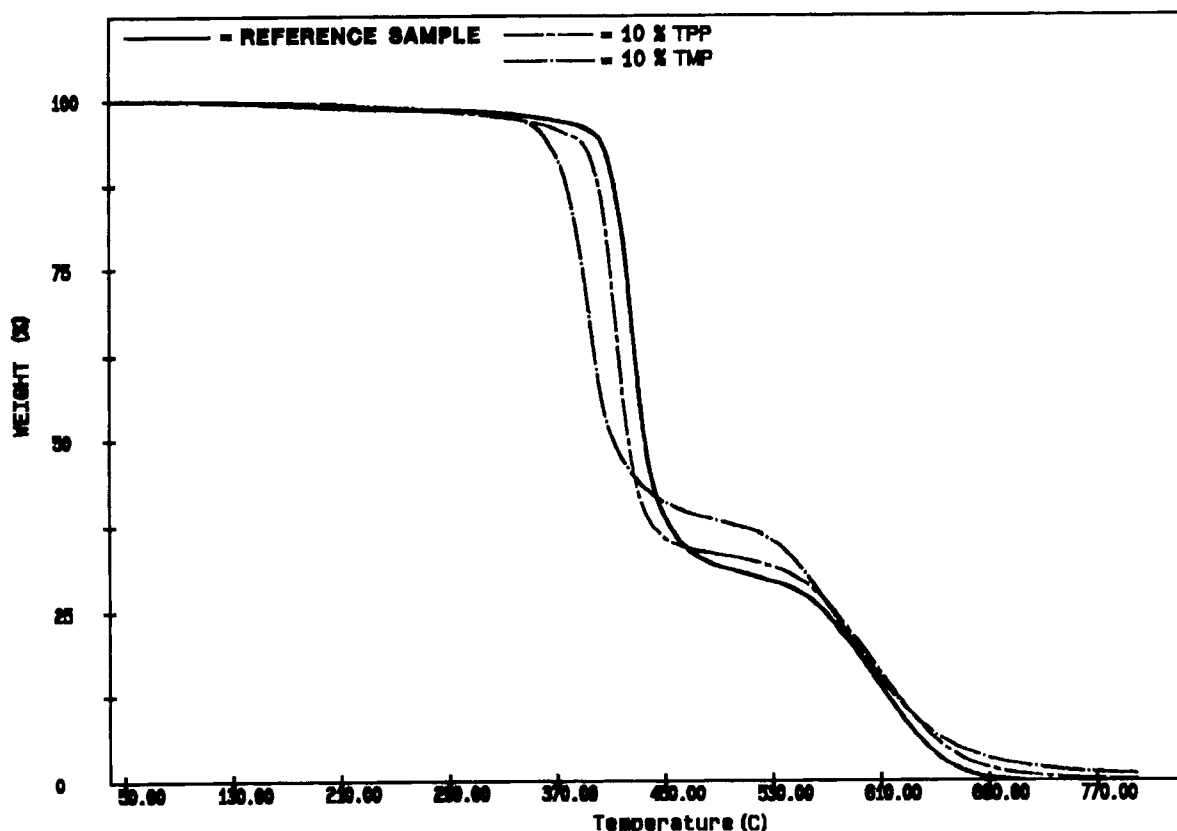


Figure 10 TGA curves of nonmodified resins, including trialkyl (or aryl) phosphates, as additives.

6). Combustion times of specimens prepared from DGEBA previously modified by dialkyl phosphate reagent were compared with those of corresponding another one chemically modified during the curing (Fig. 7). The similar combustion times noticed in relation with the used phosphorus reagent proves that chemical modification of DGEBA can be carried out *in situ* during the curing of epoxy resins without change in the fire behavior.

Thermogravimetric Studies

Thermogravimetric analyses of the epoxy-amine resins were carried out in air for all the samples.

Thermograms of thermosetted resins prepared from DGEBA 10% modified by dialkyl (or aryl) phosphates are superimposed on Figures 8 and 9. Decomposition curves are strictly the same whatever the dialkyl (or aryl) phosphate graft may be. In contrast to the DGEBA/DDS reference sample (two decomposition stages), curves show that it exists three decomposition stages for all the samples.

The first decomposition appears at the same temperature (345°C), whatever the dialkyl (or aryl)

phosphate grafts may be. It is lower than that of the DGEBA/DDS reference sample, but the mass loss during this first decomposition stage is also smaller (57%, against 69% for the reference sample). The fact that the first decomposition temperatures are lower than that of DGEBA/DDS reference sample is characteristic of intumescent char formation, which is in accordance with the observed phenomena.^{10,11}

Above 700°C, the residual mass is around 6 to 10%; while in the case of the DGEBA/DDS reference sample, the decomposition is entire. This can be assigned to the protection of the material from contact with the surrounding air by the intumescent charred mass formed during burning.

On the contrary to modified samples, including chemically bonded dialkyl (or aryl) phosphate groups, samples containing trialkyl phosphate additives show only two decomposition stages (Fig. 10). The first and second decomposition temperatures are almost close to that of DGEBA/DDS reference sample. The mass losses are also higher than those of modified DGEBA/DDS resins. The mass losses after the first decomposition stage are also more important than in the

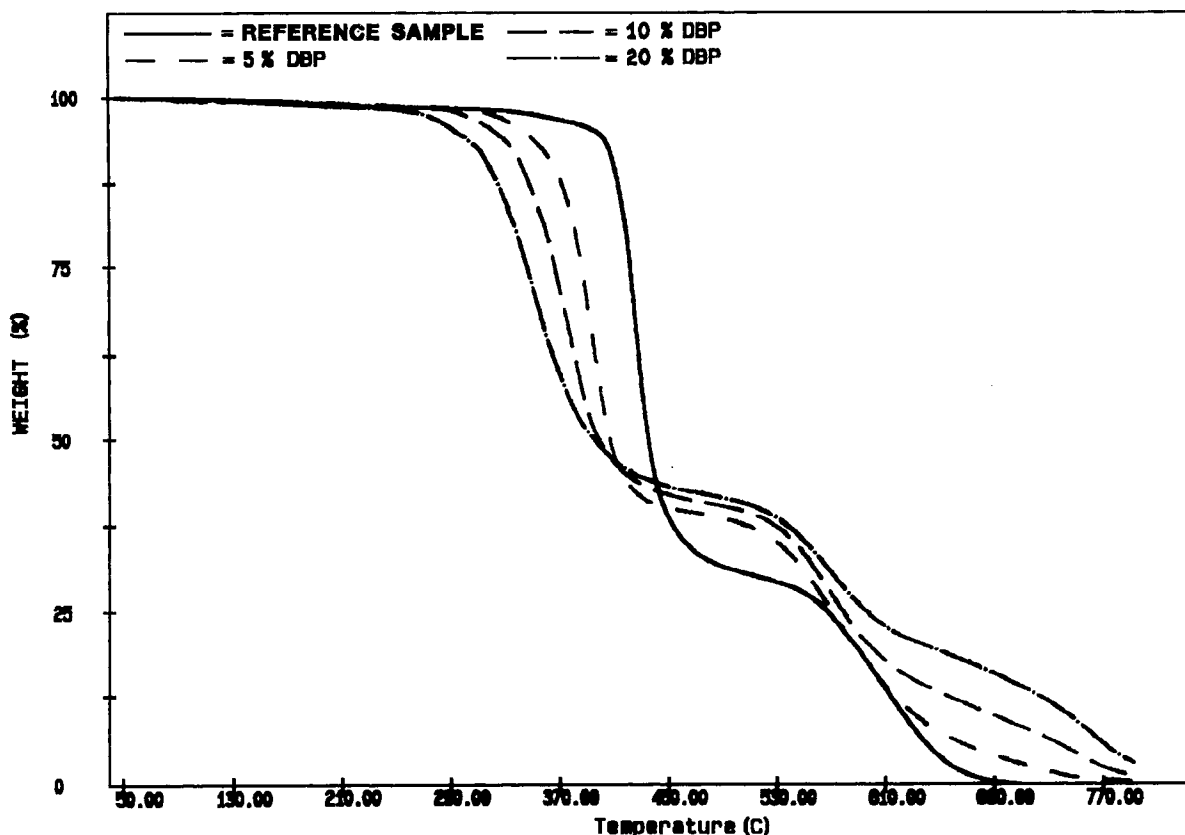


Figure 11 TGA curves of modified resins: influence of the concentration in dibutyl phosphate groups.

case of phosphorus modified resins (62 to 67%, against 57% for the phosphate grafted resins).

The relationship between thermal decomposition and dialkyl phosphate graft concentration in the thermosetted resins is shown in Figures 11 and 12. By increasing the dialkyl (or aryl) phosphate group concentration, the first decomposition temperature is shifted to lower temperature with a mass loss decrease; the second decomposition takes place more slowly, and the residual mass at 700°C is more important.

CONCLUSION

The aim of the research was to study the fire behavior of DGEBA/DDS resins partially chemically modified by dialkyl (or aryl) phosphate reagents.

The best fire-retardations were obtained with thermosetted resins bearing chemically bonded diphenyl phosphate grafts on their backbone (LOI value = 32). Moreover, they show upper fire-retardant behaviors than the nonchemically modified DGEBA/DDS ones, even resins incorporating tri-

phenyl phosphate as additive. More generally, DGEBA/DDS resins chemically modified by dialkyl (or aryl) phosphates show better fire-resistance properties compared to that containing trialkyl (or aryl) phosphate additives.

In contrast to the nonchemically modified DGEBA/DDS [with or without trialkyl (or aryl) phosphate as additive], combustion of modified DGEBA/DDS resins is accompanied by formation of intumescent char.

The decomposition curves of thermosetted resins chemically modified by dialkyl (or aryl) phosphates are strictly the same whatever the dialkyl (or aryl) phosphate graft may be. Their first decomposition temperature is lower than that of the DGEBA/DDS reference sample. This is characteristic of an intumescent fireproofing system,^{10,11} which has been observed during the flammability tests. On the other hand, their entire decomposition is reached at a higher temperature (around 800°C, against 690°C for the DGEBA/DDS reference sample).

DGEBA chemical modification by dialkyl (or aryl) phosphates can be carried out directly during the curing stage after simultaneous mixing of the

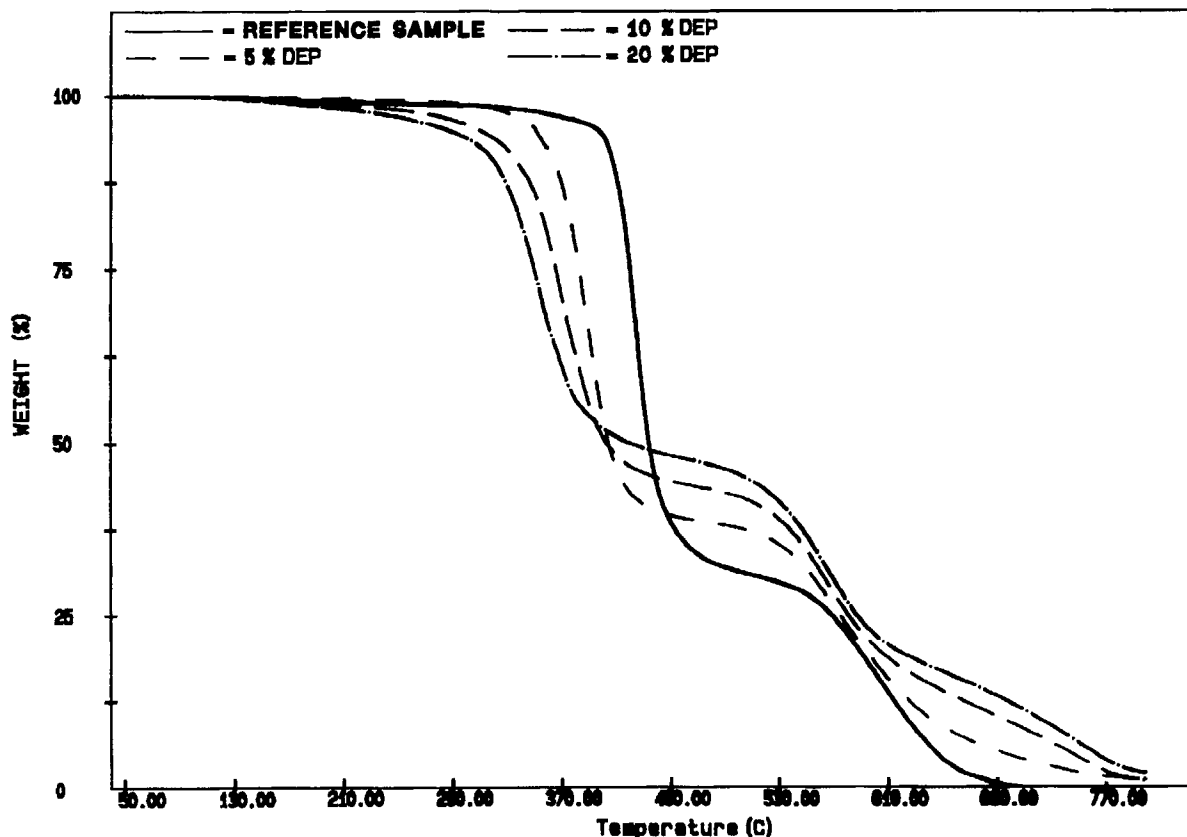


Figure 12 TGA curves of modified resins: influence of the concentration in diethyl phosphate groups.

three components [DDS, DGEBA, and dialkyl (or aryl) phosphate], without consequence on the fire-retardation behaviors.

REFERENCES

1. G. Camino, L. Costa, and G. Martinasso, *Polym. Deg. Stab.*, **23**, 359 (1989).
2. S. Maiti, S. Banerjee, and S. K. Palit, *Prog. Polym. Sci.*, **18**, 227 (1993).
3. R. M. Aseeva and G. E. Zaikov, *Adv. Polym. Sci.*, **51**, 171 (1984).
4. E. D. Weil, R. H. Hansen, and N. Patel, *Am. Chem. Soc., Symp. Ser.*, **425**, 97 (1990).
5. H. Sivriev, S. Gorgiev, and G. Borissov, *Eur. Polym. J.*, **26**, 73 (1990).
6. J. G. Dorsey, G. F. Dorsey, A. C. Rutenberg, and L. A. Green, *Anal. Chem.*, **49**, 1144 (1977).
7. D. Derouet, F. Morvan, and J. C. Brosse, to appear.
8. V. Bellenger, E. Morel, and J. Verdu, *J. Mat. Sci.*, **23**, 4244 (1988).
9. A. Sabra, T. M. Lam, J. P. Pascault, M. F. Grenier-Loustalot, and P. Grenier, *Polymer*, **28**, 1030 (1987).
10. G. Camino, L. Costa, and L. Trossarelli, *Polym. Deg. Stab.*, **7**, 25 (1984).
11. R. Delobel, M. Le Bras, N. Ouassou, and F. Alistiqsa, *J. Fire Sci.*, **8**, 85 (1990).

Received February 13, 1996

Accepted June 6, 1996