Matrix Resins Based on Bismaleimide–1,2-Polybutadienes

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Synopsis

Improved thermally stable matrix resins have been obtained by the incorporation of 1,2-polybutadiene in 4,4'-bismaleimidodiphenylmethane. The thermal curing was performed at 185–195°C for 2.5 h and at 230–235°C for 45 min to give tough crosslinked polymers. The thermal curing reaction was monitered using FT-IR and differential scanning calorimetry. Thermogravimetric analysis of the cured resins have shown improved thermal stability up to 490–480°C both in air and nitrogen atmospheres. The char yield obtained in nitrogen at 800°C was in the range of 50–49%. Graphite cloth laminates were prepared and tested. The laminates showed improved tensile strength over to parent bismaleimide. 1,2-Polybutadiene was hydrogenated using 10% palladized-charcoal. The resulting polymer was characterized by using IR and ^{1}H-NMR, which showed reduction of 15% pendent vinyl double bonds.

INTRODUCTION

There is a continuous need for modestly priced matrix resins for reinforced composites which can provide long-term thermal-oxidative stability for use at temperatures in excess of 200°C.[1] The most important requirement for a binder from the commercial point of view is materials which can be processed under low pressures and temperatures up to 225°C.

The past decade has borne out many novel polymer systems with outstanding properties. The most extensive investigated class are the polyimides, and the variety of them have been commercialized. The polyimides synthesized by condensation type reactions (C-type) have a number of disadvantages for use as matrix resins for fiber-reinforced composites. The primary disadvantage is conversion of the polymer into an intractable state prior to the complete elimination of void producing volatile materials. Therefore, for C-type polyimide resins very poor properties are achieved if the final cure step is completed prior to the application of the desired pressure. To overcome processing disadvantages, addition polyimides (A-type) were developed.[2-6] The advantage of this approach is that low molecular weight imide prepolymers endcapped with reactive maleimide rings are cured by addition reactions into highly crosslinked thermally stable polyimides without the evolution of byproducts.

It has, however, been realized by various users that applicability of these resins is somewhat limited due to their low fracture toughness. Various attempts have been made to synthesize modified addition polyimides and the results have been reported mostly in the form of patents.[7-13] Another

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approach attempted for toughning of the bismaleimides is their copolymerization with new thermoplastics and rubbers.

In this paper we report the results of the studies of bismaleimide–1,2-polybutadiene (BM–PBD) resin systems for use as binders. The thermal polymerization of various BM–PBD resins and thermal stabilities of the resulting cured resins have been reported. Graphite cloth laminates have been made and tested for their mechanical properties.

1,2-Polybutadiene has been selected for this study as this is a low melting polymer and is known to produce cyclized structure on thermal treatment.

EXPERIMENTAL

Materials, Reagents, and Solvents

The bismaleimide, 4,4′-bismaleimidodiphenylmethane(I), was prepared[15] from the corresponding diamine and maleic anhydride, mp 160–161°C. It has been selected for use in this study as this is also available commercially from Rhone-Poulenc, France.

1,2-Polybutadiene(II) is a commerical sample[14] produced by Japan Synthetic Rubber Company, Japan. It has the following characteristics: melting point < 90°C; T_g −23°C; density 0.91 g/cm³; crystallinity 25%; molecular weight 100,000 $(\overline{M}_w)$; microstructure 1,2 (92%), cis (8%), trans (0%); tacticity syndio (66%), hetero (34%), iso (0%). Chloroform was distilled over phosphorus pentoxide.

Instrumentation

Proton nuclear magnetic resonance (¹H-NMR) and ¹³C-NMR spectra were recorded on a Jeol JNX-1 100 MHz NMR spectrometer. The chemical shift (δ) is given in parts per million (ppm) with tetramethylsilane as the internal standard. Infrared spectra were recorded by using a FT-MX Nicholet IR Spectrophotometer on NaCl disks. Thermogravimetric analysis (TGA) and differential scanning claorimetry (DSC) were done using a DuPont Model 1090 thermal analyzer. A heating rate of 10°C/min was used both in air and nitrogen atmospheres. The flow rate of nitrogen was 100 mL/min. The air flow was static.

The tensile properties were determined according to ASTM D-638 on a Instron tester, with a crosshead speed of 0.01 in./min. The flammability tests were performed with a Stanton Redcroft Flammability Unit.

Partial Hydrogenation of 1,2-Polybutadiene (II)

In a 250-mL conical flask, 1,2-polybutadiene(II) (0.50 g) was dissolved in dry ethyl acetate (100 mL) by stirring at room temperature and in a warm water bath. To this solution, catalyst palladized-charcoal (Pd/C) (10%) (0.20 g) was added, and the mixture was hydrogenated at atmospheric pressure for 10 h. Another lot of Pd/C (0.20 g) was added and the hydrogenation continued for 10 h further (until there was no more adsorption of hydrogen). The mixture was filtered and the residue washed with hot ethyl acetate. The combined filtrate on distillation yielded partially hydrogenated 1,2-polybutadiene(III) (0.45 g). A 15% hydrogenation was achieved.

¹H-NMR (CDCl₃) 5.60–5.05 (bm, $CH_2=C\underline{H}$), 5.00–4.60 (m, $C\underline{H}_2=CH—$), 2.50–1.75 (bm), and 1.35–1.00 (bm) [$+CH_2—CH+$ and $+CH_2—CH_3+$].

Preparation of Bismaleimide–1,2-Polybutadiene Samples

Five resins based on bismaleimide–1,2-polybutadienes have been made as given in Table I. The typical method used was 1,2-polybutadiene being dissolved in chloroform. To the clear solution, the required amount of bismaleimide powder was added. The solution obtained was concentrated and dried to give light yellow powder.

RESULTS AND DISCUSSION

The bismaleimide, 4,4'-bismaleimidodiphenylmethane (I), is a yellow powder soluble in chloroform and aprotic solvents, viz., N,N'-dimethylacetamide (DMAC), N,N'-dimethylformamide (DMF), and N,N'-dimethylsulphoxide (DMSO). It was characterized[15] by using IR and NMR. The colorless pellet of 1,2-polybutadiene (1,2-PBD)(II) were soluble in chloroform and characterized.[14,16]

1,2-Polybutadiene(II) was hydrogenated using catalyst palladized charcoal (10%) to give hydrogenated 1,2-polybutadiene (HPBD)(III). Its proton nuclear magnetic resonance spectrum was recorded in deutrochloroform as shown in Figure 1. A 15% hydrogentation was observed as indicated by the ratio of integerations (68:92) of the vinyl protons (5.60–5.05 and 5.00–4.60 ppm) to that of aliphatic protons (2.50–1.75 and 1.35–0.95 ppm). An 8% of cis-1,4 units was present in the hydrogenated polybutadiene(III), similar to that of starting polybutadiene(II), indicating that hydrogenation preferentially reduces pendent vinyl groups. This was seen from the ratio of integrations (40:28) of the vinylic methylene (5.00–4.60 ppm) to that of vinylic methine (5.60–5.05 ppm). This type of preferential hydrogenation of 1,2-polybutadiene's pendent double bonds over cis-1,4 units has also been observed earlier[17] using different catalysts. The proton-decoupled ¹³C-NMR of hydrogenated polybutadiene(III) recorded in deutrochloroform at 25 MHz could not depict any change in tactacity. The infrared spectra of the films of 1,2-polybutadiene(II) and (III) were recorded on NaCl disks as shown in Figure 2, indicating the extent of hydrogenation.

TABLE I
Preparation of Bismaleimide–1,2-Polybutadiene Resins

Resin[a]	No	Percentage of		
		Bismaleimide	PBD	HPBD
BM	IV	100	0	0
BM–PBD5	V	95	5	0
BM–PBD10	VI	90	10	0
BM–PBD15	VII	85	15	0
BM–HPBD10	VIII	90	0	10

[a] BM = Bismaleimide, 4,4'-bismaleimidodiphenylmethane (I), PBD = 1,2-polybutadiene (II), and HPBD = hydrogenated 1,2-polybutadiene (III). Numericals after PBD represents the percentages of the PBDs used.
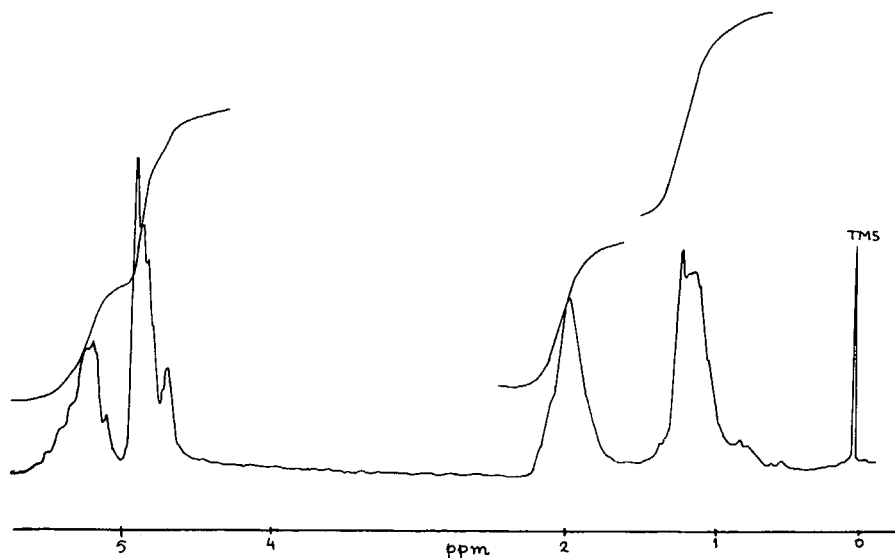
Fig. 1.   ¹H-NMR at 100 MHz of hydrogenated 1,2-polybutadiene(III) in deutrochloroform.

Five resins based on bismaleimide have been prepared (Table I) containing 15–0% of 1,2-polybutadienes. The homogeneity of these resins was tested by recording their ¹H-NMR in deutrochloroform. Figure 3 shows a typical ¹H-NMR of resin BM–PBD15(VII), indicating the presence of 15% of 1,2-polybutadiene(II) and 85% of bismaleimide(I). The vinyl double bonds required for polymerization were intact in each of the components.
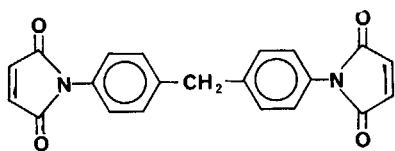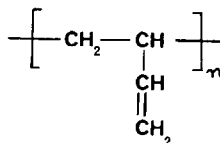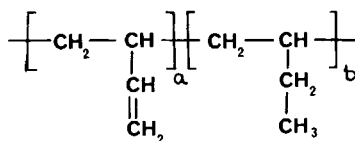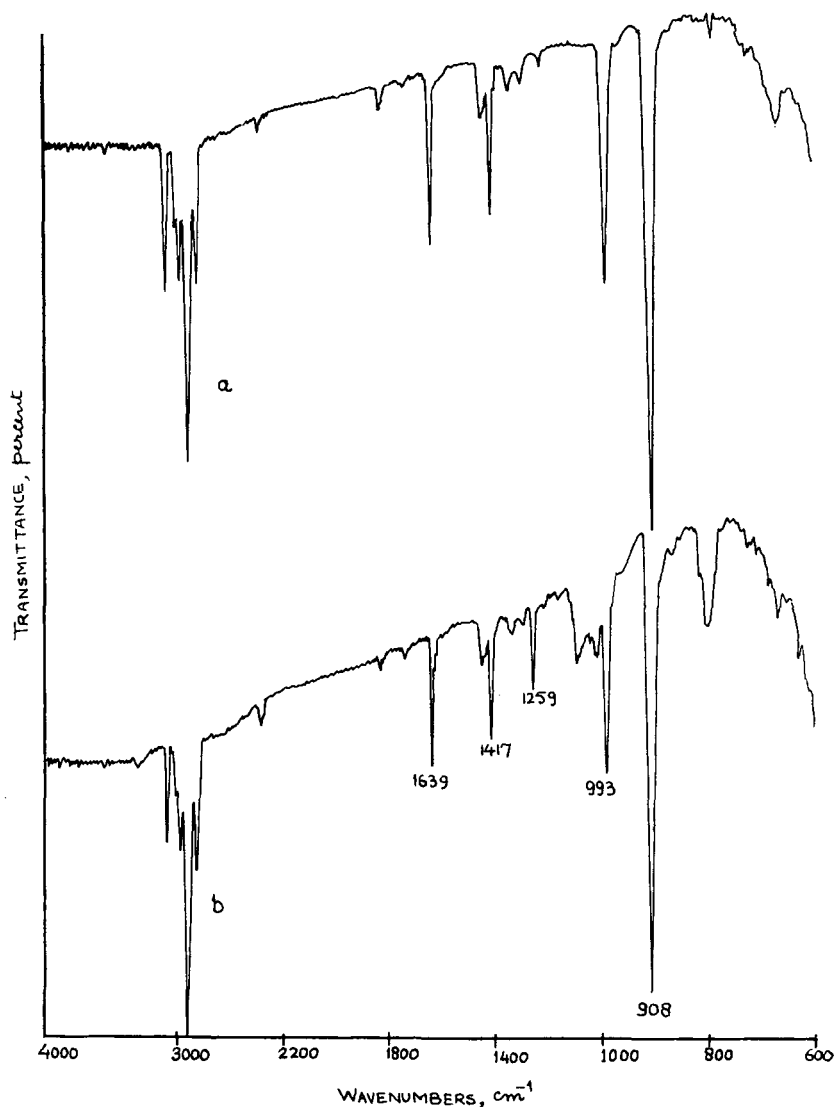

Scheme I

Fig. 2. Infrared spectra of (a) 1,2-polybutadiene(II) and (b) hydrogenated 1,2-polybuta-diene(III).

Curing Studies

Thermal curing of all the resins (IV – VIII) was carried out under identical conditions. As an example: yellow powder of BM-PBD15(VII) was heated in an aluminium dish placed in a previously heated air oven at 185–195°C for 2.5 h and at 230–235°C for 45 min. All these resins melted (<5 min) to clear fluid before vitrification has started, giving rise to tough crosslinked polymers. The cured specimens were clear, indicating that the mixture had not phase separated during the process. Scanning electron microscope examination of the cured specimens up to 2000 Å magnification also showed no phase separation. The curing reaction was monitered using IR and DSC calorimetry.
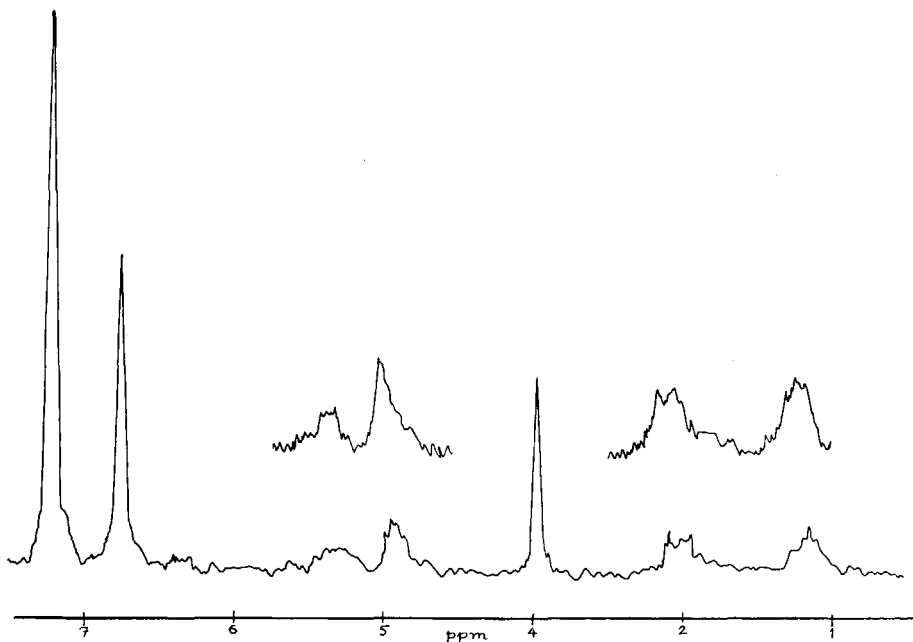
Fig. 3.   ¹H-NMR at 100 MHz of resin BM–PBD15(VII) in deutrochloroform.

The infrared spectra of sample BM–PBD15(VII) both before and after curing are given in Figure 4. The broadening of the spectra of the cured specimen indicated the polymerization.

Figure 5 shows the DSC thermogram of the uncured and cured resin BM–PBD15(VII) in air atmosphere. Two exothermic peaks were observed in the
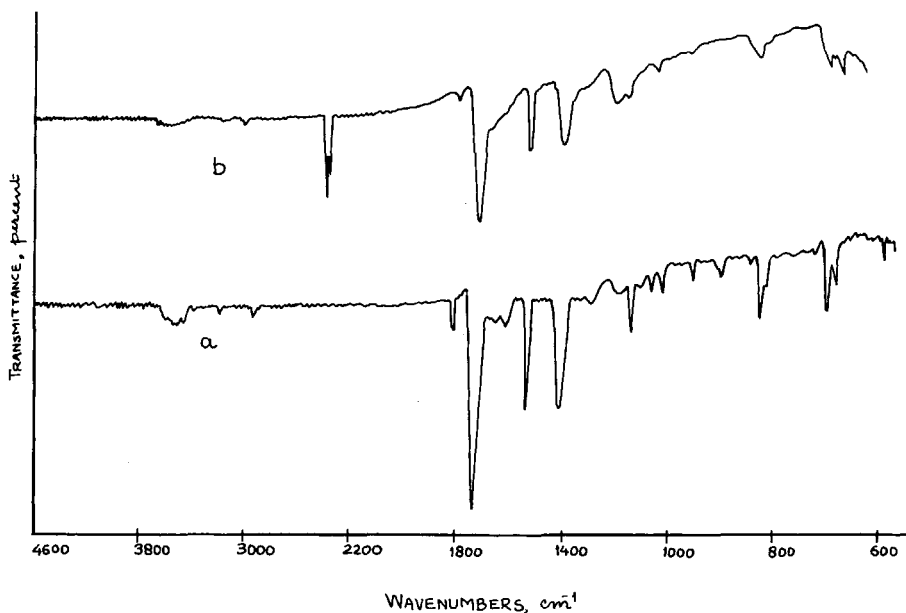

WAVENUMBERS, cm⁻¹

Fig. 4.   Infrared spectra of resin BM–PBD15(VII): (a) before curing; (b) after curing.
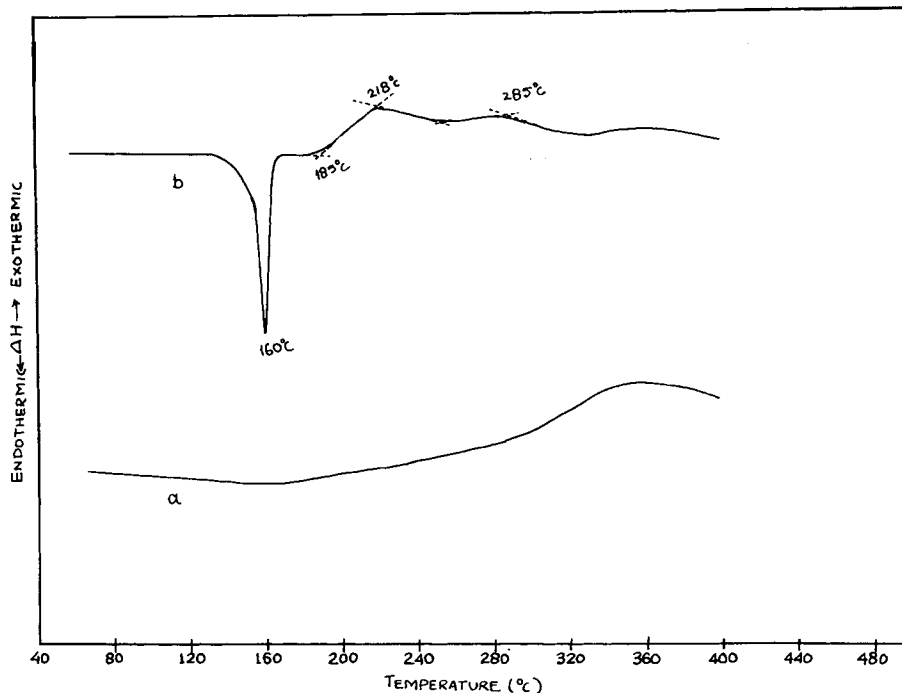
Fig. 5. Differential scanning calorimetry of cured (a) and uncured (b) resin BM–PBD15(VII); heating rate 10°C/min in air atmosphere.

uncured resin at 185–255°C and 255–321°C with their exothermic peak temperatures (Texo's) at 218 and 285°C, respectively. Observation of the endothermic peak at 160°C indicated the melting of the resin. The onset temperature observed at 185°C for the first exothermic peak indicated the start of the polymerization reaction. Absence of exothermic peaks in the DSC thermogram of the cured specimen indicated the completion of curing reaction.

Thermal Stability

The relative thermal stability of the cured resins was investigated by dynamic thermogravimetric analysis in nitrogen and air atmospheres. The analytical data are shown in Figure 6. The polymer decomposition temperature (PDT), the temperatures at which the polymers' maximum rate of weight loss occured (PDT max) and the char yields, in both nitrogen and air atmosphere, are summarized in Table II. The results show that for BM–PBD specimens the threshold temperature at which polymer decomposition starts is 490–475°C in both nitrogen and air atmosphere, while, for control specimen BM (IV), it is 415°C. A two-step decomposition was observed for BM–PBD-cured specimens in air atmosphere with maximum thermooxidative decomposition taking place mainly beyond 650°C. Anaerobic char yields of the cured specimens at 800°C were found to be in the range of 50–49%.

Energy of activation for the decomposition of the cured specimens in nitrogen atmosphere were calculated from the TGA curves by the integral
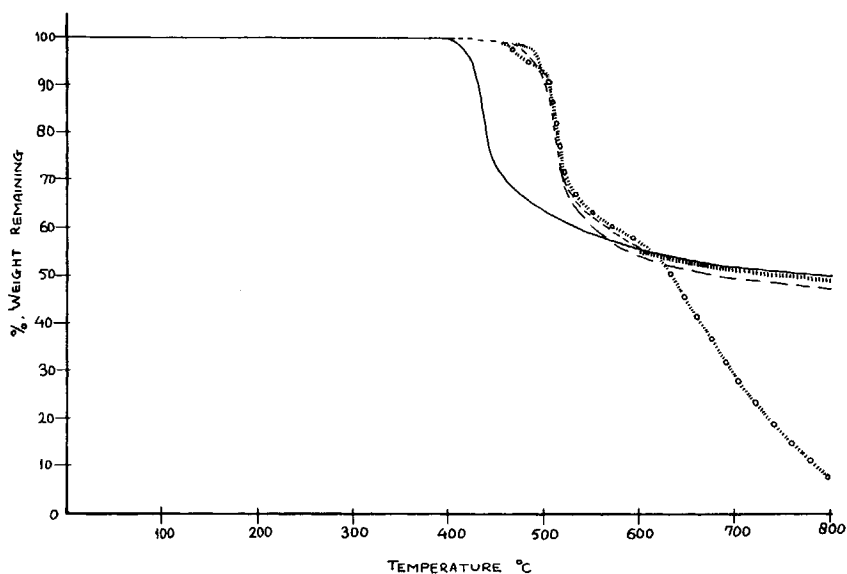
Fig. 6. Thermogravimetry analysis of cured resins. Heating rate 10°C min; flow rate 100 mL/min for nitrogen and static flow for air: (————) BM(IV) in N_2; (- - -) BM–PBD10(VI) in N_2; (— — — —) BM–HPBD10(VIII) in N_2; (‖‖‖‖) BM–PBD15(VII) in N_2; (‖‖O‖‖O‖‖O‖‖O‖‖) BM–PBD15(VII) in air.

method of Horowitz and Metzer.[18] The equation used for this calculation was:

$$\ln[\ln(1 - \alpha)^{-1}] = \frac{E\theta}{RT_s^2}$$

where α = fraction decomposed, E = energy of activation, $\theta = T\text{-}T_s$, T_s = reference temperature at which dW/dT is maximum, and R = gas constant.

Figure 7 shows the plots of $\ln \ln(1 - \alpha)^{-1}$ vs. θ, which gave straight lines with slope E/RT_s^2 from which E was calculated. The value of frequency

TABLE II
Decomposition Temperatures and Char Yields of Cured Resins

Cured resins from		PDT (°C)	PDT max (°C) (W^a)[a]	Char yield (%) 800°C	PDT	PDT max (°C) (W^a)	Char yield (%) 800°C	700°C
			In nitrogen			In air		
BM	(IV)	415	435(82)	50	—	—	—	—
BM–PBD10	(VI)	480	511(75)	50	480	511(85)	14	33
BM–PBD15	(VII)	490	511(74)	49	475	511(82)	8	28
						660(42)		
BM–HPBD10	(VIII)	480	510(72)	48	—	—	—	—

[a] W^a = weight remaining at indicated temperature.
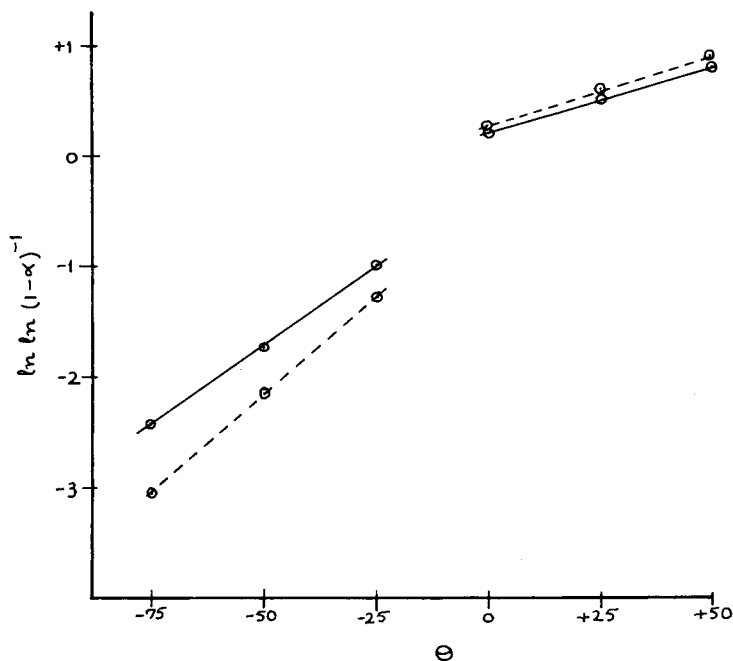
Fig. 7.   Plots of ln ln(1 − α)⁻¹ vs. θ: (——————) BM–PBD10(VI); (- - - - - -) BM–PBD15(VII).

factor Z was obtained from the expression

$$\ln(1 - \alpha) = -\frac{Z}{q}\frac{RT_s^2}{E} \cdot e^{-E/RT_s}$$

where $q = dT/dt$. The results are given in Table III.

It is interesting to point out based on the results of Tables II and III that incorporation of 1,2-polybutadiene in bismaleimide provides improved thermally stable polymers.

Composite Fabrication

Test laminates were prepared under identical conditions. The graphite cloth (Hercules magnamite type AS, W sizing, magma, Utah) was coated with a chloroform solution of any of the resins, BM(IV), BM–PBD10(VI),

TABLE III
Energy of Activation and Frequency Factor of Cured Resins in Nitrogen Atmosphere[a]

Cured resin from		Temperature range (°C)	E Energy of activation		Z, frequency factor
			(kJ/mol)	(kcal/mol)	
BM	(VI)	400–500	116	27.78	1.45×10^6
BM–PBD10	(VI)	450–550	154	36.80	7.50×10^7
BM–PBD15	(VII)	450–550	189	45.19	1.86×10^{10}

[a] Energy of activation for thermooxidative degradation of different polyimides have been reported in the literature.[19]

TABLE IV
Physical Properties of Graphite Cloth Laminates

Property tested	Test method	BM(II)	BM–PBD10 (VI)	BM–PBD15 (VII)	BM–HPBD10 (VIII)	Epoxy[a]
Resin content (%)	Nitric acid method	31	30	31	30	25
Density (g/cm³)		1.32	1.31	1.29	1.30	1.57
LOI (% O₂)	ASTM D2863	55	48	43	—	43
Tensile strength_psi (MN/m²)	ASTM D638	21 190 147	28 302 195	36 630 253	30 501 210	51 639 356

[a] Compared to the commonly used epoxy, Ciba-Geigy MY-720 (tetraglycidylamine of 4,4'-diaminodiphenylmethane) cured with 4,4'-diaminodiphenylsulfone (DDS).

BM–PBD15(VII), and BM–HPBD10(VIII). The prepregs were dried in an air-circulated oven at 50–60°C for 5–10 min. The prepregs (eight plies) were stacked and pressed between aluminium plates in a press maintained at 190°C for 2 h. The temperature was then raised to 230°C for 45 min. The pressure during curing was maintained at about 50 psi. The press was then allowed to cool slowly holding the temperature for 10–15 min each at 200, 170, and 100°C, respectively.

The resin content of each of these laminates were determined by boiling with concd nitric acid. The limiting oxygen index tests (LOI) were performed at room temperature. These laminates did not burn up to 45–40% of oxygen. The density and tensile strength of eight-ply laminates were determined.

It can be seen from the results presented in Table IV that incorporation of 1,2-polybutadiene in 4,4'-bismaleimidodiphenylmethane improves the tensile strength of graphite cloth laminates. Also observed is a decrease trend of density. The graphite cloth test laminates prepared from 15% incorporated 1,2-polybutadiene in bismaleimide showed tensile strength of 253 MN/m² compared to 147 MN/m² obtained from parent bismaleimide, indicating the usefulness of the resin. This improvement, however, is still lower than the tensile strength value of 350–500 MN/m² reported from the graphite cloth laminates prepared from epoxy resins (Table IV).

CONCLUSION

It can be concluded based on the results of TGA, energy of activation, LOI, density and tensile strength measurements that BM–PBD15(VII) is the preferred matrix resin system among the various 1,2-polybutadiene-incorporated 4,4'-bismaleimidodiphenylmethane resins studied.

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