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### **Preparation of Engineering Material as Substituted Maleimide-Epoxy Resin: Thermal Characteristics and Mechanical / Chemical Reactivity of Cured Glass Composites**

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#### **ABSTRACT**

N(4-N- phenylethanamide azo3-N-(4-hydroxy phenyl)maleimide was synthesized and modified to prepare maleimide based epoxy resin using with diglycidylether of bisphenol A (B-11). In formation of maleimide epoxy resin triphenylphosphine and methylethylketone were used as catalyst and solvent. The final compound was possessed both the maleimide and oxirane ring functional groups. The PAHMIGE-epoxy resin was characterized by elemental analysis, FT-IR and <sup>1</sup>H-NMR spectral studies were done to confirm structural existences, molecular weight determined by GPC. The curing processor of this compound with amine functional group containingcuring agents such as DDM (Diaminodiphenylmethane) and TEA (Triethylamine)were conducted and studied by differential scanning calorimetry(DCS). Thermal degradation was evaluated by thermo gravimetric analysis (TGA). Glass reinforced composites based on the PAHMIGE-epoxy-DDM / TEA systems have been prepared and some preliminary chemical / mechanical testing were also examined. The cured samples were found to have excellent thermal stability, chemical resistivity with high water absorption resistance properties.

**KEYWORDS:**Bisphenol A (B-11), Epoxy resin, DDM / TEA curing agents, Differential scanning calorimetry (DCS), Thermo-gravimetric analysis (TGA), Glass reinforced composites.

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## **INTRODUCTION**

Despite possessing many attractive features of epoxy resins, are widely used in industrial applications such as excellent chemical and solvent resistance feature, good thermal and electrical properties<sup>1</sup>, dimensional stability and ablative property. At present, epoxy resins are extensively applied in various technical applications such as coatings, composites and as adhesives<sup>[1-3]</sup>. The consumption of epoxy resin in high performance structural materials has been strongly increasing recently.

We reported the polyamides or polyimides have amide and imide functional groups with unsaturated double bond. The polymer may have terminal amino group with unsaturated double bond may participated into polymerization process or into curing reaction with either epoxy resin or acrylates / vinyls to enhance their thermal mechanical performances<sup>[4-5]</sup>. In addition, there is a lot of scope and need for improving the properties of epoxy resins to be used in advanced and high tension applications. However, epoxy resin is now prime candidate for various industrial applications<sup>[6-8]</sup> and the study of amino-ended unsaturated polyamide / imide resin and curing properties have not been attempted so far. Superior thermal stability for epoxy resin is needed for using as molding compounds, encapsulation materials in advanced electronic components and high strength composites. Generally, modifying epoxy resin with polyamides / imide compounds provide a convenient and feasible approach of enhancing the thermal stability of epoxy resins<sup>[9]</sup>. Therefore, the polyamides / imides and maleimide double bond play the major role with epoxy resins in the post-curing to formation of composite materials. The thermal strengthen of the amido / imido-epoxy resins were significantly pulled at higher both in the initial decomposition temperature (IDT) and the integral procedural decomposition temperature (IPDT)<sup>[10]</sup>. If epoxy resins modified with aromatic imides or substituted aromatic imides as maleimide / substituted maleimide compounds have also received attractive attentions, due to the similar curing conditions and processing properties of the epoxy resins and maleimides<sup>[11]</sup>. Bismaleimide and epoxy resins were also prepared and they exhibited good thermal and mechanical properties<sup>[12-14]</sup>.

Hence, in the present study comprises the synthesis and characterizations of maleimide compound with substituted hydroxyl group and epoxy resin of this maleimide compound. Maleimide-epoxy resin were consequently obtained through a simple addition reaction between the oxirane ring of epoxy compound namely diglycidyl ether of bisphenol-A (B-11) and hydroxyl group of substituted maleimide using reaction initiator and resultantly, achieved a maleimide-epoxy resin compound possessed both oxirane ring and maleimide reactive groups. Each of the reactive groups might involve incross-linking networks under thermal curing reaction with curing agents to bring

about high cross-linked reinforced resins. That's why, it was considered worthwhile to study the synthesis, characterization and curing reaction of the maleimide-epoxy resin with different curing agents bearing amino functional groups and to study the chemical, mechanical and thermal properties of the cured maleimide-epoxy resin system.

## MATERIALS

Maleic anhydride (AR), 4-N-Phenylethanamide, 4-aminophenol (AR), Diphosphorus pentoxide (AR), Tetrahydrofuran (THF), DMF, Sodium nitrate, Hydrochloric acid (Loba chemicals), Bisphenol A based epoxy resin (B-11, medium viscous liquid) supplied by Atul Limited, polymer section. DDM (Diaminodiphenylmethane) and TEA (Triethylamine) (Aldrich chemicals), TPP (Triphenylphosphine), MEK (Methyl ethyl ketone), AIBN (Loba chemicals).

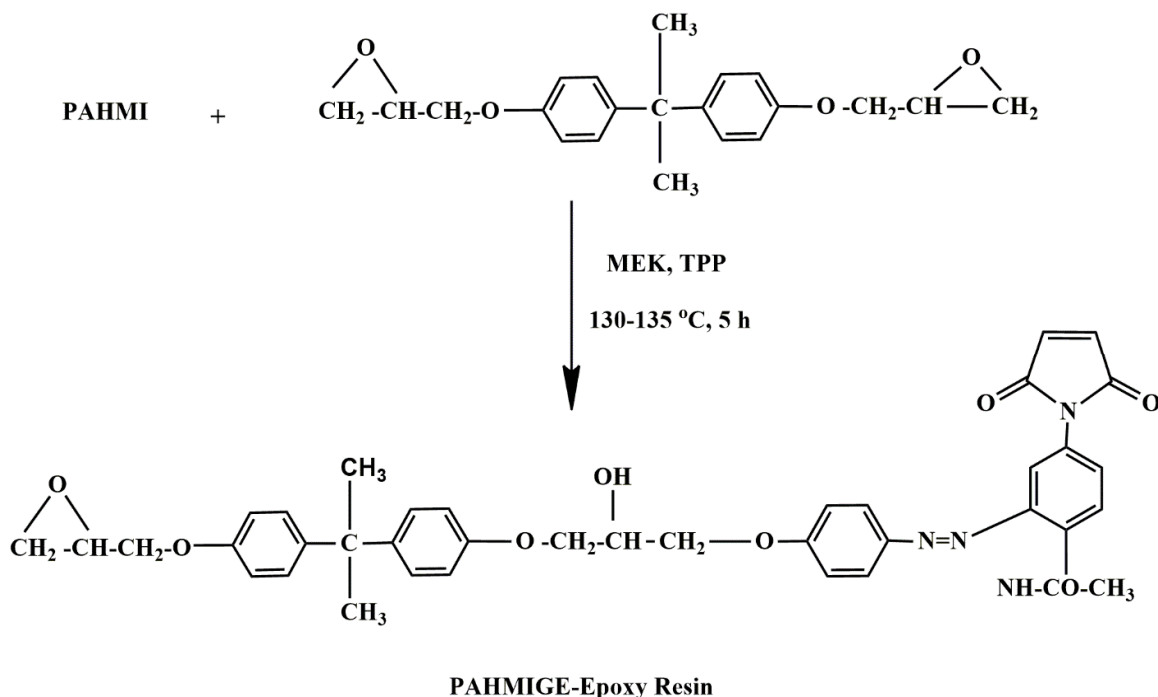
## EXPERIMENTS

### *Synthesis of N-(4-N-phenylethanamide) maleimide [PEMI] (I)*

The N-(4-N-phenylethanamide) maleimide PEMI (I) was prepared by the reaction of P-amino acetanilide (0.1 mol) and maleic anhydride (0.1 mol) according to reported method<sup>[23]</sup>. The monomer N(4-N-phenylethanamide azo3-N-(4-hydroxyphenyl)maleimide [PAHMI] was synthesized by diazotization reaction in two steps according to literature protocol<sup>[15]</sup>. The reaction solution was turned into brownish yellow slurry. After stirring for 30 min., it was filtered and washed with double distilled water and then dried at 60 °C under vacuum oven to give dried product of PAHMI compound.

### *Synthesis of N(4-N-phenylethanamide azo3-N-(4-hydroxyphenyl)maleimido-glycidylether-epoxy compound (PAHMIGE-epoxy)*

[PAHMIGE] was prepared by reacting with bisphenol A epoxy resin (B-11) and N(4-N-phenylethanamide azo3-N-(4-hydroxyphenyl)maleimide [PAHMI]. PAHMI (0.02 mol, ) and B-11 (12.50 g) were dissolved in 25 ml of methylethylketone in a 250 ml round bottomed flask with addition of TPP (0.05 g) as a reaction propellant. This solution was refluxed at 130-135 °C for 5 hours then cooled at room temperature. The solvent was recovered by evaporation-cum-condensation then liquid product was heated at 60-70 °C under vacuum for 8 hours to give viscous maleimide-epoxy product (Scheme 1).



Scheme No. 1: Synthesis of PAHMIGE-Epoxy Resin

### *Preparation of cured maleimide epoxy resin (PAHMIGE-epoxy resin)*

The cured epoxy resin was synthesized by thermally curing of PAHMIGE-epoxy resin with 4,4'-diaminodiphenylmethane (DDM) / triethylamine (TEA) and AIBN were mixed with MEK solution and cured in vacuum oven at 80 °C for 2 hours.

## COMPOSITE FABRICATION

The glass fiber reinforced composites were prepared (glass fiber: resin ratio; 60:40) by a mixture of maleimide epoxy resins and DDM, AIBN stirred for 5 mins. The suspension was then applied with a brush on a 200 × 200 mm E- type of glass fiber cloth and solvent was allowed to evaporate. The ten dried prepregs prepared then stacked one on top of another and pressed between the steel plates coated with a Teflon film release sheet and compressed in a flat platen under pressure of about 70 psi. The prepregs stacks were cured by heating at 150°C for 10 hrs. in an air-circulated oven. The composites so obtained were cooled at room temperature before the pressure was released. The composite samples were gone through machine for dimension executions.

## RESULTS AND DISCUSSION

### *Spectral Characterization*

Fourier Transform Infrared (FTIR) spectra was recorded on a FTIR Perkin-Elmer spectrophotometer model RX-I. The compounds were analyzed using the KBr pellets. The spectra were obtained in bandwidth 250-4000  $\text{cm}^{-1}$ . Nuclear Magnetic Resonance (NMR) spectra of monomer and cured compounds were analyzed on Bruker Avance II 400 MHz NMR Spectrometer.

The result of FTIR spectra revealed that the high conversions of the reaction between -OH groups and oxirane ring. In bisphenol A (B-11) showed the absorption band at 915  $\text{cm}^{-1}$  for oxirane rings but after formation of maleimide-epoxy resin (PAHMIGE-epoxy resin), absorption band of oxirane ring at 915  $\text{cm}^{-1}$  was decreased in the intensity i.e. clearly indicated the decreases in concentration of oxirane rings as the reaction of maleimide and bisphenol A was proceed. The chemical structure of the maleimide-epoxy compound (PAHMIGE-epoxy) obtained was confirmed by the presences of some absorption bands at 1398  $\text{cm}^{-1}$ ; 1394  $\text{cm}^{-1}$  (C-N), 1707  $\text{cm}^{-1}$ ; 1712  $\text{cm}^{-1}$  (C=O of imide), 1605  $\text{cm}^{-1}$ ; 1606  $\text{cm}^{-1}$  (C=C) for PAHMIGE-epoxy-DDM and PAHMIGE-epoxy-TEA respectively. FTIR absorption bands for PAHMI; 1714  $\text{cm}^{-1}$  (C=O), 3345  $\text{cm}^{-1}$  (N-H), 3262  $\text{cm}^{-1}$  (-OH), 3102  $\text{cm}^{-1}$  (CH=CH, C-H Stretching), 1634  $\text{cm}^{-1}$  (CH=CH, C-C Stretching), 1385  $\text{cm}^{-1}$  (C-N), 1595  $\text{cm}^{-1}$  (N=N) (figure 1-3).

$^1\text{H-NMR}$  spectral analysis of PAHMIGE-epoxy compound also suggested the chemical structure as showed in figure 4-6. The  $^1\text{H-NMR}$  signals of PAHMI (maleimide) at; 6.22-7.91 ppm (Aromatic), 10.06 ppm (CO-NH), 10.65 ppm (-OH) (figure ). The appearances of the signals at about 3.40 ppm (for opened oxirane ring  $-\text{OCH}_2\text{CH}(\text{OH})-$ ) and 6.02 ppm (for  $-\text{C-OH}$ ) represented the occurrences of the addition reaction between maleimide (PAHMI) and epoxy resin of bisphenol-A. The chemical shifting about 2.56 ppm, 2.40 ppm, 2.50 ppm, 3.42 ppm and 4.22 ppm and 2.52 ppm, 2.08 ppm, 3.62 ppm, 4.12 ppm demonstrated the typical oxirane /epoxy proton-signals for PAHMIGE-epoxy-DDM and PAHMIGE-epoxy-TEA respectively. In the cured compound of resins,  $^1\text{H-NMR}$  spectral studies, the signals shifting at 6.58-7.93 ppm were revealed for aromatic protons and CH=CH group of maleimides and phenyl rings of B-11.

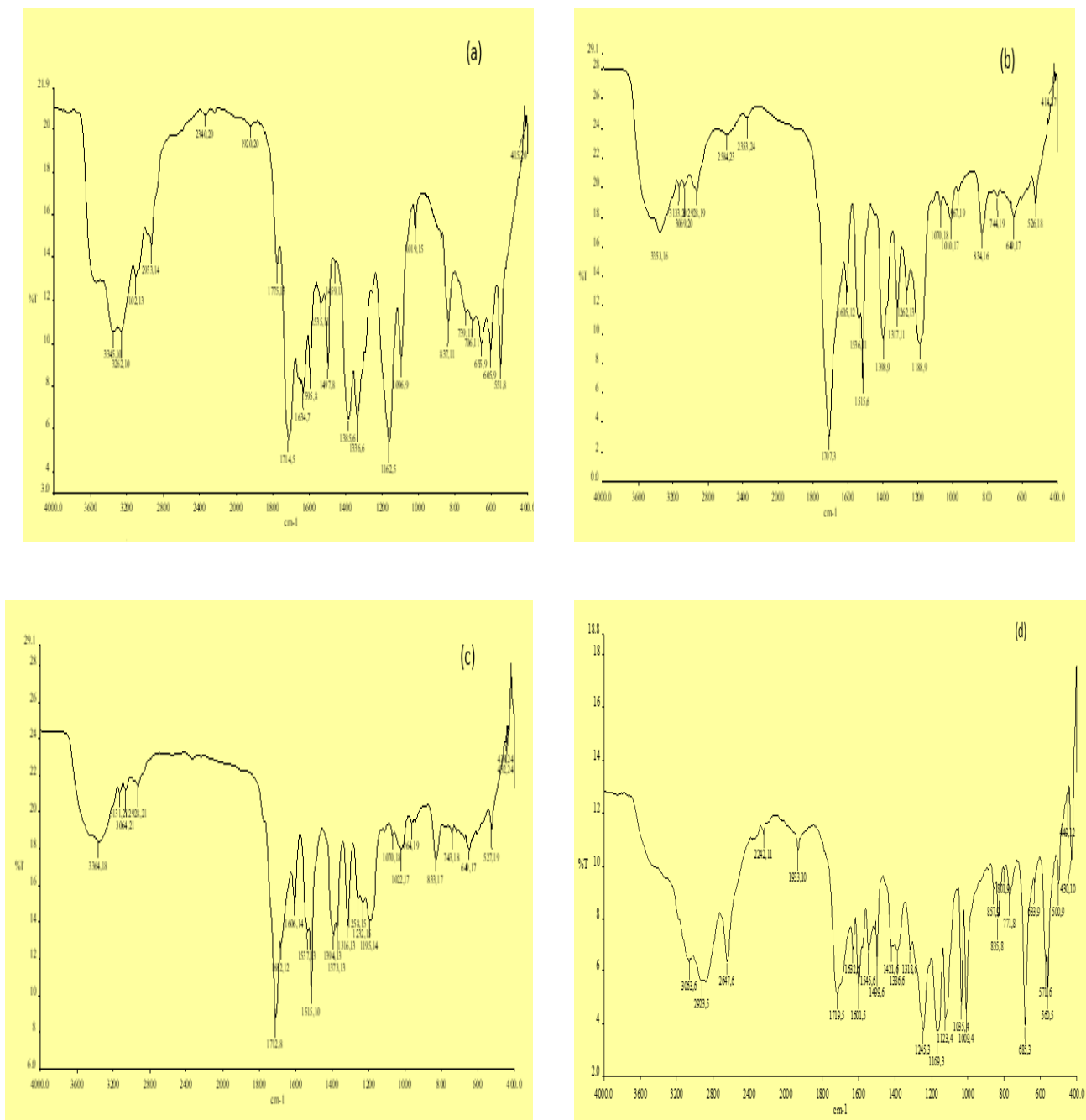


Figure No. 1: FTIR-spectra of (a) PAHMI (b) PAHMIGE-Epoxy Resin (c) PAHMIGE-Epoxy-DDM (d) PAHMIGE-Epoxy-TEA

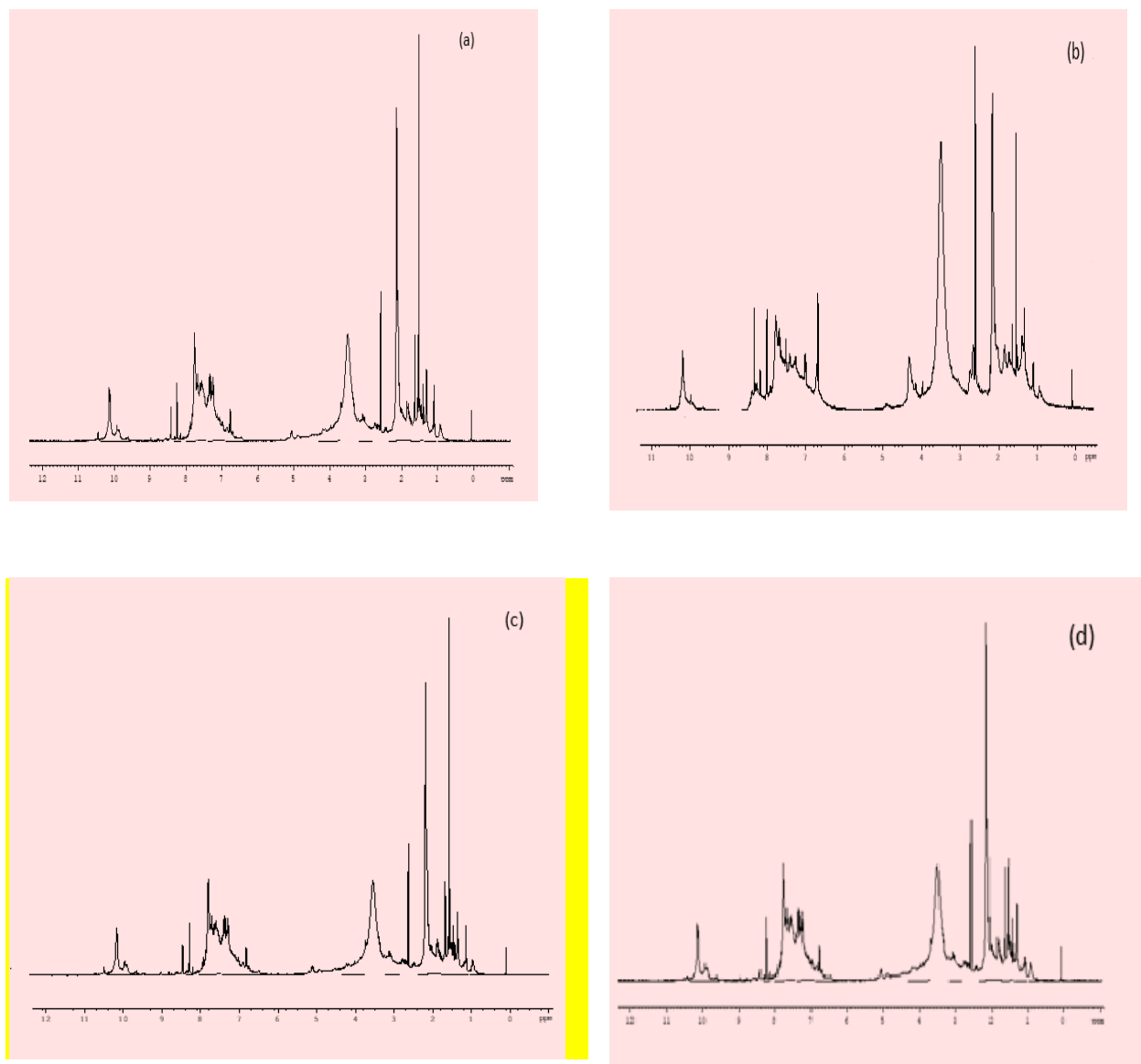


Figure No. 2: <sup>1</sup>H-NMR-spectra of (a) PAHMI (b) PAHMIGE-Epoxy Resin (c) PAHMIGE-Epoxy-DDM (d) PAHMIGE-Epoxy-TEA

### ***Molecular Weight***

The molecular weight of the PAHMIGE-epoxy resin was determined by Gel permeation chromatography (GPC) analysis. GPC is a reliable, fast and modern technique to determine the polydispersity index (PDI) and molar mass average weights of polymers. The number average and weight average molecular weights ( $M_n$ ,  $M_w$ ) and polydispersity index of epoxy resin were summarized in Table No. 1.

Table No. 1: Molecular weight and PDI values of PAHMI, PAHMIGE-Epoxy Resins

Compound	Mw	Mn	PDI (Mw/Mn)
PAHMI	1145.2	1025.2	1.11
PAHMIGE-epoxy resin	2285.8	2055.7	1.11
PAHMIGE-epoxy-DDM	2374.6	2265.5	1.04
PAHMIGE-epoxy-TEA	2342.9	2298.3	1.01

### Composite Characterizations

All chemical and mechanical testing on composite samples were carried according to ASTM D 543 standards. PAHMIGE-epoxy maleimide resin was cut into 2 cm x 2 cm small sized specimens and their edges were coated with the same matrix content to avoid the moisture absorption through edges capillary-pores. All the specimens were weighted in dry condition and noted as initial weight at room temperature. The specimens were then poured in 100 ml of various reagents as H<sub>2</sub>SO<sub>4</sub> (25% v/v), HCl (25% v/v), NaOH (25% v/v), ethanol, acetone, THF and DMF. After 7 days the specimens were taken out from all reagents, wiped and dried with tissue paper and examined for the percentage changes in weight and thickness at room temperature. The % moisture absorption was calculated from measuring by the differences of specimen's weights using the following equation.

$$\% \text{ Moisture Absorption} = \frac{\text{Wetted specimen weight} - \text{Weight of the dry specimen}}{\text{Weight of the dry specimen}} \times 100$$

The reagents absorption results were showed in Table No. 2. The moisture absorption of maleimide –epoxy resin, under the given conditions at room temperature were observed in decreasing trend as compare to epoxy resin. The moisture absorption resistance behavior was obtained due to presence of tertiary nitrogen atom in DDM and TEA. The analytical data revealed that the cured maleimide epoxy resins with curing agents (DDM and TEA) showed more resistance to water and other chemicals as compared to the without maleimide containing epoxy cured resin with the same curing agents (Table No. 2). The mechanical strength was studied as Rockwell hardness by Rockwell hardness tester model no. RAS / Saro Engg. Pvt. Ltd. India according to ASTM D 785 at room temperature. The notched izod impact strength of the maleimide-epoxy cured composites were evaluated on a Zwick Model no. 8900 Impact machine at the room temperature followed ASTM D 256 conditions and the compressive strength was analyzed on a Universal Instron testing machine model no. A-743, at the room temperature as according to ASTM D 695 and the measurement of Flexural strength was also carried out with Universal Instron Testing Machine



model no. A-7437, at room temperature according to method of ASTM D7. All mechanical tests were examined on three same specimens and average results are summarized in (Table No. 3).

**Table No. 2: Chemical resistance properties of cured PAHMIGE-Epoxy-DDM and PAHMIGE-epoxy-TEA composites**

PAHMIGE-Epoxy-DDM			PAHMIGE-Epoxy-TEA	
Reagents	Thickness	Weight	Thickness	Weight
H <sub>2</sub> O	1.12	1.93	1.45	2.05
Boiled water	1.45	2.14	1.98	2.28
10% NaOH	1.29	1.78	1.17	1.80
NH <sub>3</sub>	0.67	1.32	0.78	1.12
C <sub>2</sub> H <sub>5</sub> OH	0.69	1.15	0.85	1.16
C <sub>6</sub> H <sub>6</sub>	0.21	0.56	0.45	0.86
HNO <sub>3</sub>	0.24	0.48	0.42	0.82
H <sub>2</sub> SO <sub>4</sub>	0.79	1.15	0.29	1.84
HCl	0.43	1.25	0.54	0.82

**Table No. 3: Mechanical Properties of Cured PAHMIGE-Epoxy-DDM and PAHMIGE-Epoxy-TEA Composites**

Composites of Epoxy Resin	Rockwell Hardness (R)	Impact Strength (MPa)	Compressive Strength (MPa)	Flexural Strength (MPa)
PAHMIGE –Epoxy-DDM	123	321	298	280
PAHMIGE –Epoxy-TEA	115	297	274	245

### **Thermal Studies**

Thermal characteristics of cured maleimide-epoxy resins and their stability was investigated from “Thermo gravimetric analysis” (TGA) in presence of air atmosphere. The thermograms of the cured PAHMIGE-epoxy maleimide resins were clearly indicate that the thermal stability of cured resins was improved with the incorporation of maleimide as a rigid structured backbone unit [16-17]. Resultant, the cured maleimide-epoxy resins indicates high thermal stability as compared to simple and without maleimide cured epoxy resins. The rate of decomposition was started from 200°C and their initial weight loss is about 2%-3%. The rate of degradation increased very rapidly between 400°C to 500°C in a single step and the compounds were degraded completely above 700°C as shown in Figure No. 3. The TGA analytical data of cured maleimide-epoxy resins are showed in Table No.

4. The results are apparent that the thermal stability of cured maleimide-epoxy resins with DDM / TEA was performed better stability as compared to traditional epoxy resin.

Curing of PAHMIGE-epoxy maleimide resins was done on a Universal VG03 differential scanning calorimeter (DSC) with AIBN used as a catalyst with heating rate of 10 °C / min. DSC data of these compounds are furnished in Table 5 and reveals that cured samples give a single exothermic peak in the range 65-200 °C depending of chemical behavior of PAHMIGE-epoxy maleimide resin shown in Figure No. 4. From the DSC thermograms, the kick-off temperature ( $T_i$ ), peak exothermic temperature ( $T_p$ ) and temperature of completion of cure ( $T_f$ ) were obtained and kinetic parameters as  $E_a$  (activation energy) and  $n$  (order of reaction) were also calculated and stated in Table No. 5.

Table No. 4: TGA analytical data of cured PAHMIGE –Epoxy Resins

Compounds	% Weight loss from TGA					
	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C
PAHMIGE –epoxy-DDM	2.58	12.54	47.28	67.27	81.14	90.16
PAHMIGE –epoxy-TEA	3.21	16.22	52.33	73.41	89.48	95.52

Table No. 5: Curing Characteristics of PAHMIGE-Epoxy Resin at Heating Rate 10°C Min<sup>-1</sup>

Compound	Curing Temperature (in °C)				
	Initial Temp. ( $T_i$ )	Peak Temp. ( $T_p$ )	Final Temp. ( $T_f$ )	Activation Energy ( $E_a$ ) (kcal mol <sup>-1</sup> )	Order of Reaction ( $n$ )
PAHMIGE-Epoxy-DDM	138	147	168	35.54	1.1
PAHMIGE –epoxy-TEA	132	142	159	35.14	1.1

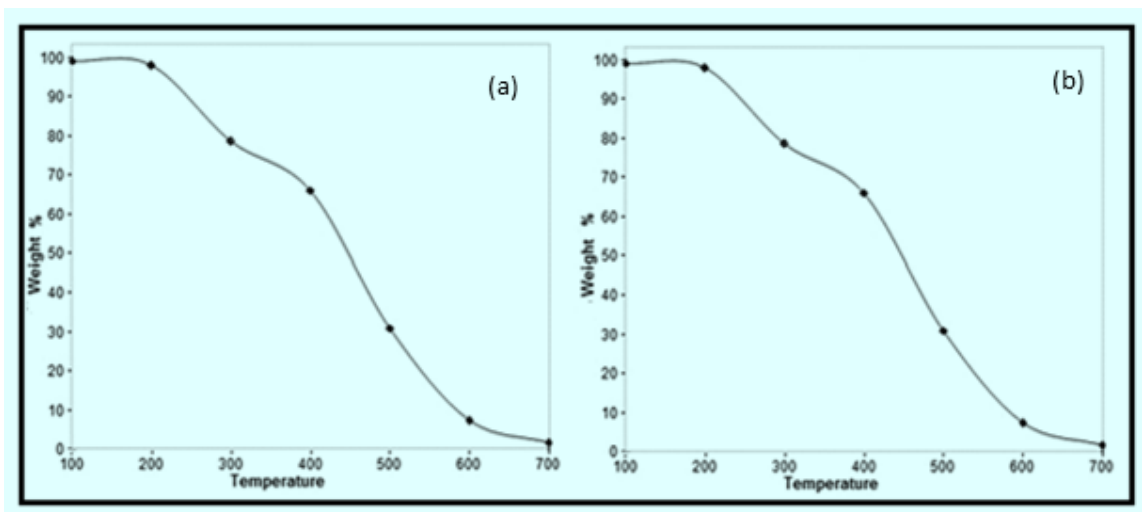


Figure No. 3: TGA thermograms of (a) PAHMIGE-Epoxy-DDM (b) PAHMIGE-Epoxy-TEA

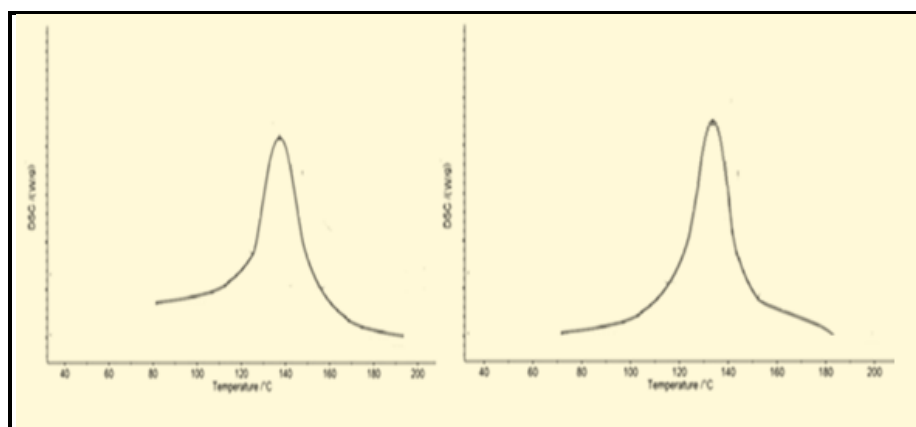


Figure No. 4: DSC exothermic peaks of (a) PAHMIGE-Epoxy-DDM (b) PAHMIGE-Epoxy-TEA

## CONCLUSIONS

N(4-N- phenylethanamide azo-3-N-(4-hydroxy phenyl)maleimide group was successfully incorporated into bisphenol A type epoxy resin (B-11) and resultantly, a compound exhibits both maleimide and oxirane ring function of effective reacting groups. The prepared PAHMIGE-epoxy resin was cured thermally with DDM and TEA exhibited excellent thermal stability. Preliminary mechanical and chemical property testing on cured maleimide-epoxy blend was conducted and it shows better and reasonable mechanical properties, chemical and water absorption resistance comparatively epoxy-resins.

Synthesized maleimide-epoxy resin, their chemical structure / reactions and molecular weight is reinforcing to subject of further work.

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