

# Amine-Terminated Oligoimides for Epoxy Curing

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## SYNOPSIS

Oligoimides of *N,N'*-4,4'-bismaleimidodiphenyl ether (DDEBM) and 4,4'-diaminodiphenylmethane (DDM) were prepared by the Michael addition reaction. The synthesized oligoimides (DDEBM-DDM) were characterized for their molecular structure by elemental analysis and IR spectroscopy. The number-average molecular weight ( $\bar{M}_n$ ) was determined by nonaqueous conductometric titration. Thermal characteristics were studied by thermogravimetry. Use of DDEBM-DDM oligomers as a curing agent for epoxy resin was studied by differential scanning calorimetry (DSC). The resin curing of the epoxy was monitored by the change in oxirane spectral band in the IR spectrum. Glass fiber reinforced composites of DDEBM-DDM-epoxy were prepared and evaluated for their physical and chemical properties. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Bismaleimide-based polymers are potential candidates as matrix resins for high-performance composites.<sup>1,2</sup> To achieve the specific properties combination, different types of reactants and reaction routes have been used to synthesis tailored bismaleimide resins.<sup>3-8</sup> The resins based on the Michael addition reaction using higher molar ratios of bismaleimide to diamine have been well documented.<sup>6-8</sup> The curing of the resin is achieved with maleimido double bonds. Thermally stable materials are also obtained by using an equimolar ratio of bismaleimide and diamine.<sup>9</sup> Use of a high molar ratio of diamine to bismaleimide can provide oligoimides having imino and terminal amino groups, which make them suitable for the curing of epoxy resin. Only a small amount of patented literature is available on the epoxy-bismaleimide-diamine oligomer system.<sup>10</sup> One of the authors has reported the synthesis of a series of bismaleimide-diamine oligomers and achieved epoxy-modified polyimides of high thermal stability and mechanical properties.<sup>11-13</sup> In continuation of the work, this article reports the synthesis of DDEBM-DDM oligomers and their curing char-

acteristics with epoxy resin. The properties of the glass-reinforced composites prepared using the synthesized oligoimides with epoxy resin were also evaluated and reported.

## EXPERIMENTAL

### Materials

*N,N'*-4,4'-Diaminodiphenyl ether and 4,4'-diaminodiphenylmethane (DDM) were procured from SDS Chemicals, India. A commercial epoxy resin, i.e., diglycidyl ether of bisphenol-A (DGEBA), having an epoxy equivalent weight of 190–210; viscosity at 25°C: 4–10P, and density at 25°C: 1.16–1.17 g/cm<sup>3</sup>. All other chemicals used were of laboratory grade.

DDEBM was synthesized by a method reported earlier.<sup>14</sup> The laminate samples were prepared using an E-type fiber glass woven fabric of 0.25 mm thickness and areal weight 270 g/m<sup>2</sup>.

### Synthesis of *N,N'*-4,4'-Bismaleimidodiphenyl Ether-4,4'-Diaminodiphenylmethane (DDEBM-DDM) Oligomers

The synthesis of oligomers was carried out using molar ratios of DDEBM and DDM of 1 : 1, 1 : 1.5, and 1 : 2. In a typical synthesis, DDM (0.02 mol)

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was brought to a molten state and DDEBM (0.01 mol) was added to it with continuous stirring over a period of 30 min, maintaining the temperature as 125–130°C. The resultant homogeneous viscous mass was poured immediately into a large amount of ice-cooled ether. This was then further washed with ether and hot dimethylformamide to remove unreacted DDM and DDEBM, respectively. The DDEBM-DDM oligomer was then vacuum-dried. The yield was > 80% (Table I).

### Preparation of Composites

A suspension mixture of DDEBM-DDM-epoxy resin in tetrahydrofuran was prepared by stirring for about 5 min. This was then applied with a brush onto a 150 × 150 mm fiber glass cloth and the solvent was allowed to evaporate. Once dried, the 10 piles of prepreg were stacked, compressed, and cured under 70 psi pressure and at 120–140°C for 12 h. The laminates so obtained were machined to the required specimen dimensions for the determination of their properties as per ASTM test methods.

### Measurements

The C, H, and N contents of all oligomers and cured epoxy products were estimated using an elemental analyzer from Carlo Erba, Italy. The IR spectra of oligomers and their epoxy-cured products were scanned in KBr pellets on a Perkin-Elmer 983 spectrophotometer. The  $\bar{M}_n$  of the oligomers was determined by a nonaqueous conductometric titration method reported earlier.<sup>15</sup> A formic acid-acetic acid mixture was used as the solvent and standard perchloric acid in acetic acid was used as the titrant. A digital conductivity meter (Toshniwal, India) was used for the titration.

Curing studies of DDEBM-DDM-epoxy resin was carried out by differential scanning calorimetry (DSC) at a heating rate of 10°C/min. A DuPont 900 differential scanning calorimeter was used. The sample weight taken for this investigation was about 4–5 mg and an empty cell was used as a reference. Thermogravimetric analysis (TGA) of oligomers and their epoxy cure products was carried out on a DuPont thermobalance in air at a heating rate of 10°C/min.

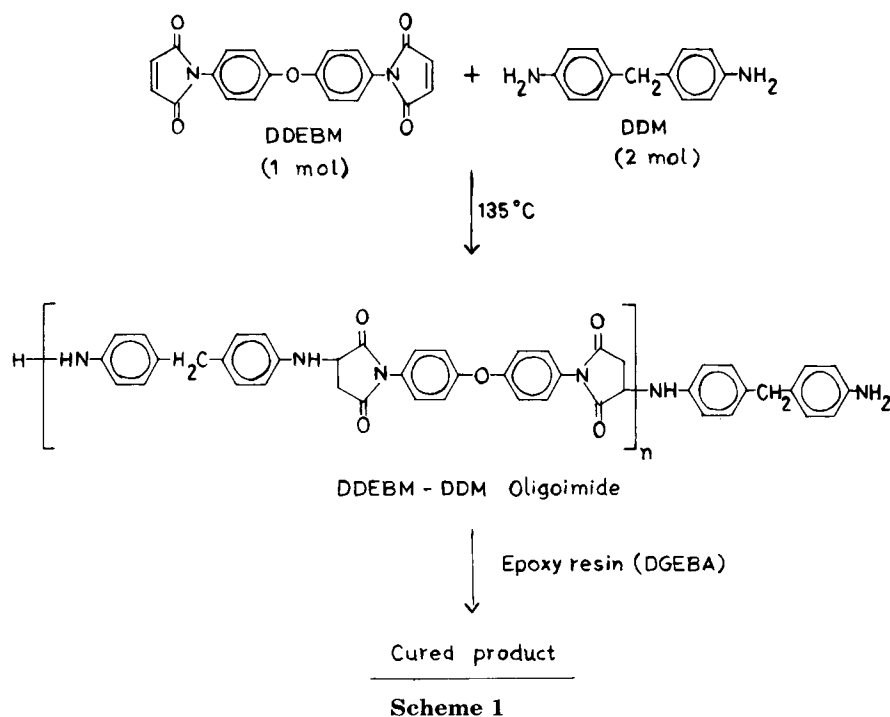
The glass fiber reinforced composites were tested for their chemical resistance, flexural strength, compressive strength, impact strength, Rockwell hardness, and dielectric strength as per ASTM D543, D790, D695, D256, D785, and D149, respectively.

Table I Analytical Data of DDEBM-DDM Oligomers

| Oligoimide Sample | Molar Ratio of DDEBM : DDM | Yield (%) | Elemental Analysis (%) |       |       |       |       |       | Conductometric Titration Curve   |                                  |            | $\bar{M}_n^b$ from First Break = $100x \times 10^{-3}$ g mol <sup>-1</sup> |
|-------------------|----------------------------|-----------|------------------------|-------|-------|-------|-------|-------|----------------------------------|----------------------------------|------------|--|
|                   |                            |           | C                      |       | H     |       | N     |       | HClO <sub>4</sub> at First Break | HClO <sub>4</sub> at Final Break | $DP = y/x$ |  |
|                   |                            |           | Calcd                  | Found | Calcd | Found | Calcd | Found | x (mmol)                         | y <sup>a</sup> (mmol)            |            |  |
| 1                 | 1 : 1                      | 90        | 70.96                  | 69.70 | 4.61  | 4.20  | 10.04 | 10.10 | 29.2                             | 172                              | 5.9        | 3322   |
| 2                 | 1 : 1.5                    | 80        | 70.86                  | 70.70 | 4.63  | 4.60  | 10.02 | 9.80  | 52.5                             | 179                              | 3.4        | 1904   |
| 3                 | 1 : 2                      | 80        | 71.00                  | 70.30 | 4.60  | 4.40  | 10.00 | 9.70  | 64                               | 179                              | 2.8        | 1562   |

<sup>a</sup> Considering one —NH— group in the repeating unit.

<sup>b</sup>  $\bar{M}_n = DP \times$  molecular weight of repeating unit.

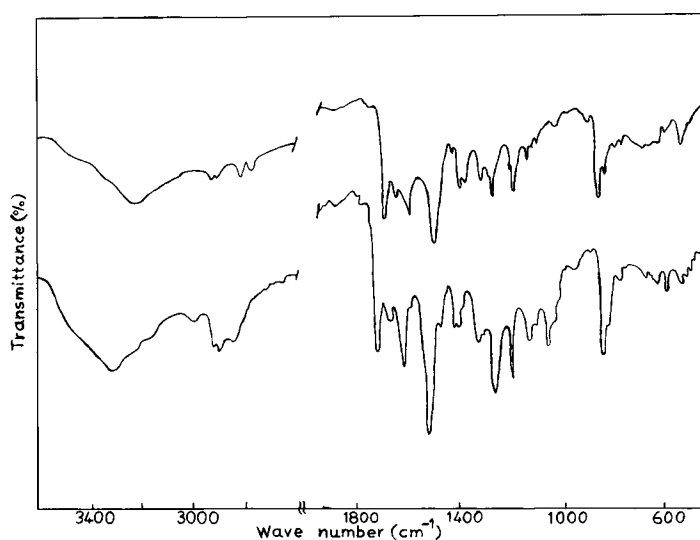


## RESULTS AND DISCUSSION

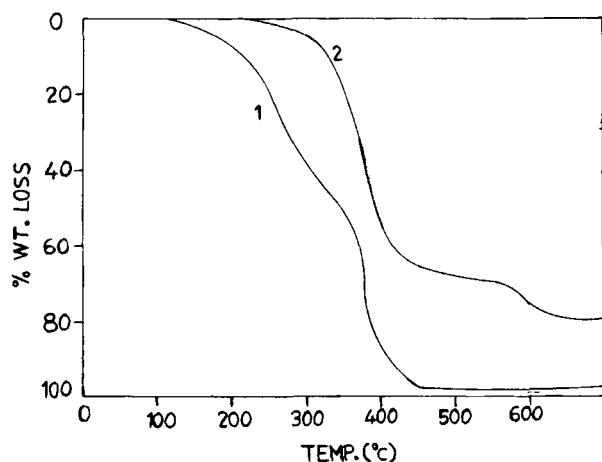
The oligoimides, i.e., DDEBM–DDM oligomers, were prepared by the Michael addition reaction using the reactant ratios given in Table I. Attempts were made to establish the synthesis of the oligomers having a low molecular weight and more reactive terminal amino groups for their suitability as epoxy curing agents. This was achieved by a modified method as

reported earlier.<sup>11–13</sup> It was observed that heating of DDEBM at 140°C did not induce addition polymerization; however, this has been reported to occur at elevated temperatures or in the presence of an initiator.<sup>16,17</sup>

Typical oligomers were yellow, softened in the range of 135–140°C, and were insoluble in common organic solvent. The C, H, and N contents were in agreement with calculated values of the predicted



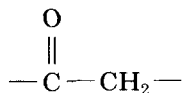
**Figure 1** Typical IR spectra of (1) DDEBM–DDM oligomer and (2) DDEBM–DDM–epoxy system.



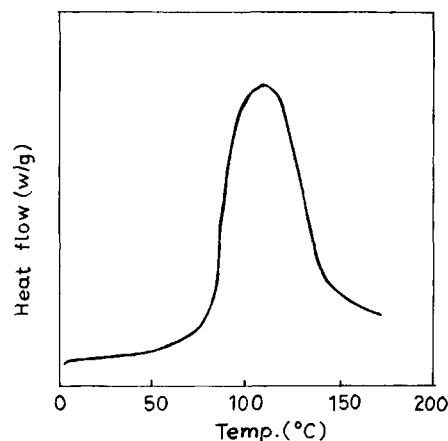
**Figure 2** TGA of (1) DDEBM-DDM oligomer and (2) DDEBM-DDM oligomer with epoxy resin.

molecular structure (Table I; Scheme 1). A red azo dye test<sup>18</sup> of all these oligomers confirmed the presence of aryl amino groups. This suggests that there are terminal  $\text{—NH}_2$  groups in the oligomers. The molecular structure of oligomers was further confirmed by IR spectroscopy (Fig. 1). Strong bands around 1700, 1650, 1050, and 730  $\text{cm}^{-1}$  were found due to the imide group.<sup>19</sup> The broad band around

3300  $\text{cm}^{-1}$  is attributed to the  $\text{N—H}$  bonds. The inflections at 3500 and 3400  $\text{cm}^{-1}$  may arise due to terminal  $\text{—NH}_2$  groups. The medium bands at 2950 and 2840  $\text{cm}^{-1}$  are attributed to the C—H of the



group present in the molecular chain.<sup>20</sup> The absence of the band at 3010–3040  $\text{cm}^{-1}$  (attributed to the



**Figure 3** Typical DSC thermogram for curing of DDEBM-DDM epoxy resin.

double bond present in DDEBM) indicates Michael addition polymerization of DDEBM and DDM. The band at 1200  $\text{cm}^{-1}$  indicates the diaryl ether linkage. The spectra of DDEBM-DDM oligomers were found to resemble the spectra of *N,N'*-diphenylaspertimide, as reported earlier.<sup>21</sup>

$\bar{M}_n$  decreases with increase in the molar ratio of DDM to DDEBM (Table I). The low values of  $\bar{M}_n$  suggest the formation of oligomers with terminal primary amino groups. On the basis of characterization studies, the most probable structure of the oligomers is shown in Scheme 1. The thermogravimetric analysis indicates that the weight loss starts at about 125°C (Fig. 2). The initial loss in weight may be due to traces of volatiles present in the sample, but the higher rate of weight loss in the temperature range of 225–400°C indicates faster degradation.

The curing characteristics of oligomers with epoxy resin were studied by DSC, using two different stoichiometric ratios, i.e., 1 : 1 and 1 : 1.2. All the oligoimide-epoxy systems showed a single exo-

**Table II** DSC Analysis : Curing Characteristics of DDEBM-DDM-Epoxy System at 10°C/Min

| Resin System<br>DDEBM : DDM | Oligomer-to-Epoxy<br>Ratio | Kick-off Temp<br>$T_i$ (°C) | Peak Temp<br>$T_p$ (°C) | Final Temp<br>$T_f$ (°C) | Activation Energy<br>( $E_a$ ) (kcal/mol) | Order of<br>Reaction<br>( $n$ ) |
|-----------------------------|----------------------------|-----------------------------|-------------------------|--------------------------|---|---------------------------------|
| 1 : 1                       | 1 : 1                      | 80                          | 113                     | 148                      | 35.36                                     | 1.25                            |
|                             | 1 : 1.2                    | 86                          | 118                     | 150                      | 34.39                                     | 1.20                            |
| 1 : 1.5                     | 1 : 1                      | 75                          | 107                     | 138                      | 33.89                                     | 0.90                            |
|                             | 1 : 1.2                    | 87                          | 112                     | 141                      | 31.46                                     | 0.95                            |
| 1 : 2                       | 1 : 1                      | 73                          | 109                     | 140                      | 30.89                                     | 0.85                            |
|                             | 1 : 1.2                    | 82                          | 114                     | 139                      | 29.76                                     | 0.85                            |

Table III Properties of Glass-reinforced Composites Based on DDEBM-DDM-Epoxy System

| Resin System<br>DDEBM : DDM | Oligomer-to-Epoxy<br>Ratio | Resin<br>Content | Specific<br>Gravity | % Wt<br>Change on<br>Exposure<br>to 25%<br>w/v NaOH | Flexural<br>Strength<br>(MPa) | Compressive<br>Strength<br>(MPa) | Impact<br>Strength<br>(MPa) | Rockwell<br>Hardness | Dielectric<br>Strength<br>(in air)<br>(kV/mm) |
|-----------------------------|----------------------------|------------------|---------------------|---|-------------------------------|----------------------------------|-----------------------------|----------------------|---|
| 1 : 1                       | 1 : 1                      | 37.00            | 1.87                | 1.20  | 300                           | 240                              | 280                         | 130                  | 13.00   |
|                             | 1 : 1.2                    | 36.80            | 1.79                | 1.00  | 310                           | 238                              | 283                         | 122                  | 11.70   |
| 1 : 1.5                     | 1 : 1                      | 35.90            | 1.84                | 1.30  | 280                           | 227                              | 267                         | 127                  | 12.90   |
|                             | 1 : 1.2                    | 37.30            | 1.87                | 1.30  | 273                           | 212                              | 255                         | 123                  | 10.80   |
| 1 : 2                       | 1 : 1                      | 34.80            | 1.77                | 1.00  | 248                           | 222                              | 278                         | 112                  | 13.20   |
|                             | 1 : 1.2                    | 35.70            | 1.74                | 1.30  | 237                           | 214                              | 269                         | 109                  | 13.20   |

thermic peak in the temperature range of 75–150°C, which indicates that the reaction of major secondary and minor primary amines with epoxy resins occur simultaneously.<sup>22</sup>

Figure 3 shows a typical DSC scan for the curing of the DDEBM-DDM-epoxy system. The kickoff temperature ( $T_i$ ), peak exotherm temperature ( $T_p$ ), and temperature of completion of cure ( $T_f$ ) were obtained from the thermograms (Table II). The data reveal that the curing temperature decreases with the decrease in the molecular weight of the oligomer. This behavior is probably due to the higher rate of diffusion of the low molecular weight DDEBM-DDM oligomer as well as increased functionality, i.e., more primary amino groups in the lower molecular weight oligomers.

The kinetic data, i.e.,  $E_a$  (activation energy) and  $n$  (order of reaction), were computed from the DSC scan (Table II) and it was found that the value of  $E_a$  decreases with the change in ratios of DDEBM to DDM in the oligomers from 1 : 1 to 1 : 2. This indicates that the epoxy curing reaction with the oligomer containing a greater amount of terminal amino groups takes place more efficiently.

The blend of DDEBM-DDM-epoxy samples were cured at about 160°C for 2.5 h. The IR spectra of these cured products show the disappearance of the oxirane ring (910  $\text{cm}^{-1}$ ). The cured products were dark brown in color, brittle in nature, and insoluble in all common organic solvents. They were also found to be stable to 25% w/v NaOH and 25% v/v HCl. Thermal analysis indicates the stability of the cured sample (Fig. 2). The weight loss is very small up to about 300°C and the rate of weight loss is high in the range of 325–400°C.

The properties of glass fiber composites of the DDEBM-DDM-epoxy system are given in Table III. The specific gravity of the composites ranges from 1.74 to 1.87 and was found to be independent of the chemical composition of the matrix resin. The chemical resistance tests show the stability of composites in common organic solvents and mineral acid (25% v/v), whereas a weight loss of about 1.0–1.3% was observed with the alkali. The mechanical properties of the composites were found to be superior to those prepared by diaminodiphenylmethane bis-maleimide-DDM-epoxy and *para*-phenylene bis-maleimide-DDM-epoxy resins.<sup>23</sup> The higher stiffness and toughness were found in the composites prepared by oligomers containing more DDM. The dielectric strength of the composites ranges from 10.80 to 13.70 kV/mm and remains unaffected by the chemical composition of the matrix system.

One of the authors (H.S.P.) is grateful to the University Grants Commission (UGC), New Delhi, for awarding him the Visiting Associateship. Thanks are also due to Dr. M. Ravindranathan, DGM (R&D), for the permission to carry out this work at the Research Centre, Indian Petrochemicals Corp. Ltd., Vadodara (India).

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Received September 9, 1995

Accepted March 30, 1996