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Hasmukh S. Patel^a; Vipul J. Shah^a

^a Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, India

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EPOXY-MODIFIED POLYIMIDES. PART III

HASMUKH S. PATEL* and VIPUL J. SHAH

Department of Chemistry
Sardar Patel University
Vallabh Vidyanagar 388120, India

ABSTRACT

The Michael addition reaction of *N,N'*-ethylene bismaleimide (EBM) and 4,4'-diamino diphenyl methane (DDM) at 1:1, 1:1.5, and 1:2 molar ratios was carried out in melt at 125–130°C. The resultant oligoimides (EBM-DDM) were characterized by elemental analysis, number of amino and imino groups, IR spectral studies, number-average molecular weight estimated by nonaqueous conductometric titration, and thermogravimetry. These oligoimides were used to cure an epoxy resin, the diglycidyl ether of bisphenol-A, and studied by differential scanning calorimetry (DSC). The unreinforced EBM-DDM-epoxy-cured products have also been prepared and characterized.

INTRODUCTION

Bismaleimide resin based on a Michael addition reaction of bismaleimide and diamine at higher molar ratios of bismaleimide to aromatic and aliphatic diamines are well documented as matrix resins for composites [1–5]. These resins mostly contain a few amino groups and many maleimido double bonds, and these double bonds play a major role in the postcuring of composite materials. The oligoimide based on bismaleimide and diamine at an equimolar ratio is reported to be thermally stable materials but have little practical importance [6–8]. The area in which the reaction of epoxy resins and bismaleimide-diamine oligomers can occur (i.e., due to primary and secondary amino functionality which can exhibit epoxy curing) has received little attention either academically or industrially in spite of well-defined applications of polyimides and epoxy resins. Only a few patents [9–11] are reported

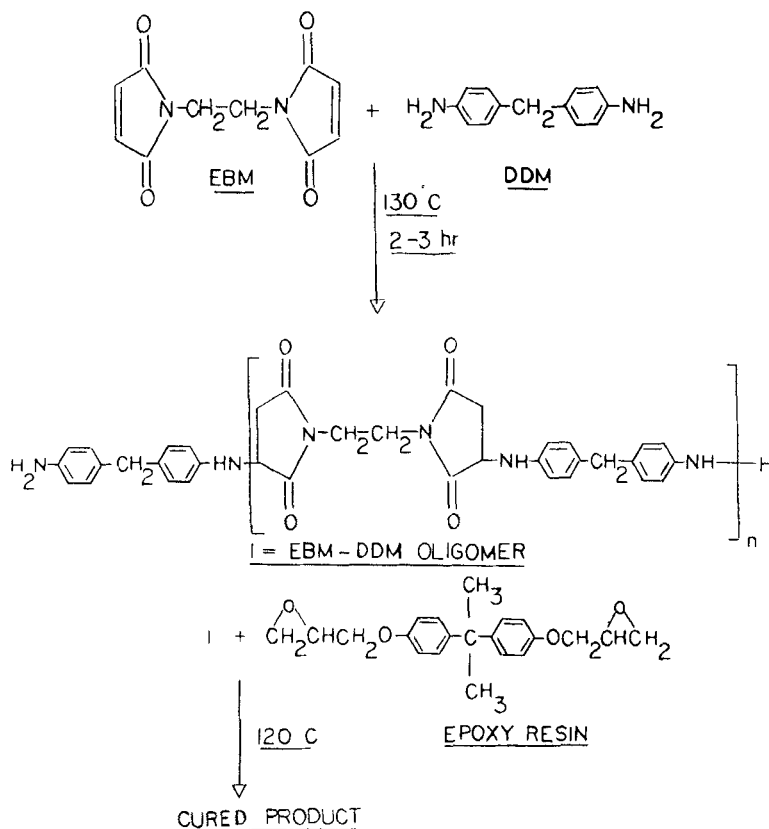
in the literature in connection with epoxy resin-bismaleimide-diamine reaction technology. Such reports indicate that epoxy-modified polyimide laminates have excellent heat resistance and mechanical properties. Reactions (i.e., crosslinking through the -NH_2 group) of such bismaleimide-diamine oligomers by the use of an epoxy resin may improve the properties greatly (especially processing and temperature performance). Hence, it was decided to explore the field of epoxy-modified oligoimides.

The present paper reports the synthesis and characterization of EBM-DDM oligomers and their reaction with an epoxy resin, the diglycidyl ether of bisphenol-A (Scheme 1). The EBM-DDM epoxy curing was studied kinetically by differential scanning calorimetry (DSC) as well as by curing unreinforced resins.

EXPERIMENTAL

Materials

4,4'-Diamino diphenyl methane and *N,N'*-ethylene diamine were obtained from SDS Chemicals, India. *N,N'*-Ethylene bismaleimide was prepared by a method reported earlier [12]. A commercial epoxy (diglycidyl ether of bisphenol-A)



SCHEME 1.

resin was obtained from Synpol Products Pvt. Ltd., Ahmedabad, India. The specifications of the epoxy resin were: epoxy equivalent weight, 190–210; viscosity at 25° C, 4–10 P; density at 25° C, 1.16–1.17 g/cm³.

All other chemicals used were of laboratory grade.

Synthesis of *N,N'*-Ethylene Bismaleimide-4,4'-Diamino Diphenyl Methane (EBM-DDM) Oligomers

The synthesis of EBM-DDM was carried out by varying the molar ratios of EBM and DDM. The ratios used were 1:1, 1:1.5, and 1:2.

A typical synthesis is as follows. To a well-stirred molten state of 4,4'-diamino diphenyl methane (3.96 g, 0.02 M), *N,N'*-ethylene bismaleimide (2.2 g, 0.01 M) was added gradually at 125–130°C over a period of 30 minutes. The resultant homogeneous viscous mass was poured immediately into a large amount of ether cooled by ice. The ether was decanted and washed twice with more ether to remove unreacted DDM. The dried powder was then washed with hot DMF (20 mL) to remove unreacted EBM. The EBM-DDM oligomer was then dried in a vacuum oven. It was yellow in color, and the yield was 75%. Details of all three oligomers are given in Table 1.

Measurements

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

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

The number-average molecular weight (\overline{M}_n) of EBM-DDM oligomers was determined by a nonaqueous conductometric titration method reported earlier [13, 14]. A formic acid-acetic acid mixture* was used as the solvent, and standard perchloric acid in acetic acid was used as a titrant. A digital conductivity meter (Toshniwal, India) was used for the titration.

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

Thermogravimetric analysis (TGA) of all oligomers and their epoxy cure products was carried out on a Du Pont thermobalance in air at a heating rate of 10°C/min (Table 2).

RESULTS AND DISCUSSION

The objective of the work reported here was to synthesize bismaleimide-aliphatic diamine oligomers and to use these for the curing of epoxies. It was feared that the larger molecular weight bismaleimide diamine oligomer could not cure

*Laboratory-grade formic acid, to which an appropriate amount of acetic anhydride was added, was used as solvent.

TABLE 1. Synthesis and Characterization

Oligomer sample	Molar ratio of EBM:DDM	Yield, %	Elemental analysis					
			C		H		N	
			Calcd	Found	Calcd	Found	Calcd	Found
1	1:1	89	66.02	65.97	5.26	5.31	13.39	13.52
2	1:1.5	80	67.00	67.08	5.39	6.44	14.02	14.21
3	1:2	75	68.65	68.50	5.98	6.19	14.31	14.62

^aConsidering one —NH— group in the repeating unit.

^b $\bar{M}_n = DP \times (\text{MW of repeating unit})$.

epoxy resin properly (e.g., a higher cure temperature might be needed). Hence, attempts were made to establish the synthesis of an EBM-DDM oligomer having a lower molecular weight and more reactive amino groups.

The synthesis of EBM-DDM oligomer was performed using a slight modification of a method reported earlier [6, 8]. As reported [6, 8], longer polymerizations yield high melting or softening materials. Consequently, the oligomerizations reported here were carried out for shorter periods. It was observed that heating of EBM at 140°C did not induce addition polymerization. This happened only at elevated temperature or by use of an initiator [15, 16]. This indicated that poly-EBM species would be absent in the EBM-DDM oligomer. The EBM-DDMs produced are in the form of yellow powders and soften at 110–130°C depending upon the nature of the oligomer. They are insoluble in common organic solvents. The C, H, and N contents of all oligomers (Table 1) are consistent with their predicted structure (Scheme 1). All three oligomers react to the red azo dye test, thereby confirming the presence of aryl amino groups. This suggests that there are terminal primary NH₂ groups in the oligomer. A typical IR spectrum of EBM-DDM is shown in Fig. 1. Examination of the IR spectra of the oligomers revealed that each spectrum comprises the strong bands around 1700, 1650, 1050, and 730 cm⁻¹ due to the presence of the imide group [17]. The broad band around 3300 cm⁻¹ is attributed to the >N—H bonds. The inflections at 3500 and 3400 cm⁻¹ may arise from terminal NH₂ groups. The medium bands at 2950 and 2840 cm⁻¹ are attributed to

the C—H of the $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—CH—} \end{array}$ group present in the polymer chain [18]. The absence of the band at 3010–3040 cm⁻¹ (attributed to the double bond present in EBM) indicates Michael addition polymerization of EBM and DDM. The bands observed in the fingerprint region are due to the aromatic moiety of DDM. In brief, the spectra of the EBM-DDM oligomer resemble in all aspects the spectrum reported earlier for the model compound *N,N'*-diphenyl aspartimide [19]. The number-average molecular weights of oligomers are given in Table 1. The data show that \bar{M}_n

of EBM-DDM Oligomers

Conductometric curve titration		$P =$ Y/X	\bar{M}_n^b from first break $\left[= \frac{100}{X \times 10^{-3}} \right]$, g/mol	Percent weight loss at °C from TGA				
HClO ₄ at first break in titration curve, X , meq	HClO ₄ at final break in titration curve, Y , ^a meq			200	300	400	500	600
39.87	239	6	2508	9.5	27.5	45	54	83
47.84	239	5	2090	10	28	47	59	86
55.64	239	4.3	1797	10	30	50	58.5	87

values decrease with an increase in the molar ratio of DDM to EBM. This also indicates that the polymerization system produced yields low molecular mass oligomer rather than the high molecular mass reported earlier [6–8]. The NH and NH₂ values per repeat unit and polymer respectively have also been calculated on the basis of conductometric titration data [20]. These are shown in Table 1. The results show that there are more –NH₂ groups present in the oligomer prepared with a high DDM:EBM ratio. On the basis of the closeness of the observed NH values and the nitrogen contents of all three oligomers, the most probable structure of the oligomers is that shown in Scheme 1.

TGA data for the oligomers are given in Table 1. Examination of these data reveals that the oligomers begin to decompose around 150°C. The rate of decomposition increases between 250 and 450°C, and the oligomers are 90% decomposed around 650°C (Fig. 2).

The cure reaction of EBM-DDM epoxy was studied for two different stoichiometric ratios of EBM-DDM, 1:1 and 1:1.2. The data obtained from DSC scans are given in Table 3. From the DSC thermograms obtained, it is seen that all the

TABLE 2. TGA of Unreinforced EBM-DDM-Epoxy Cured Materials

Resin system	Oligomer epoxy ratio	Percent weight loss at °C from TGA				
		250	300	400	500	600
EBM:DDM (1:1)	1:1	2.5	3.5	33	58	90
	1:1.2	2.9	3.5	31	61	94
EBM:DDM (1:1.5)	1:1	3	4	34	57	90
	1:1.2	4	5	30	59	89
EBM:DDM (1:2)	1:1	4.5	7.5	32	56	93
	1:1.2	5	7.7	31	59	90

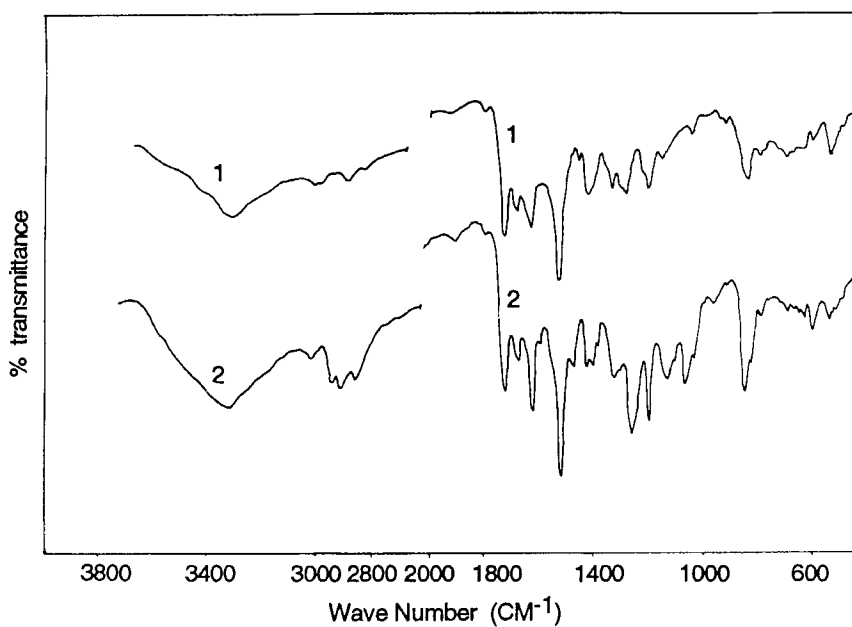


FIG. 1. IR spectra of (1) EBM-DDM oligomer and (2) EBM-DDM oligomer with epoxy resin in a 1:1 ratio.

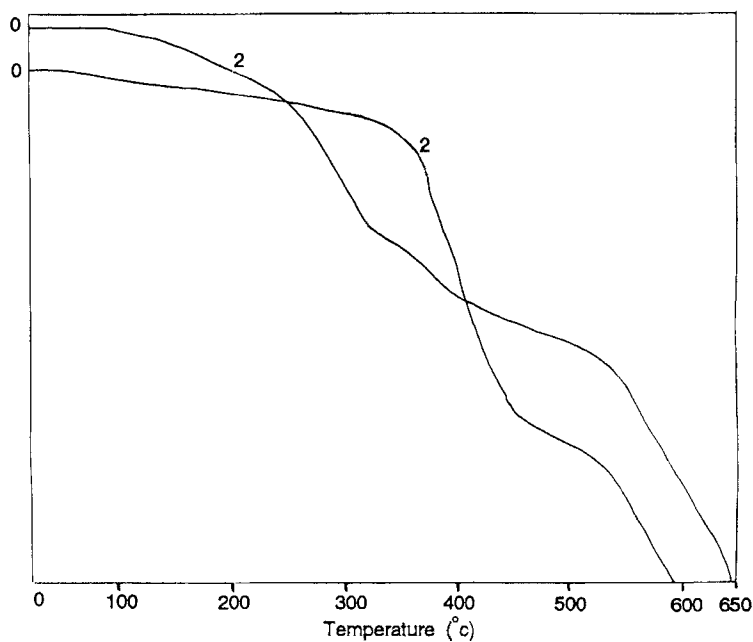


FIG. 2. TGA of (1) EBM-DDM oligomer and (2) EBM-DDM oligomer with epoxy resin in a 1:1 ratio.

TABLE 3. Curing Characteristics of EBM-DDM Epoxy Systems at Different Heating Rates

Resin system	Heating rate, °C/min	Oligomer epoxy ratio	Kick-off temp. T_i (°C)	Peak temp. T_p (°C)	Final temp., T_f (°C)	Activation energy E_a , kcal/mol	Reaction order
EBM:DDM (1:1.5)	10	1:1	125	160	169	34	0.95
		1:1.2	127	168	176	34.1	1.25
EBM:DDM (1:2)	10	1:1	120	153	164	35	0.85
		1:1.2	129	157	170	35.20	0.80
EBM:DDM (1:1)	10	1:1	114	147	157	32.20	1.20
		1:1.2	119	151	160	33.58	1.10

oligoimide cured systems have a single exothermic peak in the 114 to 176°C range. Figure 3 shows the dynamic DSC thermogram at 10°C min⁻¹. This shows that the rate of reaction of a major secondary amine and minor primary hydrogen atoms with epoxide occur simultaneously [21]. The kick-off temperature (T_i), peak exotherm temperature (T_p), and temperature of completion of cure (T_f) were obtained from the thermograms.

The data (Table 3) reveal that the curing temperature of the epoxy system increases with an increase in the molecular weight of the EBM-DDM oligomer. This behavior is probably due to the lower rate of diffusion of the high molecular weight EBM-DDM oligomer as well as the reduced functionality, i.e., more primary amino groups in the lower molecular weight oligomers (see Scheme 1). The activation energy (E_a) values for such a system (Table 3) do not vary widely, which indicates

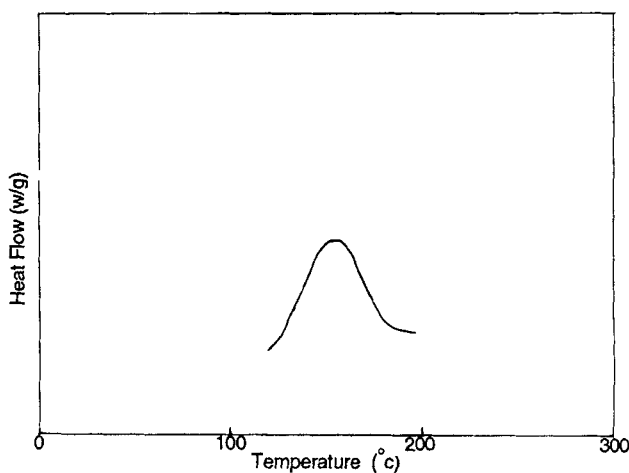


FIG. 3. DSC curve of EBM-DDM oligomer with epoxy resin in a 1:1 ratio.

that oligomer EBM:DDM (1:2) is more reactive toward the epoxy resin. Such a study shows that a small increase in the proportion of epoxy resin does not have any significant results. The kinetic parameters E_a (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 at a heating rate of 10°C. To obtain information about the properties of unreinforced crosslinked materials, larger cured specimens (~1 g) were prepared by using the same proportions and temperatures as presented in Table 3. The unreinforced cured EBM-DDM epoxy samples were prepared at 150 to 160°C for 2.5 hours, are dark brown in color, and are slightly hard materials that form powder under normal pressure. They are insoluble in all common organic solvents including formic acid. They are slightly swollen by 25% w/v NaOH and 25% v/v HCl. Thermogravimetric analysis of all the unreinforced crosslinked materials reveals that they all degrade in a single step, and that their decomposition starts around 250°C. Degradation becomes faster between 375 and 475°C. The weight loss was about 90% at 600°C in all cases.

IR spectra of three unreinforced cured products clearly show the disappearances of the oxirane ring (910 cm⁻¹). The inflections at 1170 cm⁻¹ in the spectra of the unreinforced product obtained by using a higher proportion of epoxy may be due to ether linkage arising from the homopolymerization of the epoxy resin by the formation of a tertiary amine. However, the homopolymerization of epoxy resin is only possible in the presence of a tertiary amine catalyst at elevated temperature [22].

Qualitative observation of glass reinforcement was made by using a mixture of EBM-DDM epoxy resin in an organic solvent. Laminates with good mechanical properties can be prepared (the specimen sample had an impact strength of 200 mPa and a flexural strength 308 mPa).

The syntheses of novel oligoimides with a wide range of structural variations, their use for epoxy resin curing, the optimization of fabrication conditions, and the evaluation of the properties of glass reinforced composites are in progress.

CONCLUSION

(1) Reactive oligomers have been produced at three different molecular weights from the reaction of *N,N'*-ethylene bismaleimide with 4,4'-diamino diphenyl methane.

(2) These oligoimide were characterized by a variety of techniques.

(3) The oligomers were used to cure epoxy resin (DGEBA). Reactivity parameters were calculated. Reactions were followed by IR analysis. As expected, the lower molecular weight oligomers were more reactive than their higher molecular weight counterparts.

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