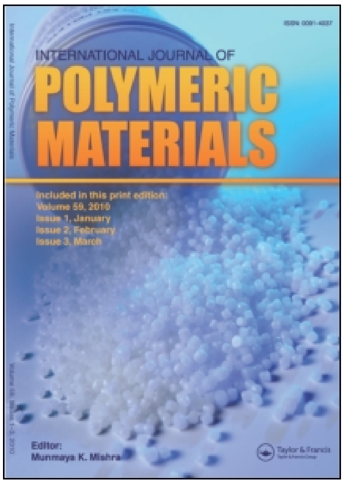

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# Epoxy Resin Based Polyamides as Epoxy Curing Agents

Rajesh Baraiya[a]; Jatin R. Thakkar[a]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

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# Epoxy Resin Based Polyamides as Epoxy Curing Agents

RAJESH BARAIYA and JATIN R. THAKKAR

*Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat, India*

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Novel bis ester 1,1'-(1-methyl ethylidene) bis[4-{1-(1-imino-4-ethyl benzoate)-2-propanolyloxy}] benzene was prepared by the reaction of epoxy resin, diglycidyl ether of bisphenol-A (DGEBA) and 4-aminoethyl benzoate. The polyamides (PAs) were prepared by the condensation of this novel bis ester with three aliphatic diamines viz; diethylene triamine (DETA), triethylene tetramine (TETA) and polyethylene amine (PEA). The resultant PAs were characterised by infrared spectroscopy (IR). The number average molecular weight ($\bar{M}n$) was estimated by non-aqueous conductometric titration.

As produced, polyamides may act as epoxy curing agent, the kinetic study of the PA-epoxy resin system has been established by differential scanning calorimetry (DSC) and the kinetic parameters have been evaluated. Neat PA-epoxy cured products have also been characterized by thermogravimetric analysis (TGA).

The glass fiber reinforced composites of the produced PA-epoxy system have been fabricated and were characterized by Flexural strength (FS), Interlaminar shear strength (ILSS) and Rockwell hardness.

*Keywords:* 4-amino ethyl benzoate; epoxy resin; polyamides; aliphatic diamines; differential scanning calorimetry; thermogravimetric analysis; composite

## INTRODUCTION

Epoxy resin matrices cured with amines are used in numerous applications [1, 2]. In their fully cured state, they have remarkable properties [3]. These properties and the low resin costs, have promoted the use of epoxy resin as substitutes for phenolics in various important applications.

The reaction of epoxy ring with amine and alcohol is well established [4] and hence the reaction of epoxy resin with an organic compound having amino and ester group like 4-amino ethyl benzoate may yield bisester derivative, which yield polyamide on further condensation with diamine.

Hitherto, polyamide formation through epoxy resin based bisester has not received attention despite well defined applications for both the epoxy resin and polyamides.

Therefore, the present paper explores the field of polyamides based on epoxy resin based on the research work carried out as is schematically presented in Scheme 1.

## RESULTS AND DISCUSSION

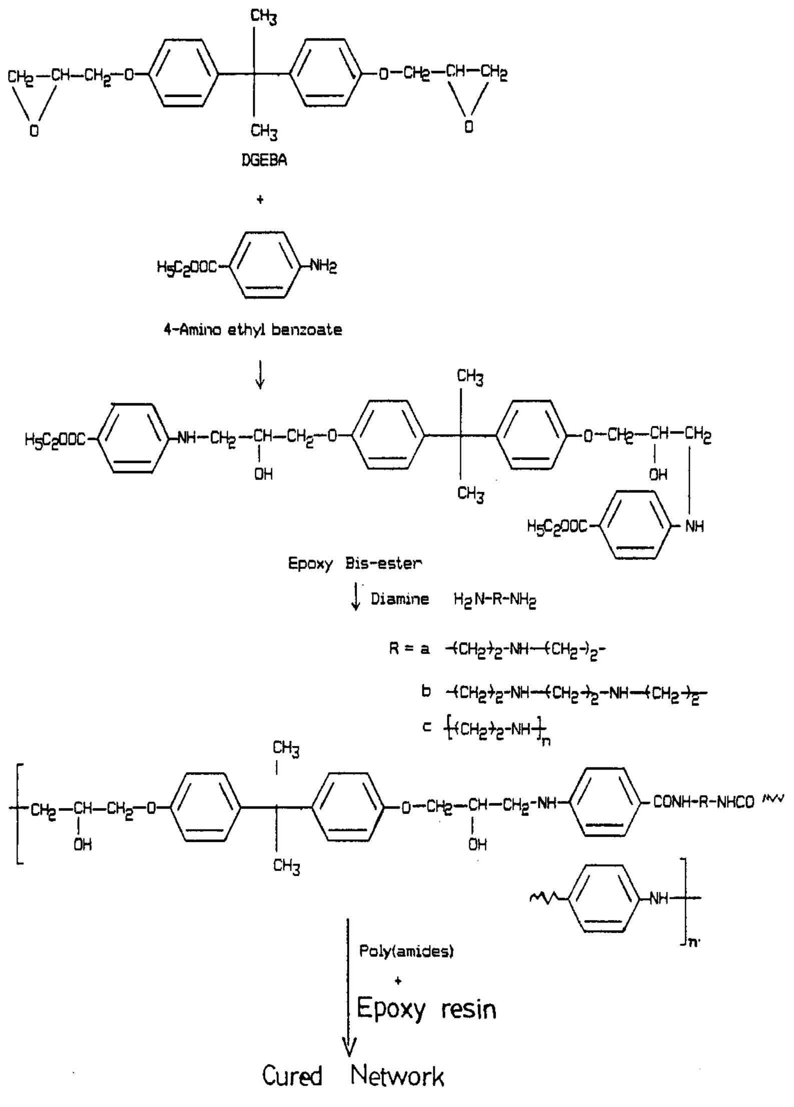
The method [4] reported in literature was followed for the reaction of epoxy resin, diglycidyl ether of bisphenol-A (DGEBA) with 4-amino ethyl benzoate (4-AEB). The resulting bisester derivative from DGE BA-4-AEB was isolated as a thick liquid.

The IR spectrum of bisester derivative comprises the group of bands around 2930–2800 cm$^{-1}$ associated with the C—H stretching vibration due to aliphatic moieties. A sharp and well resolved medium band around 1253 cm$^{-1}$ and 1044 cm$^{-1}$ may be assigned to —Ar—O —$CH_2$— and —$CH_2$—O—$CH_2$— linkages. The bands at 1600 and 1500 cm$^{-1}$ are attributed to the breathing vibrations of aromatic moieties due to bisphenol groups. The strong and sharp bands around 1300 and 1100 cm$^{-1}$ may be assigned to the secondary —OH group.

The absence of epoxy ring in the diester sample was further confirmed by the epoxy equivalent weight determination method [2]. The disappearance of epoxy ring characteristic frequency at 990 cm$^{-1}$ also confirmed the formation of bisester derivative.

The synthesis of polyamides (PAs) was carried out by reaction of the bisester derivative (i.e. DGEBA-4-AEB) with different aliphatic diamines viz., diethylene triamine (DETA), triethylene tetramine (TETA) and polyethylene amine (PEA). All the PA samples obtained were in form of thick liquid to semi solid in appearance depending upon the polymerisation. They also changed their state slightly after few months.

The examination of IR spectra of all PAs revealed that they are identical almost in all aspects. They comprise most of the features of



Scheme 1.

bisester derivative. The only discernible difference is that all the IR spectra of PAs comprises the responsible for the amide group.

The number average molecular weight ($\bar{M}n$) of all the polyamides (PAs) estimated by the non-aqueous conductometric titration [6–8] are reported in Table I, along with their —NH functionality. The $\bar{M}n$ of all the PAs are in the range of 3000 to 3500 depends on the nature of the polymers.

## Differential Scanning Calorimetric Curing Kinetics

An understanding of the curing reaction is very important to control the curing process for the end use of the resin system. In order to study the curing kinetics, the exothermic transition observed in DSC curves were analysed to obtain the characteristic temperatures like the temperature at which the curing reaction started (Ti), reached to the peak (Tp) and completed (Tf). It is evident from the data (Tab. II) that the values of Ti, Tp and Tf for the epoxy resin system in which DGEBA-4-AEB: DETA (i.e. polyamide based on epoxy resin) is used as curing agent shown the lowest values while the epoxy resin cured with DGEBA-4-AEB: PEA curing agent shows little higher values for the curing. These may be attributed to the fact that diffusion of the polyethylene amine in the epoxy resin may be lower compared to diethylene triamine or triethylene tetramine. The exothermic peak was observed on all the three systems, but no such transition was observed on the completely cured samples.

## Thermogravimetric Analysis

The curing conditions of all the resin systems were evaluated by DSC and samples of each system were cured at 130 °C for 1.5 h and 150 °C

TABLE I Number average molecular weight ($\bar{M}n$) of novel epoxy based polyamides used as curing agent

| *Code* | *Curing Agent (Polyamide)* | *—NH functionality* | *$\bar{M}n$ (by non-aqueous conductometric titration)* |
|---|---|---|---|
| A | DGEBA-4-AEB:DETA | 2.1 | 3213 |
| B | DGEBA-4-AEB:TETA | 1.9 | 3333 |
| C | DGEBA-4-AEB:PEA | 2.0 | 3412 |

DGEBA : Diglycidyl ether of bisphenol-A.
4-AEB : 4-Aminoethylbenzoate.
DETA : Diethylene triamine.
TETA : Triethylene tetramine.
PEA : Polyethylene amine.

TABLE II Curing characteristics of DGEBA by DSC using novel epoxy based polyamides as curing agents

(Heating Rate : 10°C/min)

| *System Resin:Curing Agent* | *Molar Ratio* | *Curing Temperature °C* | | | *Activation Energy Ea* | *Order of Reaction n* |
|---|---|---|---|---|---|---|
| | | *Ti* | *Tp* | *Tf* | *(Kcal/mol)* | |
| DGEBA:A | 1:1 | 62 | 77 | 102 | 47 | 0.95 |
| DGEBA:A | 1:1.5 | 55 | 76 | 98 | 44 | 1.02 |
| DGEBA:B | 1:1 | 67 | 89 | 140 | 54 | 1.10 |
| DGEBA:B | 1:1.5 | 62 | 84 | 135 | 49 | 0.98 |
| DGEBA:C | 1:1 | 72 | 113 | 154 | 58 | 0.95 |
| DGEBA:C | 1:1.5 | 65 | 105 | 149 | 52 | 1.02 |

TABLE III Thermogravimetric analysis of cured materials

| *System (Resin:Curing Agent)* | *Molar Ratio* | *% Weight Loss from TGA at °C* | | | | |
|---|---|---|---|---|---|---|
| | | *200* | *300* | *400* | *500* | *600* |
| DGEBA:A | 1:1 | 2.4 | 4.1 | 35.2 | 52 | 94 |
| DGEBA:A | 1:1.5 | 2.1 | 3.8 | 30.1 | 45 | 92 |
| DGEBA:B | 1:1 | 3.3 | 5.8 | 37.4 | 59 | 96 |
| DGEBA:B | 1:1.5 | 3.1 | 5.2 | 36.0 | 52 | 93 |
| DGEBA:C | 1:1 | 3.5 | 6.2 | 39.4 | 65 | 97 |
| DGEBA:C | 1:1.5 | 3.2 | 6.0 | 37.2 | 62 | 93 |

for 2 h and studied further to investigate their thermal stability by thermogravimetry.

To obtain information about the properties of unreinforced cross-linked materials, cured samples were powdered under normal pressure. They are insoluble in all common organic solvents. They swelled little in 25% v/v HCL and 25% W/V NaOH.

Thermogravimetry analysis of all the unreinforced cross-linked materials reveals that they degrade in a single step and start their decomposition at around 275 °C. Degradation becomes faster at 375–435 °C.

The decomposition temperature depends on the nature of polyamide used. The trend for the thermal stability of PAs was observed to be $A > B > C$ [Where A: DGEBA-4-AEB: DETA, B: DGEBA-4-AEB: TETA and C: DGEBA-4-AEB: PEA]. The lower thermal stability may be due to the proportion of amine character in the polyamide polymer chain. Therefore, the system-A shows the highest thermal stability. This may be attributed to the fact that the diffusion of the

DETA in the polymer chain may be faster and due to that, the crosslinking network formed may be strong compared to the system-C in which polyethylene amine is being used.

## Mechanical Properties

The formulations used for fabricating glass fiber reinforced composites are listed in Table IV and are coded as resin system A to C. Table IV lists the values of Flexural strength and Rockwell hardness determined at room temperature ( ≈ 30 °C).

Data included in Table IV show that Flexural strength (FS), Interlaminar shear strength (ILSS) and Rockwell hardness are affected by the nature of the epoxy based polyamides used as the curing agent. The increased interfacial bonding between the fiber and matrix may be assumed on the basis of the values of FS, ILSS and Rockwell hardness. The polyamide obtained from the system, DGEBA-4-AEB: PEA, shows better properties which may be attributed to the longer aliphatic chain length of the polyethylene amine. The flexibility caused by the longer chain length may reduce the brittleness of the cured system. This is reflected in increased FS, ILSS and rockwell hardness of the glass fiber reinforced composites.

The weight change data fall in the range 0.5–2.0% indicating no substantial effect of acetone, HCL, NaOH or water.

Since polyamides produced with the use of DETA, TETA or PEA do not lead to brittle polymeric products they may be suitable for advanced composites. The aliphatic character are considered as the key feature for the improved toughness and thereby mechanical properties of the glass reinforced composites.

TABLE IV Mechanical and electrical properties of glass reinforced composites

| *System* | *Molar Ratio* | *Flexural Strength (mpa)* | *ILSS (mpa)* | *Rockwell Hardness* | *Breakdown Voltage (KV)* |
|---|---|---|---|---|---|
| DGEBA:A | 1:1 | 178 | 18 | 109 | 10.5 |
| DGEBA:B | 1:1 | 194 | 20 | 115 | 11.8 |
| DGEBA:C | 1:1 | 201 | 24 | 121 | 12.5 |

## EXPERIMENTAL

### Materials

DGEBA was obtained from Synpol Chemicals Ltd., Ahmedabad, India having epoxy equivalent weight 190, viscosity 40–10 poise and density 1.16–1.1gm/cm$^3$ at 25 °C.

Diamines viz., diethylene triamine (DETA), triethylene tetramine (TETA) and polyethylene amine (PEA) used were laboratory grade reagents. 4-amino ethyl benzoate was synthesized according to the method given in a literature [5] (m.p. 88–90 °C).

### Synthesis of Diester Derivative Based on Epoxy Resin, DGEBA

A mixture of 4-amino ethyl benzoate 1 (2 mol.), DGEBA 2 (1 mol.) and triethyl amine (0.5 ml) in THF solvent were heated at 50–55 °C for 3 hrs. The viscous liquid was washed with solvent ether to remove unreacted DGEBA and 4-amino ethyl benzoate. The brownish viscous liquid was that vacuum distilled to remove remaining solvent species. The novel bisester formed is tested for the disappearance of epoxy ring by the IR and formaldehyde-$H_2SO_4$ test [2].

### Synthesis of polyamides (PAS)

The polyamides based on bisester and diamines listed above were prepared in the same manner. The diamine mixed with bisester thoroughly and the reaction mixture was heated at 50 °C for 2 hrs. The resultant mixture was poured into ether and washed several times. The PAs are in form of brown pasty mass.

### Measurements

Number average molecular weight ($\bar{M}n$) of epoxy based bisester and polyamides were estimated by non-aqueous conductometric titration [6–8]. Conductometric titration of each of polyamides was carried out in formic acid-acetic anhydride mixture against standard perchloric acid in acetic acid as titrant. The IR spectra was taken on

Perkin-Elmer 983 spectrophotometer. Thermogravimetry (TG) of all polymer samples were carried out on Metler TC-10/ATA-3000 thermal analyzer in air at heating rate of 10 °C/min.

## Composite Fabrication

The glass fiber reinforced composite based on such PAs-epoxy resin system were prepared by the procedure reported in the earlier communication [9]. A suspension mixture was stirred well for 5 to 10 minutes. The mixture was applied with a brush on to a 150 mm × 150 mm epoxy resin compatible fiber glass cloth (E-type glass cloth) and the solvent was allowed to evaporate. Once dried, the 12 plies of prepreg then prepared were stacked one on top of another, pressed between steel plates coated with a teflon film release and compressed in a flat plate press under 70 psi pressure. The prepreg stack was cured by heating in the press to 120–130 °C for 12 hrs. The composites so obtained was cooled to the room temperature ($\approx 30\,^{\circ}\mathrm{C}$) before the pressure was released. Test specimen were made by cutting.

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