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## Study on Novel Epoxy Based Poly(schiff reagent)s

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Novel poly(schiff reagent)s (PSs) from diketo derivative of epoxy resin were synthesised and characterised. A series of epoxy resin based poly(schiff reagent)s were synthesised by reacting an epoxy resin, diglycidyl ether of bisphenol-A (DGEBA) with 4-amino acetophenone (4-AAP) in a 1 : 2 mole ratio to afford the corresponding diketo derivative, and subsequent reaction with various aliphatic diamines in the presence of a triethyl amine as a catalyst. The resultant poly(schiff reagent)s were characterised by infrared spectroscopy (IR) and number average molecular weight ( $\bar{M}_n$ ) of PSs were estimated by non-aqueous conductometric titration. As produced, PSs having amine 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-*p*-amino phenol (TGPAP) have been investigated using PSs as a curing agent and triethyl amine as a catalyst. Thermal stability of the cured epoxy systems was studied by thermogravimetric analysis (TGA). The glass fiber reinforced composites of the produced PSs-epoxy system have been fabricated and were characterised by their mechanical properties and chemical resistance.

**Keywords:** Epoxy resin; Diamine; Differential scanning calorimetry; Mechanical properties; Chemical resistance; Thermogravimetric analysis; Schiff bases

### 1. INTRODUCTION

In the last few decades epoxy resins have gained increasing importance due to wide range of applications such as adhesives, binding,

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

The most common epoxy resin is DGEBA which has wide application 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 poly(schiff reagent)s 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 keto group like 4-amino acetophenone may yield diketo derivative. This diketo may afford poly(schiff reagent)s on further condensation with diamines. The present communication deals with the two part adhesive systems comprising a conventional epoxy resins DGEBA and TGPAP with PSs as a curing agent and TEA as a catalyst for the study of curing kinetics, thermal stability, mechanical properties and chemical resistance of composites, and to carry out comparative study of these properties.

## 2. EXPERIMENTAL

### 2.1. Materials

A commercial epoxy resin (DGEBA) 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/cm<sup>3</sup> at 25°C. TGPAP was synthesised according to a method given in the literature [6, 7]. All other chemicals used were laboratory grade reagents.

## 2.2. Synthesis of Diketo Derivative Based on Epoxy Resin

A mixture of 4-amino acetophenone (2 mol.), DGEBA (1 mol.) and triethyl amine (0.5 ml) as a catalyst were heated at 55°C for 4 hrs. The viscous liquid was washed with solvent ether to remove unreacted DGEBA and 4-AAP. The brownish viscous liquid was vacuum distilled to remove remaining solvent species. The novel diketo derivative formed was tested for the disappearance of epoxy ring by formaldehyde-H<sub>2</sub>SO<sub>4</sub> test [8] and further confirmed by IR.

## 2.3. Synthesis of Poly(schiff reagent)s (PSs)

The poly(schiff reagent)s based on diketo derivative and diamines listed above were prepared in the same manner. The diamines *viz.*, EDA, PDA, BDA and HMDA were respectively mixed with diketo derivative thoroughly and the reaction mixture was heated at 50°C for 3 hrs. The resultant mixture was poured into ether and washed several times. The PSs were in the form of brown pasty mass.

## 2.4. Measurements

The IR spectra was taken on Nicolet Impact 400 D Fourier Transform Infrared Spectrophotometer. Number average molecular weight ( $\bar{M}_n$ ) of epoxy resin based poly(schiff reagent)s were estimated by non-aqueous conductometric titration [9, 10]. Conductometric titration of each poly(schiff reagent) was carried out in formic acid-acetic anhydride mixture against standard perchloric acid in glacial acetic acid as titrant. A Du pont 900 differential scanning calorimetry was employed to obtain the data of the exothermic curing reactions. Thermogravimetric analysis (TGA) of all polymer samples have been carried out using metler TC-10/ATA-3000 thermal analyser in air at heating rate of 10°C/min.

### 2.4.1. Composite Fabrication

The glass fiber reinforced composites based on such PSs-epoxy resin system were prepared by a procedure reported in the earlier communication [11]. 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 thus prepared were stacked one on top of another, pressed between steel plates coated with a teflon release film 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 were cooled to room temperature (~30°C) before the pressure was released. Test specimen were made by cutting.

### 2.4.2. Composite Measurements

The chemical resistance of the laminated samples was measured according to ASTM D 543, having dimensions of 25 mm width and 25 mm length. Flexural strength, Inter laminar shear strength and Impact strength were measured according to ASTM methods D-770-76, D-2344-76 and D-256 respectively, using Universal Instron testing machine 1193.

## 3. RESULTS AND DISCUSSION

The diketo derivative (DGEBA-4-AAP) was prepared according to a method reported in the literature [12] and characterised by infrared spectroscopy (IR).

The IR spectrum of diketo derivative Figure 1 comprises the group of bands around 2930 and 2850  $\text{cm}^{-1}$  associated with the C—H stretching vibration due to aliphatic moieties. A sharp and well resolved medium band around 1280  $\text{cm}^{-1}$  may be assigned to —Ar—O—CH<sub>2</sub>— linkage. The bands at 3030 and 1500  $\text{cm}^{-1}$  are attributed to the aromatic breathing from bisphenol-A moiety. The strong and sharp band around 1100  $\text{cm}^{-1}$  may be assigned to the secondary —OH group. The sharp bands observed at 840 and

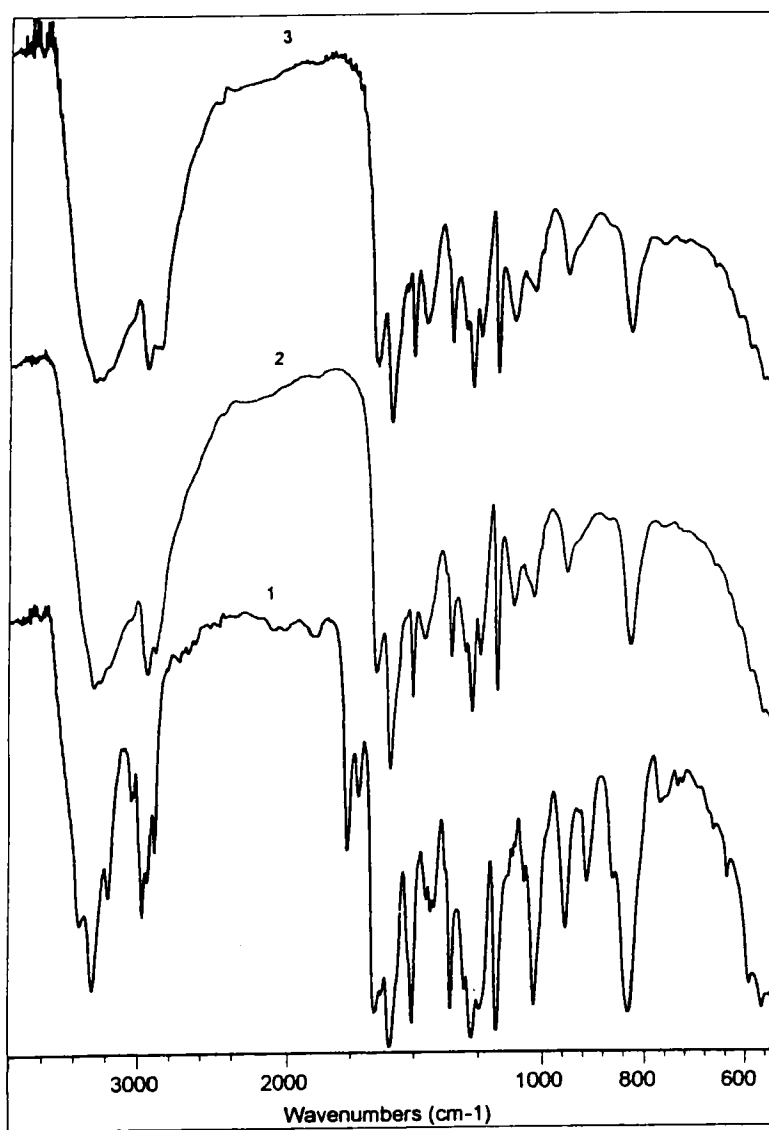


FIGURE 1 IR spectra of diketo derivative (curve: 1), Poly(schiff reagent)s of EDA and PDA (curves: 2 and 3).

$720\text{ cm}^{-1}$  may be assigned to the substituted aromatic system. The disappearance of the band at  $910\text{ cm}^{-1}$  due to epoxy ring confirmed the formation of diketo derivative. The absence of epoxy ring in the

diketo sample was further confirmed by the epoxy equivalent weight determination method. The sharp band observed at  $1730\text{ cm}^{-1}$  may be assigned to the  $\text{C}=\text{O}$  stretching vibration. The band around  $3420\text{ cm}^{-1}$  is attributed to the  $\text{N}-\text{H}$  stretching vibration due to secondary  $-\text{NH}-$  group.

The poly(schiff reagent)s were prepared by the condensation of diketo derivative with various aliphatic diamines. All the PSs 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 poly(schiff reagent) sample revealed that they are identical almost in all aspects. They comprises most of the features of diketo derivative. Other discernible frequencies of poly(schiff reagent)s are as follows. The band observed at  $3420\text{ cm}^{-1}$  is attributed to the  $\text{N}-\text{H}$  stretching vibration due to secondary  $-\text{NH}-$  group and bands at  $3480\text{ cm}^{-1}$  may arise due to  $\text{N}-\text{H}$  stretching vibration of terminal  $\text{NH}_2$  group in almost all spectra.

The number average molecular weight ( $\bar{M}_n$ ) of all the poly(schiff reagent)s (PSs) estimated by the non-aqueous conductometric titration are reported in Table I along with their  $-\text{NH}$  functionality. The  $\bar{M}_n$  of all the PSs were in the range of 3000 to 4000 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 Table II and Table 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 poly(schiff reagent)s in DSC curves were analysed to obtain the characteristic temperatures like the temperature at which the curing

TABLE I Number of average molecular weight ( $\bar{M}_n$ ) of poly(schiff reagent)s used as curing agent

Curing agent (poly(schiff reagent))	Code	$-\text{NH}$ functionality	$\bar{M}_n$
DGEBA-4-AAP:EDA	A	2.1	3290
DGEBA-4-AAP:PDA	B	2.0	3325
DGEBA-4-AAP:BDA	C	2.1	3544
DGEBA-4-AAP:HMDA	D	1.9	3780

TABLE II Curing characteristics of DGEBA by DSC using poly(schiff reagent)s as curing agent and triethyl amine as catalyst

Resin system Resin : curing agent	Proportion (%W/W)	Curing temperature (°C)			Activation energy (Ea) (Kcal/mole)	Order of reaction n
		Ti	Tp	Tf		
DGEBA : A	60 : 40	68	85	121	47	1.09
DGEBA : B	60 : 40	71	106	147	52	1.12
DGEBA : C	60 : 40	90	124	161	54	1.27
DGEBA : D	60 : 40	99	137	173	63	1.05

TABLE III Curing characteristics of TGPAP by DSC using poly(schiff reagent)s as curing agent and triethyl amine as catalyst

Resin system Resin : curing agent	Proportion (%W/W)	Curing temperature (°C)			Activation (Ea) (Kcal/mole)	Order of reaction n
		Ti	Tp	Tf		
TGPAP : A	60 : 40	53	71	95	40	1.10
TGPAP : B	60 : 40	61	88	115	45	1.14
TGPAP : C	60 : 40	77	99	137	51	1.31
TGPAP : D	60 : 40	89	115	141	57	1.20

reaction started (Ti), reached to the peak (Tp) and completed (Tf) 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 chain length of aliphatic diamines used in the poly(schiff reagent) formation. The increase in the chain length of the aliphatic diamines used in the formation of the poly(schiff reagent)s, reduces the reactivity and thus requires higher curing temperature. The longer the aliphatic chain in poly(schiff reagent), the lesser the crosslinking sites available for curing and thus the higher the activation energy. The values of activation energy in both epoxy system increase with the increase in the molecular weight of poly(schiff reagent), indicating the lower reactivity of higher molecular weight poly(schiff reagent). In both the epoxy resin systems, it is observed that trifunctional 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 lower the required curing temperature. It was also observed that the 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 poly(schiff reagent)s also affects the curing characteristics, but not significantly. The effect of slightly lowering the temperature and speeding up the curing is attributed to the higher proportion of the PSs 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.

Examination of TGA data (Tabs. IV and V) revealed that all the unreinforced crosslinked materials of both the resin systems, start their decomposition between 225–250°C depending on the nature of the poly(schiff reagent)s. The rate of weight loss is high above 400°C and is completed around 650°C. The cured samples of both resin systems loss around 50 to 60% weight when heated up to 475–525°C. Cured samples of both resin systems lost 85–97% weight

TABLE IV Thermogravimetric analysis of cured samples

System <i>Resin : curing agent</i>	Proportion (%W/W)	% weight loss from TGA at °C				
		200	300	400	500	600
DGEBA : A	60 : 40	3.0	3.6	31	44	91
DGEBA : B	60 : 40	3.3	3.9	34	50	93
DGEBA : C	60 : 40	3.7	4.7	37	53	94
DGEBA : D	60 : 40	3.9	5.8	39	59	97

TABLE V Thermogravimetric analysis of cured samples

System <i>Resin : curing agent</i>	Proportion (%W/W)	% weight loss from TGA at °C				
		200	300	400	500	600
TGPAP : A	60 : 40	2.1	3.3	22	34	83
TGPAP : B	60 : 40	2.5	3.4	25	37	88
TGPAP : C	60 : 40	2.7	3.7	29	46	89
TGPAP : D	60 : 40	3.1	4.6	35	50	91

when heated up to 650°C. Comparison of the TGA data obtained from samples of both resin systems reveals that thermal stability is significantly dependent on the nature of poly(schiff reagent) used. The decrease in the thermal stability may be due to increases in the length of the aliphatic part in the poly(schiff reagent) chain. This may be attributed to the fact that the mobility 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 TGA data obtained from both resin systems reveals that the thermal stability increased slightly but significantly in the case of trifunctional epoxy resin systems compared to difunctional resin systems, as formation of highly crosslinked network structure takes place. Finally the decomposition rate for both resin systems decreases gradually, reaching a constant weight representing the (carbonised) char. The char values observed for trifunctional resin systems are higher than that of difunctional epoxy resin systems, indicating the higher thermal stability of the trifunctional epoxy resin system. This may be accounted for by the trifunctionality of epoxy resin. It is evident from the kinetic study of the thermal degradation, that both resins achieves high thermal stability when cured with poly(schiff reagent) formed from short chain aliphatic diamines. It was also observed that trifunctional epoxy resin systems achieved higher thermal stability compared to difunctional epoxy resin systems.

The formulations used for fabricating glass cloth laminates are listed in Table VI and are coded as resin system A to D.

TABLE VI Mechanical properties of composites based on epoxy-poly(schiff reagent) system

<i>System</i>	<i>Proportion</i>	<i>Flexural strength</i>	<i>ILSS</i>	<i>Impact strength</i>
<i>Resin : curing agent</i>	<i>(%W/W)</i>	<i>(Mpa)</i>	<i>(Mpa)</i>	<i>(Mpa)</i>
DGEBA : A	60 : 40	178	20	214
TGPAP : A	60 : 40	184	23	228
DGEBA : B	60 : 40	194	24	237
TGPAP : B	60 : 40	201	26	258
DGEBA : C	60 : 40	203	26	253
TGPAP : C	60 : 40	212	27	271
DGEBA : D	60 : 40	215	28	275
TGPAP : D	60 : 40	227	29	304

Data included in Table VI show that flexural strength (FS), Interlaminar shear strength (ILSS) and Impact strength (IS) are affected by the nature of the epoxy based poly(schiff reagent)s 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 IS. The poly(schiff reagent) obtained from the system DGEBA-4-AAP:HMDA, shows better properties which may be attributed to the longer aliphatic chain of the HMDA. The flexibility caused by the longer chain length reduces the brittleness of the cured system. This is reflected in increased FS, ILSS and IS of the glass cloth reinforced laminates.

Chemical resistance studies have indicated that the epoxy-poly(schiff reagent) glass fiber composites were not affected by immersion in organic solvents (*i.e.*, ketones, alcohols, THF, DMF) and water: no change in weight or thickness was observed. It was also noted that aqueous HCL(25% V/V) did not affect the composites. However, exposure to concentrated alkali(25%W/V NaOH) resulted in weight changes. The high chemical resistance of all the composites indicates that the epoxy-poly(schiff reagent) moiety might contribute to the high level of crosslinking during composites fabrication.

Since poly(schiff reagent)s produced with the use of EDA, PDA, BDA or HMDA do not lead to brittle polymeric products, they may be suitable for advanced composites. The aliphatic character is considered as the key feature for the improved toughness and thereby mechanical properties of the composites.

#### 4. CONCLUSION

The overall advantages of PSs-epoxy resin systems are as follows:

- The poly(schiff reagent)s prepared from DGEBA can successfully be used as curing agent for epoxy resins.
- Trifunctional epoxy resin (TGPAP) required lower curing temperature than difunctional epoxy resin (DGEBA).
- DSC and TGA studies revealed that poly(schiff reagent) based on short chain aliphatic diamine is more reactive and more thermally stable curing agent than poly(schiff reagent) based on long chain aliphatic diamine.

- TGPAP shows higher thermal stability than DGEBA.
- All the poly(schiff reagent)s show excellent resistance to acid, alkali, water and organic solvents.

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