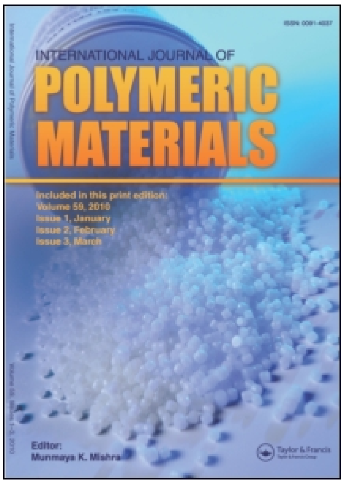

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Novel Bismaleimide—Epoxy Resin System

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Novel diamine namely N,N′-bis[1-(4-aminophenyl)ethanonyl]-1,4- benzenediamines (BAED) has been prepared and reacted with various bismaleimides at diamine:BM (1:2) ratio. The resulted bismaleimide-BAED oligoimide have been characterized by elemental analysis, IR spectral studies, number average molecular weight ($\overline{Mn}$) estimated by, non-aqueous conductometric titration and thermogravimetry. Some of bismaleimide-BAED oligomide have been modified by addition (i.e. curing reaction) of epoxy resin viz; diglycidyl ether of bisphenol-A and studied by differential scanning calorimetry (DSC). The glass and carbon reinforced composites have also been prepared and characterized by mechanical properties.

KEY WORDS Ketoamine triblock monomer, oligoimide, epoxy resin, glass reinforced composites, carbon reinforced composites.

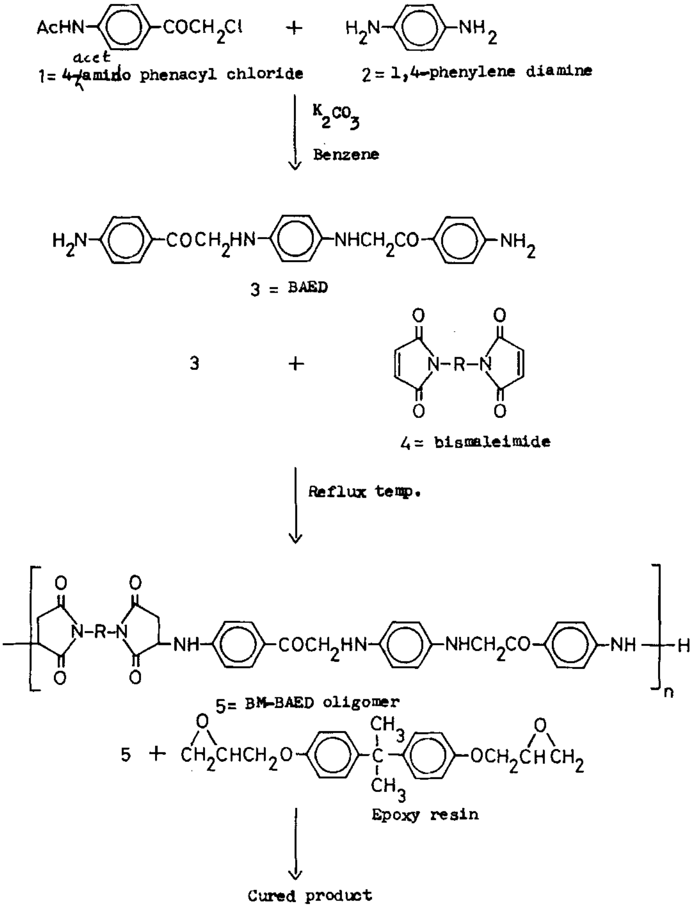
INTRODUCTION

Bismaleimide resins are brittle in nature due to high crosslink density and aromatic structure of the backbone. Attempts have been made in the past to improve processability and fracture toughness of bismaleimide resins by nucleophilic reaction to maleimideo double bond. Resin formulations based on bismaleimide and nucleophiles such as diamines,[1-3] dihydrazide,[4] amino acid hydrazide[5] and bisphenols[6] have been developed. Copolymerisation of maleimido double bond with vinylic compounds helps in improving the processability of bismaleimide resins.[7]

Recently we reported a new class of oligoimide-epoxy system developed for glass and carbon reinforced composites.[8-11] In continuation of this work the work presented here is in connection with synthesis of novel diamine (i.e. BAED) containing keto-amine group, its Michael addition reaction with bismaleimide resins and modification of oligoimide by epoxy resin into glass and carbon fibre reinforcement. The entire work has been traced in Scheme I.

RESULTS AND DISCUSSION

The objective of the work reported here was to synthesize novel bismaleimide-diamine oligomers and to use these for the curing of epoxies. It was feared that



SCHEME I

the larger molecular weight bismaleimide-diamine oligomer could not cure epoxy resin properly (e.g. a higher cure temperature may be needed). Hence attempts were made to establish the synthesis of oligomer having lower molecular weight and more reactive amino groups.

The synthesis of bismaleimide-diamine oligomer was performed using a slight modification of the method reported earlier.[18,19] As reported,[18,19] longer polymerizations yield high melting or softening materials. Consequently oligomerizations reported here were carried out for shorter periods, it was observed that heating of bismaleimide at 140°C did not induce addition polymerization. This happened only at elevated temperature or by use of an initiator.[20,21] This indicated that there would be absence of polybismaleimide species in the bismaleimide-diamine oligomer. The bismaleimide-diamine oligomer produced are in the form of yellow powder and soften at 130–150° depending upon the nature of the oligomer. They are insoluble in common organic solvents. The C, H, N contents of all oligomers (Table I) are consistent with their predicted structure (Scheme I). All the oligomers showed the red azo dye test confirming the pres-

TABLE I

Synthesis and characterization of oligomer

Bismaleimide used	Molar ratio of BM:BAED	Yield	Elemental Analysis C calc.	C found	H calc.	H found	N calc.	N found	$\overline{Mn}$	% wt. loss at °C from TGA 250	300	400	500
EBM	1:2	90	64.66	64.64	5.05	5.00	14.14	14.04	1365	3	15	59	83
PBM	1:2	85	67.28	67.30	4.67	4.75	13.08	13.00	1480	4	19	64	86
MBM	1:2	83	67.28	67.30	4.67	4.70	13.08	12.98	1486	3	20	69	85
BBM	1:2	75	70.19	70.25	4.73	4.75	11.69	11.55	1650	2	17	71	90
DDMBM	1:2	80	70.49	70.50	4.91	5.00	11.47	11.35	1680	3	18	67	87

ence of aryl amino groups. This suggests that there are terminal primary NH_2 groups in the oligomer.

Examination of the IR spectra not shown of the oligomers reveals that each spectrum comprises the strong bands around 1700 cm^{-1}, 1650 cm^{-1}, 1050 cm^{-1} and 730 cm^{-1} due to the presence of the imide group [22]. The inflections at 3500 cm^{-1} and 3400 cm^{-1} may arise from terminal NH_2 groups. The absence of the band at 3010–3040 cm^{-1} (attributed to the double bond present in bismaleimide) indicates the Michael addition polymerization of bismaleimide and BAED. The bands observed in the fingerprint region are due to the aromatic moiety. In brief, the spectra of the bismaleimide-diamine oligomer resemble in all aspects the spectrum reported earlier of the model compound N,N′-diphenyl aspartimide.[23] The number average molecular weight of oligomers are given in Table I. It was observed that $\overline{Mn}$ values decrease with increase in molar ratio of diamine to bismaleimide. This also indicates that the produced polymerization system yields low molecular mass oligomers rather than the high molecular mass reported earlier.[18,19] The NH and NH_2 values per repeat unit and polymer chain respectively have also been calculated on the basis of conductometric titration data.[24] These are shown in Table I. The results show that there would be more —NH_2 groups present in the oligomer prepared with a high ratio of diamine to bismaleimide. On the basis of closeness of observed NH values and nitrogen contents of all oligomers, the most probable structure of oligomer is that shown in Scheme I.

The TGA data of all oligomers are given in Table I. Examination of TGA data reveals that the oligomers start their decomposition around 200°C. The rate of decomposition increases between 250°C and 550°C, and oligomers decompose 90% around 600°C are shown typically in Figure 1. The cure reaction of oligoimide-epoxy was studied for the ratio of 1:1. The data obtained from DSC scans are given in Table II. From the DSC thermograms obtained it was seen that all the

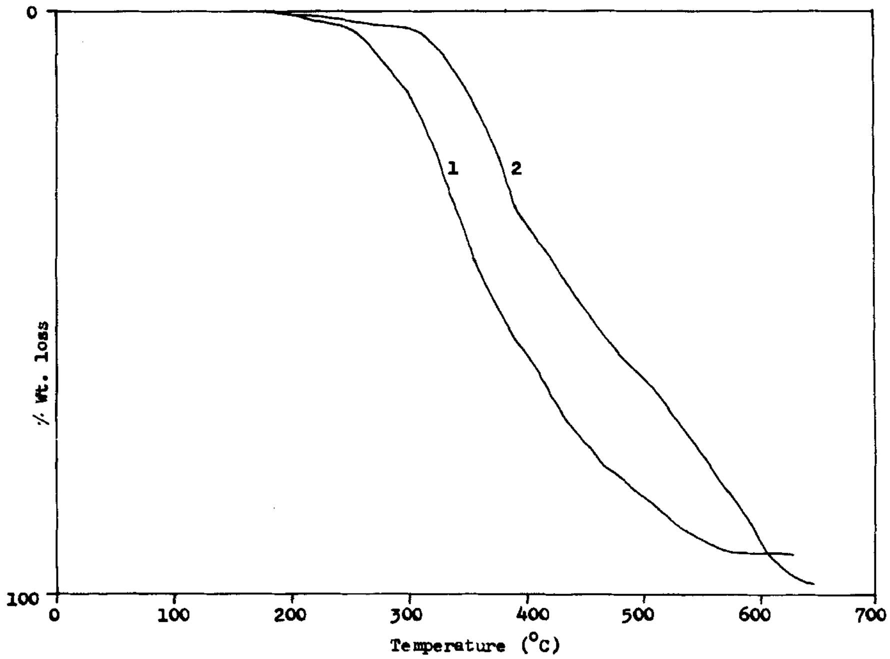


FIGURE 1 TGA of: 1) EBM-BAED oligomer, 2) EBM-BAED oligomer with epoxy resin in the ratio 1:1.

TABLE II

Curing characteristic of BM-BAED-epoxy system

Resin system	Oligomer to epoxy ratio	Kick off temp. Ti(°C)	Peak temp. Tp(°C)	Final temp. Tf(°C)	Activation energy Ea Kcal/mol	Order of reaction
EBM-BAED	1:1	150	220	231	30.8	0.95
PEM-BAED	1:1	169	210	222	33.58	1.2
MBM-BAED	1:1	156	200	215	33.2	1.1
BBM-BAED	1:1	223	248	261	41.0	1.25
DDMBM-BAED	1:1	200	225	250	42.0	0.95

oligoimide cured systems gave single exothermic peak in the range 150–261°C. Figure 2 shows the typical DSC thermogram at 10°C/min. This shows that the rate of reaction of major secondary amine and minor primary hydrogen atoms with epoxide occurs simultaneously.[25] From the thermograms the kick of temperature

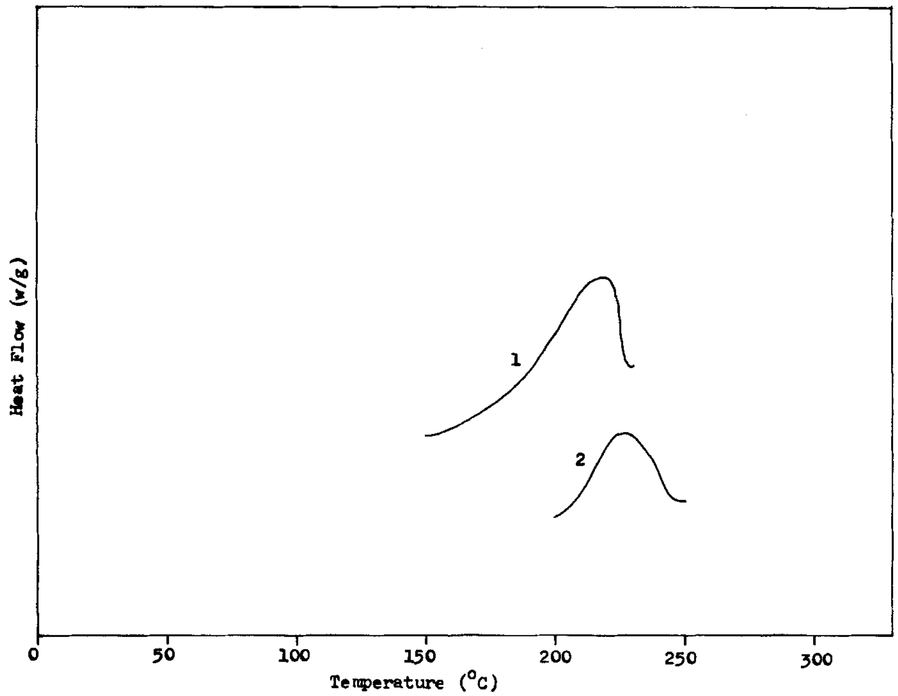


FIGURE 2 DSC curve of: 1) EBM-BAED oligomer with epoxy resin in the ratio 1:1, 2) DDMBM-BAED oligomer with epoxy resin in the ratio 1:1.

(*Ti*), peak exotherm temperature (*Tp*) and temperature of completion of cure (*Tf*) were obtained.

It was observed that the curing temperature of the epoxy system increases with an increase in the molecular weight of the oligomer. This behaviour is probably due to the lower rate of diffusion of the high molecular weight oligomer as well as the reduced functionality, hence reactivity, compared with the lower molecular eight oligomers (see Scheme I). The values of activation energy (*Ea*) for such a system (Table II) increase with increase in the molecular weight of oligomer indicating the lower reactivity of higher-molecular-weight oligomer. The kinetic parameters such as *E* (activation energy) and *n* (order of reaction) were calculated by assuming that the curing reaction obeys Arrhenius type kinetics and that the peak maximum represents a point of constant conversion. To obtain information about the properties of unreinforced crosslinked materials, larger cured specimens were prepared using the same proportions and temperatures as stated in Table II. The unreinforced cured oligoimide-epoxy samples are dark brown in colour and are slightly hard materials that form powder under normal hand pressure. They are insoluble in all common organic solvents including formic acid. They are swelled little by 25% v/v HCl and 25% w/v NaOH. Thermogravimetric analysis of all the unreinforced crosslinked materials reveals that they all degrade in a single step and start their decomposition at around 250°C. Degradation becomes faster between 300°C and 500°C. IR spectra of unreinforced cured products clearly show disappearances of the oxirane ring (910 cm^{-1}). The inflections at 1170 cm^{-1} in the

TABLE III

TGA of unreinforced BM-BAED-epoxy cured materials

Resin system	Oligomer epoxy ratio	% wt. loss at °C from TGA				
		250	300	400	500	600
EBM-BAED	1:1	2	3	37	63	91
PBM-BAED	1:1	2.5	4	31	69	93
MBM-BAED	1:1	2	3	34	62	90
BBM-BAED	1:1	2	5	39	71	94
DDMBM-BAED	1:1	3	7	42	70	90

TABLE IV

Mechanical and electrical properties of glass reinforced composites based on BM-BAED epoxy system

Resin system	Oligomer to epoxy ratio	Percentage change on exposure to 25 % (w/v) NaOH		Specific gravity	Flexural strength (mPa)	Compressive strength (mPa)	Impact strength (mPa)	Rockwell hardness	Electrical strength (in air) (kV/mm)
		Thickness	Weight						
EBM-BAED	1:1	1.0	1.3	1.81	175	205	201	112	12.5
PBM-BAED	1:1	1.1	1.2	1.59	292	250	286	118	13.5
MBM-BAED	1:1	0.8	1.3	1.82	207	245	240	128	16.0
BBM-BAED	1:1	0.9	0.9	1.76	125	160	152	132	17.0
DDMBM-BAED	1:1	1.0	0.8	1.75	170	192	202	122	13.6

spectra of unreinforced product obtained by using a higher proportion of epoxy may be due to the ether linkage arising from the homopolymerization of the epoxy resin by formation of tertiary amine. However, the homopolymerization of epoxy resin is only possible in the presence of tertiary amine catalyst at elevated temperature.[26]

Glass reinforced and carbon reinforced oligoimide epoxy composites prepared are in form of dark brown and black sheets respectively. The specific gravity of all these composites is in the range 1.59–1.82 for glass laminates (Table IV) and 1.67–

TABLE V

Mechanical and electrical properties of carbon reinforced composites based on BM-BAED epoxy system

Resin system	Oligomer to epoxy ratio	Percentage change on exposure to 25 % (w/v) NaOH		Specific gravity	Flexural strength (mPa)	Compressive strength (mPa)	Impact strength (mPa)	Rockwell hardness	Electrical strength (in air) (kV/mm)
		Thickness	Weight						
EBM-BAED	1:1	0.75	1.1	1.71	160	190	200	96	10
PBM-BAED	1:1	1.2	1.6	1.79	280	239	273	108	11.5
MBM-BAED	1:1	0.8	0.9	1.69	200	230	243	123	13.0
BBM-BAED	1:1	0.95	0.95	1.73	120	145	150	136	12.0
DDMBM-BAED	1:1	1.0	1.2	1.67	150	170	195	105	11.9

1.79 for carbon laminates (Table V). Results indicate that there is no appreciable change in the composites specific gravity with respect to the nature of the bismaleimide and processing temperature. Chemical resistance studies indicated that the oligoimide glass and carbon fibre composites were not affected by immersion in organic solvents (DMF, Ketones, alcohols, DMSO, 1,4-dioxane, THF). No change in weight or thickness was observed. It was also noted that concentrated hydrochloric acid (25% v/v) did not affect the composites. However, exposure to concentrated alkali (25% w/v NaOH) resulted in changes in thickness and weight (Tables IV and V). The high chemical resistance of all the composites indicates that the bismaleimide moiety might contribute to high level of crosslinking, of epoxy resin with oligoimide during composite fabrication.

The neat cured products obtained by oligoimide and epoxy resin are yellow amorphous powders. They did not melt up to 200° and insoluble in mineral acids and organic solvents. The film or cast of necked system is too brittle and therefore the hardness and other study are not presented. Since bismaleimide produces a highly crosslinked and brittle polymeric product[27] not be well applied for advanced composites. Several modifications by addition of vinyl monomers, diamines, elastomers to the bismaleimide system have been examined to improve the toughness and mechanical properties.[28] The addition of epoxy resin to oligoimide having more epoxy reactive —NH group system may increase the toughness of the final product. Such type of oligoimide epoxy resin and other polymer have only been patented recently[29,30,31] and no information received regarding the properties of glass and carbon fibre reinforced composites.

The dielectric strength of all the composites are presented in Tables IV and V for glass laminates and carbon laminates respectively. The values of the electrical strength of the present composites are low. This could result in the presence of a charred path, over which subsequent discharge could take place more and more readily. Additionally a minute leakage of current may arise from surface contamination.

EXPERIMENTAL

Materials

4-Acetamido phenacyl chloride (1) was prepared by method reported earlier.[12] A novel diamine† was prepared by condensation of (1) and 1,4-phenylene diamine (2) in presence of K_2CO_3 in benzene following the method reported by one of us (HSP).[13] Commercial epoxy resin namely diglycidyl ether of bisphenol-A (DGEBA) was obtained from Synpol Products Pvt. Ltd. Ahmedabad, India. Specification of epoxy resin are: epoxy equivalent weight 190–210; viscosity 4–10 p at 25°C; density at 25° 1.16–1.17 gm/cm^3.

All the bismaleimides were prepared by the process reported previously.[14]

E type fiber glass woven fabric (polyimide compatible) of 0.25 mm thick (Unnati Chemicals, India) of arral weight 270 gm/m^2 was used for composite preparation. Carbon fiber (12 K) obtained from Indian Petrochemicals Corporation Limited, Baroda.

All other chemicals were used of laboratory grade.

Synthesis of Oligomer

Synthesis of bismaleimide-diamine (BM-BAED) oligomer was carried out by the molar ratios of bismaleimide to diamine namely 1:2. The typical synthesis is as follows.

A suspension of diamine (0.02 M) (i.e., BAED) and bismaleimide (0.01 M) in acetone was refluxed for 6 hour. The resultant suspension was then poured into ice cooled large amount of solvent ether. The ether was decanted and washed twice with more ether to remove unreacted BAED. The dried powder was then washed with hot DMF (20 ml) to remove unreacted bismaleimide. The bismaleimide-diamine oligomer was then dried in vacuum oven. It was yellow in colour and yield was 75%. The details about all oligoimide are given in Table I.

Composite Fabrication

A suspension mixture of BM-BAED oligomer epoxy resin in tetrahydrofuran was prepared and was stirred well for 2 to 5 min. The suspension mixture was applied with a brush on to a 150 mm × 150 mm polyimide compatible fibre glass cloth and the solvent was allowed to evaporate. Once dried, the 10 plies of prepreg thus prepared were stacked one on top of another, pressed between steel plates coated with a Teflon film release and compressed in a flat platen press under about 70 psi pressure. The prepreg stack was cured by heating in the press to 120–140° for

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†Analysis of novel diamine (3) (BAED): νCO = 2953 cm^{-1}, νCH2 = 2880, 2950 cm^{-1}, νNH (Secondary) = 3430 cm^{-1}. The spectrum is resemble to that of model compound.[15]

12 h. The composites so obtained was cooled to 45°C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimensions.

The carbon fibre composites were prepared by using 30 tows of (12″ each) carbon fibre, wherein the fibres were allowed to pass through the suspension and then compression moulded under the similar moulding conditions as used in case of glass fibre composites.

Measurements

The C, H, N contents of all oligoimides and their epoxy cure products were estimated using an Elemental Analyser from Carlo Erba, Italy.

The IR spectra of all oligoimides and their epoxy cured products were scanned in KBr pellets on a Perkin Elmer 983 spectrophotometer.

The number average molecular weight ($\overline{Mn}$) of oligoimides were determined by a non-aqueous conductometric titration[16,17] method reported earlier.[12,13] A formic acid-acetic acid mixture‡ was used as the solvent and the standard perchloric acid in acetic acid was used as the solvent and the standard perchloric acid in acetic acid was used as titrant. A digital conductivity meter (Toshniwal, India) was used for the titration.

Curing of oligoimide-epoxy resin was carried out by differential scanning calorimetry. A Du Pont 900 DSC was used for this study. The instrument was calibrated using standard materials of known heat of fusion.

Curing was carried out using a single heating rate (10°/min). The weight of the sample for this investigation was in the range of 4 to 5 mg and an empty cell was used as a reference.

Thermogravimetric analysis (TGA) of all oligomers and their epoxy cure products was carried out on Du Pont thermobalance in air at a heating rate of 10°C/min.

All the chemical, mechanical and electrical tests of the prepared composites were conducted according to ASTM or IS methods.

CONCLUSIONS

(1) Reactive oligomers have been produced from the reaction of different bismaleimides with BAED.
(2) These oligomers were characterized by a variety of techniques.
(3) The oligomers were used to cure epoxy resin (DGEBA). Reactivity parameters were calculated. Reaction were followed by IR analysis.
(4) Merging of versatile polymers say epoxy resin and bismaleimide resin could afford the material for advanced glass/carbon fibre reinforced composites with better toughness and temperature resistance.

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‡Laboratory grade formic acid to which inappropriate amount of acetic anhydride was added, which was used as solvent.

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