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Novel Epoxy Based Polyamides

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Novel epoxy resin based polyamides (EPAs) were prepared by the condensation of bisester derivative namely 1,1'-(1-methylethylidene) bis[4-{1-(1-imino-3-ethylbenzoate)-2-propanolyloxy}]benzene, (BE) 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 EPAs were characterized by infrared spectroscopy (IR) and number average molecular weight (\overline{Mn}) of EPAs were estimated by non-aqueous conductometric titration.

As produced, EPAs having amido groups may act for curing of epoxy resins. Differential scanning calorimetric (DSC) curing kinetics of the epoxy resins *viz.*, diglycidyl ether of bisphenol-A (DGEBA) and triglycidyl ether of p-amino phenol (TGPAP) have been investigated using EPAs as a curing agent and triethyl amine (TEA) as a catalyst. Thermal stability of the cured epoxy systems were studied by thermogravimetric analysis (TGA).

Keywords: Epoxy resin; bisester; polyamides; aliphatic diamines; differential scanning calorimetric; thermogravimetric analysis

INTRODUCTION

In the last few decades epoxy resins have gained increasing importance due to wide range of applications such as adhesives, binding, construction materials, composites, coatings, mouldings and textile finishing. Epoxy resins are two part systems that undergo rapid, exothermic reactions to completion, without undesirable side effects. Due to invaluable properties like versatility towards number of curing agents;

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modifiers and diluents; good handling characteristics; toughness because of ether linkages; low shrinkages and inertness; epoxy resins forms an important class within the family of thermoset materials [1, 2].

The most common epoxy resin is DGEBA which has wide applications in many fields, however have some inferior properties with respect to thermal stability and hence many modifications have been made within its structure for gaining the desired properties.

Another resin, TGPAP is being used increasingly in adhesives and composites for high temperature applications [3, 4].

These properties of the cured epoxy resins may be modified by using suitable curing agents. Generally, diamines are used as curing agent for epoxy resins, but they are toxic in nature. In connection with our interest in development of novel non-toxic curing agents which improves the properties of cured epoxy resin, we have developed novel curing agents having epoxy and polyamide properties.

The reaction of epoxy ring with amine and alcohol is well established [5] and hence the reaction of epoxy resin with an organic compound having amino and ester group like 3-amino ethyl benzoate may yield bisester derivative. This bisester may afford polyamides on further condensation with diamines.

The great deal of work on epoxy resin based polyamides has been carried out in our laboratory [6, 7]. The work was mainly based on curing study of epoxy resin (DGEBA) using EPAs as curing agent. The present communication deals with the two part adhesive systems comprising a conventional epoxy resins, DGEBA and TGPAP with EPAs as a curing agent and TEA as a catalyst for the study of curing kinetics, thermal stability, and to carry out comparative study of these properties.

EXPERIMENTAL

Materials

A commercial epoxy (DGEBA) resin was obtained from Synpol Chemicals Ltd., Ahmedabad, India having epoxy equivalent weight 190–210, viscosity 4–10 poise and density 1.16–1.17 gm/cm³ at 25°C. Diamines *viz.*, 1,2-ethylene diamine (EDA), 1,3-propylene diamine

(PDA), 1,4-butylene diamine (BDA) and 1,6-hexamethylene diamine (HMDA) and triethyl amine (TEA) used were laboratory grade reagents. 3-amino ethyl benzoate (3-AEB) was synthesized according to the method given in literature (b.p. 172–175°C) [8]. TGPAP was synthesized according to the method given in literature [9, 10].

Synthesis of Bisester Derivative Based on Epoxy Resin (DGEBA)

A mixture of 3-amino ethyl benzoate 1 (2 mol.), DGEBA 2 (1 mol.) and triethyl amine (0.5 ml) as a catalyst were heated at 50–55°C for 3 hrs. The viscous liquid was washed with solvent ether to remove unreacted DGEBA and 3-amino ethyl benzoate. The brownish viscous liquid was vacuum distilled to remove remaining solvent species. The novel bisester formed is tested for the disappearance of epoxy ring by formaldehyde-H₂SO₄ test [11] and further confirmed by IR.

Synthesis of Polyamides (EPAs)

The polyamides based on bisester and diamines listed above were prepared in the same manner. The diamines *viz.*, 1,2-EDA, 1,3-PDA, 1,4-BDA and 1,6-HMDA were respectively 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 EPAs were in the form of brown pasty mass.

Measurements

Number average molecular weight (\bar{M}_n) of epoxy resin based polyamides were estimated by non-aqueous conductometric titration [12–14]. Conductometric titration of each polyamides were carried out in formic acid–acetic anhydride mixture against standard perchloric acid in glacial acetic acid as titrant. The IR spectra was taken on Nicolet Impact 400D Fourier Transform Infrared Spectrophotometer. A Du Pont 900 differential scanning calorimetry was employed to obtain the data of the exothermic curing reactions. The samples were scanned from 30 to 250°C at a scanning rate of

10°C/min. Thermogravimetric analysis (TGA) of all polymer sample have been carried out using Metler TC-10/ATA-3000 thermal analyzer in air at heating rate of 10°C/min.

RESULTS AND DISCUSSION

The bisester derivative (DGEBA-3-AEB) was prepared according to method reported in literature [3] and characterized by infrared spectroscopy (IR).

The IR spectrum of bisester derivative (Fig. 1) comprises the group of bands around 2930 and 2850 cm^{-1} associated with the C—H stretching vibration due to aliphatic moieties. A sharp and well resolved medium band around 1280 cm^{-1} may be assigned to —Ar—O—CH₂— linkage. The bands at 3030 and 1500 cm^{-1} are attributed to the aromatic breathing from bisphenol-A moiety. The strong and sharp band around 1100 cm^{-1} may be assigned to the secondary -OH group. The sharp bands observed at 840 and 720 cm^{-1}

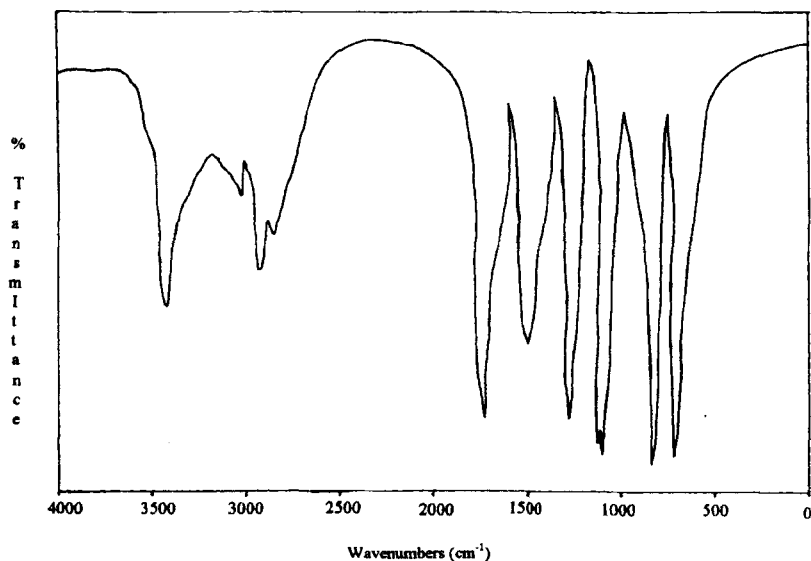


FIGURE 1 IR spectra of DGEBA-3-AEB (bisester).

may be assigned to the substituted aromatic system. The disappearance of the band at 910 cm^{-1} due to epoxy ring confirmed the formation of bisester derivative. The absence of epoxy ring in the bisester sample was further confirmed by the epoxy equivalent weight determination method. The band around 3420 cm^{-1} is attributed to the N—H stretching vibration due to secondary —NH— group. The sharp band observed at 1730 cm^{-1} may be assigned to the C=O stretching vibration due to aromatic ester group.

The polyamides were prepared by the condensation of bisester derivative with four aliphatic diamines *viz.*, 1,2-ethylene diamine (EDA), 1,3-propylene diamine (PDA), 1,4-butylene diamine (BDA) and 1,6-hexamethylene diamine (HMDA). All the EPA samples obtained were in the form of thick liquid to semi solid in appearance depending upon the polymerization. They also changed their state slightly after few months.

The examination of IR spectra (one of them was presented in Fig. 2) of all polyamide sample revealed that they are identical almost in all aspects. They comprises most of the features of bisester derivative. Other discernible frequencies of polyamides are as follows. The band observed at 3420 cm^{-1} is attributed to the N—H stretching vibration due to secondary —NH— group and bands around 3480 cm^{-1} may arise due to the N—H stretching vibration of terminal NH_2 group in almost all spectra. All the IR spectra of polyamides comprises the group of bands around 3200 , 1510 , 1770 and 1710 cm^{-1} which is responsible for the amide group.

The number average molecular weight (\bar{M}_n) of all the polyamides (EPAs) estimated by the non-aqueous conductometric titration [12–14] are reported in Table I, along with their —NH functionality. The \bar{M}_n of all the EPAs were in the range of 2500 to 3500 depending on the nature of the polymers.

An understanding of the curing reaction is very important to control the curing process for the end use of the resin system. The resin systems studied for the DSC curing kinetics are shown in Tables II and III. In order to study the curing kinetics, the exothermic transition observed in some specific temperature range depending upon the nature of aliphatic diamines selected for the epoxy based polyamides in DSC curves were analyzed to obtain the characteristic temperatures like the temperature at which the curing reaction started (T_i), reached

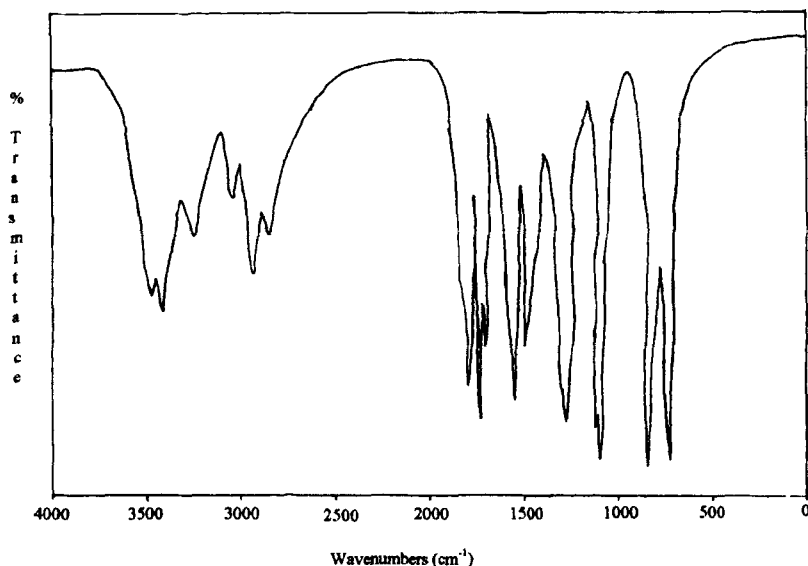


FIGURE 2 IR spectra of DGEBA-3-AEB: BDA (polyamide).

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
A	DGEBA-3-AEB: EDA	1.9	2850
B	DGEBA-3-AEB:PDA	2.1	3010
C	DGEBA-3-AEB :BDA	2.0	3290
D	DGEBA-3-AEB: HMDA	2.1	3440

DGEBA: Diglycidyl ether of bisphenol-A; 3-AEB: 3-aminoethyl benzoate; EDA: 1,2-ethylene diamine; PDA: 1,3-propylene diamine; BDA: 1,4-butylene diamine; HMDA: 1,6-hexamethylene diamine.

to the peak (T_p) and completed (T_f) along with the values of activation energy and order of reaction for the curing reaction.

The data obtained from the DSC thermograms revealed that the curing temperature of both the epoxy resin systems increases with an increase in the chain length of aliphatic diamines used in the polyamide formation. The increase in chain length of the aliphatic diamines used in the formation of polyamides, reduces the reactivity and thus require higher curing temperature. Longer the aliphatic chain

TABLE II Curing characteristics of DGEBA by DSC using epoxy based polyamides as curing agent and triethylamine as catalyst.

Resin system	Proportion	Curing temperature (°C)			Activation energy (Ea) (Kcal/mole)	Order of reaction n
		T _i	T _p	T _f		
DGEBA : A	60 : 40	65	86	118	42	1.01
DGEBA : B	60 : 40	72	102	144	50	1.10
DGEBA : C	60 : 40	90	122	155	55	1.20
DGEBA : D	60 : 40	98	132	170	61	1.03

TABLE III Curing characteristics of TGPAP by DSC using epoxy based polyamides as curing agent and triethylamine as catalyst.

Resin system	Proportion	Curing temperature (°C)			Activation energy (Ea) (Kcal/mole)	Order of reaction n
		T _i	T _p	T _f		
TGPAP : A	60 : 40	51	73	94	41	1.02
TGPAP : B	60 : 40	60	86	112	46	1.10
TGPAP : C	60 : 40	72	96	130	52	1.03
TGPAP : D	60 : 40	86	112	139	58	1.20

in polyamide, lesser the crosslinking site available for curing and thus higher the activation energy. The values of activation energy in both epoxy system increases with increase in the molecular weight of polyamide indicating the lower reactivity of higher molecular weight polyamide. In both the epoxy resin system, it is observed that tri-functional epoxy resin *i.e.*, TGPAP resin having higher crosslinking site than difunctional epoxy resin *i.e.*, DGEBA resin and so that higher the reactivity and thus require lower curing temperature. It was also observed that ease of curing of TGPAP can be attributed to its higher functionality. The energy of activation value is lower for the system having rapid curing rate. The change in ratio of epoxy 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 EPAs used for the curing. The kinetic parameters such as activation energy and 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 for 10°C/min heating rate.

The curing conditions of all the resin systems were evaluated by DSC and samples of each system were cured following information obtained from the DSC curve. The cured samples designated as unreinforced crosslinked materials were studied further to investigate their thermal stability by thermogravimetry. All the samples were powdered under normal pastel pressure. They were insoluble in all common organic solvents. They swelled little in 25% v/v HCL and 25% w/v NaOH.

Examination of TGA data (Tabs. IV and V) revealed that all the unreinforced crosslinked materials of both the resin systems, start their decomposition between 200–225°C depending upon the nature of the polyamides. The rate of weight loss is high around 500–525°C and completed around 650°C. The cured samples of both the resin systems loss around 50 to 60% weight when heated upto 475–525°C. The cured sample of both the resin systems loss 85–97% weight when heated upto 650°C. Comparison of the TGA data obtained from the samples of both the resin systems reveals that thermal stability decrease slightly but significantly depends on the nature of polyamide used. The decreasing characteristics of the thermal stability may be due to increasing in the aliphatic chain length in the polyamide polymer chain. This may be attributed to the fact that the diffusion of the EDA in the polymer chain may be faster than that of HMDA and due to that, the crosslinking network formed may be strong compared to system in which HMDA is being used. Comparison of the TG data obtained from both the resin systems reveals that the thermal stability increased slightly but significantly in the case of trifunctional epoxy resin systems compared to difunctional epoxy resin systems, as formation of highly crosslinked network structure takes place. Finally the decomposition rate for both the resin systems decrease gradually reaching at constant weight representing the (carbonized) char. The

TABLE IV Thermogravimetric analysis of cured samples

System	Proportion (%w/w)	% Weight loss from TGA at °C				
		200	300	400	500	600
Resin : curing agent						
DGEBA : A	60 : 40	3.3	3.9	34	49	93
DGEBA : B	60 : 40	3.5	4.1	37	55	94
DGEBA : C	60 : 40	3.8	4.8	38	57	95
DGEBA : D	60 : 40	3.9	5.5	39	65	97

TABLE V Thermogravimetric analysis of cured samples

System Resin : curing agent	Proportion (%w/w)	% Weight loss from TGA at °C				
		200	300	400	500	600
TGPAP:A	60:40	2.3	3.4	25	35	86
TGPAP:B	60:40	2.6	3.7	28	40	88
TGPAP:C	60:40	3.0	4.1	31	46	89
TGPAP:D	60:40	3.3	4.6	35	52	91

char values observed for trifunctional epoxy resin systems is higher than that of difunctional epoxy resin systems indicates the higher thermal stability of trifunctional epoxy resin system which may be accounted for the trifunctionality of epoxy resin. It is evident from the kinetic study of the thermal degradation, that the both the resin achieves high thermal stability when cured with polyamide formed from the short chain aliphatic diamines. It was also observed that trifunctional epoxy resin systems achieves higher thermal stability compared to difunctional epoxy resin systems.

CONCLUSIONS

The overall advantages of EPA-epoxy systems are as follows.

- (i) The polyamides prepared from DGEBA can successfully be used as curing agent for the epoxy resins (*i.e.*, EGEBA & TGPAP).
- (ii) From the DSC, it revealed that polyamide based on short chain aliphatic diamine is more reactive curing agent than polyamide based on long chain aliphatic diamine in both the epoxy resin system.
- (iii) Trifunctional epoxy resin (TGPAP) required lower curing temperature than difunctional epoxy resin (DGEBA).
- (iv) From the TGA, it revealed that polyamide having long chain aliphatic diamine is least thermally stable than polyamide having short chain aliphatic diamine in both the epoxy resin system.
- (v) TGPAP shows higher thermal stability than DGEBA.
- (vi) All the polyamides shows excellent resistance to acid, alkali, water and organic solvents.

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