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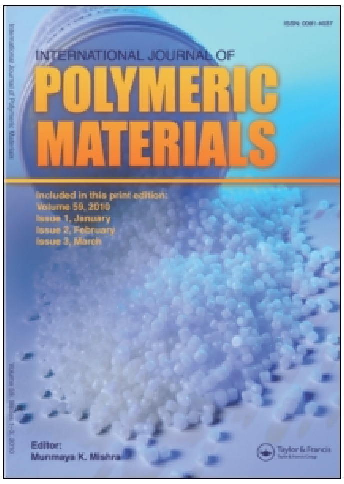

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Studies on Novel Bismaleimide Resins: Part I

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A new amine-terminated bismaleimide resin was prepared by the Michael addition reaction of N, N'-1,4-phenylene bis (maleimide) PBM with tris (2-aminoethyl) amine TREN® at 1:1 and 1:2 molar ratios in acetone at reflux temperature. The resultant PBM-TREN® oligoimides were characterized by elemental analysis, IR spectroscopy and thermogravimetry. These oligoimides were used to cure epoxy resin, namely diglycidyl ether of bisphenol – A, and studied by differential scanning calorimetry(DSC). The unreinforced PBM-TREN®-epoxy cured product has also been prepared and characterized. A study of glass reinforcement based on the PBM-TREN®-epoxy system is in progress.

Keywords: Michael addition reaction; bismaleimide; epoxy resin

INTRODUCTION

Epoxy resins have been used in the past as matrix resins for the fabrication of glass fibre reinforced composites. However, these resins show only limited temperature capability and poor performance in hot humid environments. Bismaleimide resins, on the other hand, exhibit excellent properties under such stress and are very attractive materials for advanced composites suitable for high temperature applications.

Bismaleimide resins are brittle in nature due to high crosslink density and aromatic structure of the backbone. Attempts have been

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*Work performed at Clarkson University.

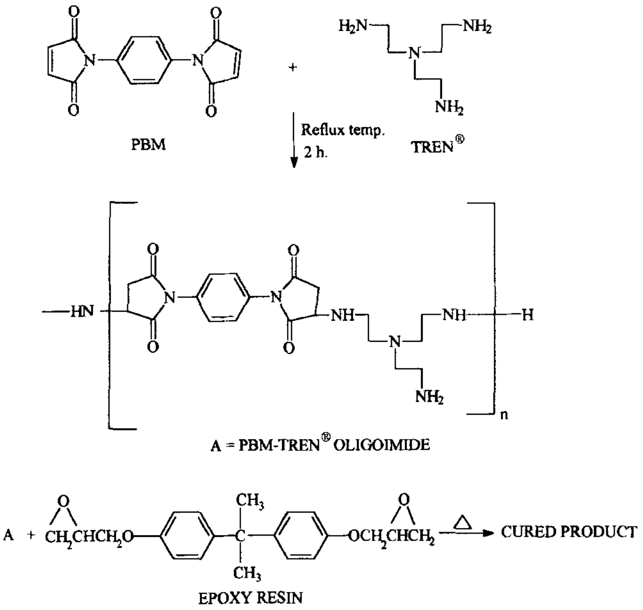
made in the past to improve processability and fracture toughness of bismaleimide resins by nucleophilic reaction at the maleimido double bonds. Resin formulations based on bismaleimide and nucleophiles such as diamines [1 – 3], dihydrazide [4], aminoacid hydrazide [5] and bisphenols [6] have been developed. Copolymerization of the maleimido double bond with vinylic compounds helps in improving the processability of bismaleimide resins [7].

Bismaleimide resins based on a Michael addition reaction of bismaleimide and aromatic and aliphatic diamines at higher molar ratios of bismaleimide are well documented as matrix resins for composites [2, 3, 8 – 10]. These resins mostly contain few amino groups and many maleimido double bonds, and these double bonds play the major role in the post-curing processes. The polyimides based on bismaleimide and diamine at an equimolar ratio are reported to be thermally stable materials but have less practical importance [11 – 13]. Reactions of epoxy resins and amine terminated bismaleimides which have primary and secondary amino functionality for epoxy curing have received little attention either academically or industrially, in spite of well defined applications of polyimides and epoxy resins. Only few patents [14 – 16] are reported in the literature in connection with epoxy resin-oligoimide reaction technology. Such reports indicate that epoxy resin-oligoimide laminates have excellent heat resistance and mechanical properties. Reactions (i.e. crosslinking through the —NH group) of such types of oligoimide by the use of epoxy resin may improve the properties greatly, especially processing and temperature performance.

The present paper comprises the synthesis and characterization of PBM-TREN® oligomers and their reaction with epoxy resin, namely diglycidyl ether of bisphenol-A (Scheme I). The PBM-TREN®-epoxy curing was studied kinetically by DSC as well as by curing of the unreinforced resins.

RESULTS AND DISCUSSION

The chain extension reaction of bismaleimide by tris (2-aminoethyl) amine and use of the oligomer for epoxy curing is summarized in Scheme I.



SCHEME I

The synthesis of PBM-TREN® oligomer was performed using a slight modification of the method reported earlier [11 – 13], in which longer polymerization times yield high melting or softing materials. Consequently, oligomerizations reported here were carried out for shorter periods. It was observed that refluxing PBM alone in acetone did not induce addition polymerization. This happened only at elevated temperature or by use of an initiator [17,18]. This indicated that poly-PBM species were all but absent in the PBM-TREN® oligomers. The PBM-TREN® produced was in the form of yellow powder which softened at 100–120°C depending upon the aliphatic/aromatic nature of the oligomer. It was insoluble in common organic solvents.

The C,H,N content of the 1:1 oligomer (Tab. I) is consistent with the predicted structure (Scheme I). The 1:2 oligomer has the same calculated values. A typical IR spectrum of PBM-TREN® is shown in Figure 1. The strong bands around 1700 cm^{-1}, 1650 cm^{-1}, 1050 cm^{-1} and 730 cm^{-1} are due to the presence of the imide group [19].

TABLE I Synthesis and Characterization of PBM-TREN® Oligomers

No.	*Molar ratio of PBM:TREN®*	*Yield*	*Elemental Analysis (%)*						*% Wt. Loss at °C from TGA*					
			C		*H*		*N*		*200*	*300*	*400*	*500*	*600*	*700*
			Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*						
1	1:1	95	57.97	57.93	6.28	6.21	20.29	18.25	8	25	42	60	79	96
2	1:2	89	57.97	–	6.28	–	20.29	–	8	30	45	68	93	98

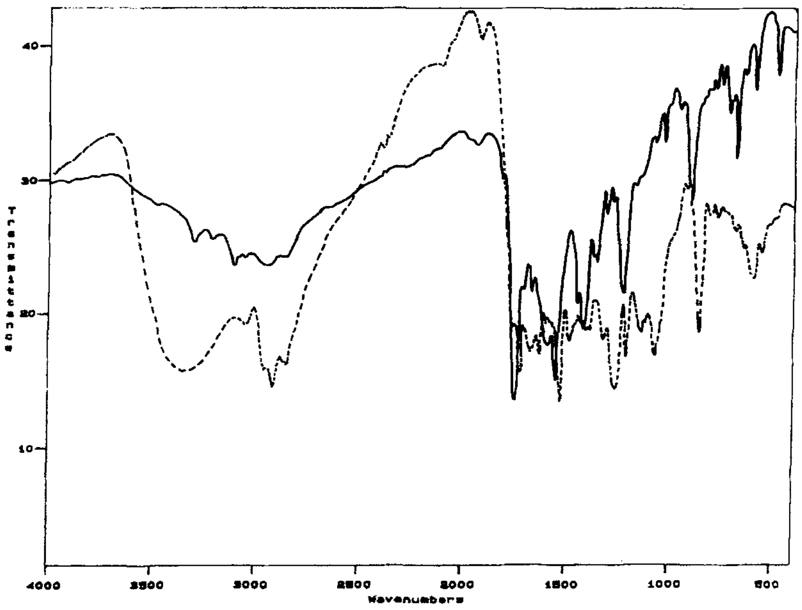


FIGURE 1 FTIR of PBM-TREN® oligomer (———) and PBM-TREN®-Epoxy cured product (---).

The broad band around 3300 cm^{-1} is attributed to the N-H bond. The inflections at 3500 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 desired Michael addition polymerization of PBM and TREN® occured. In brief, the spectrum of the PBM-TREN® oligomers resembles in all aspects the spectra reported earlier of the model compound N,N'-diphenylaspartimide [20].

The TGA data for the 1:1 and 1:2 oligomers are given in Table I. As shown in Figure 2, Curve 1, the oligomer 1:1 start their decomposition around 150°C, the rate increases between 250°C and 500°C, and the oligomer decompose completely around 700°C.

The cure reaction of PBM-TREN®-epoxy was studied for stoichiometric ratios of PBM-TREN®: epoxy namely 1:1. The data obtained from DSC scans are given in Table II. The DSC thermogram of the oligoimide cured systems gave a single exothermic peak in the

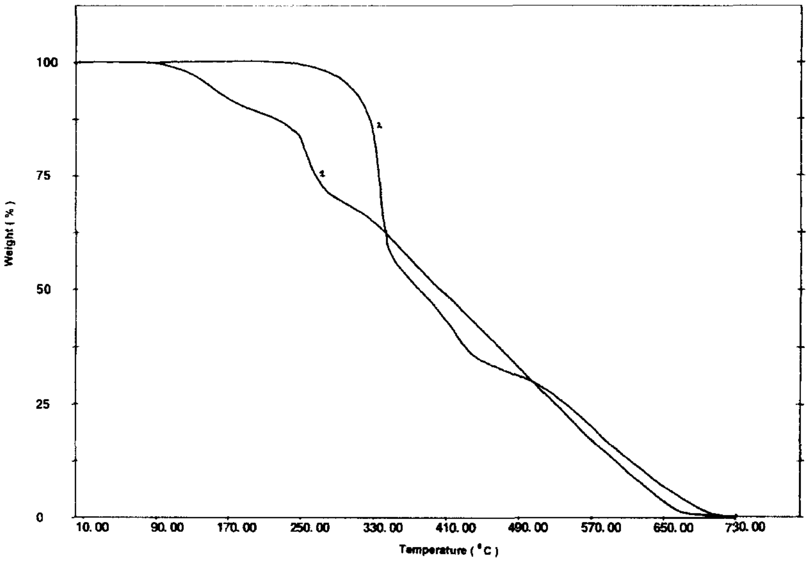


FIGURE 2 TGA of 1. PBM-TREN® oligomer; 2. PBM-TREN® oligomer with epoxy resin in the ratio 1:1.

TABLE II Curing Characteristic of PBM-TREN®-Epoxy system

Resin System	*Oligomer to Epoxy ratio*	*Kick-off Temp.* T_i*(°C)*	*Peak Temp.* T_p*(°C)*	*Final Temp.* T_f*(°C)*
PBM:TREN® 1:1	1:1	195	220	235

range 195 to 235°, which indicates that the reaction of secondary and primary amines with epoxy resins occur simultaneously [21]. The kick-off temperature (T_i), peak exothermic temperature (T_p) and temperature of completion of cure (T_f) were obtained (Tab. II).

As reported earlier [22], the curing temperature of the epoxy system increases with a decrease in the molar ratio of bismaleimide to amine indicate increase in the molecular weight. 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 weight oligomers. To obtain information about the properties of unreinforced cured materials, larger cured specimens were prepared using the same proportion and temperatures. The TGA data of all unreinforced cured materials are given in Table III. The unreinforced cured PBM-TREN®-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 but swell when placed in 25% v/v HCl or 25% v/v NaOH. Thermogravimetric analysis of unreinforced crosslinked materials exhibits greater thermal stability than the oligomer alone and does not commence decomposition until about 300°C (Fig. 2, Curve 2). This characteristic is one of the objectives of the present research. IR spectra of unreinforced cured products clearly show disappearance of the oxirane ring (910 cm^{-1}).

EXPERIMENTAL

Materials

Tris (2-aminoethyl) amine TREN® was obtained from the Pressure Chemicals Company. P-phenylene diamine was from Fisher Scientific Company. The N,N'-1,4-phenylene bismaleimide was prepared by a method reported earlier[23]. Commercial epoxy resin based on diglycidyl ether of bisphenol-A was obtained from RBC Industries, Inc. Specifications of the epoxy resin are as follows,

1) Epoxy equivalent weight : 195–205
2) Viscosity : 500–700 cps
3) Density : 1.10 gm/cm^3

All other chemicals used were of laboratory grade.

TABLE III TGA of unreinforced PBM-TREN®-Epoxy cured materials

Resin System	*Oligomer Epoxy ratio*	*% Wt. loss at °C from TGA*					
		200	*300*	*400*	*500*	*600*	*700*
PBM:TREN® 1:1	1:1	0	6	56	70	87	99
PBM:TREN® 1:2	1:1	0.4	9	46	71	79	95

Synthesis of Chain Extended Bismaleimides

Chain extension of bismaleimide with TREN® was carried out in acetone. The molar ratios of bismaleimide to amine were 1:1 and 1:2. A suspension of 0.02M TREN® and 0.01M bismaleimide in acetone was refluxed for 2h. A solution containing insoluble gel at the bottom was obtained. The acetone was removed using rotatory evaporator and into the resultant mass was immediately poured a large amount of ether precooled to 0°C, and the mixture kept it cold for three hours. During which time the product partially solidified the ether was decanted and the product washed twice with more ether. The dried powder was then washed with hot DMF to remove unreacted bismaleimide. The yellow PBM-TREN® oligomers were then air dried, the yield was 85–95 %. The details about all oligomers are in Table I.

Measurements

The carbon, hydrogen, nitrogen content of oligomers were obtained from Galbraith Laboratories.

The IR spectra of all oligomers and their epoxy cured products were scanned in KBr pellets on 2020 Galaxy series FTIR.

Curing of PBM-TREN®-epoxy resin was carried out by Differential Scanning Calorimetry at a heating rate of 10°C min^{-1}. A Perkin Elmer DSC-4 was used for this study. The instrument was calibrated using standard materials of known heat of fusion. The weight of the sample for this investigation was in the range of 4–5 mg and empty cell was used as a reference. Thermogravimetric analysis of all oligomers and their epoxy cured products was carried out on Perkin Elmer TGA7 thermobalance in nitrogen at a heating rate of 50°C/min.

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