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Indra K. Varma[a]; George M. Fohlen[a]; John A. Parker[a]
[a] Chemical Research Projects Office NASA-Ames Research Center, California

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Phosphorus-Containing Imide Resins. I*

INDRA K. VARMA,[†] GEORGE M. FOHLEN, and JOHN A. PARKER

Chemical Research Projects Office
NASA-Ames Research Center
Moffett Field, California 94035

ABSTRACT

Recently we reported the general features of bisimide resins based on bis(m-aminophenyl)methylphosphine oxide. Graphite fabric composites fabricated from one of these resins did not burn in pure oxygen even at 300°C. However, curing of these resins was done above 270°C. It is desirable to have organic matrix resins with lower curing temperatures. We now report the synthesis of several bisimides and triimide resins based on tris(m-aminophenyl)phosphine oxide. These monomers were prepared according to the procedure of Searle or Martin et al. by reacting triamine with appropriate amounts of maleic anhydride, citraconic anhydride, dichloromaleic anhydride, and benzophenone tetracarboxylic dianhydride. Cross-linked imide resins insoluble in DMF were obtained by thermal polymerizations at 180°C with some of these monomers. Anaerobic char yields at 800°C in the range of 60-70% were obtained. A four-ply graphite cloth laminate prepared from one of these resins at 180°C, and after postcuring at 220°C for 4 h, had a limiting

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[†] National Research Council-NASA Research Associate 1979-1981. Permanent address: Center of Materials Science & Technology, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016, India.

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oxygen index above 100. The glass transition temperature of this laminate (as evaluated by DMA) was 385°C.

INTRODUCTION

The application of composites (defined as a combination of resins and fiber reinforcement) in the aerospace industry has grown considerably in the past decade after the first production of horizontal stabilizers for several aircrafts. The major motivation of such growth has been the reduced weight and fuel consumption. However, other important factors influencing the widespread applications of composites in aircraft and the automotive industries are 1) cost, 2) durability, and 3) high temperature capabilities. It is desirable to have flame-resistant resins in the fiber-reinforced composites. A variety of graphite and glass fiber-reinforced composite formulations mainly based on epoxy and polyimides has been developed in recent years. Most of these laminates burn in oxygen, and limiting oxygen index (LOI) values of 41-52 have been reported for graphite cloth laminates [1].

Recently we reported [2, 3] the general features of bisimide resins based on bis(m-aminophenyl)methylphosphine oxide. Graphite cloth laminates fabricated from one of these resins did not burn in pure oxygen even at a temperature of 300°C. However curing of these resins was done at temperatures above 230°C. The aim of the present investigation was to develop polyimide resins, based on tris(m-aminophenyl)phosphine oxide, processable at lower temperatures. The imide functional group was selected because 1) the compounds are simple to manufacture and 2) the ethylenic double bond readily undergoes thermal polymerization and is easily reacted with organic amino compounds. The ease of polymerization of trismaleimides may be influenced by the nature of substituent at the olefinic bond [2-4]. The effect of the electron-donating methyl group and the electron-attracting chlorine atoms was therefore investigated by preparing triscitraconimides and trisdichloromaleimides.

An attempt was also made to prepare bisimides from tris(m-aminophenyl)phosphine oxide. These compounds would contain a free amino group along with the two cyclic imide groups. The facile addition of nucleophiles, particularly primary and secondary amines, to the electron-deficient double bonds of maleimides has been extensively investigated [5-9]. It is expected that bisimides based on tris(m-aminophenyl)phosphine oxide would polymerize and crosslink at lower temperatures due to the presence of amino groups in these monomers. The presence of phosphorus in the main polymer chain is expected to impart good adhesion and flame-resistant properties.

EXPERIMENTAL

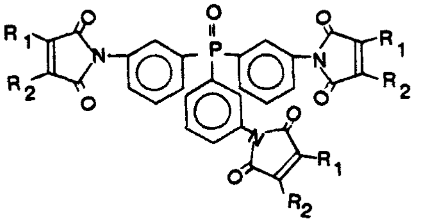
Starting Materials

Tris(m-aminophenyl)phosphine oxide was prepared from triphenylphosphine oxide (M&T Chemicals Inc.) by nitration with a concentrated H_2SO_4-HNO_3 mixture and subsequent reduction with stannous chloride dihydrate and concentrated HCl. The melting point of the crystalline amine was 258-263°C. In the mass spectrum of the amine, the M-1 ion (m/e 322) arising due to the loss of a hydrogen atom was the base peak. Characteristic absorptions due to P=O (1160 cm^{-1}), P–C_6H_5 (1435 cm^{-1}), and amino groups were observed in the infrared spectrum of the amine.

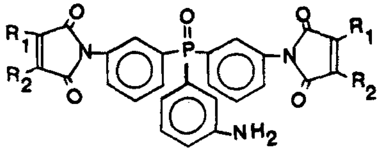
Maleic anhydride (MA) (J. T. Baker), citraconic anhydride (CA) (Aldrich Chemical Co.), and benzophenone tetracarboxylic acid dianhydride (BTDA) (Gulf Oil) were used as supplied. Dichloromaleic anhydride (DA) (Aldrich Chemical Co.) was recrystallized from hexane.

Preparation of Imide Monomers

Several trisimide and bisimide monomers were synthesized in the present work:



(TRISIMIDE)



(BISIMIDE)

WHERE $R_1 = R_2 = H$

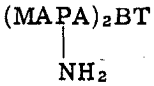
OR

$R_1 = R_2 = Cl$

OR

$R_1 = H, R_2 = CH_3$

TABLE 1. Resins Prepared[a]

I.	MA_3PA	V.	MA_2PANH_2
II.	CA_3PA	VI.	CA_2PANH_2
III.	DA_3PA	VII.	DA_2PANH_2
IV.	$MA_2PABTPAMA_2$	VIII.	 $(MA\underset{NH_2}{P}A)_2BT$

[a]MA = maleimidyl group.
DA = dichloromaleimidyl group.
CA = citraconimidyl group.
PA = tris(m-phenyl)phosphine oxide group.
BT = benzophenone tetracarboxyl diimide group.

Throughout the text the imides are referred to by the number designated in Table 1 (Compounds I-VIII).

The procedure of Searle [10] was used to prepare trisimides and bisimides from MA, CA, and BTDA. The triamine (0.05 mol) was dissolved in dimethylformamide, and 0.165 mol (for trisimide) or 0.11 mol (for bisimide) of maleic anhydride or citraconic anhydride was added with constant stirring. Cyclization of the amic-acid intermediate was carried out either by treating with a sodium acetate: acetic anhydride mixture at room temperature or by refluxing the DMF solution for 45-60 min. Samples IV and VIII were prepared by first reacting the appropriate amount of MA with the triamine and then introducing BTDA in the reaction mixture. After stirring for 10-14 h, thermal cyclization was done at 150°C.

Imides were precipitated from their DMF solution by water and purified from toluene-acetone and petroleum ether and subsequently dried in vacuum oven at 70-80°C. The trisimide and bisimide based on DA were prepared according to the procedure of Martin et al. [11] by refluxing the amine and anhydride in glacial acetic acid for 1-2 h and isolating the product by precipitation in water. The product was recrystallized from chloroform/petroleum ether.

Samples I, II, V, and VI were also prepared by reacting appropriate quantities of amine and anhydride in glacial acetic acid and refluxing for 10-14 h. The imide monomers were precipitated in water, filtered, and washed with sodium bicarbonate solution. The dried substances were then crystallized from chloroform/petroleum ether.

Characterization

Infrared spectra of imide monomers in the KBr pellets or as thin films cast from chloroform solution on salt plates were recorded by

TABLE 2. Analytical Results of Imide Monomers[a]

Sample no.	Formula	Elemental composition (%)				
		C	H	N	P	Cl
I	$C_{30}H_{18}N_3PO_7$	62.21	3.50	7.78	4.68	-
		(63.95)	(3.22)	(7.46)	(5.49)	
II	$C_{33}H_{24}N_3PO_7$	65.18	4.11	6.88	5.04	
		(65.48)	(3.99)	(6.94)	(5.11)	
III	$C_{30}H_{12}N_3PO_7Cl_6$	46.71	1.63	5.43	3.74	27.92
		(46.79)	(1.57)	(5.46)	(4.02)	(27.62)
IV	$C_{69}H_{38}N_6P_2O_{15}$	64.49	3.6	6.92	5.41	
		(66.14)	(3.06)	(6.71)	(4.94)	
V	$C_{26}H_{18}N_3PO_5$	62.23	4.45	8.92	6.27	
		(64.59)	(3.75)	(8.69)	(6.41)	
VI	$C_{28}H_{22}N_3PO_5$	65.33	4.46	7.31	5.42	
		(65.75)	(4.33)	(8.21)	(6.06)	
VII	$C_{26}H_{14}N_3PO_5Cl_4$	50.62	2.48	6.98	5.2	18.67
		(50.2)	(2.25)	(6.76)	(4.99)	(22.84)
VIII	$C_{61}H_{38}N_6P_2O_{11}$	65.48	4.17	7.77	5.18	
		(67.01)	(3.50)	(7.72)	(5.66)	

[a] Figures in parentheses indicate calculated values.

a Perkin-Elmer 180 spectrophotometer or a Nicolet-MX1-FTIR spectrophotometer. Mass spectra were recorded at 70 eV on a Hewlett-Packard MS-5980 instrument by the direct inlet procedure. A Varian T-60 NMR spectrophotometer was used to record the ^1H-NMR spectra of bisimides and trisimides in $CDCl_3$ or DMSO-d_6.

Dynamic Thermal Analysis

A DuPont 990 thermal analyzer was used to evaluate thermal behavior of imide monomers and their polymers. All measurements were carried out in a nitrogen or air atomosphere at a flow rate of 100 cm^3/min. A heating rate of 10°C/min was used.

Curing of Imide Monomers

Polymers were prepared by thermal polymerization. A known weight of the monomer was heated from room temperature to the

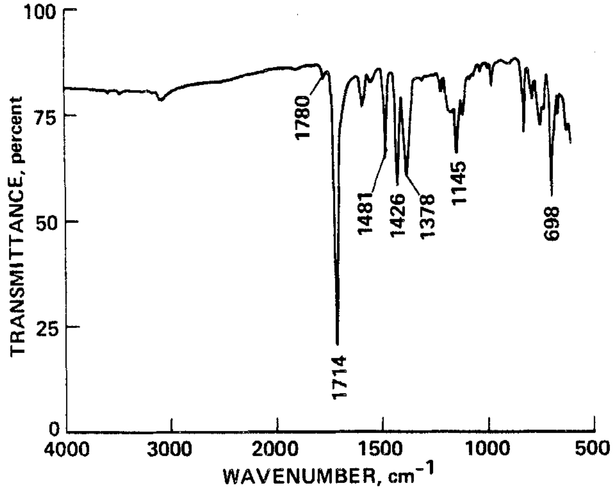


FIG. 1A. Infrared spectra of N,N', N''-tris(maleimidophenyl)-phosphine oxide.

desired temperature and maintained for a desired interval of time. Solubility in DMF was used as a criterion for cross-linking reaction.

COMPOSITE FABRICATION

Test laminates were prepared by coating graphite cloth (8 harness satin weave cloth) designated as a style 133 fabric, with a DMF solution of trisimide IV and bisimide V and VIII. The prepregs were dried in an air oven at 125-135°C for 20 min. The dried prepregs (4-9 plies) were stacked and pressed between aluminum plates covered with a tetrafluoroethylene film. The laminate was then cured in a flat platen press at 180°C at a pressure of 125-140 psi for 2 $\frac{1}{2}$ h. Postcuring of the laminate was done at 218 ± 2°C for 16 h. The resin content of the laminates was determined by the hydrazine method [12].

The laminates were tested for a number of physical properties: short beam shear (ASTM D 2344-76), flexural strength (ASTM D 790-70), and tensile strength (ASTM D 638-68). The flammability tests were performed with a Stanton- Redcroft Flammability Unit and the LOI was determined according to ASTM D 2863-74.

A modified DuPont 980 dynamic mechanical analyzer, which measures modulus and damping, was used to study the composite systems and to evaluate glass transition temperatures.

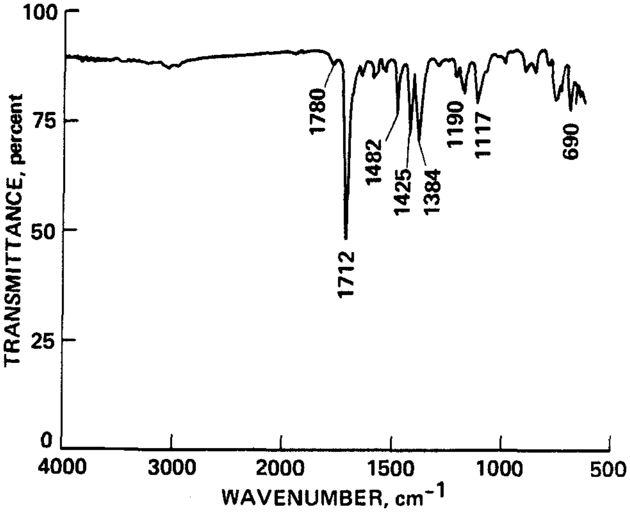


FIG. 1B. Infrared spectra of N,N',N''-tris(citraconimidophenyl)-phosphine oxide.

RESULTS AND DISCUSSION

Characterization of Imide Monomers

The imide monomers were characterized by elemental analysis (Table 2) and infrared spectroscopy. Characteristic absorption bands due to imide rings were observed at 1710-1733 and 1775-1780 cm^{-1}. Other absorptions due to P=O (at 1160-1190 cm^{-1}), P–C_6H_5 (at 1425 cm^{-1}) C_6H_5 (at 1590-1593 and 1480-1483 cm^{-1}) and C–N (at 1375 cm^{-1}) were also observed. In Samples III and VII an additional band due to C–Cl was present at 880-884 cm^{-1}. The infrared spectra of trisimides are given in Fig. 1.

In Sample VII, along with the above-mentioned characteristic absorptions, a strong band was observed around 1650 cm^{-1} (Fig. 2C). Such a band has been observed in poly(maleimide-amines) and has been attributed to the carbonyl group conjugated with the –NH– group [13-15]. This suggests a partial displacement of chlorine by the free amino group in this bisimide. The chlorine content of this sample was lower than the calculated values (Table 1). In Samples V and VI additional absorption bands due to the –NH– groups were observed in the 3100-3300 cm^{-1} region (Fig. 2A and 2B).

The mass spectrum of only Sample III could be recorded. In other samples extensive char formation on the ion probe was observed. Isotopic cluster due to 6-chlorine atoms was observed in Sample III

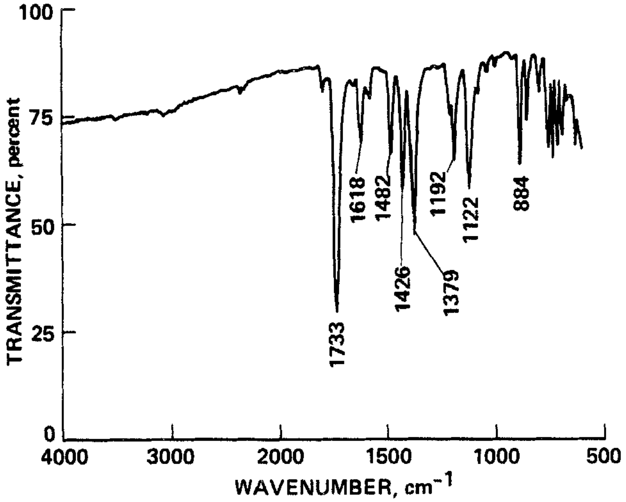


FIG. 1C. Infrared spectra of N,N',N''-tris(dichloromaleimidophenyl)phosphine oxide.

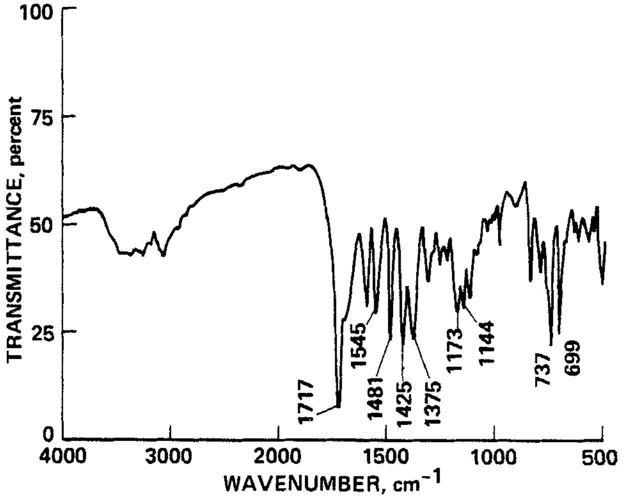


FIG. 2A. Infrared spectra of Compound V.

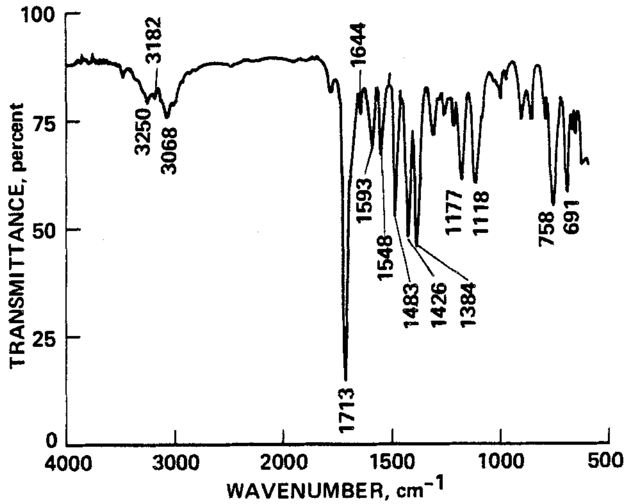


FIG. 2B. Infrared spectra of Compound VI.

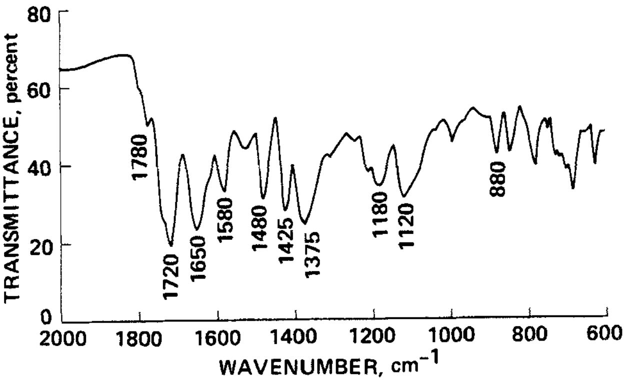


FIG. 2C. Infrared spectra of Compound VII.

and base peak appeared at m/e 87 (C_3ClO^+ ion). The molecular ion (m/e 767) was of low intensity. Some of the prominent fragment ions in order of decreasing relative intensity were at m/e 87 (100), 89 (35.3), 94 (33), 90 (20), 96 (19), 122 (18.2), 124 (10.4), and 177 (10.1).

In the ^{1}H-NMR spectra of trisimides I and II, the olefinic protons were present at 6.7 and 6.5 ppm, respectively (Fig. 3). New groups

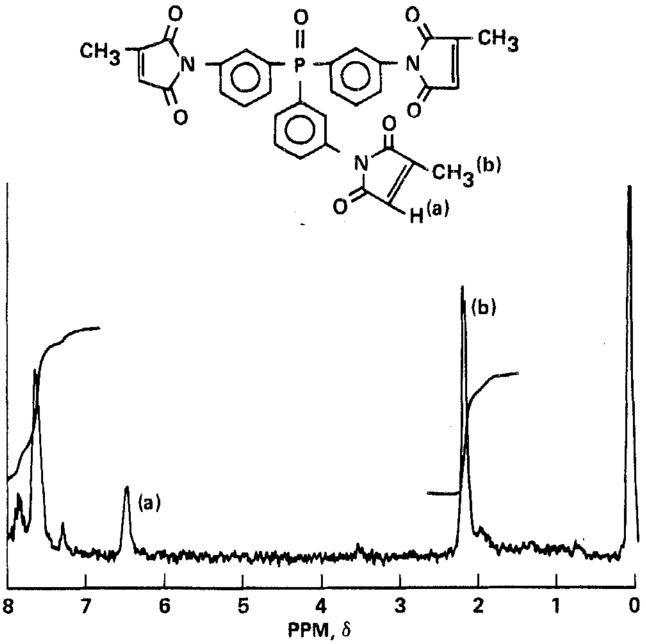


FIG. 3. ^{1}H-NMR spectrum of N,N',N''-tris(citraconimidophenyl)-phosphine oxide.

of bands which could be ascribed to the –NH– group appeared in Compounds V and VI around 2.0 ppm.

Curing of Imide Monomers

Broad exothermic peaks in the temperature range of 150-330°C were observed in imide monomers by DSC (Fig. 4). The position of this exotherm depended on the nature of the substituent around the double bond of the imide group. The presence of an electron-donating methyl group reduced it by 50°C (CA_3 PA) while an increase in temperature was observed by substituting chlorine atoms (DA_3 PA). However, in compounds V and VI the effects of substituents were not observed. A sharp endothermic transition associated with melting was observed only in Compound III.

Curing of these imide monomers was investigated at several temperatures ranging from 180 to 325°C. Solubility in DMF was used as a criterion of the cross-linking reaction. DMF insoluble products from Monomer III were obtained only when heating was

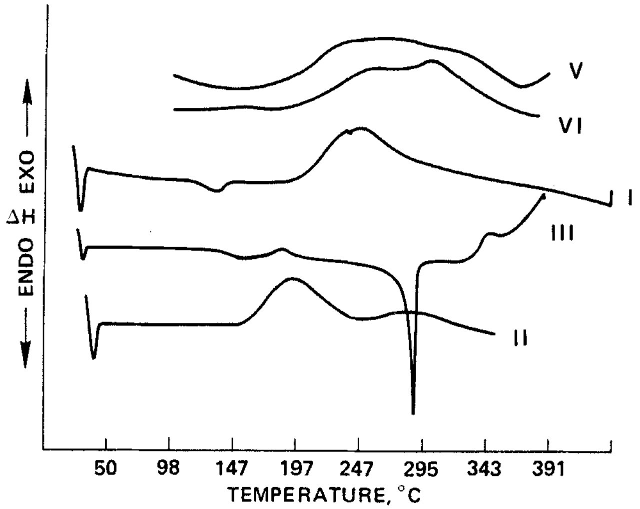


FIG. 4. DSC thermograms of imide resins.

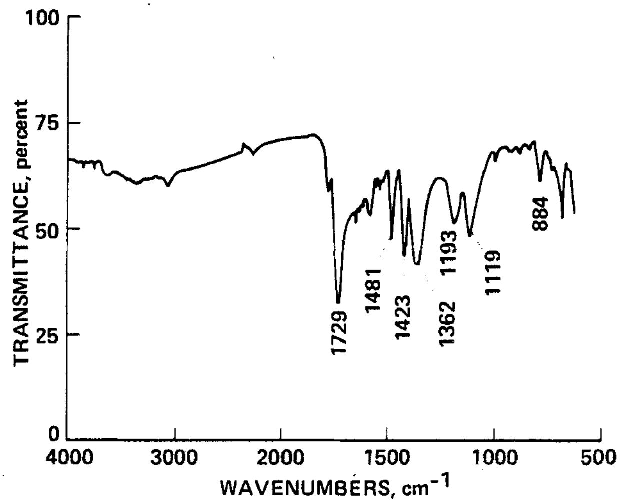


FIG. 5. Infrared spectrum of N,N',N''-tris(dichloromaleimidophenyl)phosphine oxide after heating at 325°C for 25 min.

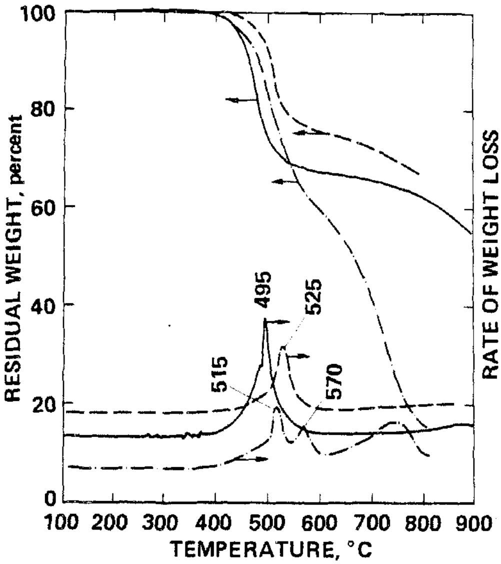


FIG. 6. Primary thermograms of imide resins in nitrogen atmosphere: (– –) Compound II, (—) Compound VI, and (- ·) Compound II in air atmosphere.

done above 300°C. Such a heat-treated sample, however, showed a decrease in intensity of the C–Cl band in the IR spectrum (Fig. 5). This indicated a loss of chlorine during such thermal treatment.

Thermal Behavior of Cured Polymers

The relative thermal stability of Resins I-VIII cured at temperatures ranging from 220-325°C was evaluated by dynamic thermogravimetry in air and nitrogen atmospheres. These resins were stable in both air and nitrogen atmosphere up to 300°C (Fig. 6) but started losing weight above this. The temperature of maximum rate of weight loss (obtained from a differential thermogram, recorded simultaneously) and anaerobic char yields at 800°C were obtained from the primary thermograms and the results are given in Table 3. It is obvious from these results that Resins IV and VIII could be cured at lower temperature and also give a high char yield. In the presence of air, almost complete loss in weight was observed above 800°C.

TABLE 3. Thermal Characteristics of Imide Resins in Nitrogen Atmosphere

Sample no.	Cure temperature (°C)	Time (min)	Solubility in DMF (%)	T_{max} [a] (°C)	Y_c [b] (%)
I	232	120	4.9	520	64.5
II	232	120	6.1	525	66.0
III	232	120	100.0	410, 580	48.0
	305	30	20.0	420, 580	61.0
	325	30	-	570	65.0
IV	224[c]	100	-	340, 520	64.0
	290	30	4.1	540	70
V	232	120	6.8	440, 540	61
VI	232	120	32	495	62.5
VII	232	120	9.4	350, 560	56
VIII	224[c]	100	-	330, 520	68.5
	232	120	1.25	340, 520	69-71

[a] T_{max} = temperature of maximum rate of decomposition.
[b] Y_c = char yield in nitrogen atmosphere at 800°C.
[c] 100 min at 180°C plus 100 min at 224°C.

Mechanical Properties of Laminates

Dynamic analysis of a 4-ply laminate from Resins IV and VIII and cured at 180°C for $2\frac{1}{2}$ h was carried out on a DuPont 980 DMA apparatus. The testing was performed in the temperature range of 25-450°C using a programmed incremental heating rate. Typical modulus and tan δ curves are shown in Fig. 7. Modulus started to decrease above 140°C in the sample which was not postcured. The decrease may be due to fewer cross-bonds in the resins. In a rerun of the same sample on DMA, a shift in the inflection temperature to 200°C was observed. In order to increase the high temperature capabilities of these laminates, postcuring was done above 200°C for $4\frac{1}{2}$ h. Such a treatment resulted in a further increase in the inflection temperature above 260°C. The modulus vs temperature curve can be characterized by noting the inflection temperature (T_1), the temperature at the midpoint (T_2), or the temperature of the peak position

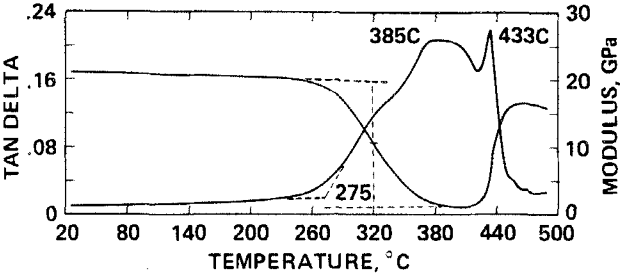


FIG. 7. Dynamic mechanical analysis results of 4-ply graphite cloth laminate of resin IV postcured at 218 ± 2°C.

TABLE 4. Effect of Heating at 218 ± 2°C on the Transition Temperatures of Graphite Cloth Laminates Based on Resin IV

Heating time (h)	Transition temperatures (°C)		
	T_1	T_2	T_3
0	240	315	372
$4\frac{1}{2}$	275	320	385
$14\frac{1}{2}$	305	350	396

(T_3). The values of T_1, T_2, and T_3 for a laminate postcured at 218 ± 2°C for $4\frac{1}{2}$ h are given in Fig. 7. The results of heating the laminate to different time intervals at 218 ± 2°C are summarized in Table 4. An increase in T_1, T_2 and T_3 is observed when postcuring was done for longer time intervals.

It was therefore decided to postcure these laminates at 218°C for several hours before determining mechanical properties. Such a treatment will increase the cross-link density and make the resin network more rigid. 7-9 ply graphite cloth laminates based on Resins IV, V, and VIII were fabricated. Postcuring of the laminates was done at 218 ± 2°C for 16 h. The LOI of all the laminates was above 100 (Table 5). The mechanical properties of the laminate fabricated from Resin VIII, which had a BTDA unit in between the maleimide groups, were better than the laminate based on Resin V. No delamination was observed by boiling test Laminates IV and VIII in water for 20 h.

This study clearly indicates that graphite cloth laminates having outstanding flame-resistant properties could be fabricated from imide resins based on tris(m-aminophenyl)phosphine oxide.

TABLE 5. Mechanical Properties of Graphite Fabric Laminates Based On Imide Resins Derived from Tris(m-aminophenyl)phosphine Oxide

Property tested	Laminate 1[a]	Laminate 2[b]	Laminate 3[c]
Flexural strength 10^3 (psi)	76.04	96.04	-
Flexural modulus 10^6 (psi)	21.42	-	-
Energy ft lb	14.32	-	-
Tensile strength 10^3 (psi)	45.79	46.64	-
LOI	100	100	100
Char yield	61	70	70
Shear strength 10^3 psi	2.94	3.3	2.82
Resin content	18.3	21.3	19.3

[a] Based on Resin V.
[b] Based on Resin VIII.
[c] Based on Resin IV.

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