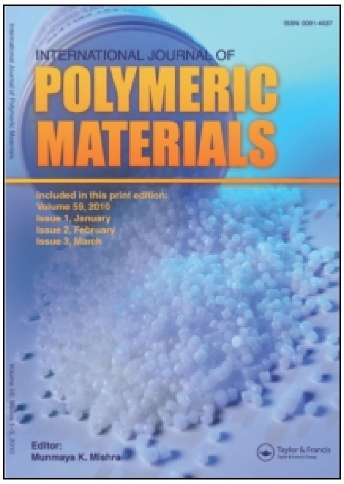

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Rajesh Baraiya[a]; Jatin R. Thakkar[a]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

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Novel Epoxy Based Polyamides—I

RAJESH BARAIYA and JATIN R. THAKKAR

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388120, Gujarat, India

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Novel bis ester namely 1,1′-(1-methylethylidene) 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-amino ethyl benzoate. The polyamides (PAs) were prepared by the condensation of bis ester derivative with various aliphatic diamines viz., 1,2-ethylene diamine (EDA), 1,3-propylene diamine (PDA), 1,4-butylene diamine (BDA) and 1,6-hexamethylene diamine (HMDA). The resultant novel epoxy resin based PAs were characterized by infrared spectroscopy and number average molecular weight ($\bar{M}n$). 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).

KEY WORDS 4-amino ethyl benzoate epoxy resin, polyamides, aliphatic diamines, thermogravimetric analysis.

INTRODUCTION

Epoxy resins have attained a prominent position in industry. In their fully cured state they have remarkable properties to solvents, acids, base and heat, in addition the low cost of these resins has prompted their use as substitutes for phenolics in various important applications.[1,2] The reaction of epoxy ring with amine and alcohols is well established[3] and hence the reaction of epoxy resin with an organic compound having amino and ester group like 4-amino ethyl benzoate may yield the bis ester derivative. This bis ester may afford polyamide with diamine.

Hitherto, most of the commercial polyamides are prepared from dibasic acids and diamines, the area in which the polyamide formation through epoxy resin (a commercial versatile material) based biester has not received attention academically as well as technically in spite of well defined applications of epoxy resin. Hence, it was thought interesting to explore the field of polyamides based on epoxy resin. The present paper comprises the initial work in this direction.

RESULTS AND DISCUSSION

The reaction of epoxy resin DGEBA with 4-aminoethylbenzoate (4-AEB) was performed according to the method reported in literature.[3] The resulting bis-ester deriv-

TABLE I

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

CODE	Curing Agent (Polyamide)	-NH functionality	$\overline{Mn}$ (by non-aqueous conductometric titration)
A	DGEBA-4-AEB:EDA	1.9	2990
B	DGEBA-4-AEB:PDA	2.0	3110
C	DGEBA-4-AEB:BDA	2.1	3320
D	DGEBA-4-AEB:HMDA	2.1	3450

DGEBA : Diglycidyl ether of bisphenol-A

4-AEB : 4-Aminoethylbenzoate

EDA : 1,2-Ethylene diamine

PDA : 1,3-Propylene diamine

BDA : 1,4-Butylene diamine

HMDA : 1,6-Hexane diamine

ative from DGEBA-4-AEB was isolated as a thick liquid. The yield was around 80%. The IR spectrum of bisester derivative based on DGEBA comprises the group of bonds around 2930–2800 cm^{-1} indicates the C—H stretching vibrations 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 groups.

The absence of an epoxy ring in the diester sample was further confirmed by the epoxy equivalent determination method.[4] The disappearance of epoxy ring characteristic frequency at 990 cm^{-1} also confirmed the formation of biester derivative.

The synthesis of polyamides (PAs) was carried out by reaction of the bisester derivative (i.e. DGEBA-4-AEB) with different aliphatic diamines. All the PA samples were obtained in good yields.

The examination of IR spectra of all PAs revealed that they are identical almost in all aspects. They comprise most of features of 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 weights ($\bar{M}n$) of all the polyamides (PAs) estimated by the non-aqueous conductometric titration method[5–7] are reported in Table I. They are in the range of 2000 to 3450 depending on the nature of the polymers.

TABLE II

Curing characteristics of DGEBA by DSC using novel epoxy based polyamides as curing agent (Heating rate: 10°C/min)

System Resin:Curing Agent	Molar Ratio	Curing Temperature °C			Activation Energy Ea (Kcal/mol)	Order of Reaction n
		Ti	Tp	Tf		
DGEBA:A	1:1	58	74	98	43	1.01
DGEBA:A	1:1.5	51	71	92	41	1.02
DGEBA:B	1:1	63	84	143	49	1.10
DGEBA:B	1:1.5	58	79	137	46	0.90
DGEBA:C	1:1	68	108	156	54	1.20
DGEBA:C	1:1.5	61	101	157	51	1.08
DGEBA:D	1:1	75	115	171	59	1.03
DGEBA:D	1:1.5	71	104	165	55	0.99

Differential Scanning Calorimetric Curing Kinetics

The resin systems studied for the DSC curing kinetics are shown in Table II. The exothermic transition was observed in some specific temperature range depending upon the nature of aliphatic diamines selected for the novel epoxy based polyamides. Table II lists some of the temperature data viz., the temperatures at which the curing reaction started (*Ti*), peaked (*Tp*) and completed (*Tf*) along with the values of activation energy and order of reaction for the curing reaction.

A comparison of the curing behaviour of different epoxy systems reveals that the values of *Ti*, *Tp* and *Tf* decrease with the increase in the aliphatic chain length of the diamines used in the synthesis of polyamides. The less reactive systems (i.e. PA based on HMDA) shifts the DSC curve towards the higher temperature range than that of more reactive system (i.e. PA based on EDA). The increase in chain length of the diamines used for the formation of novel epoxy based polyamides, reduces the reactivity and thus requires higher curing temperature. The change in ratio (Table II) of DGEBA to polyamides also affect the curing characteristics, but not much significantly. The effect of slightly lowering the temperature and speeding up the curing is attributed to the higher proportion of the PAs used for the curing.

Thermogravimetric Analysis

The curing conditions of all the resin systems were evaluated by DSC and samples of each system were cured following the information obtained from the DSC curves. The cured samples were studied further to investigate their thermal stability by thermogravimetry.

Examination of TGA data (Table III) reveals that the synthesised PAs sample start their decomposition between 210 and 223°C depending upon the nature of the poly-

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	2.8	4.9	30.2	48	92
DGEBA:A	1:1.5	2.5	4.2	28.3	43	89
DGEBA:B	1:1	3.2	5.5	32.3	54	93
DGEBA:B	1:1.5	2.9	5.1	31.2	53	91
DGEBA:C	1:1	3.4	5.8	34.4	59	94
DGEBA:C	1:1.5	3.1	5.2	33.6	53	91
DGEBA:D	1:1	3.8	6.5	36.9	64	96
DGEBA:D	1:1.5	3.3	6.1	32.8	61	94

amides. The rate of weight loss is high around 430°C and completed around 600°C. The trend for the thermal stability of the PAs was observed to be $A > B > C > D$, [where, *A*: DGEBA-4-AEB:EDA polyamide; *B*: DGEBA-4-AEB:PDA polyamide; *C*: DGEBA-4-AEB:BDA polyamide; *D*: DGEBA-4-AEB:HMDA polyamide]. The decreasing characteristics of the thermal stability may be due to increasing in the aliphatic chain length in the polyamide polymer chain. The major advantages of produced PAs lie in their solvent, weather, acid and alkali resistance.

The fabrication and study of glass fiber reinforced composites of this novel PA-epoxy systems is under progress and will be communicated shortly.

EXPERIMENTAL

Materials

DGEBA was obtained from Synpol Chemicals Ltd., Ahmedabad, India having epoxy equivalent weight 190, viscosity 40-10 poise and density 1-16-1.1 gm/cm^3 at 25°C.

Diamines viz. 1,2-ethylene diamine (EDA), 1,3-propylene diamine (PDA), 1,4-butylene diamine (BDA) and 1,6-Hexanediamine (HMDA) used were laboratory grade reagents. 4-amino ethyl benzoate was synthesized according to the method given in a literature[8] (m.p. 88 to 90°C).

Synthesis of Diester Derivative Based on Epoxy Resin, DGEBA

A mixture of 4-amino ethyl benzoate 1 (2 mol), DGEDA 2 (1 mol) and triethylamine (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 DGEABA and 4-aminoethyl benzoate. The brownish viscous liquid was that vacuum distilled to remove remaining solvent species. The novel biester formed is tested for the disappearance of epoxy ring by the IR and formaldehyde H_2SO_4 test.[4]

Synthesis of Polyamides (PAs)

The polyamides based on bisester and diamines listed above were prepared in the same manner. The above listed diamines viz. 1,2-EDA, 1,3-PDA, 1,4-BDA and 1,6-HMDA were respectively mixed with bisester. The reaction was carried out at 50°C for 2 hrs.

The $\bar{M}n$ values of PAs are furnished in Table I.

Measurements

Number average molecular weight ($\bar{M}n$) of epoxy based bisesters and polyamides were estimated by non-aqueous conductometric titration.[5-7] Conductometric titration of each of polyamides was carried out in formic acid-acetic anhydride mixture against standard perchloric acid in acetic 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.

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