

Structural Modification of Brominated Epoxy Resins by Reaction with Phosphoric or Poly(phosphoric Acid)

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Synopsis

A modification process of some commercial brominated epoxy resins by reacting them with phosphoric or poly(phosphoric acid) is described. The influence of the reactants ratio on the thermal stability of the modified resins was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The resin obtained from complete esterification of phosphoric acid showed the highest thermal stability. In addition, the resins prepared by reacting phosphoric acid with brominated epoxy resins of different molecular weight were thermally characterized by DSC and TGA. Most of the modified resins were thermally more stable than the corresponding unmodified resins. The chemical reactions that possibly take place during the process are discussed. Furthermore, the structure of the modified resins was investigated by Fourier-transform-infrared (FT-IR) spectroscopy.

INTRODUCTION

The majority of the epoxy resin formulations are considered to have flammability characteristics ranging from slow burning to self-extinguishing. It is possible to produce fire-resistant systems by the use of chlorinated, brominated, or phosphorylated substances. The halogen or phosphorus may be contained in the resin, in the curing agent or modifier, or in an additive specifically designed for epoxy resins. Epoxy resins containing halogen may be prepared from halogenated hydroxy compounds such as tetrabromobisphenol A and tetrachlorobisphenol A. The presence of halogen renders these resins flame-retardant. The ability of the resins to retard or extinguish burning is due to the evolution of hydrogen halide upon decomposition at elevated temperatures. The brominated resins are more effective than those chlorinated and consequently prevailed commercially. The brominated resins are more stable than the chlorinated, but, as soon as the evolution of hydrogen bromide starts, it is faster than that of hydrogen chloride, and the system is more effectively blanketed. A bromine content of 13–15% by weight is required to render an unfilled cured epoxy resin system flame-retardant while in an identical system 26–30% by weight chlorine is necessary to obtain the same result.¹ Brominated epoxy resins are generally

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used in blends with other epoxy resins to confer flame retardancy while maintaining physical properties in applications such as adhesives and laminates.

The present investigation is concerned with a modification of some brominated epoxy resins by reacting with phosphoric or poly(phosphoric acid). The brominated epoxy resins that were structurally modified are commercially available. The reactions of epoxidies with phosphoric acid, phosphorous acid, or phosphorus oxychloride are of interest, since they may lead to the preparation of phosphorus-containing resins.² Several phosphorus-bearing compounds like hydroxy alkylphosphines,³ phosphate and pyrophosphate esters,⁴ phosphonates,^{5,6} complex compounds of boron trifluoride with phosphines,⁷ and dialkyl phosphites⁸ have been proposed as crosslinking agents for epoxy resins. The present investigation aims at incorporating phosphorus in some brominated epoxy resins and at improving not only their thermal stability but also fire resistance.

EXPERIMENTAL

Materials

The diglycidyl ether-type brominated polymeric additives (BPA) were produced by Makhteshim Chemical Works Ltd. They contained 50% aromatically bound bromine and had different molecular weights. The following three BPAs were used as starting materials: F2200 with an epoxy equivalent weight (EEW) 330, F2001P with an EEW 545, and F2300 with an EEW 1850. An aqueous solution 85% of phosphoric acid, poly(phosphoric acid), and triphenyl phosphine of commercial grade were utilized.

General Procedure for Chemical Modification of the Brominated Epoxy Resins

Method A. A stainless steel vessel containing granular BPA was stirred and heated to about 130°C. After melting of BPA, a catalytic amount (0.15% by weight) of pulverized triphenyl phosphine was added under stirring. To the vigorously stirred mixture an appropriate amount of phosphoric or poly(phosphoric acid) was added. An exothermic reaction was observed and the mixture completely solidified after about 15 min. The solid product obtained was subsequently pulverized and heated to 80°C into a vacuum oven overnight. The reaction yield was almost quantitative.

Method B. BPA and phosphoric or poly(phosphoric acid) were placed into a ceramic mill. After rotation of the mill for 2 h, a catalytic amount (0.15% by weight) of triphenyl phosphine was added and rotation was continued for 1 h more to obtain a homogenous mixture. Small batches (about 100 g) of this mixture were heated to 120°C into a vacuum oven for 6–8 h, and the solid product obtained was subsequently pulverized.

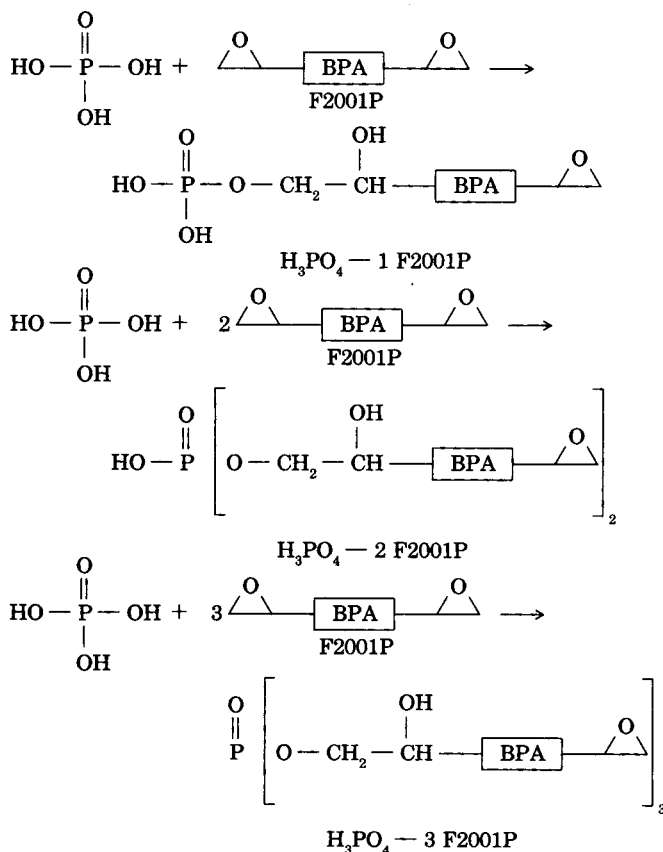
Characterization Methods

DSC and TGA thermograms were run on a DuPont 1090 Thermal Analyzer under nitrogen atmosphere. The experimental conditions were 80 cm³/min N₂ and a heating rate of 20°C/min.

Fourier-transform-infrared spectra were recorded on a Nicolet MX-1 IR spectrometer with KBr pellets.

RESULTS AND DISCUSSION

Various phosphorus- and bromine-containing epoxy resins were prepared by reacting the diglycidyl ether-type brominated polymeric additives (BPA) with phosphoric acid. The influence of the reactants ratio on the thermal stability of the modified resins was at first investigated. The products obtained by reacting F2001P, a BPA with moderate molecular weight, with phosphoric acid under various reactant ratios may be presented as follows:



Throughout the text the epoxy resins obtained are referred to by the symbols shown above.

The reaction may be carried out with or without catalyst. In the present work triphenyl phosphine was utilized as catalyst. The reaction was extremely fast and was complete within a few minutes at 130°C. Side reactions that will be discussed below may lead to a crosslinked system. The rapid crosslinking of epoxy resins occurring in the presence of phosphoric acid is, however, a serious disadvantage from the point of view of composite preparation due to processing difficulties.

Since BPAs have a melting temperature lower than 120°C and they are thermally stable, their reaction with phosphoric acid was carried out in

bulk at temperatures above the melting temperature of the starting material. The water of phosphoric acid solution may hydrolyze the ester P—O—C linkages or react with epoxy groups. Since molecular weight and melt viscosity increase as the reaction progresses, removal of water from the reaction mixture becomes increasingly difficult even under reduced pressure.

The reaction of BPA with phosphoric acid was thermally investigated by DSC. A homogenous mixture of phosphoric acid and resin F2001P (under a mole ratio 1:3) in the presence of a catalytic amount of triphenyl phosphine gave the thermogram b shown in Figure 1. The endotherm at about 60°C corresponds to the melting of F2001P. A broad exothermic peak appears from 70 to 230°C. Since the thermograms of the starting material F2001P as well as of the reaction product do not show exotherm at the same temperature range, the exothermic peak is believed to be due to the reaction heat evolved. The heat of reaction cannot be calculated from the DSC trace because of water evaporation.

The thermal stability of the products obtained by reacting the resin F2001P with phosphoric acid under various reactant ratios was evaluated by DSC and TGA (Figs. 2 and 3). The large exothermic peaks appeared in the DSC thermograms of resins are attributed to pyrolysis as is verified from the corresponding TGA traces. Some thermal characteristics of the resins calculated from their DSC and TGA thermograms are listed in Table I. Specifically, T_1 is the onset temperature, T_2 the temperature corresponding to the exothermic peak position, and ΔH_{pyr} the enthalpic change associated with pyrolysis that was automatically calculated by the thermal analyzer. The polymer decomposition temperature (PDT), the maximum polymer decomposition temperature (PDT_{max}), and the temperature of complete pyrolysis (TCP) are included among the thermogravimetric data. The PDT and TCP were determined from the intersection of the tangent to the steepest portion of the curve with its strain line before and after the polymer degradation, respectively. The PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred.

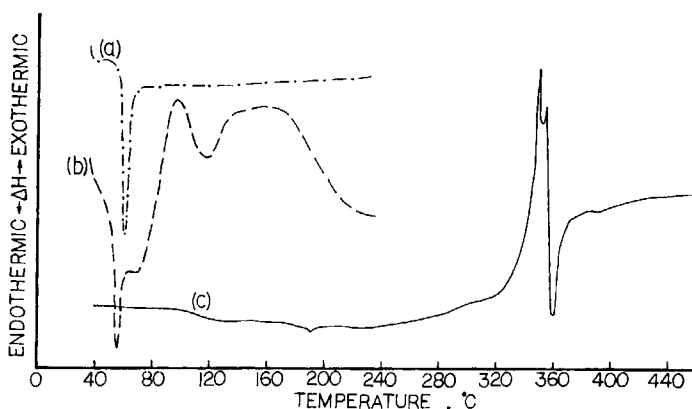


Fig. 1. DSC thermograms in N_2 atmosphere of: (a) resin F2001P; (b) a mixture of H_3PO_4 and F2001P (mole ratio 1:3) in the presence of triphenyl phosphine (0.15% by weight); (c) resin H_3PO_4 -3 F2001P.

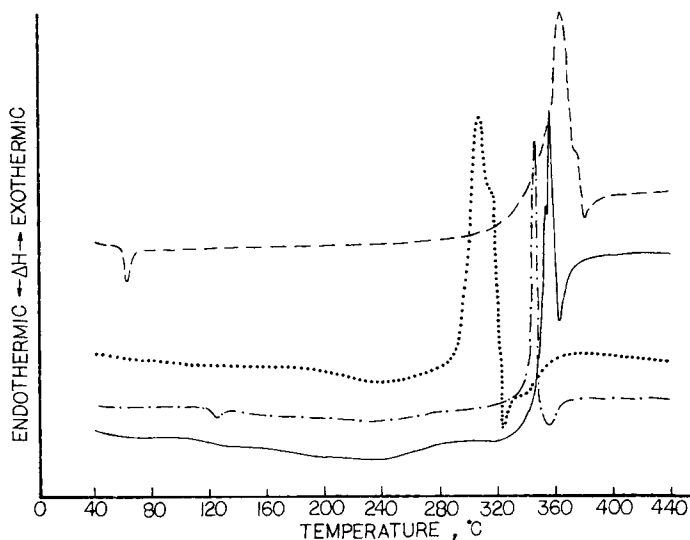
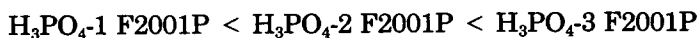


Fig. 2. DSC thermograms in N_2 atmosphere of resins F2001P (- - -), H_3PO_4 -1 F2001P (· · ·), H_3PO_4 -2 F2001P (- · · ·), and H_3PO_4 -3 F2001P (—).

It can be seen that all phosphorylated resins exhibit a T_2 and PDT_{max} lower than those of the control resin F2001P. This suggests that the phosphorus-containing resins are more easily pyrolyzed than the F2001P resin. The P—O—C linkages may undergo thermal cleavage or hydrolysis.

Comparing phosphorylated resins shows that the T_2 and PDT_{max} increase as follows:



Since the molecular weight of the phosphorus-bearing resins follows the same trend, this type of behavior should be attributed to the increased molecular weight. In the partially esterified phosphoric acid the free P—O—H may react with epoxy groups of other molecules, thus reducing the epoxy functionality of the resin or may catalyze the hydrolysis of the P—O—C linkages.

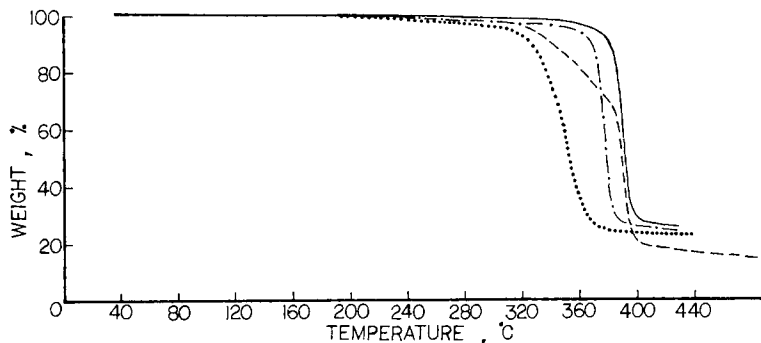


Fig. 3. TGA thermograms in N_2 atmosphere of resins F2001P (- - -), H_3PO_4 -1 F2001P (· · ·), H_3PO_4 -2 F2001P (- · · ·), and H_3PO_4 -3 F2001P (—).

TABLE I
Phosphorus Content and Some Thermal Characteristics of the Resins Obtained by Reacting H_3PO_4 with Resin F2001P under Various Reactant Ratios

Resin	Theoretical phosphorus content (%)	DSC data			TGA data			
		T_1 (°C)	T_2 (°C)	ΔH_{pyr} (J/g)	PDT (°C)	PDT _{max} (°C)	TCP (°C)	Char yield (% at 400°C)
F2001P	0	351	362	118	344	390	418	20
H_3PO_4 -1 F2001P	2.60	296	307	150	321	348	370	24
H_3PO_4 -2 F2001P	1.36	341	345	64	356	377	393	27
H_3PO_4 -3 F2001P	0.92	340	349	67	369	388	406	29

From Table I it can be seen that the ΔH_{pyr} of $\text{H}_3\text{PO}_4\text{-2}$ F2001P is higher than that of $\text{H}_3\text{PO}_4\text{-1}$ F2001P and lower than that of $\text{H}_3\text{PO}_4\text{-3}$ F2001P. The possibility of the partially esterified phosphoric acid to give more side reactions may be responsible for this behavior.

Whereas the resin F2001P shows a relatively low and sharp melting temperature (58–62°C) the phosphorylated resins exhibit a higher and broad melting or softening temperature. The melting or softening temperatures of resins calculated from their DSC traces have as follows: $\text{H}_3\text{PO}_4\text{-1}$ F2001P, 201–277°C; $\text{H}_3\text{PO}_4\text{-2}$ F2001P, 204–276°C; and $\text{H}_3\text{PO}_4\text{-3}$ F2001P, 173–276°C.

The phosphorus-containing resins give a somewhat higher char yield under anaerobic conditions as compared to the control resin F2001P, a fact indicative of the superiority of these resins with respect to flammability. A remarkable property of the BPAs is the high degree of fire resistance. It is reasonable to expect that the combination of phosphorus and bromine to further increase fire resistance of the resins due to synergism of these two elements. From comparing phosphorylated resins it can be seen that the char yield increases slightly with increasing molecular weight of resins although their phosphorus content is reduced.

So far it has been demonstrated that the resin obtained from complete esterification of phosphoric acid exhibits the highest thermal stability. The influence of molecular weight of BPA on the thermal characteristics of the completely esterified phosphoric acid is examined next.

The products prepared by reacting phosphoric acid with each of the resins F2200, F2001P, and F2300 under a mole ratio 1:3 and the same experimental conditions were thermally characterized. Figures 4, 5, and 6 show the DSC and TGA thermograms of these resins as well as of the starting materials in nitrogen atmosphere. Figure 7 shows their isothermal TGA diagrams obtained at 250°C under anaerobic conditions. Some thermal characteristics of the resins calculated from their DSC and TGA traces are summarized in Table II. The DSC thermograms of all starting materials show sharp

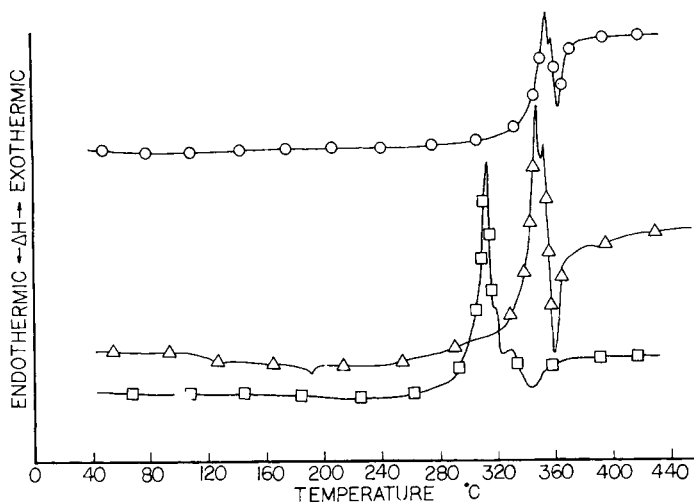


Fig. 4. DSC thermograms in N_2 atmosphere of resins $\text{H}_3\text{PO}_4\text{-3}$ F2200 (—□—), $\text{H}_3\text{PO}_4\text{-3}$ F2001P (—△—), and $\text{H}_3\text{PO}_4\text{-3}$ F2300 (—○—).

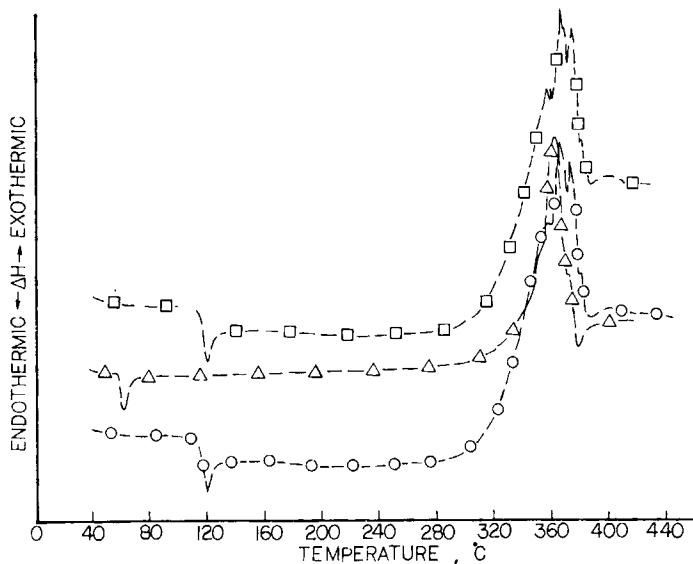


Fig. 5. DSC thermograms in N_2 atmosphere of resins F2200 (-□-), F2001P (-△-), and F2300 (-○-).

endothermic peaks associated with melting. The DSC thermograms of the phosphorus-containing resins, however, do not show definite endotherms but only large exotherms corresponding to pyrolysis. From the DSC and TGA data it is apparent that the thermal stability of the phosphorylated resins increases with increasing molecular weight. It should be noted that the thermal stability of the starting materials follows the same trend. The isothermal TGA diagrams of resins (Fig. 7) very clearly show their degree of thermal stability. It should be emphasized that all phosphorus-containing resins except for H_3PO_4 -3 F2300 show a considerably higher thermal stability as compared to the corresponding starting materials. This is very important from the technological point of view. Since esterification of phosphoric acid increases the molecular weight of BPAs, the improved thermal stability should be attributed to the increased molecular weight. Resin H_3PO_4 -3 F2300, however, exhibits a lower thermal stability as compared to

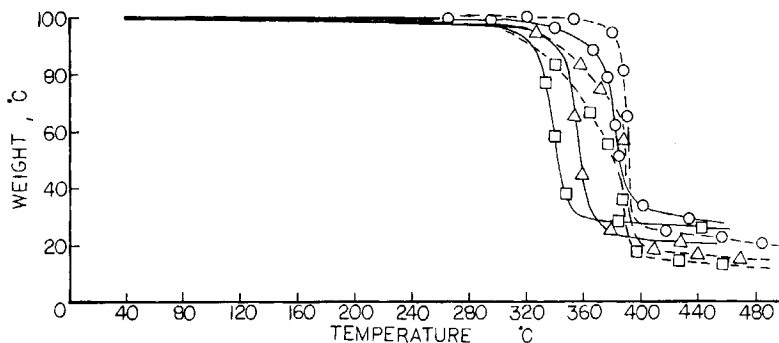


Fig. 6. TGA thermograms in N_2 atmosphere of resins F2200 (-□-), F2001P (-△-), F2300 (-○-), H_3PO_4 -3 F2200 (—□—), H_3PO_4 -3 F2001P (—△—), and H_3PO_4 -3 F2300 (—○—).

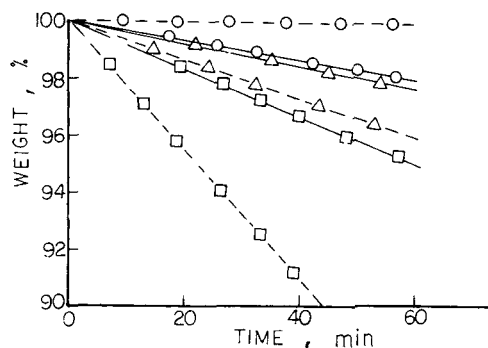
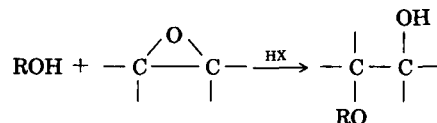


Fig. 7. Isothermal at 250°C TGA diagrams in N_2 atmosphere of resins F2200 (-□-), F2001P (-△-), F2300 (-○-), H_3PO_4 -3 F2200 (-□-), H_3PO_4 -3 F2001P (-△-), and H_3PO_4 -3 F2300 (-○-).

control resin F2300. Such a behavior shows that the increase of molecular weight of a BPA by esterification of phosphoric acid does not continue increasing its thermal stability beyond a limiting value of the molecular weight.

The present investigation has been expanded to include esterification of poly(phosphoric acid), $H_6P_4O_{13}$, with resin F2001P. The ratio of reactants $H_6P_4O_{13}$ /F2001P was 1:6 to obtain a completely esterified poly(phosphoric acid). The reaction product ($H_6P_4O_{13}$ -6 F2001P) is expected to contain 1.8% phosphorus. Figure 8 shows the DSC thermogram of the reaction mixture as well as the DSC and TGA thermograms of the reaction product in N_2 atmosphere. The DSC thermogram of the mixture shows an exotherm from 68°C to 120°C due to exothermic reaction. The heat of reaction was 55 J/g. The exothermic peak at 320°C in the DSC thermogram of the product corresponds to the pyrolysis ($\Delta H_{pyr} = 113$ J/g). The following thermogravimetric data of the reaction product were calculated from its TGA trace: PDT, 315°C; PDT_{max}, 338°C; TCP, 361°C, and char yield at 400°C, 25%. These data indicate that resin $H_6P_4O_{13}$ -6 F2001P is thermally less stable than H_3PO_4 -3 F2001P resin.

Taking into consideration the possible side reactions, it seems likely that the structure of the modified brominated resins to be complex. In addition to the esterification reaction, an etherification reaction catalyzed by acids⁹ takes place:



The OH for etherification is supplied from the reaction of an epoxy group with phosphoric or poly(phosphoric acid). The etherification reaction should lead to a crosslinked system. The ratio of the etherification to esterification reaction will determine the cured properties and the optimum combining ratio of ingredients. Consequently, the reaction of a BPA with phosphoric or poly(phosphoric acid) produces a 3-dimensionally crosslinked system

TABLE II
 Thermal Characteristics of the Resins Obtained by Complete Esterification of H_3PO_4 with Brominated Epoxy Resins of Different Molecular Weight

Resin	DSC data				TGA data				
	T_1 (°C)	T_2 (°C)	ΔH_{DVF} (J/g)	PDT (°C)	PDT _{max} (°C)	TCP (°C)	Char yield (%, 400°C)	Isothermal weight loss (%) ^a	
F2200	346	370	120	326	368	422	17	13.9	
H_3PO_4 -3 F2200	305	315	100	315	337	359	28	5.0	
F2001P	351	362	118	344	390	418	20	4.1	
H_3PO_4 -3 F2001P	340	349	67	369	388	406	29	2.4	
F2300	355	367	40	384	390	394	27	0.1	
H_3PO_4 -3 F2300	346	357	42	357	380	400	35	2.1	

^a At 250°C in N_2 atmosphere after 1 h.

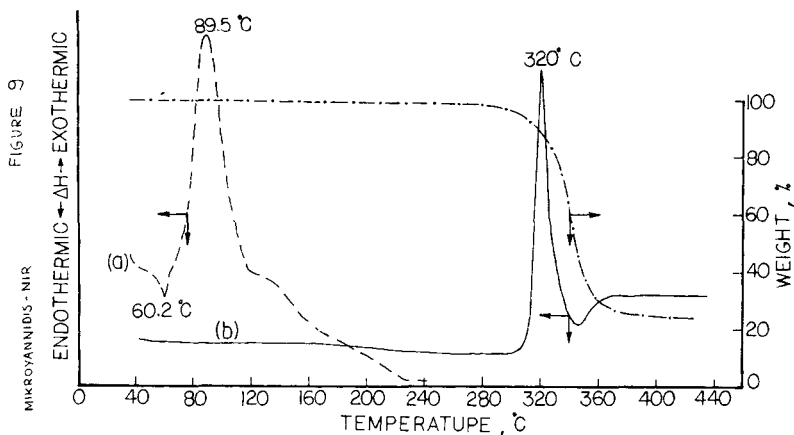


Fig. 8. DSC thermograms in N_2 atmosphere of (a) a mixture of $H_6P_4O_{13}$ and F2001P (mole ratio 1:6) in the presence of triphenyl phosphine (0.15% by weight); (b) resin $H_6P_4O_{13}$ -6 F2001P. TGA thermogram in N_2 atmosphere of resin $H_6P_4O_{13}$ -6 F2001P (---).

rather than a polyfunctional epoxy resin. The crosslinking should be responsible for the improved thermal stability of the modified brominated epoxy resins.

An attempt was made to elucidate the structure of the modified epoxy resins by infrared spectroscopy. Figure 9 shows typical FT-IR spectra of the modified resin H_3PO_4 -3 F2001P as well as of the corresponding unmodified resin F2001P. The spectrum of the modified resin shows a broadening of the peaks. Both resins show two medium absorption bands in the region of $600\text{--}500\text{ cm}^{-1}$ associated with C—Br links. The following characteristic absorption bands of the epoxy groups¹⁰ appear in the spectrum of the resin F2001P: $1271\text{--}1251$, 1130 , and 870 cm^{-1} . It has been reported¹⁰ that only the band in the region of $1240\text{--}1270\text{ cm}^{-1}$ could be identified with any reasonable certainty as pertinent to the epoxy group. In the spectrum of

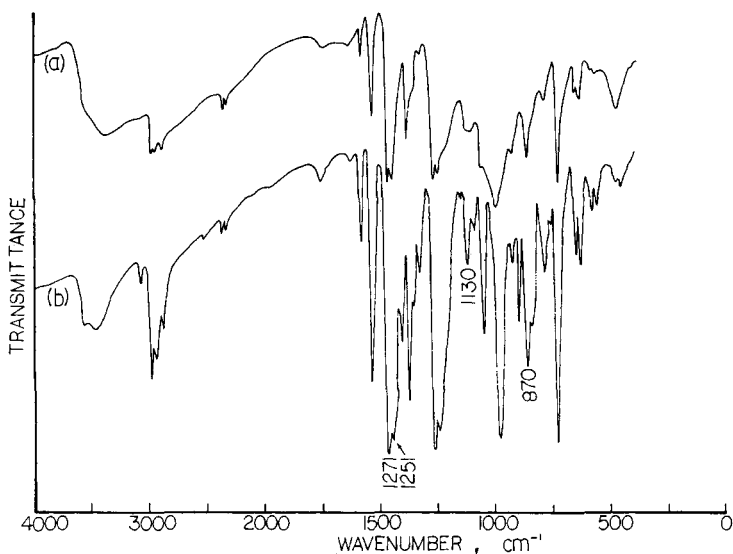


Fig. 9. FT-IR spectra of resins (a) H_3PO_4 -3 F2001P and (b) F2001P.

the modified resin the aforementioned bands except the 1271–1251 cm^{-1} band have been weakened. This suggests a decrease of the epoxy group concentration in the modified resin. Since the P=O group absorbs in the region of 1350–1250 cm^{-1} , the P=O band as well as the band at 1271–1251 cm^{-1} associated with the epoxy group overlap, thus precluding an estimate of the epoxy group concentration. The two spectra (Fig. 9) differ considerably in the region of the 1050–990 cm^{-1} , where the P—O—C linkages absorb. It should be noted that the C—O—C linkages of the aliphatic ethers absorb in the approximate range 1150–1060 cm^{-1} .

The modified brominated epoxy resins show a lower solubility range as compared with starting materials. The unmodified resins, for example, are readily soluble in methyl ethyl ketone whereas resin H₃PO₄-3 F2001P is dissolved in a mixture of methyl ethyl ketone–dioxane (1:1 by volume) after stirring at ambient temperature for 4–5 days. The lower solubility range of the modified resins should be attributed both to crosslinked structure and their increased molecular weight.

CONCLUSIONS

Commercial brominated epoxy resins were structurally modified by reacting with phosphoric or poly(phosphoric acid). In addition to the esterification reaction, an etherification reaction took place that formed a crosslinked system. The resins obtained from complete esterification of phosphoric acid were more thermally stable as compared to those prepared from a partial esterification of phosphoric acid. Most of the modified resins showed a higher thermal stability than the corresponding unmodified resins.

The main part of the present work was performed at NASA Ames Research Center in Moffett Field, California. The authors thank the staff of the Chemical Research Projects Office of this Research Center for providing facilities.

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Received March 27, 1984

Accepted May 10, 1984