



# ***SYNTHESIS AND CHARACTERIZATION OF NOVEL HEAT RESISTANT EPOXY RESIN BASED ON N, N'-BIS (4-HYDROXY-6-METHYL-2- PYRIMIDYL) PYROMELLITIC DIIMIDE***

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## **ABSTRACT**

Processable heat resistant polymers are a recent development in the search for thermostable polymers in which a compromise is required between processability and thermal resistance. Several approaches have been tried to improve the processability without much loss of thermal stability. Two novel BTDA and PMDA based epoxy resins containing imide and pyrimidyl groups will be synthesized through a three step procedure, which is cured with 4,4'-diaminodiphenyl-methane(DDM) and characterized using FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C- NMR. The solubility of these polyimides were tested in several solvents and found that they have good solubility in polar aprotic solvents such as NMP, DMF, DMAc, etc. The curing behavior was investigated with differential scanning calorimetry (DSC) using 4, 4'-diaminodiphenyl-methane(DDM) as curing agent. The physical properties of the cured polymers were evaluated with and thermogravimetric analysis (TGA). The results show that the cured polymers exhibit higher glass transition temperature (T<sub>g</sub>244-250°C) and better thermal stability compared with those commercial available polyimides.

**Keywordst; Thermal properties, TGA and DSC**

## **1. INTRODUCTION**

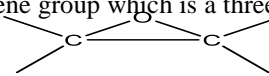
In the last twenty years there has been a flurry of activity in the synthesis of new polymer systems. This interest has developed largely as a result of the increased need for advanced materials. It is evident that material advances have been the key to significant technology break through throughout history. In less than twenty years, advanced composites have become established as efficient high- performance structural materials and their use is expanding rapidly. In the recent years high value specialty polymers, such as those used in some engineering and aerospace engineering are being used in more demanding applications that require even higher specifications[1,2]. High performance polymers such as polyimides have become an increasingly important class of materials in the field of aerospace and microelectronics industry.

## **EPOXY RESINS**

Epoxy resins are generally recognized as work house products among the category of thermosetting polymers due to their outstanding mechanical properties and good handling characteristics. The use of epoxy resins in industry extends back over fifty years since their introduction commercially and they find an extremely wide range of applications as coatings, adhesives and matrix resins in different fields like electronics, aerospace industry etc. Though epoxy resins were first synthesized in 1891, commercial epoxy resins were marketed only in 1940. The earliest epoxy resins marketed were the reaction products of bisphenol-A and epichlorohydrin and this is still the major route for the manufacture of most of the epoxy resins marketed today[3]. The main advantages of epoxy resins are their good mechanical properties, minimum shrinkage after cure and suitable weather, chemical and electrical resistance. The term epoxy resin is applied to both the prepolymer and to the cured resins.



Epoxy resin in the unreacted form contains an epoxide, oxirane or ethoxylene group which is a three membered ring consisting of an oxygen atom attached to two connected carbon atoms i.e.,



The epoxide function is usually a 1,2-epoxide that appears in the form,  $\text{H}_2\text{C}-\text{CH}-\text{CH}_2$ , called the glycidyl group, which is attached to the remainder of the molecule by an oxygen, nitrogen or carboxyl linkage and are termed as glycidylether, glycidylamine or glycidylester respectively[4,5].

### Synthesis of different types of epoxy resins

Two basic processes are used in the manufacture of epoxy resins: (i) the reaction of epichlorohydrin with compounds containing reactive hydrogen atoms, such as phenols or amines, and (ii) the peroxide oxidation of olefins[6,7,8].

#### Epoxidation using epichlorohydrin

Diglycidyl ether of bisphenol-A (DGEBA) and its higher homologues synthesized by reacting bisphenol-A with epichlorohydrin in presence of aqueous caustic soda (Scheme 1.1.) constitute of major portion of commercially used epoxy resins. The reaction is always carried out with an excess of epichlorohydrin so that the resulting resin has terminal epoxy groups. By varying the manufacturing conditions and amount of epichlorohydrin, resins of low, intermediate or high molecular weight can be produced. As the value of 'n' in DGEBA increases, the resin progresses from a viscous liquid to a solid having high softening point. Besides DGEBA resins novolac epoxy resins are widely used in industry. These resins are polyglycidyl ethers of novolac resins and vary from the standard bisphenol-A-based resin in their multifunctionality[9,10]. Novolac epoxy resins are prepared by reacting novolac resins with epichlorohydrin

## 2 EXPERIMENTAL SECTION

### 2.1 Materials and methods

Acetone, Methanol and anhydrous potassium carbonate were purchased from Sisco Research Laboratories Pvt Ltd. Hydrochloric acid (HCl, spectrochem, india), Epichlorohydrin (SRL, India), 2-amino-4-hydroxy-6-methyl-pyrimidine (SRL, India), Maleic anhydride (E-Merck, India), triethylamine (Spectrochem, india), N-methyl-2-pyrrolidone (Alrich, wiscons, USA), purified by refluxing with calcium hydroxide distilled under reduced pressure and stored over molecular sieves 4A°, diethyl amine (Spectrochem, mumbai, india), P-toluene-sulphonic acid monohydrate (Ferak, USA), Acetic anhydride (Fischer, india), sodium acetate (Nacalai, extra pure reagent), 2,6-dimethyl phenol, p-phenylenediamine (SRL, India), 1-chloro-4-nitrobenzene and anhydrous calcium chloride were purchased from (Qualigen chemicals, India). 4,4'-diamino diphenyl methane (DDM), 4,4',3,3'-benzophenonetetracarboxylic dianhydride and pyromellitic dianhydride were purchased from (Lancaster, USA).

### 2.2 MONOMER SYNTHESIS

#### SYNTHESIS OF PMDA BASED EPOXIDE TERMINATED DIIMIDES

##### 2.1 Synthesis of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl) pyromellitic acid(1)

4g (0.0183mol) of 2-amino-4-hydroxy-6-methyl-pyrimidine and 42 ml of acetone were put into a 250 ml four necked round-bottomed flask equipped with a stirrer, a reflux condenser, a dropping funnel and nitrogen inlet. The mixture was heated to 40°C in a water bath to let the 2-amino-4-hydroxy-6-methyl-pyrimidine dissolve well in acetone. Then, the solution of pyromellitic acid dianhydride dissolved in 27 ml of acetone was added dropwise at 40°C for another 5 h. After the reaction was completed, the resultant mixture was filtered and then washed with acetone three times. A lustrous white powder (indicated as **1** in Scheme 1) was obtained. Yield: 80 %, (m.pt: 195°C).

##### 2.2 Synthesis of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitimide(2)



5 g of **1**, 22 ml of of N,N'-dimethylformamide and 7.5 ml of toluene were added to a 100 ml four necked round-bottomed flask equipped with a heating oil bath, a magnetic stirrer, Dean-stark condenser and nitrogen inlet. After completely dissolved, 0.05 g of p-toluene sulphonic acid (pTSA) was added, then the mixture was heated to 130°C and refluxed for 8 h. The generated water was removed from the mixture by azeotropic distillation. After the reaction was completed, the mixture was concentrated to remove some of the solvent and then poured into distilled water at 0°C and stirred for 0.5 h. The mixture was filtered and washed with water three times, the solid product was then placed in the vacuum oven to remove the traces of solvent and water. A brown colored solid product (indicated as **2**) was obtained. The sequence of the reactions is shown in Scheme 1. Yield: 65 % (m.pt:263°C).

### 2.3 Synthesis of Glycidyl ether of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitimide (epoxide terminated diimides) (**3**)

1 g of **2** and 8 ml of epichlorohydrin were put into a 100 ml four necked round-bottomed flask equipped with a magnetic stirrer, a syringe pump and a modified reflux condenser. Benzyltrimethylammonium chloride of 0.02 g was added as phase transfer catalyst and 5 ml of DMF was added into it. The reaction mixture was heated to 100°C in an oil bath and then 4g of 30 wt % aqueous NaOH was added gradually over a period of 1 h by syringe pump and further reacted at the reflux temperature for 4 h. After cooling down, the reaction solution was filtered to remove the salt and the organic phase was washed with water three times. The solution was concentrated and poured into ethyl ether with stirring, then filtered to collect the solid product. The crude product was washed with ethyl ether and dried in a vacuum oven. A yellow-colored solid product (indicated as **3**) was obtained. Yield: 73% (m.pt:290°C), (EEW=262.0g/equiv). The chemical reaction is outlined in Scheme 1.

### 2.4 SYNTHESIS OF BTDA BASED EPOXIDE TERMINATED DIIMIDES

#### Synthesis of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl) benzophenone tetra carboxylic acid dianhydride [**1**]

4g (0.0124mol) of 2-amino-4-hydroxy-6-methyl-pyrimidine and 42 ml of acetone were taken in a 250 ml four necked round-bottomed flask equipped with a heating water bath, a stirrer, a reflux condenser, a dropping funnel and nitrogen inlet. The mixture was heated to 40°C to let the 2-amino-4-hydroxy-6-methyl-pyrimidine dissolve well in the acetone. Then, the solution of benzophenone tetra carboxylic acid dianhydride dissolved in 27 ml of acetone was added dropwise at 40°C for another 5 h. After the reaction was completed, the resultant mixture was filtered and then washed with acetone three times. A lustrous white powder (indicated as **1** in Scheme 1) was obtained. Yield: 82 %, (m.pt:240°C).

#### 2.5 Synthesis of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl) benzophenone tetra carboxylic acid diimide [**2**]

5 g of **1**, 22 ml of of N,N'-dimethylformamide, 7.5 ml of toluene were added to a 100 ml four necked round-bottomed flask equipped with a magnetic stirrer, Dean-stark condenser and nitrogen inlet. After completely dissolved, 0.05 g of p-toluene sulphonic acid (pTSA) was added, then the mixture was heated to 130°C in an oil bath, and refluxed for 8 h. The generated water was removed from the mixture by azeotropic distillation. After the reaction was completed, the mixture was concentrated to remove some of the solvent and then poured into distilled water at 0°C and stirred for 0.5 h. The mixture was filtered and washed with water three times, the solid product was then placed in the vacuum oven to remove the traces of solvent and water. A brown colored solid product (indicated as **2**) was obtained. The reaction equation is shown in Scheme 1. Yield: 70 % (m.pt:250°C).

#### 2.6 Synthesis of Glycidyl ether of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)benzophenone tetra carboxylic acid diimide (epoxide terminated diimides) [**3**]

1 g of **2** and 8 ml of epichlorohydrin were put into a 100 ml four necked round-bottomed flask equipped with a heating oil bath, a magnetic stirrer, a syringe pump and a modified reflux condenser. Benzyltrimethylammonium chloride of 0.02 g was added as phase transfer catalyst and 5 ml of DMF was added into

it. The reaction mixture was heated to 100°C and then 4ml of 30 wt % aqueous NaOH was added gradually over a period of 1 h by syringe pump and further reacted at the reflux temperature for 4 h. After cooling down, the reaction solution was filtered to remove the salt, and the organic phase was washed with water three times. The solution was concentrated and poured into ethyl ether with stirring, then filtered to collect the solid product. The crude product was washed with ethyl ether and dried in a vacuum oven. A yellow-colored solid product (indicated as **3**) was obtained. Yield:75% (m.pt:265°C), (EEW=324.0g/equiv).The chemical reaction is outlined in **Scheme 1**.

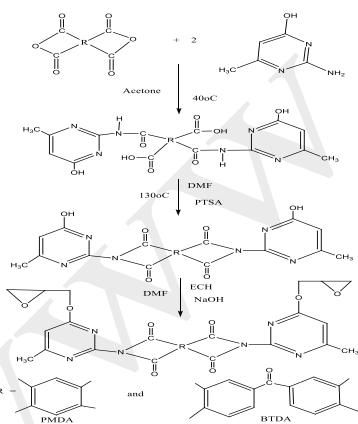
### 3. CURING PROCEDURE

The epoxy resin and the curing agent DDM were mixed in a 1:1 equivalent ratio and dissolved in the mixture of N,N'-dimethylformamide and acetone at room temperature. Then, the solvent was evaporated under vacuum and the blends were placed in the refrigerator before performing the DSC measurement. The other reactants were heated on hot plates and cured at 120°C for 1 h, 240°C for 1 h. Then, the cured resins were cooled slowly to room temperature to get the required product for TGA measurements.

### 3.1SYNTHESIS OF POLYIMIDES

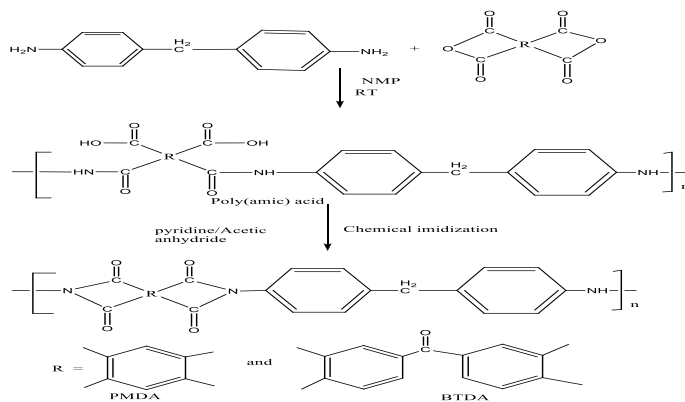
Utilizing DDM as diamine monomer, two kinds of novel polyimides were synthesized by polycondensation of diamine with PMDA and BTDA. DDM (3g, 0.0093 mol) was dissolved in NMP in a100ml three necked flask fitted with a nitrogen inlet and mechanical stirrer, then PMDA (3.68g, 0.0186 mol) was added to the solution with stirring and the reaction was allowed to take place for 24 hrs at room temperature to yield a viscous poly (amic acid) solution with 15% of solid content. The polyimides were obtained by chemical imidization method. A mixture of 6 ml acetic anhydride and 4 ml pyridine was added into the PAA solution and was stirred for 24 hrs at room temperature. The solution containing polyimides was poured into ethanol to produce a precipitate, the precipitate was collected by filtration and washed with ethanol thoroughly, and then it was dried at 80°C for 2 hr and 120°C for 6 hr under vacuum, successively. Polyimide DDM/BTDA was synthesized by the polymerization of 1-equivalent of BTDA with 2-equivalent of DDM, at 15% solid content in NMP using the same method as for polyimide DDM/PMDA.

#### SCHEMES:



Scheme-1 Synthesis of Epoxide terminated diimides

Scheme for DDM based imide



Scheme 2 Synthesis of polyimides

## RESULTS AND DISCUSSION

### 4. MONOMER SYNTHESIS

#### SYNTHESIS OF PMDA BASED EPOXIDE TERMINATED DIIMIDES

#### 4.1. Synthesis of N,N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitic acid

N,N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitic acid was synthesized from 2-amino-4-hydroxy-6-methyl-pyrimidine and pyromellitic dianhydride. **Figure 1** shows the FTIR spectrum of N,N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitic acid. Characteristic bands observed at 1782 and 1702  $\text{cm}^{-1}$  shows the asymmetric and symmetric stretching vibrations of C=O group. The band appearing at 3500  $\text{cm}^{-1}$  shows the OH- groups.

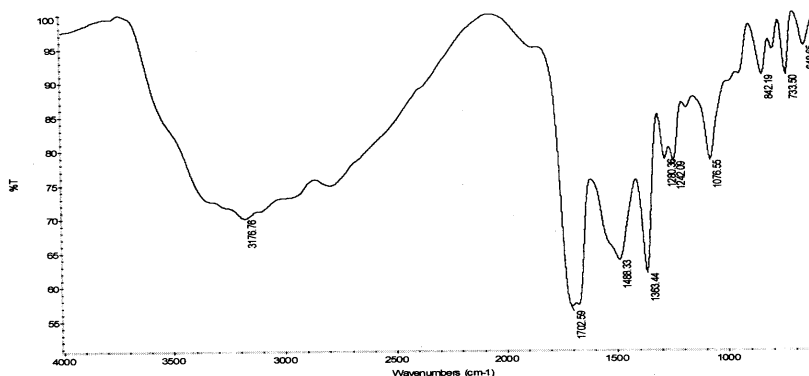


Figure-1 FT-IR Spectrum of PMDA based Diol (STEP-1)

#### 4.2 Synthesis of N,N'-bis(2-amino-4-hydroxy-6-methylpyrimidyl) pyromellitimide

N,N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitimide was synthesized from N,N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitic acid and DMF. **Figure 2** shows the FTIR spectrum of N,N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitimide. Characteristic bands observed at 1789 and 1721  $\text{cm}^{-1}$  shows the asymmetric and symmetric stretching vibrations of C=O group. The band appearing around 3500-3400  $\text{cm}^{-1}$  shows the OH- groups. The band appearing at 1383  $\text{cm}^{-1}$  shows the CN-stretching vibrations.  $^1\text{H-NMR}$  (400MHZ,  $\text{CDCl}_3$ , ppm);  $\delta$ - 2.35 ppm (s,6H,1),  $\delta$ -5.0 ppm (s,2H,2),  $\delta$ -5.73 ppm (s,2H,3),  $\delta$ -9.0 ppm (s,2H,4). The signal at 20 ppm is attributed to the methyl carbon attached to the heteroaromatic ring. The signal at 167 ppm is attributed to the carbonyl carbon which is present in the imide ring. The signal at 160.7 ppm is due to the carbon which is attached to the imide ring. The signals obtained in the range of 100-160 ppm are attributed to the aromatic carbons. The FT-IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  confirm the structure of N,N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitimide.

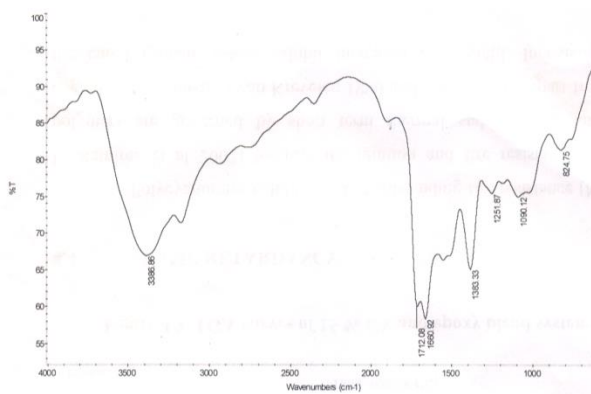


Figure-2 FT-IR Spectrum of PMDA based Diol (STEP-2)

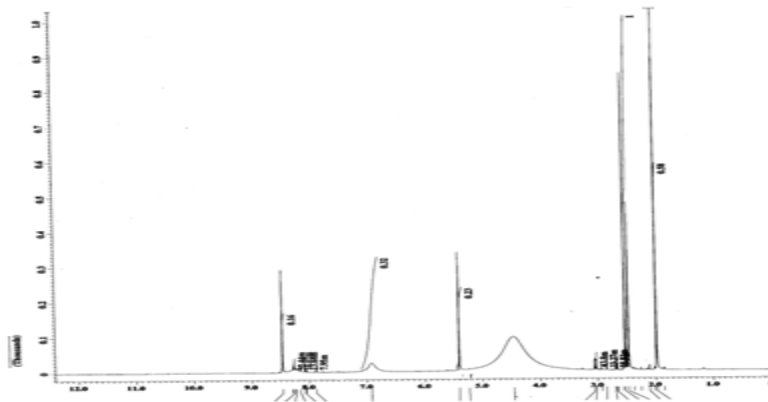


Figure-7 <sup>1</sup>H-NMR Spectrum of PMDA based fully imidized diol (STEP-2)

#### 4.3 Synthesis of glycidyl ether of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitimide

Figure 3 shows the FTIR spectrum of glycidyl ether of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitimide. Characteristic bands observed at 1780 and 1711 cm<sup>-1</sup> shows the asymmetric and symmetric stretching vibrations of C=O group. The band appearing at 911cm<sup>-1</sup> indicates the presence of oxirane ring. The band appearing at 1383cm<sup>-1</sup> shows the CN- stretching vibrations. <sup>1</sup>H-NMR (400MHZ, CDCl<sub>3</sub>, ppm); δ- 2.35 ppm (s,6H,1), δ-2.36-2.63 ppm (m,4H,2), δ-3.04 ppm (m,2H,3), δ-3.95-4.20 ppm (m,4H,4), δ-5.97 ppm (s,2H,5), δ-9.00 ppm (s,2H,6). <sup>13</sup>C-NMR spectrum of the N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitimide. The signals at 44, 51 and 76 ppm are attributed to the oxirane ring. The signal at 24 ppm is attributed to the methyl carbon. The signal at 166.7 ppm is due to the carbon which is attached to the imide ring. The signal at 165 ppm is due to the carbonyl carbon which is present in the imide ring. The signals obtained in the range of 100-160 ppm are attributed to the aromatic carbons. The FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C- NMR confirm the structure of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl) pyromellitimide.

#### 4.4 SYNTHESIS OF BTDA BASED EPOXIDE TERMINATED DIIMIDES

##### 4.4.1 Synthesis of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl) benzophenonetetracarboxylic acid

N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)benzophenonetetracarboxylic acid was synthesized from 2-amino-4-hydroxy-6-methyl-pyrimidine and benzophenonetetracarboxylic acid dianhydride. Characteristic bands observed at 1779 and 1717 cm<sup>-1</sup> shows the asymmetric and symmetric stretching vibrations of C=O group. The band appearing at 3500cm<sup>-1</sup> shows the OH- groups.

##### 4.4.2 Synthesis of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl) benzophenonetetracarboxylic diimide.

The FTIR spectrum of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl)pyromellitimide. Characteristic bands observed at 1789 and 1712 cm<sup>-1</sup> shows the asymmetric and symmetric stretching vibrations of C=O group. The band appearing around 3500-3400cm<sup>-1</sup> shows the OH- groups. The band appearing at 1383cm<sup>-1</sup> shows the CN-stretching vibrations. Figure 8 shows the <sup>1</sup>H-NMR (400MHZ, CDCl<sub>3</sub>, ppm); δ- 2.35 ppm (s,6H,1), δ-5.0 ppm (s,2H,2), δ-5.73 ppm (s,2H,3), δ-8.13 ppm (d,2H,4), δ-8.23 ppm (d,2H,5), δ-8.57 ppm (s,2H,6). The signal at 24 ppm is attributed to the methyl carbon attached to the heteroaromatic ring. The signal at 167 ppm is attributed to the carbonyl carbon which is present in the imide ring. The signal at 160.7 ppm is due to the carbon which is attached to the imide ring. The signals obtained in the range of 100-160 ppm are attributed to the aromatic carbons.



#### 4.4.3 Synthesis of glycidyl ether of N, N'-bis(2-amino-4-hydroxy-6-methyl-pyrimidyl) benzophenonetetracarboxylicdiimide.

The FTIR spectrum of Glycidyl ether of N, N'-bis (2-amino-4-hydroxy-6-methyl-pyrimidyl)benzophenonetetracarboxylicdiimide. Characteristic bands observed at 1779 and 1720  $\text{cm}^{-1}$  shows the asymmetric and symmetric stretching vibrations of C=O group. The band appearing at 911  $\text{cm}^{-1}$  indicates the presence of oxirane ring. The band appearing at 1383  $\text{cm}^{-1}$  shows the CN- stretching vibrations.  $^1\text{H-NMR}$  (400MHZ,  $\text{CDCl}_3$ , ppm);  $\delta$ - 2.35 ppm (s,6H,1),  $\delta$ -2.36-2.63 ppm (m,4H,2),  $\delta$ -3.04 ppm (m,2H,3),  $\delta$ -3.95-4.20 ppm (m,4H,4),  $\delta$ -5.97 ppm (s,2H,5),  $\delta$ -8.13 ppm (d,2H,6),  $\delta$ -8.23 ppm (d,2H,7),  $\delta$ -8.57 ppm (s,2H,8). The signals at 44, 50 and 69 ppm are attributed to the oxirane ring. The signal at 25 ppm is attributed to the methyl carbon. The signal at 166.7 ppm is due to the carbon which is attached to the imide ring. The signal at 167 ppm is attributed to the carbonyl carbon which is present in the imide ring. The signal at 96 ppm is due to the carbonyl carbon which is present inbetween the benzene rings. The signals obtained in the range of 100-160 ppm are attributed to the aromatic carbons.

#### 4.5 SYNTHESIS OF POLYIMIDES

##### SYNTHESIS OF PMDA BASED POLYIMIDE

PMDA based Polyimide was synthesized from 4,4'-diaminodiphenylmethane and pyromellitic dianhydride (PMDA).  $^1\text{H-NMR}$  (400MHZ,  $\text{CDCl}_3$ , ppm);  $\delta$ -3.96 ppm (s,2H,1),  $\delta$ -7.96 ppm (d,2H,2),  $\delta$ -7.21 ppm (d,2H,3),  $\delta$ -8.34 ppm (s,2H,4). The signal at 41.3 ppm is attributed to the methylene carbon. The signal at 167 ppm is attributed to the carbonyl carbon which is present in the imide ring. The signal at 130 ppm is due to the carbon which is attached to the imide ring. The signals obtained in the range of 125-135 ppm are attributed to the aromatic carbons. The FT-IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  confirm the structure of PMDA based polyimide.

##### SOLUBILITY

The solubility of polyimides was tested in various organic solvents and the results are summarized in table 2. The synthesized polyimides are soluble in polar aprotic solvents such as NMP, DMF, DMAc etc.

##### DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The glass transition temperature of the polymers were evaluated by differential scanning Calorimetry was carried out for polyimides (1a – 1d) at a heating rate of 10°C. The glass transition temperature of epoxy terminated polyimides are in the range of 244-250°C. The representative DSC curve is shown in figure.

##### THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermal stability of the polyimides in nitrogen was evaluated from TG analysis and is shown in Figures. The polyimide-1a has thermal stability upto 430°C ( $T_{10}$ ) and has the residual mass value 12.51% at 800°C under nitrogen. The polyimide-1b has thermal stability upto 380°C ( $T_{10}$ ) and has the residual mass value 22.42% at 800°C under air. The polyimide-1c has thermal stability upto 360°C ( $T_{10}$ ) and has the residual mass value 30.12% at 800°C. The polyimide-1d has thermal stability upto 365°C ( $T_{10}$ ) and has the residual mass value 32.55% at 800°C. From this it is inferred that, the epoxy terminated polyimides exhibits much higher thermal stability than the commercial polyimides.

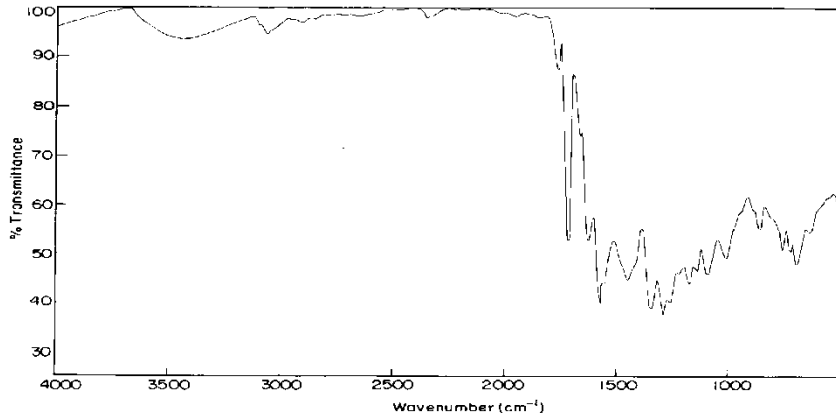


Figure-3 FT-IR Spectrum of PMDA based Epoxy terminated diimide (STEP-3)

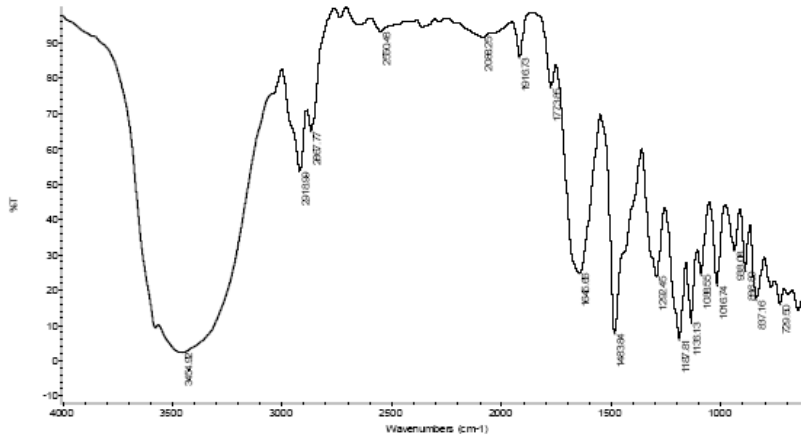


Figure-4 FT-IR Spectrum of BTDA based amic acid diol (STEP-1)

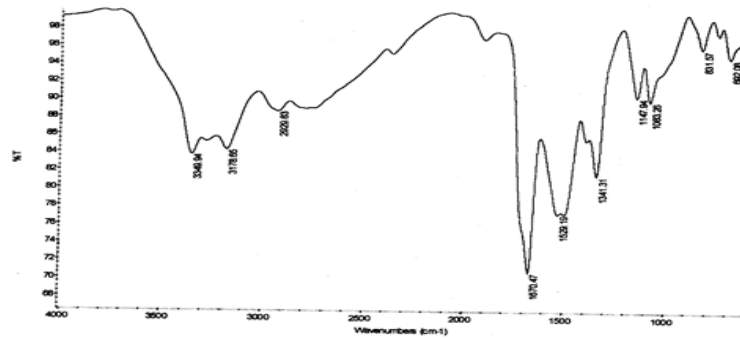


Figure-5 FT-IR Spectrum of BTDA based fully imidized diol (STEP-2)

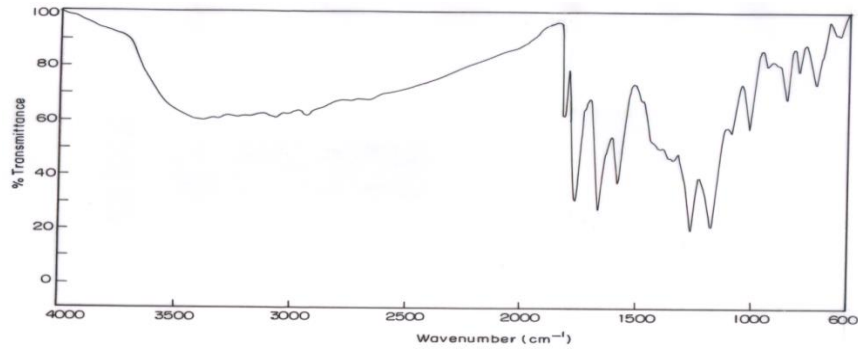


Figure-6 FT-IR Spectrum of BTDA based epoxy terminated diimide (step-3)

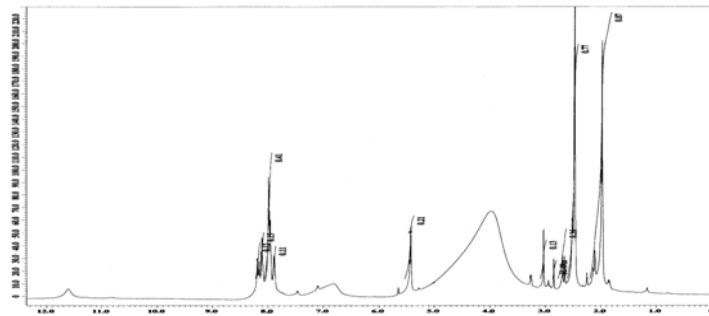


Figure-8 <sup>1</sup>H-NMR Spectrum of BTDA based fully imidized diol (STEP-2)

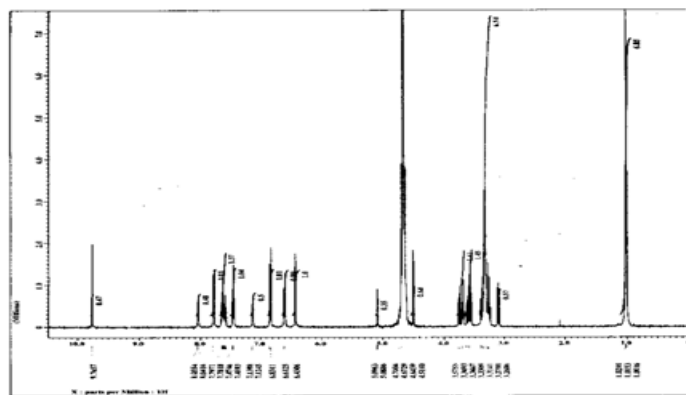


Figure-9 <sup>1</sup>H-NMR Spectrum of PMDA based epoxy terminated diimide

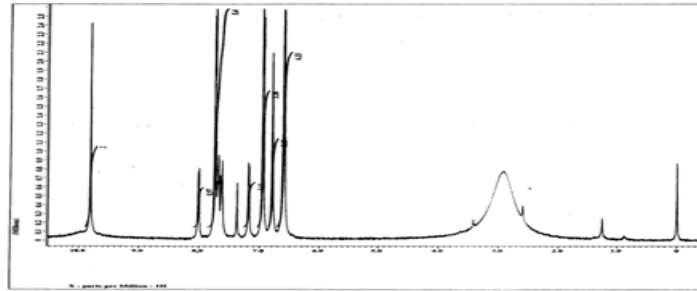


Figure-10 <sup>1</sup>H-NMR Spectrum of BTDA based epoxy terminated diimide

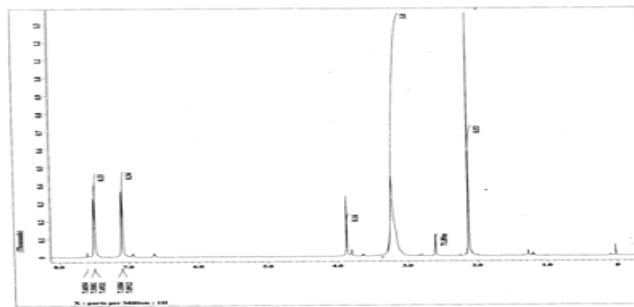


Figure-11 <sup>1</sup>H-NMR Spectrum of PMDA and DDM based polyimide

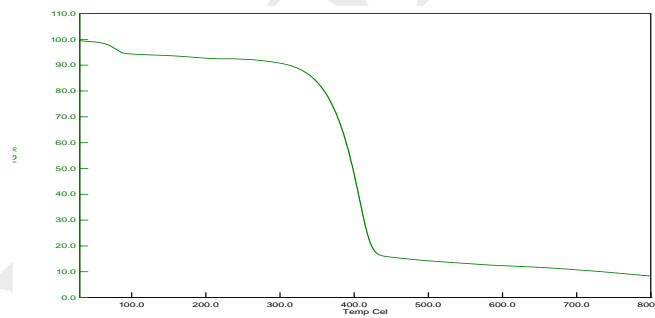


Figure-17 TGA curve of PMDA based cured Epoxy terminated diimide-1b (air atmosphere)

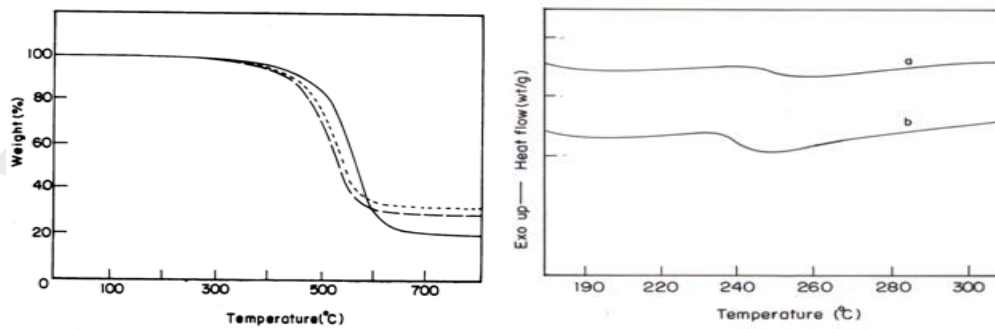


Figure-18 TGA curve for polyimides DSC curves for the epoxy resin based polyimides

Table-1 Thermal properties of the polyimides

Polyimide code	Polyimide	T <sub>10</sub> %(°C)	Char yield (%)
PI-1a	PMDA based epoxy resin	430	12.51
PI-1b	BTDA based epoxy resin	380	22.42
PI-1c	PMDA based PI	360	30.12
PI-1d	BTDA based PI	365	32.55

Table-2 Solubility behaviour of polyimides

CODE	Polyimide	NMP	DMF	DMSO	DMAc	THF
PI-1a	PMDA based epoxy resin	++	++	++	++	++
PI-1b	BTDA based epoxy resin	++	++	++	++	++
PI-1c	PMDA based PI	++	++	++	++	++
PI-1d	BTDA based PI	++	++	++	++	++

++-Completely soluble at room temperature; +-Completely soluble on heating

## CONCLUSIONS

Two novel pyrimidyl/imide epoxy resins were synthesized from 2-amino-4-hydroxy-6-methyl-pyrimidine and the corresponding dianhydride. Two different polyimides were synthesized from the diamine DDM. The structures of the compounds synthesized were confirmed by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR techniques. The solubility of the polyimides in various test solvents was studied. These polymers are soluble in polar aprotic solvents such as NMP, DMF, DMAc. The TGA analysis shows that the epoxy resin based polyimides exhibits higher thermal stability than the DDM based polyimides. (T<sub>10</sub> weight % 360-430°C). DSC result shows the T<sub>g</sub> of epoxy resin based polyimides (244-250°C). From the above studies it has been observed that, with the incorporation of pyrimidyl and imide groups into the backbone, the resulting epoxy polymer cured with DDM showed higher glass transition temperature and excellent thermal stability than the commercial available polyimides.

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