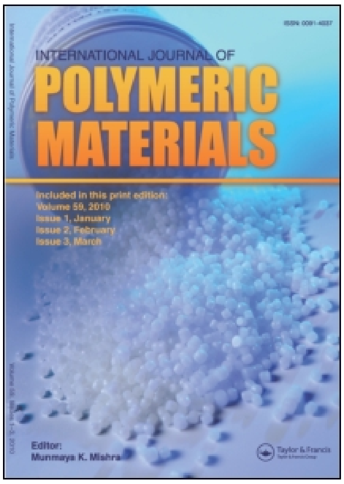

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Novel Epoxy Curing Agents from Epoxy Resin Based Dialdehyde Derivative

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A series of epoxy based curing agents were synthesised by the reaction of dialdehyde derivative 1,1′-(1-methylethylidene) di[4-{1-(1-imino-4-benzaldehyde)-2-propanolyloxy}] benzene of epoxy resin with a different aromatic diamines. The dialdehyde derivative was synthesised by the reaction of epoxy resin (DGEBA) with 4-amino benzaldehyde (4-ABA) in presence of triethyl amine (1% by wt. Of resin) as a catalyst. All this curing agents were characterised by their number average molecular weight ($\overline{M}n$), elemental analyses and infrared spectrophotometry (IR). As produced, polymers may act as a epoxy curing agent, the thermal characteristics of the synthesised PK-epoxy resin system were investigated by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Keywords: Epoxy resin; curing agent; dialdehyde derivative; infrared spectrophotometry; differential scanning calorimetry

1. INTRODUCTION

Epoxy resins have been widely used as an engineering materials because of their extra ordinary toughness, good mechanical resistance [1,2]. Considerable amount of research work have been made on the relation between the properties of cured resins and structure of epoxy compounds. These studies were mostly based on bisphinol-A type epoxy resin with various kinds of hardeners like amines, anhydrides, *etc.* [1,2].

The most common epoxy resin is DGEBA which has wide applications in many fields, however have some inferior properties with

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respect to 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. In connection with our interest in development of novel curing agents which improves the properties of cured epoxy resin. The reaction of oxirane ring with amine and alcohol group has been well established [5] and hence the reaction of epoxy resin with an organic compound like 4-amino benzaldehyde may afford curing agents on further condensation with diamines.

The present communication deals with the two part adhesive systems comprising a conventional epoxy resins, DGEBA and TGPAP with PKs as a curing agent and present/absent of TEA as a catalyst for the study of curing kinetics, thermal stability and to carry out comparative study of the there properties.

2. EXPERIMENTAL DETAILS

2.1. Materials

Epoxy resin triglycidyl-p-amino phenol (TGPAP) was synthesised according to the method given in a literature [6, 7]. Commercial epoxy resin diglycidyl ether of bisphenol-A (DGEBA) was obtained from *Synpol Products Pvt. Ltd.*, Ahmedabad, India. The specifications of DGEBA are as follows:

(1) Epoxy equivalent weight	190
(2) Viscosity at 25°C	40 – 100 poise
(3) Density at 25°C	1.16 – 1.17 g cm^{-3}

All other chemicals used were of laboratory grade.

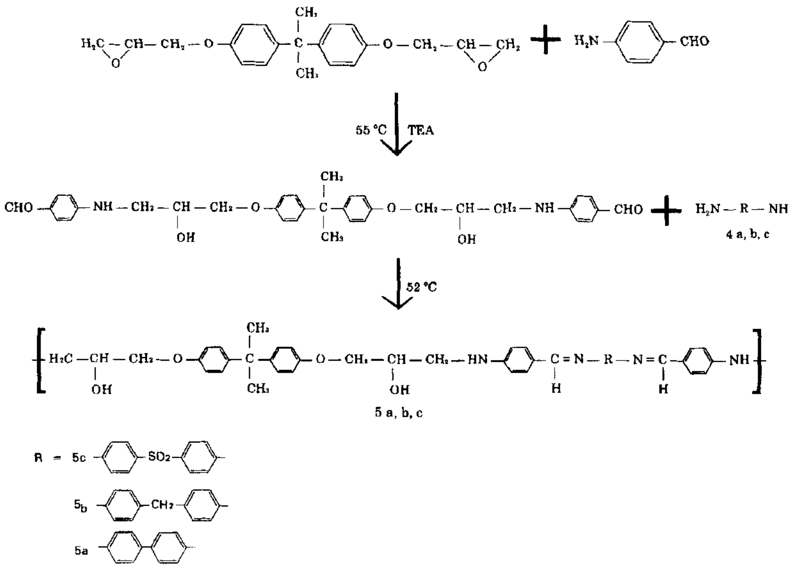
2.2. Preparation of Dialdehyde Derivative Based on Epoxy Resin Diglycidyl Ether of Bisphenol-A (DGEBA): Formation of 1,1′-(1-methylethylidene) di[4-{1-(1-imino-4-benzaldehyde)-2-propanolyloxy}] Benzene (3)

A mixture of DGEBA (1 mol), 4-amino benzaldehyde (2) (2 mol) and three to four drops of triethylamine was heated at 70 ± 5°C for 10 hours.

The resulting mixture was poured into a large amount (~ 250 ml) of dry ether. The ether was decanted and the viscous liquid was again washed with dry ether to remove unreacted amino benzaldehyde and DGEBA. The dark brown viscous liquid was then vacuum distilled to remove remaining solvent species. Analysis of the resultant dialdehyde derivative, designed as 3 (Scheme 1), are as follows:

	C (%)	H (%)	N (%)
($C_{35}H_{38}N_2O_6$) Calculated	72.16	6.52	4.81
(582) Found	71.08	6.97	4.82

$\overline{Mn}$(vpo) = 580 (in DMF at 70 ± 1°C)



SCHEME 1 Proposed structure of the curing agent.

The novel dialdehyde derivative formed is tested for the disappearance of epoxy ring by formaldehyde-H_2SO_4 test [8] and further confirmed by IR.

2.3. The Curing Agents/Poly(Schiff Reagent)s was Synthesised by the Reaction of 3 with 4a, 4b and 4c

The poly(ketimene)s based on dialdehyde derivative and diamines listed above were prepared in the same manner. The diamines *viz.*, DDM, DDS and Benzidine were respectively mixed with dialdehyde derivative thoroughly and the reaction mixture was heated at 50 ± 1°C for 4 hours. The resultant mixture was poured in to ether and washed several times. The PKs were in the form of brown pasty mass.

2.4. Measurements

The C, H and N contents of all the curing agents sample were estimated by means of a Carlo Ebra elemental analyser (Italy). The IR spectra was taken on Nicolet Impact 400D fourier Transform Infrared Spectrophotometer.

Number average molecular weight ($\overline{Mn}$) of all samples were estimated by Gel permeation chromatography (GPC) with a model HLC-830 from Shimazu Seisakusho. The curing behaviour of all the resin system was studied by differential scanning calorimeter. Thermogravimetry (TG) of all polymer samples was carried out on a Mettler TC-10/ATA-3000 thermal analyser in air, at a heating rate of $10\,\mathrm{k\,min^{-1}}$.

3. RESULTS AND DISCUSSION

The reaction of epoxy resin DGEBA (1) with 4-amino benzaldehyde (2) in the presence of triethylamine was performed according to the method reported in the literature [9]. The resulting dialdehyde derivative was isolated as a dark brown thick liquid. The yield was around 60–70%. The C, H and N contents of 3 are in good agreement with the structure proposed in Scheme 1. Examination of the IR spectrum of 3 indicated the characteristic group frequencies. The tentative assignment to the vibrational frequencies supports the proposed structure in Scheme 1. The group of bands around $2930-2800\,\mathrm{cm^{-1}}$ indicates the C—H stretching vibrations due to aliphatic moieties. A sharp and well resolved medium band around $1253\,\mathrm{cm^{-1}}$ may be assigned to —Ar—O—CH_2— linkages. The bands at 1600 and $1500\,\mathrm{cm^{-1}}$ are attributed to the breathing vibration of aromatic moieties due to the presence of bisphenol groups. The strong and sharp band around $1100\,\mathrm{cm^{-1}}$ may be assigned to the secondary —OH group. The sharp bands observed at 840 and $720\,\mathrm{cm^{-1}}$ may be assigned to the substituted aromatic system. The band around

$3420\,\text{cm}^{-1}$ is attributed to the N—H stretching vibration due to secondary —NH— group. The disappearance of band $910\,\text{cm}^{-1}$ due to epoxy ring confirmed the formation of dialdehyde derivative.

The absence of an epoxy ring in the dialdehyde sample was further confirmed by the epoxy equivalent determination method. The effect of TEA on epoxy resin was found to be negligible as there was no significant change in the properties of the epoxy resin when heated at 70°C under similar experimental conditions. However, the properties are changed at elevated temperature or by the addition of Lewis acids [10]. The dialdehyde(3) was obtained as a viscous liquid, which remained in this form even after six to seven months storage in a vacuum desiccator. The molecular weight of 3 was estimated by the VPO method and found to be 580 in good agreement with the predicted structure (Scheme 1).

The entire curing agents (PK) formation through the polycondensation reaction of the dialdehyde derivative 3 with diamine 4a, b, c is shown in Scheme 1. All the PK samples obtained were in the 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 PKs sample revealed that they are indentical almost in all aspects. They comprises most of the features of dialdehyde derivative. The only discernible difference is that all the IR spectra of PKs comprises the bond at $1600-1620\,\text{cm}^{-1}$ was responsible for the $C=N$ group. The elemental analyses of all the PKs samples, shown in Table I, are consistent with their predicated structure (Scheme 1).

The number average molecular weight ($\overline{Mn}$) of all the PKs were estimated by the Gel Permeation Chromatography are reported in Table I. The ($\overline{Mn}$) of all PKs in the range of 4000 to 5000 depends on the nature of the polymers.

The data obtained from the differential scanning calorimetry (DSC) run at 10°C/min are given in Table I. The DSC thermograms showed that all the epoxy resin system gave a single exothermic peaks in the range of 150 to 250°C. The temperature at which curing starts (Ti), peak exotherm temperature (Tp) and temperature of completion of curing (Tp) are reported in Table II. The data reveal that the curing temperature of the epoxy resin systems depends on the nature of the curing system (say, curing agent and presence or absence of catalyst).

TABLE I Characterization of curing agents

Code	Curing agent	Yield (%)	Elemental analysis						IR spectra characteristics (cm^{-1})						$\overline{M}n$
			C(%)		H(%)		N(%)		— CH_2 — and — CH_3 —	Secondary — NH —	Secondary — OH	Ar — O — CH_2	— CH	— C = N —	
			Calc.	found	Calc.	found	Calc.	found							
A	DGEBA-4-ABA : DDS*	87	69.99	97.3	5.83	5.72	5.97	5.68	2930 2850 2950	3420	1300 1100	1253 1054	3030	1610	2840
B	DGEBA-4-ABA : DDM**	86	75.11	75.09	6.56	6.58	8.54	8.68	2932 2853 2950	3420	1310 1100	1250 1045	3030	1615	2620
C	DGEBA-4-ABA : BEN	90	76.99	76.82	6.41	6.47	6.57	6.98	2930 2850 2950	3420	1310 1100	1250 1145	3030	1608	2595

*DDS : 4,4′-diamino Diphenyl Sulfone.

**DDM : 4,4′-diamino Diphenyl Methane.

TABLE II Curing characteristics of DGEBA and TGPAP by DSC (Heating Rate: 10°C/min)

System *Resin: curing agent*	*Ratio*	*Curing temperature °C* *Ti*	 *Tp*	 *Tf*	*Activation energy Ea (Kcal/mol)*	*Order of reaction n*
DGEBA:A	60:40	134	168	192	50	1.13
DGEBA:B	60:40	146	171	208	56	1.27
DGEBA:C	60:40	160	190	217	58	1.10
TGPAP:A	60:40	118	143	173	42	0.98
TGPAP:B	60:40	127	151	192	47	0.90
TGPAP:C	60:40	143	166	198	48	0.91
DGEBA:A:TEA*	59:40:1	98	114	130	38	1.04
DGEBA:B:TEA*	59:40:1	107	129	141	40	1.09
DGEBA:C:TEA*	59:40:1	120	137	158	43	0.99
TGPAP:A:TEA*	59:40:1	81	101	117	27	0.92
TGPAP:B:TEA*	59:40:1	92	113	125	31	0.93
TGPAP:C:TEA*	59:40:1	99	121	134	37	1.01

* TEA added 1% on the bases of curing agent.

The curing temperature and activation energy of both the resin systems increases with an increase in the molecular weight of curing agent indicating the lower reactivity of higher molecular weight curing agent. In both the epoxy resin system, it is observed that trifunctional epoxy resin (TGPAP) having higher crosslinking site than difunctional epoxy resin (DGEBA) and so that higher the reactivity and thus require lower curing temperature. The energy of activation value is lower for the system having rapid curing rate. In both the resin systems incorporation of a catalyst (triethylamine) lower down the curing temperatures. These may be ascribed to a higher catalytic character of tertiary nitrogen present in the TEA.

The values of activation energy (Ea) for such systems have no wide variation. The kinetic parameters Ea and order of reaction(n) were calculated by assuming that curing reactions obeys Arrhenius type kinetic and that the peak maximum represents a point of constant conversion at a heating rate of 10°C/min. The data indicate that the system in which TEA used required less energy of activation which also reflect the enhanced catalytic effect of triethylamine.

The cured samples (after DSC) designated as unreinforced crosslinked materials were studied further to investigate their chemical resistance and thermal stability by thermogravimetry. All the samples were powdered under normal pastel pressure. The samples of each system were put in 100 ml standard reagents (water, 25% NaOH, 25% HCl, acetone) for seven days. After exposure to chemical reagents, each sample was examined on the basis of physical properties like discolouration, loss of gloss and change in weight. The weight change data falls in the range of 1 to 4.9% indicating no substatical effect of water, acetone, acid and alkali.

The unreinforced cured epoxy samples were analysed for their thermal stability by thermogravimetry analysis (TGA). Table III shows, the results obtained from TGA revealed that resins degrate in a single step and start their decomposition at around 300°C. The rate of decomposition increases between 350 to 400°C. The cured resin decomposes 90% at around 600°C.

The thermal stability of the resin system may be accounted for the aromatic character of both the epoxy resin as well as curing agents. Comparison of the TGA data obtained from both the resin systems reveals that the thermal stability increased slightly but significantly in the case of trifunctional epoxy resin systems, as formation of highly crosslinked network structure take place.

Finally, the decomposition rate for both the resin systems decrease gradually reaching at constant weight representing the (carbonised) char. The char values observed for trifunctional epoxy resin systems is higher than that of difunctional resin systems indicated the higher thermal stability of trifunctional epoxy resin systems. Which may

TABLE III Thermogravimetric analysis of cured materials

System		*% Weight loss from TGA at °C*					
Resin: curing agent	*Ratio*	250	300	400	500	600	650
DGEBA : A	60 : 40	3.3	5.8	33.0	59.1	80.7	92.9
DGEBA : B	60 : 40	3.7	6.0	34.7	60.9	83.1	95.3
DGEBA : C	60 : 40	4.5	7.3	35.8	62.5	85.5	96.1
TGPAP : A	60 : 40	2.4	4.1	30.3	52.7	79.1	91.6
TGPAP : B	60 : 40	2.6	4.3	33.5	54.9	80.0	93.6
TGPAP : C	60 : 40	2.7	4.7	34.9	56.3	82.2	95.0
DGEBA : A : TEA*	59 : 40 : 1	2.9	4.1	30.1	52.7	80.7	90.7
DGEBA : B : TEA*	59 : 40 : 1	3.3	5.8	32.8	59.7	82.1	92.8
DGEBA : C : TEA*	59 : 40 : 1	3.4	6.3	34.3	62.2	84.3	94.4
TGPAP : A : TEA*	59 : 40 : 1	2.1	3.4	28.7	50.0	77.7	89.3
TGPAP : B : TEA*	59 : 40 : 1	2.3	3.9	29.1	52.8	79.1	92.8
TGPAP : C : TEA*	59 : 40 : 1	2.7	4.0	30.0	54.0	80.9	93.7

*DGEBA : Diglycidyl Ether of Bisphenol-A; TGPAP : Triglycidyl-P-Amino Phenol; TEA : Triethyl Amine.

accounted for the trifunctionality of epoxy resin. It is evident from the kinetic study of the thermal degradation, that the both the resin systems, thermal stability increase with increases in aromatic character of curing agent. Thus, 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 PK used.

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