

## The Structure and Cure Mechanism of 2, 3-bis (benzimidazolyl) Pyridine with an Epoxy Resin System

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*2, 3-bis (benzimidazolyl) pyridine was synthesised and characterised by CHN analysis and techniques like infrared spectra, mass spectra and NMR studies. The structure was established using the X-ray crystallography technique.*

*The cure behaviour of 2, 3-bis (benzimidazolyl) pyridine has been investigated with bisphenol-A based epoxy resin with an anhydride hardener. The study has revealed that this ligand behaves like an accelerator by reducing the cure and gel times of the resin system. Kinetic studies based on DSC showed that the rate of curing increased with enhanced concentration of this accelerator. The electrical properties of the cured epoxy resin were unaffected with lower concentrations of 2, 3-bis (benzimidazolyl) pyridine. A mechanism for curing has been proposed based on infrared spectral studies which indicate the involvement of the secondary and tertiary nitrogen of 2, 3-bis (benzimidazolyl) pyridine which enhances the cross-linking of the resin system.*

**Key words:** *accelerator, crystal structure, epoxy resin, 2, 3-bis (benzimidazolyl) pyridine*

### 1.0 INTRODUCTION

Epoxy resins are currently among the most intensively investigated compounds as electrical insulators owing to their remarkable chemical resistance, good adhesion, extraordinary toughness, high mechanical strength and good heat resistance. When properly cured, they yield tough materials, which find application in industrial flooring, foam and electrical insulation. The applications of epoxy resins depend on the nature of curing. Generally, curing takes place in the presence of a hardener or a curing agent. Anhydrides are used as curing agents for epoxy resins, and the latter are used in casting and lamination. Bases such as tertiary amines are commonly used to accelerate the curing process. Chemical reactions that take

place during the period of curing determine the properties of the cured thermoset. Organometallic compounds are known to act as curing agents for various epoxy resin systems [1-3]. Several acetyl acetonates act as latent accelerators for anhydride cure of bisphenol-A based resins [4-8].

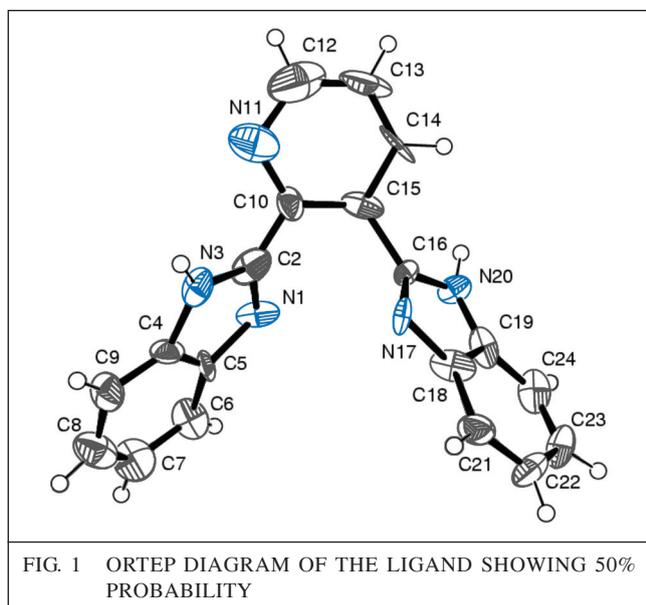
In the present work, an attempt has been made to use 2, 3-bis (benzimidazolyl) pyridine as accelerator for curing epoxy-anhydride system. 2, 3-bis (benzimidazolyl) pyridine was synthesised and its crystal structure has been established by X-ray crystallography. The cure and kinetic aspects of the resin and the anhydride in the presence of these compounds have been studied. Gel time and storage life studies have also been carried out. Electrical properties such as loss factor of the resin-anhydride system

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have been investigated. A cure mechanism has been suggested for the epoxy resin with carboxylic anhydride in the presence of 2, 3-bis (benzimidazolyl) pyridine suggesting the involvement of tertiary and secondary nitrogen atoms.



## 2.0 EXPERIMENT

**Materials used:** Bisphenol-A based epoxy resin, Lapox C-17 with an epoxy content of 5.2–5.5 eq/kg, K-12 hardener (anhydride content of about 94%) and commercial accelerator K-112 were procured from Cibatul, India and were used as such. Silica flour (w-12 grade) of 300 mesh was also procured from Cibatul India and it was dried at 110°C for 3 hours and then used as filler. 2, 3-bis (benzimidazolyl) pyridine was synthesised using 2, 3-pyridine decarboxylic acid (Merck) and Orthophenylene diamine (Merck).

**Physical measurements:** Elemental analysis was performed with a Thermo Finnigan Flash 1112 CHN analyser. ESMS was recorded on a Micromass Q-ToF micro instrument (electrospray ionisation, ES1). <sup>1</sup>H, NMR measurement was carried out with a Bruker AMX400 spectrometer in CDCl<sub>3</sub> as the solvent at 400 MHz with tetramethylsilane as external reference. The structure of the ligand has been determined by single crystal X-ray crystallography (BRUKER SMARX CCD) and (EDax by JEOL, JFC-1100E ion sputtering device). The gel time

characteristics of the resin system were determined using Gel norm Gel timer (Switzerland). Differential scanning calorimeter with data station (Perkin Elmer DSC-2C) was used for cure kinetic studies. The viscosity measurements were made using Brookfield viscometer (Model-RVT). The capacitance and loss factor values were determined as per ASTM D 150 specifications. The cure process was followed using FTIR spectra. The spectra of the samples as KBr pellets were recorded using FTIR-Spectrometer 2000 (Perkin Elmer).

In order to measure the gel time characteristics of the resin system, about 5 to 10 g of the resin mix was taken in a tube provided with a spiral wire for agitation. This was introduced into a bath maintained at a particular temperature. The mixture was allowed to attain thermal equilibrium and then the spiral wire was mechanically moved up and down. The viscosity of the resin system gradually increased and a rubbery mass was formed. At this stage the movement of the wire gets arrested. The time taken for the entire process was noted as gel time. The viscosity measurements were made for the resin system in presence of 0.5 phr (parts per hundred) of benzimidazole and the number of days taken for a tenfold increase in viscosity was recorded and tabulated as the storage life.

Dynamic DSC scans of the epoxy systems were carried out in the temperature range 40–400°C at varying heating rates of 5–40°C/min. The temperature corresponding to the T<sub>m</sub> of the curing exotherm was determined at various concentrations of the benzimidazole. The electrical and thermal measurements were carried out as per IS: 1998 specifications. To find the possible cure mechanism of the epoxy resin system with 2, 3-bis (2-benzimidazolyl) pyridine, equal quantities of the resin and the hardener were accurately weighed and treated with a known quantity of 2, 3-bis (benzimidazolyl) pyridine. The mixture was stirred and the sample film was cured in the KBr pellet at 100°C and infrared spectra were recorded periodically once every 15 minutes for 6 hours.

## 2.1 Preparation of 2, 3-bis (benzimidazolyl) pyridine (2, 3-b bZ py)

2, 3-pyridine dicarboxylic acid (0.05 m mole) was added to a mixture of o-phenylene diamine (0.1 m mole) in syrupy phosphoric acid (50 ml) and stirred for 4 hours in a sand bath at 240°C. The greenish blue melt that was obtained was poured into cold water and subsequently neutralised with 10% sodium carbonate solution. A pink-coloured solid was separated and it was recrystallised from ethanol and the resultant white needles were checked for their melting point (70-80% yield).

## 2.2 Structure by X-ray crystallography

A suitable single crystal was mounted on a glass fibre and the three dimensional intensity data was collected using BRUKER SMART APEX CCD equipped with a sealed X-ray tube. The compound crystallises in the orthorhombic space group P21cn with 4 molecules in the unit cell. The structure was solved using SHELXS-97 program by DIRECT methods and the subsequent difference Fourier methods. The non-H atoms were refined anisotropically while the H atoms were allowed to ride with the respective non-H atoms. The final R factor converged to 0.077. The relevant crystallographic details are given in Table 1.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Structure of 2, 3-bis (benzimidazolyl) pyridine

The molecule has got a buckled conformation which is substantiated by the torsion angle C2-C10-C15-C16-21.0(4). The benzimidazole rings are twisted by N11-C10-C2-N1 133.3(4), C14-C15-C16-N17 127.2(4) to avoid the steric repulsion between them with respect to the pyridine ring. In the unit cell, the molecules are stabilised by N-H...N type of intra-molecular dimeric hydrogen bonds. The molecular packing down the B axis shows a channel with dimensions 3.83Å x 7.09Å. This runs to infinity down the B axis. The two benzimidazole rings are subtending at an angle of 66.39(6). See Figs. 1, 2 and 3.

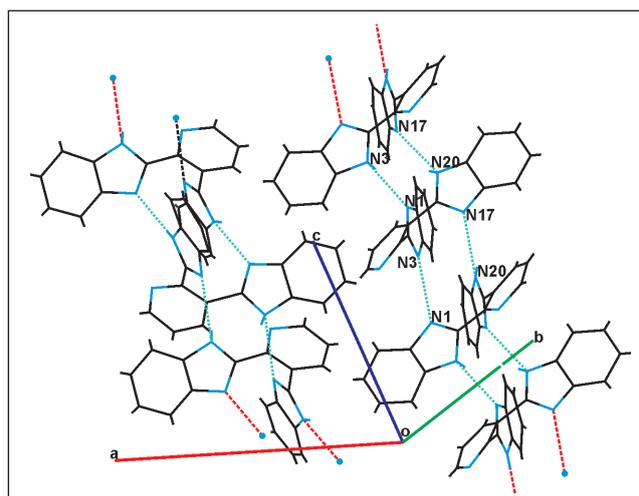


FIG. 2 PACKING DIAGRAM SHOWING THE N-H...N DIMER FORMATION

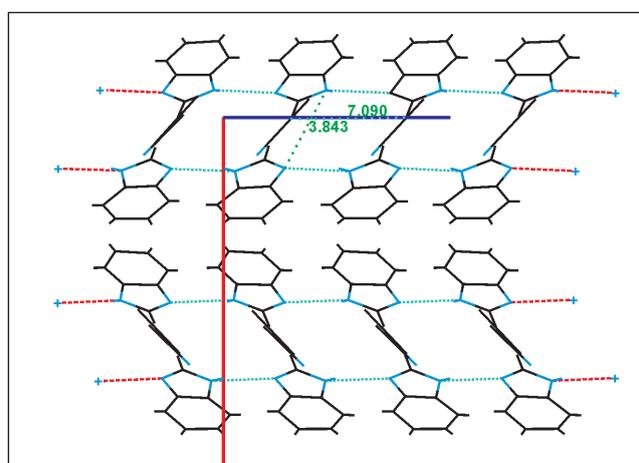


FIG. 3 PACKING DOWN B AXIS SHOWING THE CHANNEL

1. Elemental analysis calculated: C 73.28,  
Found: C 73.28; H 4.3147 H 4.211  
N 22.2817 N 22.504
2. Infrared spectral studies

The band assignments are made in the case of benzimidazole [16–17] and related heterocycles [18]. A band at 3044  $\text{cm}^{-1}$  may be due to  $\nu\text{N-H}$ , 1613  $\text{cm}^{-1}$  due to  $\nu\text{C=N}$  and 1600  $\text{cm}^{-1}$  due to  $\nu\text{C=C}$ . A band at 1585  $\text{cm}^{-1}$  is assigned to  $\nu\text{C=C}$  skeletal in plane vibrations, and 1529  $\text{cm}^{-1}$  to  $\nu\text{N-H}$ . Bands at 1277  $\text{cm}^{-1}$ , 1006  $\text{cm}^{-1}$  and 613  $\text{cm}^{-1}$  may arise due to benzimidazole ring vibrations. A band at 1223  $\text{cm}^{-1}$  may be due to in plane CH deformation and ring breathing mode. The band around 760  $\text{cm}^{-1}$  and 741  $\text{cm}^{-1}$  are

assigned to N-H out of plane deformation and CH out of plane deformation of benzimidazole and CH out of plane deformation of pyridine ring.

### 3. NMR studies

The  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3 + \text{DMSO-}$  and 6, and drop exhibited resonances is shown in Fig. 5 For the protons of pyridine and benzimidazole rings, the resonances are observed in the chemical shift range (7.3 – 7.781).

Py ring

Benzimidazole ring

H-4	H-5	H-6	H-4'	H-5'	H-6'	H-7'
8.5			7.772	7.382	7.382	7.772

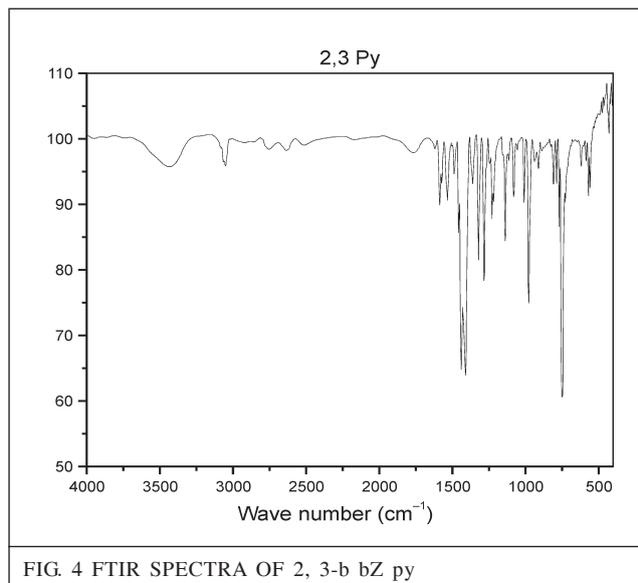


FIG. 4 FTIR SPECTRA OF 2, 3-b bZ py

The IR spectra of 2, 3-bis (benzimidazolyl) pyridine is given in Fig. 4.

The prominent absorption peaks were observed at:

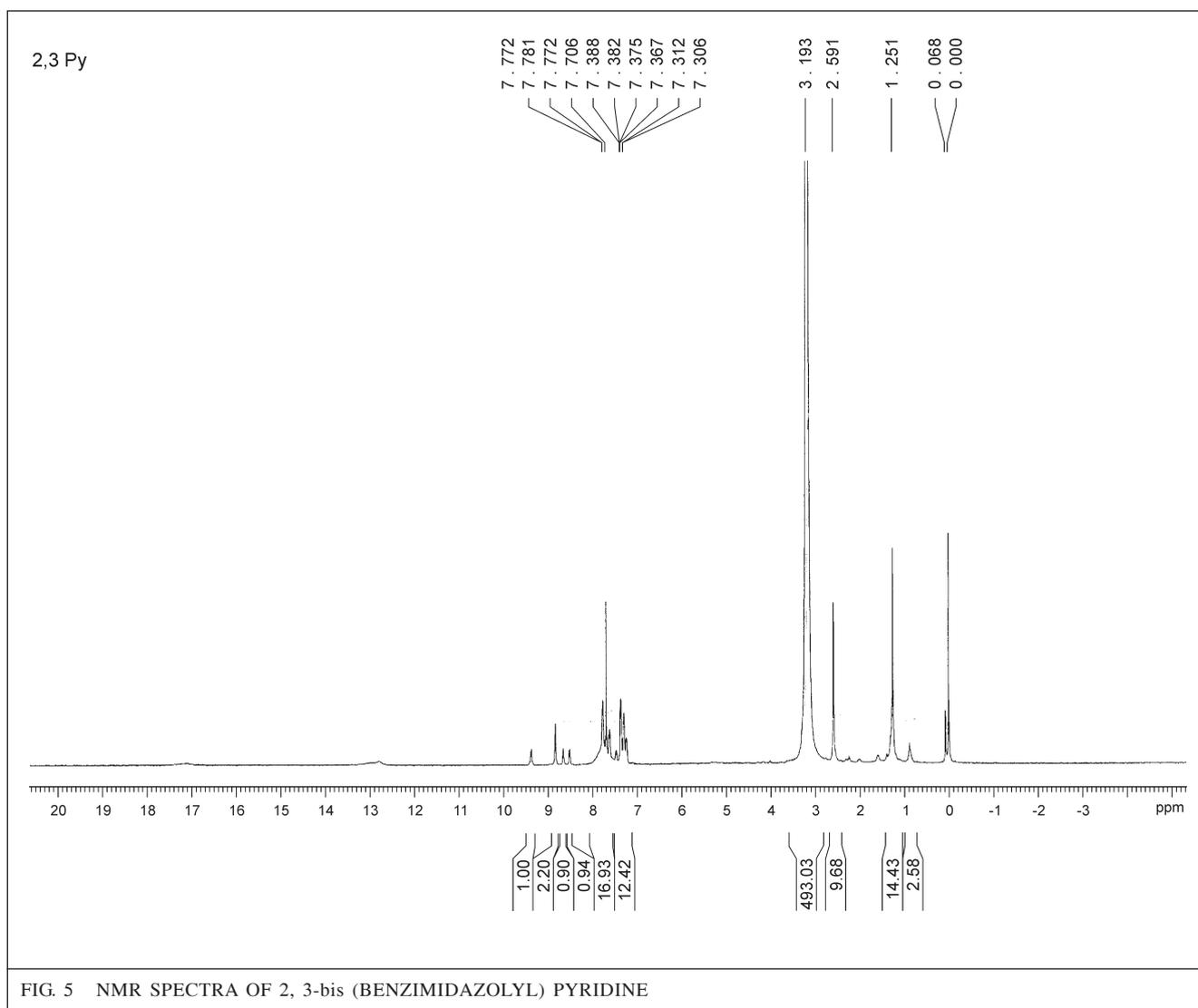
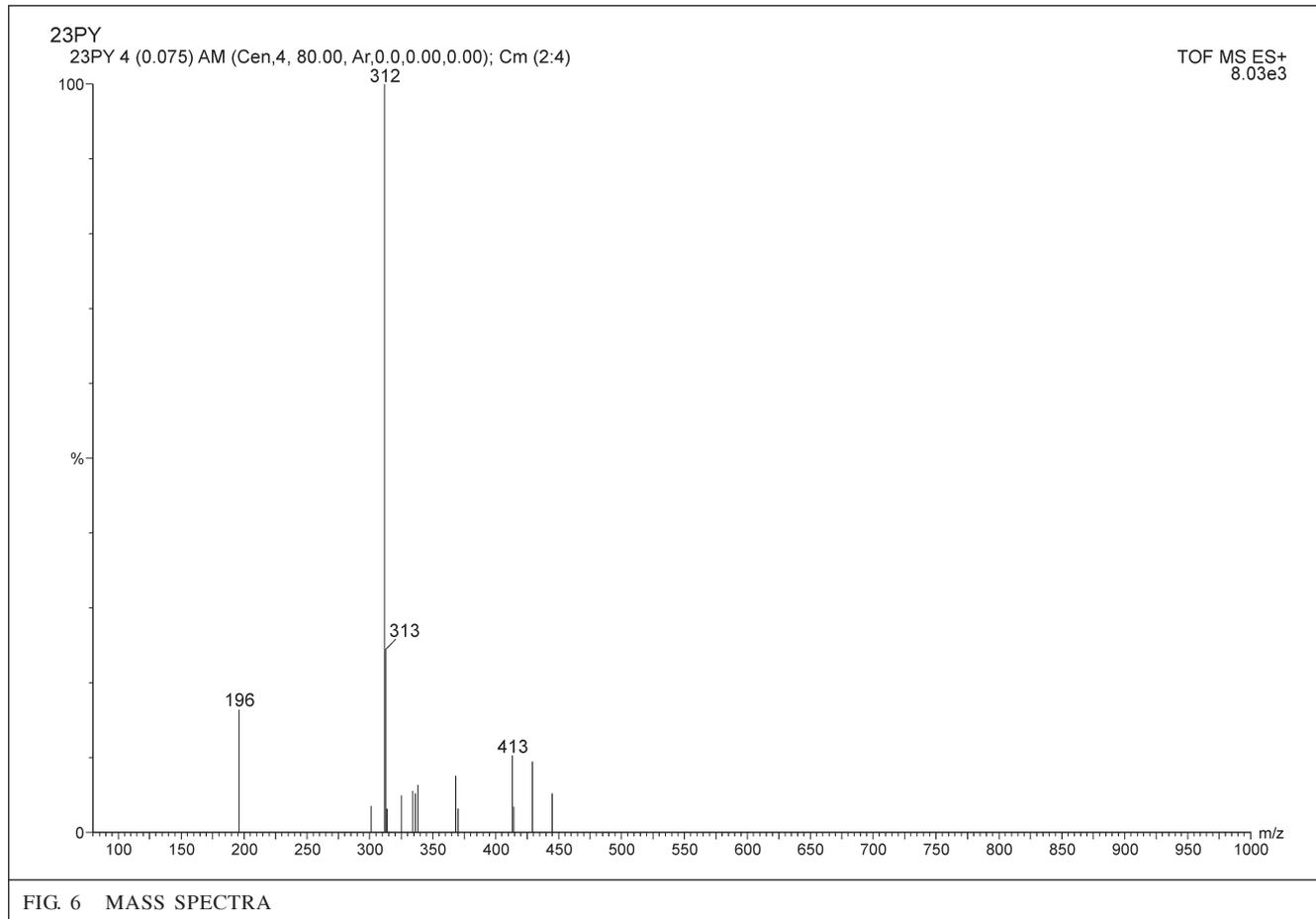


FIG. 5 NMR SPECTRA OF 2, 3-bis (BENZIMIDAZOLYL) PYRIDINE



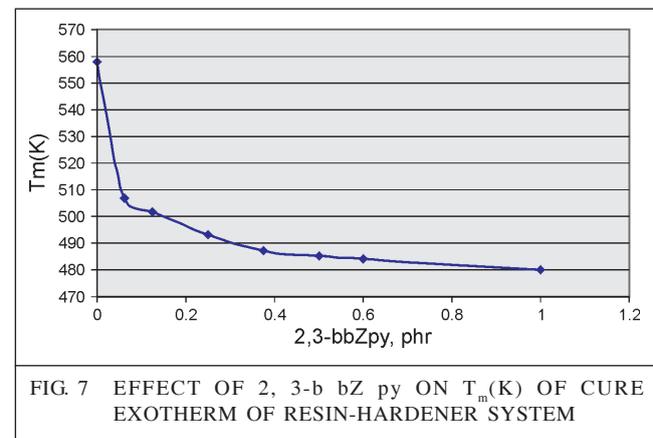
### 3.2 Resin-hardener stoichiometry

The resin-hardener stoichiometry was determined using dynamic DSC runs by plotting enthalpy change  $\Delta H$  against the amount of hardener used and the stoichiometry was found to be 1:1[6]. For commercial applications, the epoxy system is generally associated with a suitable filler. In the present study, silica flour was added as filler in such a way that the control system had the formulation of resin, hardener and filler in the ratio of 1:1:3.

### 3.3 Effect of 2, 3-bis (benzimidazolyl) pyridine on Resin-Hardener System

The observed temperature minimum ( $T_m$ ) value of the cure exotherm was plotted against concentration of the 2, 3-bis (benzimidazolyl) pyridine. Such a plot is shown in Fig. 7. The rate of decrease in the  $T_m$  value was appreciable upto 0.5 phr of 2, 3-bis (benzimidazolyl) pyridine and thereafter it remains almost

constant. In view of this, further evaluation was carried out upto 0.5 phr of the benzimidazole.



### 3.4 Gel time and storage life

The effect of 2, 3-bis (benzimidazolyl) pyridine on the gel time and storage life of the epoxy resin system at different temperatures was monitored. The values obtained are listed in Table 1. The results indicate that the gel times for the resin system in the presence of 2, 3-bis (benzimidazolyl) pyridine are lower when

compared to the control system and the values decrease with increase in temperature. The values are better than a commercial accelerator.

2,3-b bZ py, phr	Gel time (minutes)					Storage life (days)
	373K	393K	413K	433K	453K	
0.0000	110	690	257	114	43	46
0.0625	186	101	31	22	12	27
0.1250	148	71	25	17	09	22
0.2500	120	52	23	12	08	20
0.3750	92	41	19	09	06	18
0.5000	80	29	17	08	06	15
K-112 commercial accelerator (0.375 phr)	101	47	13	12	18	18

It is observed that with increase in concentration of 2, 3-bis (benzimidazolyl) pyridine, the gel time values of the epoxy resin system decreases. Also the values decrease with increase in temperature at a given concentration of the ligand. The storage life also decreases with increase in concentration of the accelerator. The values are comparable to that of a commercial accelerator.

### 3.5 Kinetic studies and cure schedules

By considering the degradation process as a simple chemical reaction, Toop [12] has derived an expression to evaluate the thermal life of wire enamels. Also, several reports are available based on thermal analytical techniques. This concept has been used for the purpose of finding out the cure schedules [13] using the cure kinetics, which is based on the data obtained from DSC.

Dynamic DSC scans of the epoxy systems were carried out in the temperature range of 40-400° C at varying heating rates of 5 to 40° C/min. The temperatures corresponding to the peak minimum ( $T_m$ ) of the curing exotherm were determined at various phr of the 2, 3-bis (benzimidazolyl) pyridine. The energy of activation ( $E_a$ ) for the curing reaction was calculated by plotting log (heating rate) versus

( $1/T_m$ ). Using these values, the pre-exponential factor ( $Z$ ) and also the rate constant ( $k$ ) were evaluated [10–11]. The  $E_a$  value for the curing of epoxy system in the presence of various 2, 3-bis (benzimidazolyl) pyridine has been found to be in the range of 12 – 19 kcal/mol (Table 2). Generally the rate constant was found to increase with enhanced concentrations. It has been observed that with enhanced concentrations of the accelerator, the rate constant was found to increase from  $21 \times 10^{-3}$  min at 140°C to  $46 \times 10^{-3}$  min at the same temperature. The activation energy was found to decrease from 19.2 kCal/mol at zero concentration to a value of 12.17 kCal/mole at 0.5 phr of the accelerator. The exponential factor increased with increase in concentration of 2, 3-bis (benzimidazolyl) pyridine. Table 2 also indicates the cure time of the epoxy resin system in the presence of the accelerator. The data indicates a large decrease in cure time values at the concentrations studied. The values are 41 minutes at 0.0625 phr of the ligand whereas the cure time is about 290 minutes in the absence of the accelerator and also comparable to a commercial accelerator. This suggests the ligand acts as a good curing agent.

2,3-b bZ py, phr	$E_a$ , kCal/mol	$k \times 10^{-3}$ min, 140°C	$Z \times 10^6$ (range)	Cure time, min, 140°C
0.0000	19.24	21	27 - 30	293
0.0625	19.18	38	18 - 25	41
0.1250	18.6	40	7 - 15	34
0.2500	17.38	42	5 - 8	28
0.3750	13.34	46	4 - 6	21
0.5000	12.17	49	8 - 5	16
K112 commercial accelerator (0.375 phr)	16.1	45.2	1.3	15

The SEM analysis was carried out on the resin samples both in the cured and uncured forms. The EDAX mode was employed to analyse the filler dispersion in the resin matrix carried out on to the surfaces of samples.

The picture shows that the polymer matrix has a uniform phase in which all the additives are dispersed indicating a different phase than that of the polymer matrix.

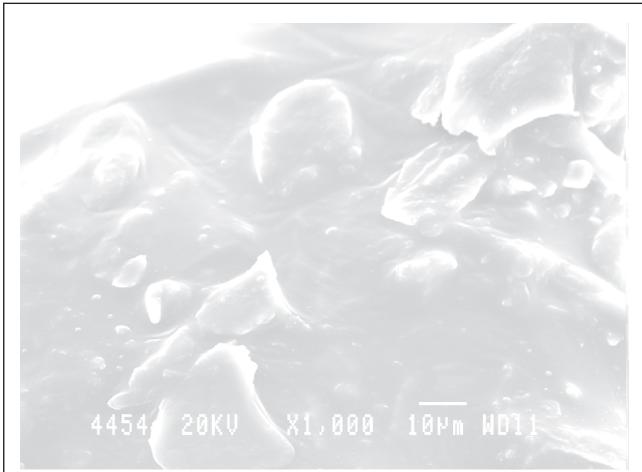


FIG. 8A BLANK SYSTEM

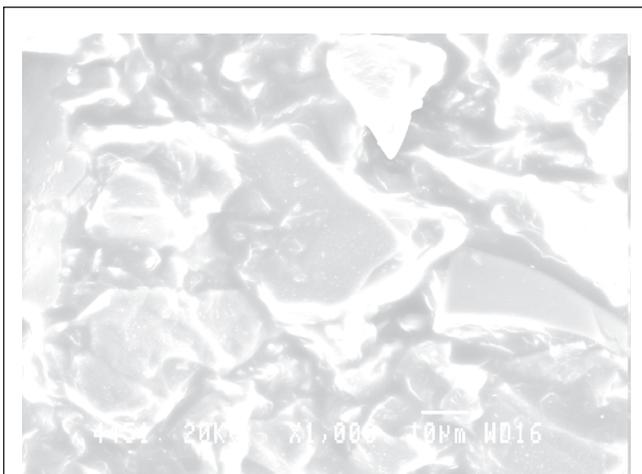


FIG. 8B 0.25 PHR POST CURED SAMPLE 2



FIG. 8C 0.25 PHR UNCURED SAMPLE 2

### 3.6 Electrical properties

For applications in high voltage insulation involving generators, transformers and AC motors, the highest voltages used usually dictate the limitations. Hence, the present epoxy samples were subjected to variations of voltage. The capacitance and the loss factor of the cured epoxy resin system at different concentrations of the ligands and their complexes have been studied both at room temperature as well as at higher temperatures. At room temperature, there is no difference in terms of the loss factor of the cured system. The loss factor data obtained for the epoxy system with variation in temperature is shown in Fig. 9. The graph indicates that the trend in loss factor values is almost the same with different concentrations of the ligand and at 0.25 phr, the loss factor values are lower than the blank system and at 0.375 phr the loss factor values are almost equivalent to the blank system. The tandelta tip up for the ligand under study is indicating lower temperature than the blank system. This suggests that at the concentrations of the ligand studied, one of the important electrical properties is not deteriorated for the epoxy system.

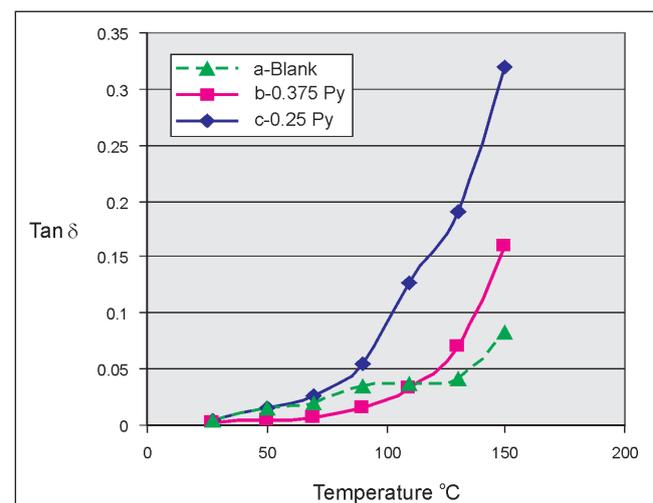
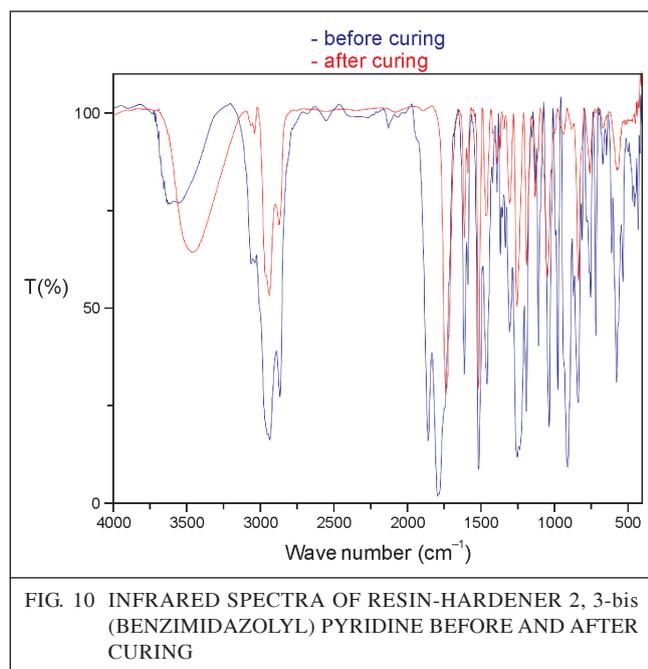


FIG. 9 TAN  $\delta$  VS TEMPERATURE FOR THE EPOXY SYSTEM A) BLANK B) 2, 3-b bZ py (0.375 phr) AND C) 2, 3-b bZ py (0.25 phr)

### 3.7 Cure mechanism

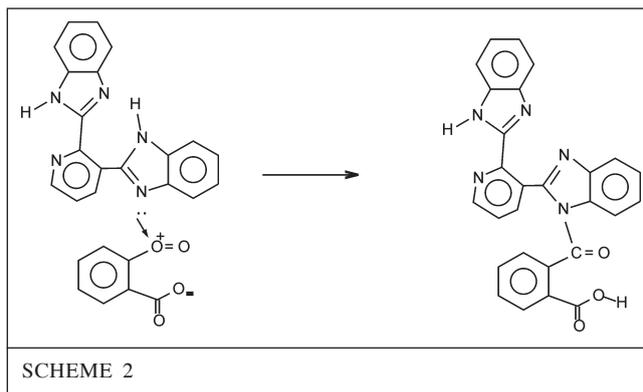
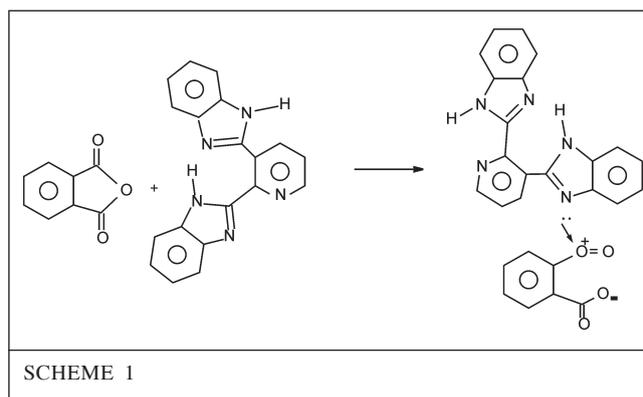


In epoxy chemistry, usually cyclic anhydrides are used as hardeners. These groups do not react directly with epoxy groups. In order for the polymerisation reaction to happen, the anhydride ring must be opened. This can be done by any Lewis base [14]. The resulting carboxyl ion, in turn opens the epoxy ring. This further opens the second anhydride ring and the polymerisation proceeds.

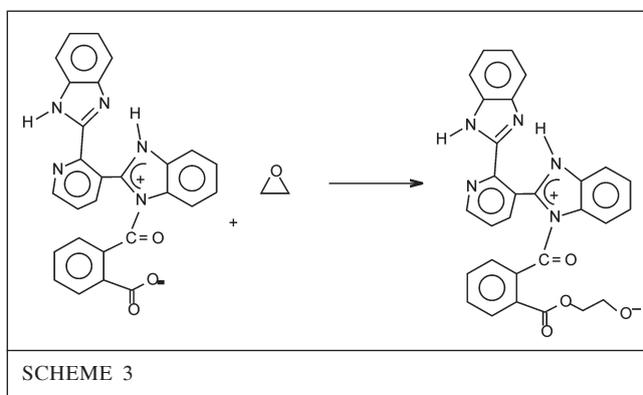
IR spectral studies of the curing of resin-hardener system with 2, 3-bis (benzimidazolyl) pyridine gives substantial evidence for this theory.

The peaks at  $1853\text{ cm}^{-1}$  and  $1786\text{ cm}^{-1}$  due to anhydride are affected as the reaction proceeds. The former decreases in intensity whereas the latter is shifted to  $1729\text{ cm}^{-1}$  without appreciable change in its intensity. This is indicative of the two carbonyl groups reacting in different ways.

The tertiary nitrogen would open up the anhydride ring through Coulombic interaction with one of the carbonyl groups (Scheme 1). Subsequently, the carbonyl group may interact covalently with the imine hydrogen of 1, 3-bis (2-benzimidazolyl) benzene resulting in a covalent O-H bond as shown in Scheme 2.



Alternatively, in the presence of epoxide, the carbonyl group would open up the epoxy ring, facilitating the curing of the resin-hardener system. The reaction is depicted in Scheme 3.



These are indicated in the IR curves as follows:

The symmetrical stretching or ring breathing frequency of the epoxy ring which occurs at  $1244\text{ cm}^{-1}$  originally [15] decreased indicating the opening of the epoxy ring. The asymmetrical ring stretching of the epoxy ring at  $905\text{ cm}^{-1}$  virtually disappears on curing. The C-H stretching vibrations of the epoxy rings which occurred at  $2943\text{ cm}^{-1}$  gradually disappears. Formation of O-H bond is evident by the

3595  $\text{cm}^{-1}$  band moving to a lower frequency 3469  $\text{cm}^{-1}$  with increased intensity of a band at widening. Appearance of a band at 1124  $\text{cm}^{-1}$  shows the formation of asymmetrical C-O-C stretching of ether group.

A peak at 1504  $\text{cm}^{-1}$  due to C=C stretching and CH bending of the benzimidazole has shifted and merged with 1452  $\text{cm}^{-1}$  band of the hardener. Both the hardener and 2, 3-bis (benzimidazolyl) pyridine exhibit a peak at 968  $\text{cm}^{-1}$  and this band is attributed to the ring breathing vibration. Another band at 827  $\text{cm}^{-1}$  of 2, 3-bis (4-benzimidazolyl) pyridine ring vibration merges with a peak at 858  $\text{cm}^{-1}$  of the hardener. The 728  $\text{cm}^{-1}$  band due to the out of plane CH deformation vibration of benzimidazole and benzene ring has shifted to 708  $\text{cm}^{-1}$ . It was observed that the intensities of these bands decreased as the curing of the resin hardener system progressed. This suggests an increase in the extent of cross-linking.

#### 4.0 CONCLUSIONS

The addition of accelerators such as benzimidazole derivatives and their complexes to the resin system decreases the cure time. The addition of 2, 3-bis (benzimidazolyl) pyridine enhances the curing activity of bisphenol-A based resin and its activity is comparable to that of the commercial accelerator. The kinetic data indicates that the rate of curing is enhanced in the presence of the 2, 3-bis (benzimidazolyl) pyridine. The storage life of the catalysed system is also affected to certain extent in the presence of the accelerator but is comparable to a commercial accelerator.

In the epoxy-anhydride system, 2, 3-bis (benzimidazolyl) pyridine enhances the rate of curing. The anhydride hardener reacts with the tertiary nitrogen of 2, 3-bis (benzimidazolyl) pyridine and disrupts the anhydride ring.

Further, the opening up of the epoxy ring leads to gelation and polymerisation with enhanced cross-linking.

The addition of 2, 3-bis (benzimidazolyl) pyridine to the resin system does not affect the important electrical properties of the cured resin system.

#### 5.0 ACKNOWLEDGEMENT

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