

Addition Polyimides. I

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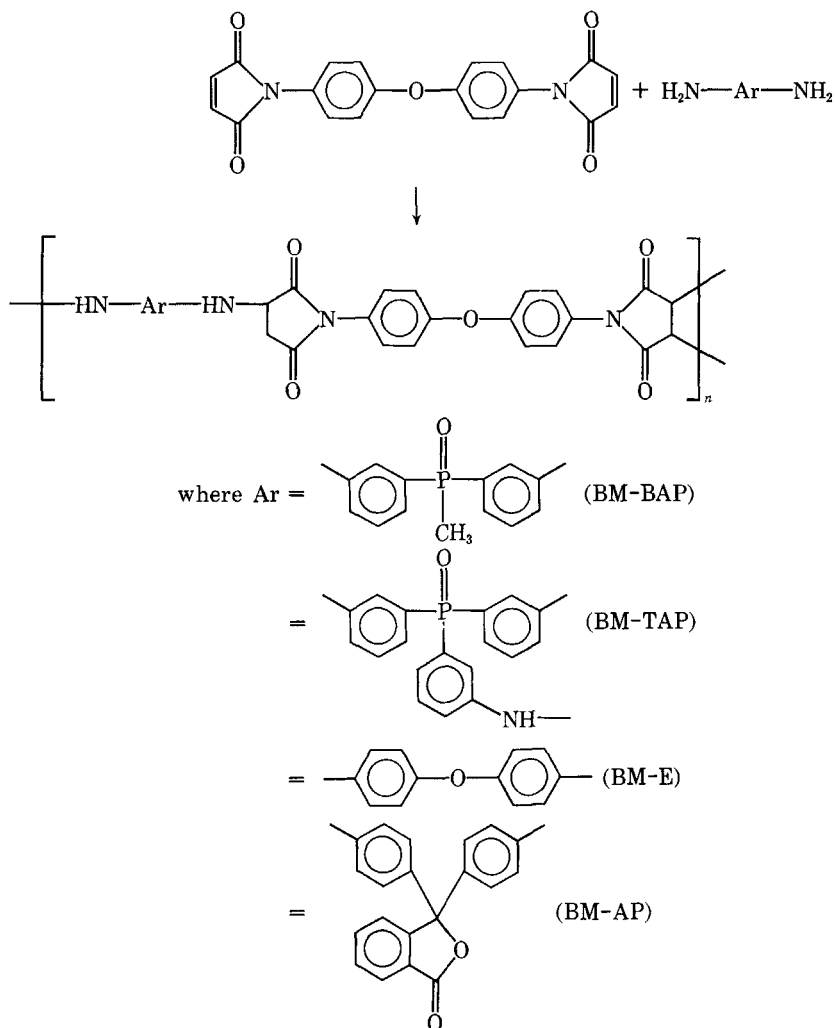
Synopsis

Crosslinking of 4,4'-(bismaleimido)diphenyl ether (BM) was investigated in presence of bis(*m*-aminophenyl) methylphosphine oxide (BAP), tris(*m*-aminophenyl)phosphine oxide (TAP), diaminodiphenyl ether (E) and 3,3-bis(*p*-aminophenyl)phthalide (AP). These crosslinked resins were examined for thermal stability by thermogravimetric analysis. A slight decrease in initial decomposition temperature, the temperature of maximum rate of weight loss, was observed, though the char yield in nitrogen atmosphere at 800°C did not change appreciably. Glass-cloth-reinforced laminates were fabricated from BM and amine mixtures. An improvement in mechanical properties was observed in the presence of phosphorus-containing di- and triamines.

INTRODUCTION

Low molecular weight imide prepolymers, end-capped with reactive maleimide rings, can be thermally polymerized to yield highly crosslinked brittle resin matrices having good high-temperature mechanical properties.¹⁻⁶ The applications of these polymers for structural composites in combination with high modulus fibers is somewhat limited due to their brittleness. Stoichiometric mixing of bismaleimide with a diamine leads to the formation of linear polymers (polyaspartimides) with poor thermal stability.⁷ These polymers, however, could be cast into coherent, flexible films. Thus by a careful selection of bismaleimide to amine ratio, it is possible to control the crosslink density and to retain the outstanding thermal stability of these polymers. Such a modified bismaleimide resin with improved flow properties and somewhat better extensibility is available under the trade mark Kerimid 601 from Rhone-Poulenc.⁸ Several resin formulations are possible by varying the structure of the diamino compounds used for the bismaleimide synthesis⁹ or for Michael reaction with bismaleimides.¹⁰ Crosslinked polymers based on aliphatic bismaleimide and cardiac diamines have been described in the literature.¹¹

We have recently reported the outstanding thermal stability and flame resistance of bismaleimides prepared from phosphorus containing di- and triamines.¹²⁻¹⁴ It was considered to be of interest to study the Michael reaction of such diamines with bismaleimides. In this paper, we report the properties of 4,4'-bismaleimidodiphenyl ether (BM) crosslinked thermally in the presence of bis(*m*-aminophenyl)methylphosphine oxide (BAP), tris(*m*-aminophenyl)phosphine oxide (TAP), 4,4'-diaminodiphenyl ether (E), and 3,3-bis(*p*-aminophenyl)phthalide (anilinephthalein) (AP). Crosslinking of bismaleimide in the presence of amines is expected to give rise to following structures in the backbone:



(Throughout the text these polymers are referred to by the letter designations shown in the parentheses.)

EXPERIMENTAL

Starting Materials

Maleic anhydride (BDH) was purified by refluxing with acetic anhydride (BDH) and subsequent crystallization. Anhydrous sodium acetate (BDH) was obtained by fusion.

Diaminodiphenyl ether (Fluka) was used as such. 3,3-bis(*p*-aminophenyl)-phthalide (mp 202–203°C, brown color) was prepared by the method reported in literature. Synthesis of bis(*m*-aminophenyl)methyl phosphine oxide from triphenylphosphine (Aldrich Chemical Co.) has been described elsewhere.¹⁵ Tris(*m*-aminophenyl)phosphine oxide was prepared from triphenylphosphine oxide (Koch Light) by nitration with a mixture of fuming nitric acid and concd

H₂SO₄ and subsequent reduction with SnCl₂·2H₂O and concd HCl. The mp of the crystalline amine was 260°C.¹⁶

4,4'-Bismaleimidodiphenyl ether (BM) was prepared by the cyclodehydration of bismaleamic acid precursor with acetic anhydride and sodium acetate using a modification of the method described by Searle.¹⁷ Diaminodiphenyl ether (E) (0.1 mol) was dissolved in dry acetone and maleic anhydride (0.22 mol) was added in two portions over a period of 10 min. The solution was refluxed for 3 h in nitrogen atmosphere. Cyclization of the amic-acid intermediate was carried out by treating with fused sodium acetate/acetic anhydride mixture and refluxing the solution for another 2 h. The solution was then poured in cold water. The yellow-orange precipitates were collected by filtration, repeatedly washed with water, and dried at 60–70°C in vacuum. The product was dissolved in chloroform, passed through a silica gel column, and eluted with chloroform. The solution was concentrated and kept for sometime, when pure BM crystals separated out (mp 175–176°C).

A DMF solution of amines and bismaleimide BM were mixed at room temperature and the solution placed in shallow aluminum dishes. The solvent was slowly evaporated and then these dishes were placed in an oven preheated to the desired temperature. After keeping at the fixed temperature for certain times the dishes were cooled in a desiccator, and polymers varying in color from orange, dark red, or brown were obtained.

The extent of crosslinking was determined from the quantity of the insoluble fraction remaining after extraction with DMF, which is a good solvent for amines as well as BM. Percentage solubility of these polymers in DMF was calculated by weighing the polymers before and after the extraction:

$$\% \text{ solubility} = \frac{W_0 - W_1}{W_0} \times 100$$

where W_0 = initial wt of the polymer and W_1 = wt of insoluble material.

Characterization

A DuPont 990 thermal analyzer was used to evaluate the thermal behavior of these crosslinked polymers. All the measurements were carried out in a nitrogen atmosphere at a flow rate of 100 cc/min or in air (static condition). A heating rate of 10°C/min was used.

Composite Fabrication

Test laminates were prepared by RP-8 epoxy compatible glass fabric weighing 280 g/m². Ten pieces of 6 in. × 6 in. glass fabric were coated with a 30% (w/w) polymer solution. The prepregs were dried in air at room temperature for 2–3 h and then kept at 120°C for 30 min in a circulating air oven.

The dried prepregs were stacked and pressed between aluminum plates covered with an aluminum foil. The resulting laminate was then cured in a flat platen press at 180–185°C for 1 h and then at 200–205°C for another 1 h. Post-curing was done at 220°C for 16 h.

Resin content was determined by hydrazine method.¹⁸ 0.4–0.6 g of laminate was treated with hydrazine hydrate (BDH) at room temperature for 4–5 h. The

temperature was then gradually increased to boil the solution and kept there for 5–10 min. After cooling to room temperature, the fibrous residue was filtered (sintered glass funnel), washed with acetone several times, and then dried to a constant weight at 110°C.

Interlaminar shear strength (SH) was determined according to ASTM D2344-76. A span-to-depth ratio of 5:1, a crosshead speed of 0.08 in./min, and a sample width of 0.5 in. were used.

$$SH = (0.75 \times P_B)/bd$$

where P_B = load at the moment of break (lb), b = width of specimen (in.), and d = specimen thickness (in.).

The flexural properties of the composites were determined using a span-to-depth ratio of 32:1. All samples had a width of 0.5 in., and a crosshead speed of 0.08 in./min was employed (ASTM D790-70).

$$\text{flexural strength} = 3PL/2bd^2$$

where P = load at the moment of break (lb), L = support span (in.), b = width of specimen (in.), and d = specimen thickness (in.).

The tensile strength was evaluated by using a gauge length of 2.0 in. on an

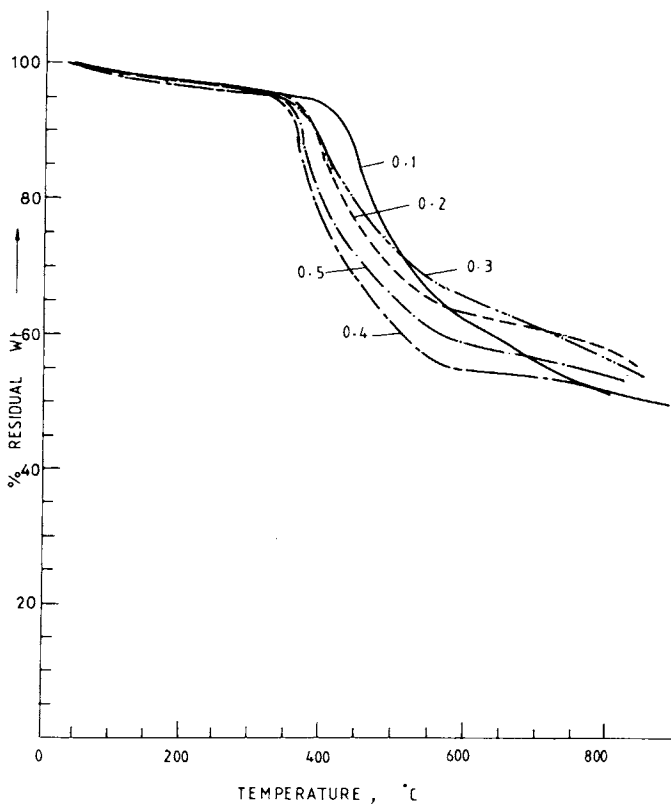


Fig. 1. Thermogravimetric traces of 4,4'-(bismaleimido)diphenyl ether (cured in the presence of various molar concentrations of tris(*m*-aminophenyl)phosphine oxide) in nitrogen atmosphere.

Instron 1120 according to ASTM D638-68. A crosshead speed of 0.08 in./min was used, and the sample width was 0.25 in.

The limiting oxygen index (LOI) of test laminates was determined using a Stanton Redcroft Flammability Unit (ASTM D 2863-74). Samples measuring 4 in. \times 0.25 in. were cut and placed in a holder in the flame chamber. The mixture of nitrogen and oxygen passed upward through the chimney at a flow rate of 18 L/min. The LOI, which is the quantity of oxygen (by volume) in a mixture of oxygen and nitrogen which supports burning, was then evaluated:

$$\text{LOI} = \text{O}_2 / (\text{O}_2 + \text{N}_2)$$

RESULTS AND DISCUSSION

The effect of temperature, time, and concentration of the diamine on the extent of crosslinking reaction was investigated. Appreciable solubility in DMF was obtained when the temperature of crosslinking was kept below 200°C. Heating at 200°C for several hours resulted in a crosslinked product with less than 2% solubility in DMF. Therefore, it was decided to study the thermal behavior of a polymer crosslinked at 200°C for 16 h.

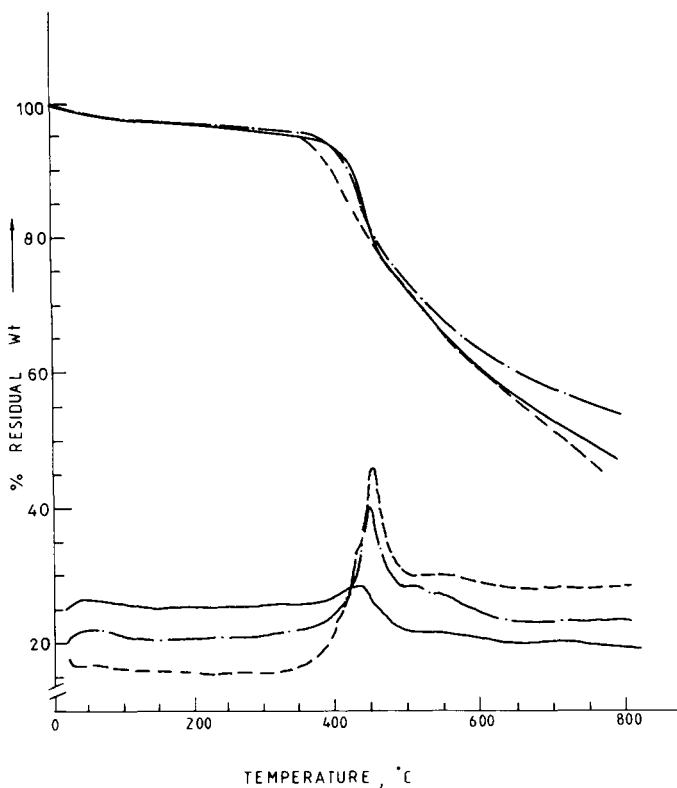


Fig. 2. Thermogravimetric traces of 4,4'-(bismaleimido)diphenyl ether (BM) (cured in the presence of various molar concentrations of anilinephthalein) in nitrogen atmosphere: (—) 0.1; (---) 0.2; (- - -) 0.3.

TABLE I
Effect of Concentration of Tris(*m*-Aminophenyl)phosphine Oxide on Thermal Behavior of Imide Resins in Nitrogen Atmosphere

Sample	Molar ratio of TAP:BM	% Solubility in DMF	IDT (°C)	IPDT (°C)	T_{\max} (°C)	Y_c^a (%)
1	0.1	0.99	420	560	475	53.0
2	0.2	0.61	390	554	430	58.0
3	0.3	0.30	387	543	420	57.5
4	0.4	0.51	360	526	410	52.5
5	0.5	0.84	360	535	410	54.0

^a Anaerobic char yield at 800°C.

The effect of various concentration of tris(*m*-aminophenyl)phosphine oxide and anilinephthalein on solubility in DMF was studied by curing the bismaleimide at 200°C for 16 h. Under these conditions, the bismaleimide was almost completely cured, and less than 1% material could be extracted with DMF. Thermal behavior of these cured resins was investigated by thermogravimetric analysis. A systematic decrease in the initial decomposition temperature was obtained on increasing the molar ratio of amine:BM from 0.1 to 0.5 (Figs. 1 and 2). Similarly, a decrease in temperature of maximum rate of decomposition and integral procedural decomposition temperature¹⁹ was observed (Tables I and II). However, the char yields (Y_c) in nitrogen atmosphere were either unaffected by the amines or increased on increasing the amine concentration. These results thus clearly indicate that char-forming condensation reactions are enhanced in the presence of amines. However, the overall stability of the crosslinked polymer is somewhat decreased when amines in high molar ratios are used.

Initial decomposition temperature and T_{\max} in air and nitrogen atmosphere were almost similar in various samples (Table III). Two T_{\max} were observed in air atmosphere. The lower one around 445°C may be attributed to the decomposition reaction of polyimide while the other around 635°C may be attributed to oxidation reactions. Complete loss in weight was observed in air atmosphere at about 750°C (Fig. 3).

Curing of BM in the presence of 4,4'-diaminodiphenyl ether (E) and bis(*m*-aminophenyl)methylphosphine oxide was carried out only at 0.1 molar concentration of amine to BM. In Table III, values of IDT, IPDT, T_{\max} and Y_c

TABLE II
Effect of Concentration of Aniline Phthalein on Thermal Behavior of Imide Resins^a

Sample	Molar ratio of AP:BM	% Solubility in DMF	IDT (°C)	IPDT (°C)	T_{\max} (°C)	Y_c^b (%)
1	0.1	1.47	405 (410)	530 (550)	463, 555, 630 (457)	(46.5)
2	0.2	0.11	405 (420)	532 (555)	445, 550, 635 (450)	(53.0)
3	0.3	1.01	390 (380)	530 (553)	430, 545, 637 (435)	(45.0)

^a Figures in parenthesis indicate the values in nitrogen atmosphere.

^b Anaerobic char yield at 800°C.

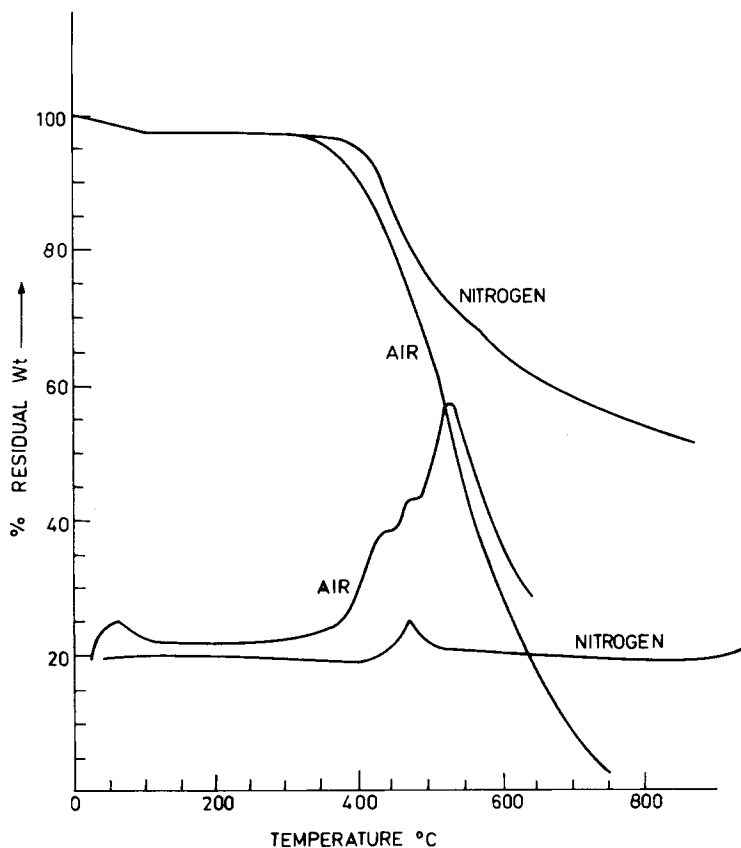


Fig. 3. Thermogravimetric traces of BM resin [cured in presence of 1:0.1 molar ratio of tris(*m*-aminophenyl)phosphine oxide] in air and nitrogen atmosphere.

values of the imide resins crosslinked in presence of different diamines are given. From these results it can be concluded that a variation in the structure of the diamine has no significant effect on the thermal behavior of bismaleimide.

Glass-cloth-reinforced laminates were prepared from BM containing different

TABLE III
Decomposition Temperatures of Imide Resins^a

Property tested	Sample	BM-E (0.1) ^b	BM-BAP (0.1) ^b	BM-AP (0.2) ^b	BM-TAP (0.1) ^b
IDT (°C)		375	370	405	390
		(420)	(420)	(420)	(420)
IPDT (°C)		482	503	532	523
		(557)	(567)	(555)	(560)
T_{\max} (°C)		435, 515	440, 525	445, 550, 635	445, 530
		(458)	(457)	(450)	(475)
Y_c^c (wt %)		55.0	56.5	53.0	53.0

^a Figures in parentheses represent the values in nitrogen atmosphere.

^b Represents the molar ratio of amine to BM.

^c Anaerobic char yield at 800°C.

TABLE IV
Properties of Glass-Cloth-Reinforced Imide Resins

Property tested \ Sample	BM-E (0.1) ^a	BM-BAP (0.1) ^a	BM-AP (0.2) ^a	BM-TAP (0.1) ^a
Resin content (%)	20.0	21.6	29.0	30.0
LOI (vol %)	>100	>100	>100	>100
Tensile strength (psi × 10 ³)	25.25 ± 2	41.29 ± 2	22.60 ± 6	32.35 ± 2
Tensile modulus (psi × 10 ⁶)	0.95 ± 0.2	4.13 ± 0.1	0.44 ± 0.1	0.54 ± 0.1
Shear strength (psi × 10 ³)	1.15 ± 0.1	2.75 ± 0.2	2.53 ± 1.0	4.30 ± 0.3
Flexural strength (psi × 10 ³)	21.27 ± 3	33.06 ± 3	20.23 ± 5	44.68 ± 2

^a Represents the molar ratio of amine to BM.

diamines, and were tested for various physical properties (Table IV). None of these laminates could be burned in even pure oxygen environment at room temperature according to the ASTM D2863-74 test. Tensile strength and modulus of the laminate based on BM-BAP was best among all these samples. Laminates based on phosphorus-containing diamines had better mechanical properties than those based on aniline phthalein or 4,4'-diaminodiphenyl ether. It is thus possible to improve the mechanical properties of glass-cloth-reinforced imide resins by incorporation of phosphorus-containing diamines.

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