

Effect of Triallyl Cyanurate on the Properties of *bis*-Maleimide Resins

INDRA K. VARMA, S. P. GUPTA and D. S. VARMA, *Centre for Materials Science and Technology and Department of Textile Technology, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi, 110016*

Synopsis

This paper describes the improved processibility of 4,4'-*bis*-maleimidophenyl methane (BM) chain extended by 4,4'-diaminodiphenyl methane (DADPM) by coreaction with triallyl cyanurate (TAC). Curing of BM, chain-extended BM, and mixture of BM and DADPM (1 : 0.3 molar ratio) in the presence of 5, 10, 15, and 20% (w/w) of TAC was followed by differential scanning calorimetry (DSC) and thermal stability of cured resins was evaluated by thermogravimetric analysis. TAC had insignificant effect on char yield (at 800°C) of BM resin. Glass- and graphite fabric-reinforced composites were fabricated using chain-extended BM containing 10% TAC and methyl ethyl ketone (MEK) as solvent. Interlaminar shear strength was found to be 7620 psi for graphite fabric laminate containing 40% resin. Good retention of mechanical properties of laminates at 220°C up to 320 h was observed.

INTRODUCTION

Advanced fiber-reinforced polyimide matrix composite materials are attractive for aerospace structures due to their outstanding specific strengths, specific stiffness, thermo-oxidative stability, and excellent retention of properties in hot-wet environments. A wide variety of thermosetting polyimides, end-capped with reactive maleimide, norbornene, or acetylenic unsaturation, have been developed in the last 15 years with an aim to improving the processing conditions while retaining high temperature capabilities and mechanical strength of polyimides.

Very attractive high temperature thermosets are based on *bis*-maleimides, which are being increasingly used as matrix resins for carbon fiber-reinforced composites. These monomers are cured by a thermally induced addition reaction to give highly cross-linked void-free network polymer. There are, however, certain problems with *bis*-maleimide such as solvent retention in the prepregs, brittleness of the polymers due to high cross-link density, and the high temperatures used for curing. Attempts have been made to overcome these shortcomings by Michael addition reaction with diamines or coreacting with reactive diluents.

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Some of the commercially available polyamine-*bis*-maleimide resins (Rhône Poulenc, Keremid 601)¹ are prepared by reacting 4,4'-*bis*-maleimidophenyl methane (BM) with 4,4'-diaminodiphenyl methane (DADPM) either in solution or melt. The processing solvent is *N*-methyl pyrrolidone (NMP). Similarly Technochemie M751 resin has to be processed from NMP to form laminates.^{2,3} For ease of processing, preregs are required with drape and tack, which means leaving some solvent in the preregs. This residual high boiling solvent (i.e., NMP or DMF) causes considerable degradation in the final laminate properties perhaps due to plasticization at high temperature or void formation. There is, therefore, a need to develop *bis*-maleimide resin which can be processed by using low boiling solvents like methyl ethyl ketone, acetone, or methylene chloride.

Coreaction of *bis*-maleimides with thermostable reactive-monomer can combine the properties of both types of resins.⁴⁻⁶ This coreactant can homopolymerize to give thermally stable materials and can also participate in free radical copolymerization with *bis*-maleimide.

We now report processing of polyamino *bis*-maleimide based on 4,4'-*bis*-maleimidodiphenyl methane (BM) from MEK solution. Triallyl cyanurate (TAC) was used as a coreactant.

Thermal behavior of BM, chain-extended BM by Michael reaction with 4,4'-diaminodiphenyl methane (DADPM) or tris(*m*-aminophenyl) phosphine oxide (TAP) in acetone solution; [molar ratio (1 : 0.3)], BM : DADPM mixture (1 : 0.3 molar ratio) in presence of TAC was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Glass fabric- and graphite fabric-reinforced composites were fabricated from MEK solution and room temperature mechanical properties were determined. Effect of heating laminates at 220°C for several hours on mechanical properties was also evaluated.

EXPERIMENTAL

Materials. 4,4'-*bis*(maleimidophenyl) methane (BM) (m.p. 156–160°C) was prepared by the cyclodehydration of *bis*-maleamic acid precursor with acetic anhydride and sodium acetate.⁷ The crude BM was purified by passing a chloroform solution through silica gel (60–120 mesh) (yield = 70%). 4,4'-Diaminodiphenyl methane (Fluka) (DADPM) was used as such. Tris (*m*-aminophenyl)phosphine oxide (TAP) was prepared according to procedure reported elsewhere.⁸ Triallyl cyanurate (TAC) was commercially available and used as such.

Chain extension reaction of BM with amines (1 : 0.3 molar ratio) [(DADPM)/TAP] was done in solution using methyl ethyl ketone (MEK) or acetone as a solvent. Refluxing BM with DADPM in acetone solution yielded a homogeneous solution after 3–4 h. Acetone was removed by using a rotary evaporator and shining powder of *bis*-maleimide-amine adduct was obtained. Chain extension reaction in MEK instead of acetone could also be carried out for prepreg preparation. Homogeneous solution in MEK was obtained after refluxing BM and DADPM (molar ratio 1 : 0.3) for 2–3 h and this solution, containing 40–50% (w/v) of adduct, was used directly for coating the glass/graphite fabric.

Curing of *bis*-maleimides. BM and DADPM containing different proportions of TAC (0–20%) and benzoyl peroxide (.05–2% w/w of the total resin content) were placed in shallow aluminum dishes and cured at $180 \pm 5^\circ\text{C}$ for 1 h in an air oven. Thermal stability of these cured samples in nitrogen atmosphere was evaluated by using a DuPont 1090 thermal analyzer having a TGA module-951. A heating rate of $10^\circ\text{C}/\text{min}$ and sample size of 11 ± 2 mg was used.

Curing characteristics of various *bis*-maleimide resin samples in nitrogen atmosphere were studied by using DuPont DSC module-910. A heating rate of $10^\circ\text{C}/\text{min}$ and sample size of 10 ± 3 mg were used.

Laminate Fabrication. Epoxy-compatible glass fabric (Pilkington Glass Co., RP-6 weighing $200 \text{ g}/\text{m}^2$) was used for prepreg preparation. The graphite fabric, Torayca 6341, 8H satin weave was a gift sample supplied by Toray Co. Japan. Glass fabric or graphite fabric 7×7 inches were coated with chain-extended *bis*-maleimide resin solution in MEK containing 10% (w/w) TAC and benzoyl peroxide. The drying was done at room temperature for 1 h and then at 100°C for 1 h in an air oven.

Ten plies (glass fabric) or seven plies (graphite fabric) of prepregs were used for laminates fabrication. The dried prepregs which were slightly tacky were stacked and pressed between glazing sheets covered with an aluminum foil. Compression moulding was done on a Carver Laboratory Press at 180°C (pressure 100 psi) for 1 h, and then at 205°C (pressure 100 psi) for 1 h. Postcuring was done at $220 \pm 10^\circ\text{C}$ for 16 h.

Evaluation of Properties of Laminates. Resin content was determined by hydrazine method. A 0.2–0.3 g of laminate was treated with hydrazine hydrate (Sarabhai Chemicals) at room temperature for 30 min and then the temperature was gradually increased to boiling for half an hour. After cooling to room temperature, the fibrous residue was filtered (sintered glass funnel), washed with acetone several times, and dried to a constant weight.

The mechanical properties of laminates were determined by using an Instron Model No. 1121. Interlaminar shear strength was determined according to ASTM-D 2344-76. A span-to-depth ratio 5 : 1, crosshead speed of 0.0394 inch/min, and sample width of 0.5 inch was used.

$$\text{SH} = \frac{0.75 \times p_B}{b \cdot d}$$

Where p_B = load at the moment of break (lb), b = width of specimen (in.), and d is specimen thickness (in.).

The flexural properties of the composites were determined by using a span-to-depth ratio of 32 : 1. All samples had a width of 0.5 in. and a crosshead speed of 0.0394 inch/min was used (ASTM-D 790-70).

$$\text{Flexural strength} = \frac{3/2 p \cdot L}{b \cdot d^2}$$

where p = load at the moment of break (lb),

L = support span (in.), and b and d are the width and thickness of the specimen, respectively.

The dynamic mechanical properties of laminates were determined using a DuPont DMA-982 module by keeping heating rate $5^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

In DSC trace of BM a sharp endotherm indicating melting was observed around $158\text{--}160^{\circ}\text{C}$ (Fig. 1). Mixing of BM with DADPM (1 : 0.3 molar ratio) and addition of TAC to this mixture resulted in a decrease in melting

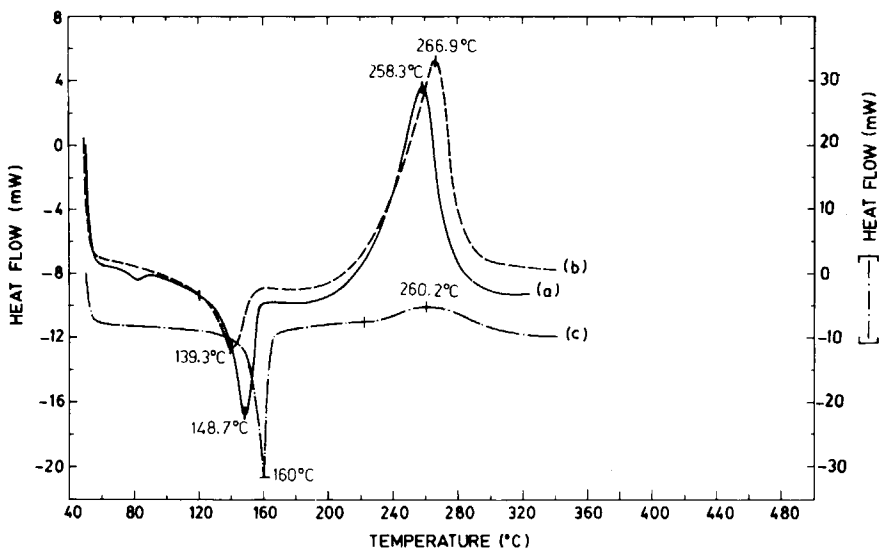


Fig. 1. DSC traces of BM resin (c) and BM:DADPM resin mixture (1 : 0.3 molar ratio) in presence of 5% (a) and 20% (b) TAC.

TABLE I
Effect of TAC and Benzoyl Peroxide on Fusion Endotherm of
BM : DADPM (1 : 0.3 molar ratio)

S. no.	TAC content (%)	BP (%)	T_1' ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_2' ($^{\circ}\text{C}$)	ΔH_f (J/g)
1.	0	1.0	130.0	145.0	160.0	43.1
2.	5	0.047	120.0	148.7	160.0	53.6
	5	2.0	95.0	148.0	162.0	57.1
3.	10	0.090	116.0	142.9	156.0	42.1
	10	2.0	100.0	142.3	160.0	62.1
4.	15	0.130	104.0	143.0	156.0	42.1
	15	2.0	100.0	137.0	155.0	44.8
5.	20	0.166	100.0	139.3	158.0	45.7
	20	2.0	95.0	136.1	158.0	50.0

TABLE II
Effect of TAC and Benzoyl Peroxide on Curing Exotherm of
BM : DADPM (1 : 0.3 molar ratio)

S. no.	TAC content (%)	BP (%)	T_1 (°C)	T_{exo} (°C)	T_2 (°C)	ΔH (J/g)
1.	0	1.0	190.0	250.2	290.0	249.0
2.	5	0.047	224.8	258.3	304.0	250.0
	5	2.0	221.0	268.5	310.0	252.0
3.	10	0.090	231.1	262.9	298.0	226.0
	10	2.0	226.6	261.5	310.0	306.0
4.	15	0.130	224.8	265.5	296.0	224.0
	15	2.0	219.3	261.7	310.0	291.0
5.	20	0.166	232.4	266.9	294.0	288.0
	20	2.0	223.4	267.5	320.0	304.0

transition. From the DSC traces, characteristic temperatures were noted for defining this endothermic transition. These include the temperature of initial deviation from base line (T_1'), endothermic peak position (T_m), and temperature marking the end of endotherm (T_2'). T_1 and T_2 were obtained by extrapolation of front side or back side of the endothermic transition. The heat of fusion ΔH_f was calculated from the area under the endothermic transition. The results are summarized in Table I. An increase in concentration of benzoyl peroxide in the resin mixture did not influence T_m of the sample.

Exothermic transitions associated with polymerization of maleimide double bond and/or vinylic double bond of TAC were observed in temperature range of 190–300°C. Heat of curing (ΔH) exothermal peak position (T_{exo}), on-set temperature of curing reaction (T_1), and temperature of completion of reaction (T_2) were determined from DSC traces (Table II). Addition of 5% TAC to BM : DADPM mixture resulted in an 30°C increase in T_1 values. Further increase in TAC content did not influence T_1 significantly. Addition of TAC only marginally affected T_{exo} and T_2 temperatures. An increase in ΔH values were observed on increasing benzoyl peroxide content in the resin, indicating

TABLE III
Effect of Triallylcyanurate (TAC) on the Thermal characteristics of *bis*-maleimide (BM)

S. no.	TAC content (%)	BP (%) (w/w)	T_m (°C)	T_1 (°C)	T_{exo} (°C)	ΔH (J/g)
1.	5	.05	154	238	266	109
2.	10	.10	151	249	273	—
3.	15	.15	148	236	264	153
4.	20	.20	147	236	265	171
5.	25	.25	143	236	263	176

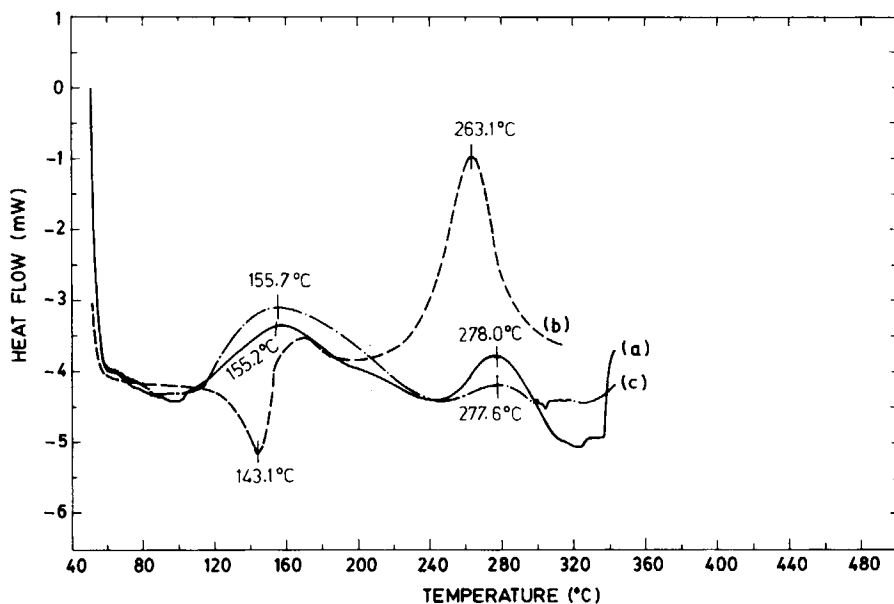
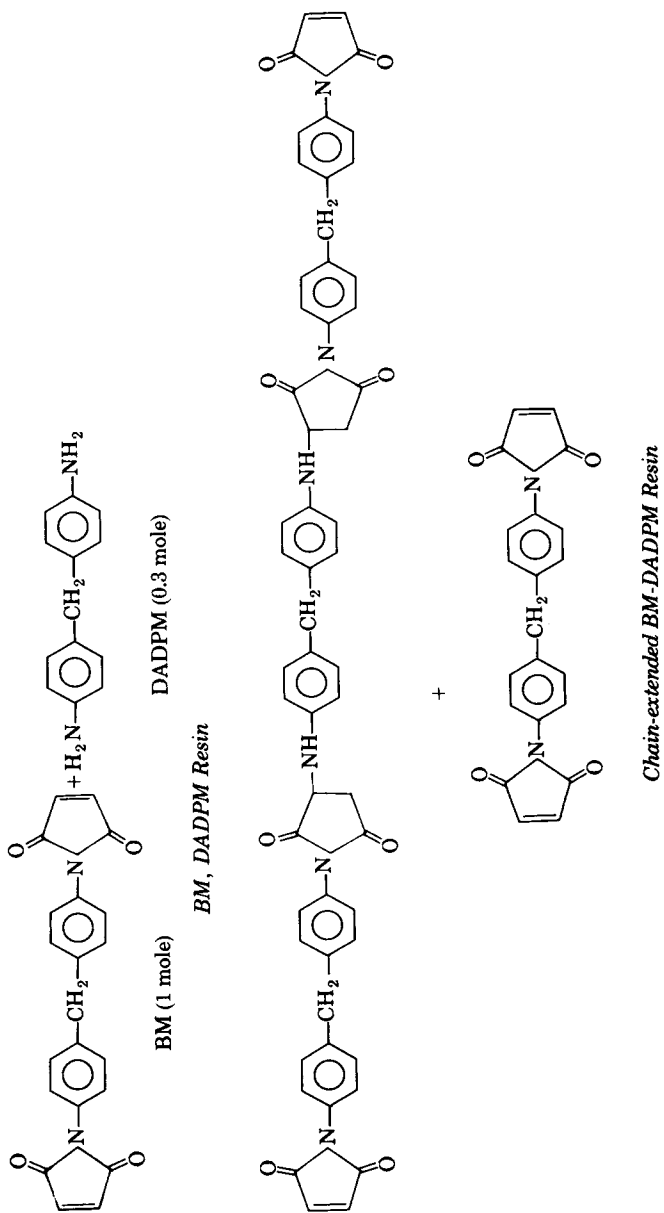


Fig. 2. DSC traces of chain-extended BM-DADPM resin (c) in presence of 5% TAC (a) and 25% TAC (b).

thereby higher cross-linking of the resin during cure. T_{exo} values on the other hand, were unaffected by increasing benzoyl peroxide (Table II).

Effect of TAC on the curing behavior of BM was also investigated and results are given in Table III. An increase in ΔH was observed by increasing TAC/benzoyl peroxide content of the resin. T_m decreased on addition of TAC.

Chain-extended BM-DADPM or BM-TAP resins did not show sharp endothermic transitions associated with melting (Figs. 2 and 3). However, two exothermic transitions, with peak positions at 155.7 and 277.6°C were observed in BM:DADPM. Addition of 5% TAC only slightly affected these exotherms. Increase in TAC content to 25% resulted in the appearance of an endotherm at $\sim 143^\circ\text{C}$. An $\sim 15^\circ\text{C}$ reduction in the higher temperature exotherm was also observed (Table IV). Increase in benzoyl peroxide from 0.05 to 2% on BM-DADPM resin containing 5% TAC resulted in broadening of exotherm and loss of bimodal character. The T_{exo} position also shifted to lower temperature ($\sim 40^\circ\text{C}$) (Table IV). A significant increase in ΔH values was observed at higher concentration of benzoyl peroxide. These results thus indicate that BM-DADPM resin containing TAC starts curing at relatively low temperatures and this curing is facilitated by an increase in concentration of free radical initiator. However, in the case of BM resin containing DADPM and TAC, the free radical initiator had no significant effect on position of T_{exo} (Table II). This difference between chain-extended BM-DADPM resin and BM-DADPM resin mixture may be attributed to the amine-catalyzed decomposition of peroxide at low temperatures in the samples containing free amine. The two resin systems can be depicted as follows:



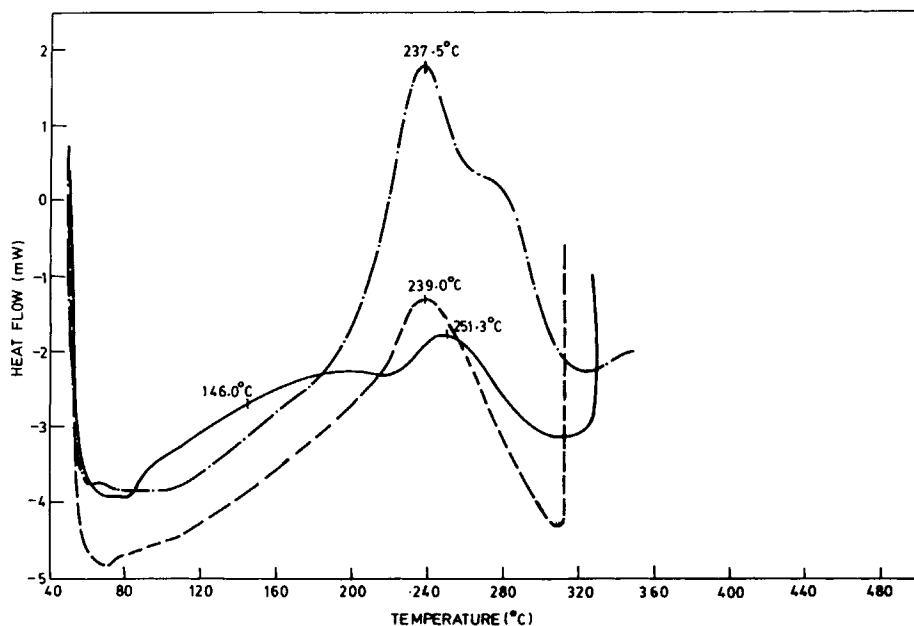


Fig. 3. DSC traces of chain-extended BM-DADPM-TAC resin containing 2% (w/w) benzoyl peroxide (---) 15% TAC, (- - -) 5% TAC, and (—) 0% TAC.

No significant change in curing characteristics of BM:TAP resins was observed on addition of TAC.

The activation energy for curing reactions of BM:DADPM (1:0.3 molar ratio) resin mixture containing TAC was determined according to dynamic method using the Borchardt-Daniels DSC kinetics program,⁹ which permits the calculation of activation energy E , pre-exponential factor (Z), and order of reaction (n) from a single DSC scan of a reaction exotherm. The method assumes that the reaction follows n th-order kinetics, i.e.,

$$\frac{d\alpha}{dt} = K_{(T)}(1 - \alpha)^n$$

where α = fractional conversion (dimension less);

$K_{(T)}$ = specific rate constant at temperature $t(s)^{-1}$;

n = reaction order (dimensionless).

The method also assumes that the temperature dependence of reaction rate follows the Arrhenius expression. Typical Arrhenius plots of $\ln K_{(T)}$ vs. $1/T$ are given in Figure 4. The results are given in Table V.

Relative thermal stability of cured resin (at $180 \pm 5^\circ\text{C}$ for 1 h) was evaluated by thermogravimetry. Initial decomposition temperature (IDT), temperature of maximum rate of weight loss (T_{\max}), final decomposition

TABLE IV
Effect of Triallylcyanurate (TAC) on the Thermal
Characteristics of Chain-Extended *bis*-Maleimide

S. no.	Bisimide	TAC content (%)	BP (%) (w/w)	T_1 (°C)	T_{exo} (°C)	ΔH (J/g)
1.	BM-DADPM	0	1.0	112.4	155.7	54.5
				257.7	277.7	3.68
2.	BM-DADPM	5	0.05	100.6	155.2	48.8
				250.6	278.0	19.9
			2.00	177.0	238.0	177.0
3.	BM-DADPM	10	0.10	111.0	154.9	16.5
				254.2	276.7	37.7
			2.0	194.4	236.0	161.0
4.	BM-DADPM	15	2.0	197.2	237.0	216.0
5.	BM-DADPM	20	2.0	193.0	235.0	238.0
6.	BM-TAP	5	0.05	167.0	205.0	95.0
7.	BM-TAP	15	0.15	180.0	219.0	144.0
8.	BM-TAP	25	0.25	193.0	232.0	227.0

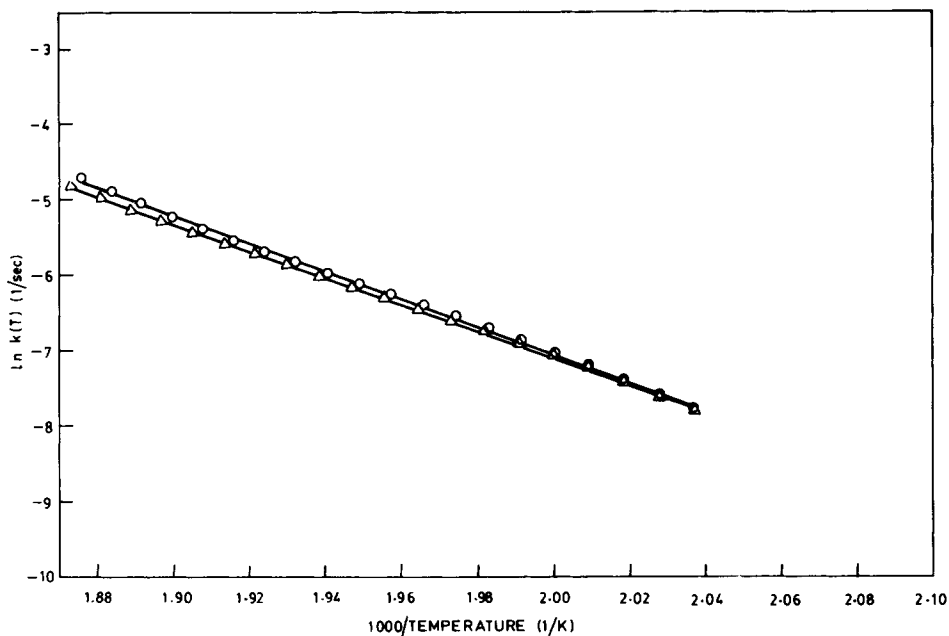


Fig. 4. Arrhenius plots of cure rate constant of BM-DADPM-TAC resin vs. reciprocal temperature (Δ) 5% TAC and (\circ) 20% TAC.

temperature (T_f), and char yield (Y_c) were noted from TG traces. Addition of TAC to BM resulted in a slight decrease in IDT, and T_{max} (Fig. 5) and (Table VI). All these resins were stable up to 400°C and started decomposing above this temperature. In cured BM:DADPM mixtures (1:0.3 molar ratio) containing TAC a two-step decomposition was observed (Fig. 6). About 5% weight loss was observed at 200°C. These results are summarized in Table VII. The

TABLE V
Thermal Degradation of BM: DADPM Resin in Nitrogen
Atmosphere-Evaluation of Kinetic Parameters

S. no.	TAC content (%)	Activation energy KJ/mole	Reaction order	log Z min ⁻¹
1.	5	148.0	1.44	14.2
2.	10	144.0	1.01	13.8
3.	15	129.0	1.04	12.4
4.	20	152.0	1.54	14.6

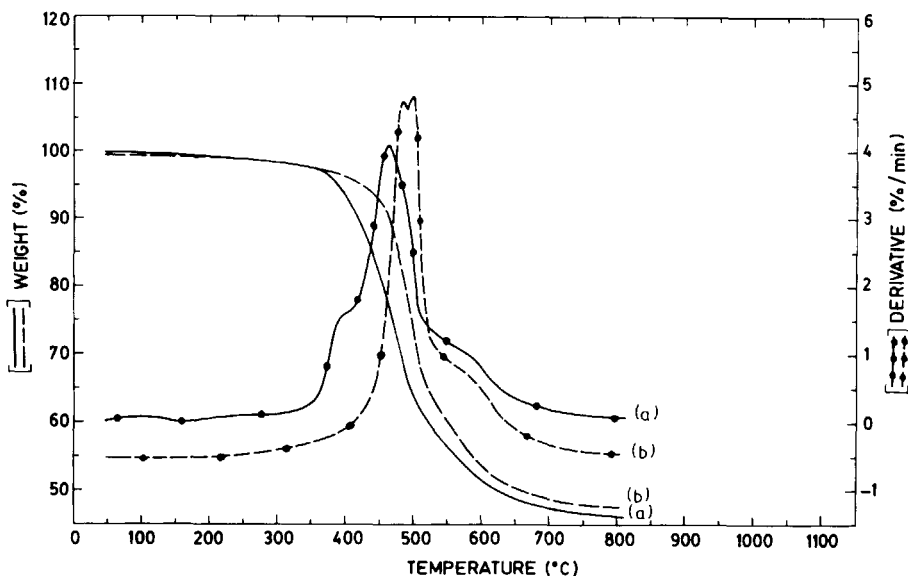


Fig. 5. TGA traces in nitrogen atmosphere of cured BM resin containing 20% TAC (a) and 10% TAC (b).

TABLE VI
Thermal Behavior of BM Resin Blended with
TAC and Cured at 180°C for 1 h

S. no.	TAC content (%)	IDT (°C)	T _{max} (°C)	T _i (°C)	Y _c (%)
1.	5	475.4	499.6	536.2	44
2.	10	452.4	489.0	541.2	47
3.	15	421.0	466.8	552.8	44
4.	20	410.1	483.3	534.2	46

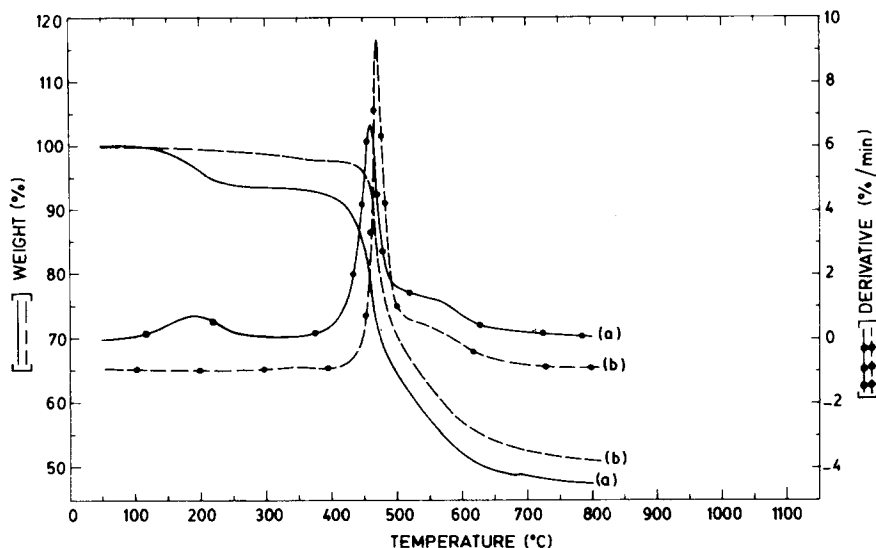


Fig. 6. TGA traces in nitrogen atmosphere of (b) cured BM : DADPM resin mixture and (a) BM : DADPM resin mixture containing 20% TAC.

TABLE VII
Thermal Behavior of BM : DADPM Resin Blended
with TAC and Cured at 180°C for 1 h

S. no.	TAC content (%)	IDT (°C)	T_{max} (°C)	T_f (°C)	Y_c (%)
1.	5	447.2	469.0	514.0	47
2.	10	440.0	464.0	515.0	47
3.	15	439.0	462.4	511.2	48
4.	20	434.2	461.0	511.1	47

chain extension of BM by DADPM resulted in a decrease in char yield. IDT and T_{max} values were (Table VIII) also lower than BM resin or BM : DADPM mixtures. Addition of TAC to this resin did not affect thermal degradation.

Mechanical properties of glass/graphite fabric reinforced chain-extended BM : DADPM resin containing 10% TAC (Table IX) was determined. The interlaminar shear strength for glass and graphite fabric laminates was found to be 4540 and 7620 psi, respectively.

TABLE VIII
Thermal Behavior of Chain-Extended BM-DADPM/TAC Cured at 180°C for 1 h

S. no.	TAC content (%)	IDT (°C)	T_{max} (°C)	T_f (°C)	Y_c (%)
1.	0	391.6	428.2	485.2	35
2.	5	384.9	426.4	480.9	33
3.	10	387.0	428.5	482.7	34

TABLE IX
Physical Properties of Glass/Carbon Fiber-Reinforced
Chain-Extended BM Resin Containing 10% (w/w) TAC

Properties	Test method	Glass fiber	Carbon fiber
Resin content (% w/w)		37.1	42.0
FS ($\text{psi} \times 10^4$)	ASTM-D 790-70	3.46 (SD \pm .59)	5.25 (SD \pm .41)
FM ($\text{psi} \times 10^5$)	ASTM-D 790-70	3.87 (SD \pm .60)	7.62 (SD \pm .64)
ILSS ($\text{psi} \times 10^3$)	ASTM-D 2344-76	4.59 (SD \pm .08)	7.05 (SD \pm .21)
After heating at $220 \pm 10^\circ\text{C}$ for			
(I) 100 h	—	—	6.69 (SD \pm 0.26)
(II) 185 h	—	4.78 (Sd \pm .26)	—
(III) 320 h	—	2.96 (SD \pm .22)	6.20 (SD \pm .03)
IV 460 h	—	—	3.73 (SD \pm .12)

Ageing of glass/graphite fabric-reinforced composites was done up to 460 h at $220 \pm 10^\circ\text{C}$ and interlaminar shear strength was determined at various time intervals. No significant change in ILSS was observed up to 185 h for glass fabric and 320 h for graphite fabric composites, but properties deteriorated beyond this time interval and a decrease in ILSS was observed. The glass transition temperature of these laminates were determined by DMA (Figs. 7 and 8) and were found to be $280/285^\circ\text{C}$ (on the basis of $\tan \delta$ curve).

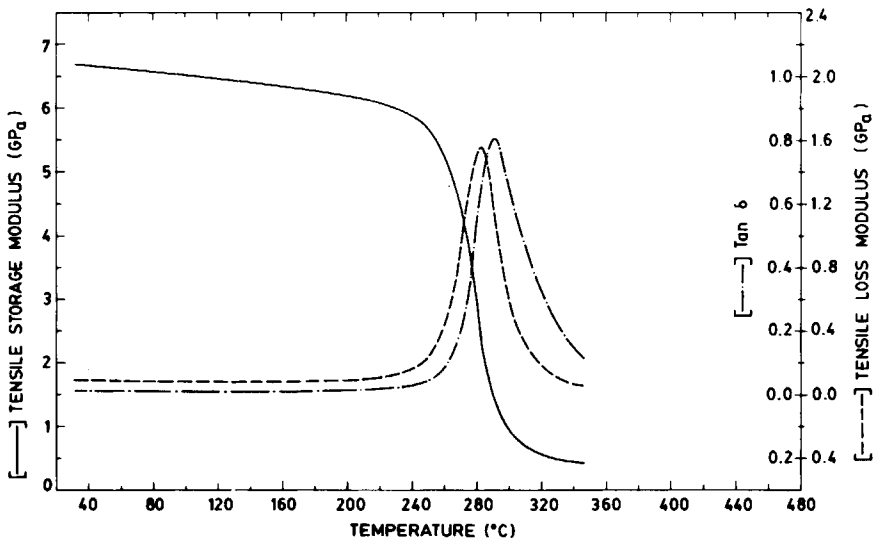


Fig. 7. DMA scan of glass fabric-reinforced chain-extended BM:DADPM resin laminate containing 10% TAC.

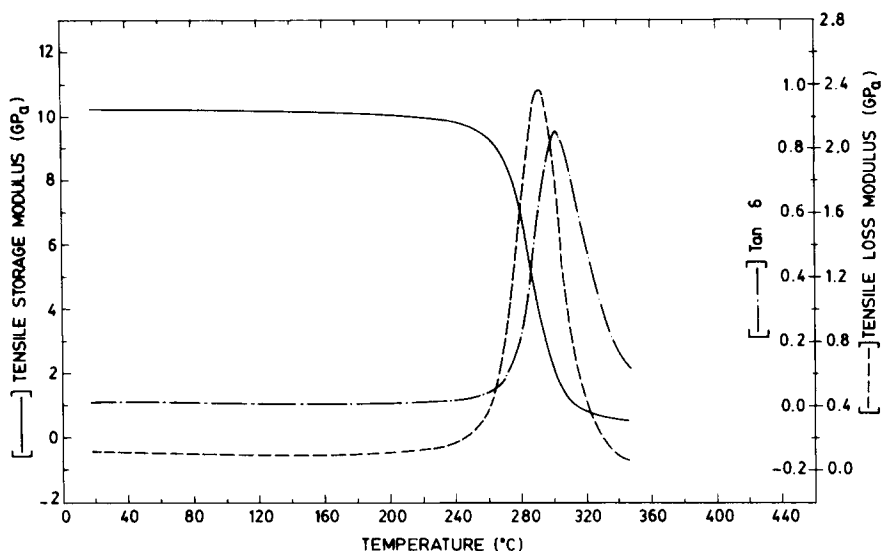


Fig. 8. DMA scan of carbon fabric-reinforced chain extended BM:DADPM resin laminate containing 10% TAC.

These results thus indicate that the above advanced composites based on *bis*-maleimide and TAC with excellent mechanical properties can be fabricated from MEK solution.

CONCLUSIONS

The following conclusions can be drawn on the basis of this work:

1. The melting temperature of 4,4'-*bis*-maleimidophenyl methane (BM) is reduced by addition of reactive diluent triallyl cyanurate and the decrease is proportional to the concentration of TAC (5–20% w/w). The melting temperature was also reduced by addition of 4,4'-diaminodiphenyl methane (DADPM) (molar ratio of BM : DADPM = 1 : 0.3). In chain-extended BM-DADPM resin or BM-TAP resin, sharp endothermic peak representing of T_m was not observed.

2. Exothermic transition associated with curing of BM, BM : DADPM resin mixture, and chain-extended BM-DADPM were influenced by the addition of TAC and free radical initiators. An increase in concentration of benzoyl peroxide resulted in a higher heat of curing reaction. A broadening of exotherm was also observed. Temperature of maximum rate of curing also decreased ($\sim 40^\circ\text{C}$).

3. Activation energy for the curing reaction of BM-DADPM mixture (containing 2% benzoyl peroxide) was only slightly affected by the addition of TAC and was in the range of 129–152 KJ/mole.

4. Thermal stability of cured resin was not influenced by its TAC content.

5. Glass and carbon cloth prepreps prepared from methyl ethyl ketone solution of chain-extended BM-DADPM resin containing TAC had better tackiness than those which did not contain TAC.

Advanced fiber-reinforced composites with excellent mechanical properties could be obtained by processing these resin systems from MEK solution.

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