

Preparation and Curing Studies of Maleimide Bisphenol-A Based Epoxy Resins

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Maleimide modified epoxy compounds were prepared by reacting *N*-(4-hydroxyphenyl) maleimide (HPM) with diglycidylether of bisphenol-A. Triphenylphosphine was used as catalyst and methylethylketone as solvent. The resulting compound possessed both the oxirane ring and maleimide group. The curing reaction of the maleimide epoxy compound with amine curing agents such as 1-(2-aminoethyl) piperazine (AEP) and 5-amino-1,3,3-trimethylcyclohexane methylamine isophorone diamine, IPDA) were studied. Incorporation of maleimide groups in the epoxy resin provides cyclic imide structure and high cross-linking density to the cured resins. The cured samples were found to have good thermal stability, chemical resistance (acid/alkali/solvent) and water absorption resistance.

Key Words : Epoxy resin, Maleimide

Introduction

Epoxy resins are widely used in industrial applications owing to their many attractive properties, such as excellent chemical and solvent resistance, good thermal and electrical properties.¹ At present epoxy resins are extensively used in various technical applications such as coatings, composites and as structural adhesives.² The use of epoxy resin in high performance structural materials has been increasing recently. There is a lot of scope and need for improving the properties of epoxy resins to be used in advanced applications. For example, epoxy resin with superior thermal stability is needed for using as molding compounds and encapsulation materials in advanced electronic components. Generally, modifying epoxy resin with polyamides or imido compounds²⁻³ provide a convenient approach of enhancing the thermal stability of epoxy resins. Therefore, epoxy resins were cured with reactive polyimides,²⁻⁴ polyamic acid,⁵ and imido-modified curing agents⁶ to introduce imide structure into epoxy resin. The thermal stability of the above mentioned imido epoxy resins was significantly leveled up both in the initial decomposition temperature (IDT) and the integral procedural decomposition temperature (IPDT).⁷ On the other hand, epoxy resins modified with maleimide compounds have also received attractive attentions, due to the similar curing conditions and processing properties of the epoxy resins and maleimides.⁸⁻¹² Maleimide epoxy resins generally showed appropriate properties between epoxy and maleimide resins.¹³ Thus both the intercrossed and the interpenetrating systems (IPN) based on bismaleimides and epoxy resins were prepared and they exhibited good thermal and mechanical properties.⁸⁻¹²

In the present work, a maleimide compound with hydroxyl group was first synthesized. Maleimide epoxy compounds were consequently obtained through a simple addition reaction between the oxirane ring of epoxy compounds and

hydroxyl group of maleimide. The resulting maleimide epoxy compounds possessed both oxirane ring and maleimide reactive groups. Each of the reactive groups might form cross-linking networks under thermal curing reaction with curing agents to bring about high cross-linking density. So it was considered worthwhile to study the synthesis, characterization and curing reaction of the maleimide epoxy compounds with different amines and to study the properties of the cured resin systems (For water resistance and chemical resistance properties).

Experimental Section

Materials and measurements. Maleic anhydride and 4-aminophenol were purchased from S.d.Fine chemicals. The following bisphenol-A based epoxy resins were used. (Lapox* make supplied by ATUL Ltd, polymer division); (i) Lapox B-11 (medium viscous liquid; Viscosity at 25 °C, 9000-12000 m pas), and (ii) Lapox B-13 (High viscous liquid; Viscosity at 25 °C, 12000-16000 m pas). AEP (1-(2-aminoethyl) piperazine) and IPDA (isophorone diamine) were supplied by Aldrich Chemicals. Triphenylphosphine (TPP), dimethyl formamide (DMF) and toluene were obtained from Merck chemicals. Infrared spectra were recorded using Nicolet FT-IR spectrometer using KBr. Elemental analyses were carried out in Liquid Crystal Department, Raman Research Institute, Bangalore. The ¹H NMR spectra of MIE compound is recorded in Sophisticated Instrument Facility, Indian Institute of Science, Bangalore. TGA/DTA for cured samples is recorded in National Chemical Laboratory, Pune.

Synthesis of *N*-(hydroxyphenyl) maleamic acid (HPMAc). In a 2-necked flask equipped with a mechanical stirrer and a reflux condenser, maleic anhydride (0.88 mol, 86.4 g) dissolved in 700 mL acetone was charged. The solution was stirred at ambient temperature, and 4-aminophenol (0.80 mol, 87.2 g) was added in portions over 30 min. The reaction

mixture turned into yellow slurry. After stirring for 1.5 h the slurry was filtered. The solid was washed with acetone, and then dried at 60 °C under vacuum to give light green powder product. Yield 95%. Molecular Formula: C₁₀H₉NO₄. Elemental analysis: Found % (Calcd %) C: 57.90 (57.97), H: 4.38 (4.35), N: 6.80 (6.76). IR (KBr, cm⁻¹): 3312 (N-H), 3200 (O-H), 1703 (-COOH), 1621 (C=O) and 1600 (C=C).

Synthesis of *N*-(4-hydroxy phenyl) maleimide (HPM).

In a 3-necked flask equipped with a mechanical stirrer, water segregation, and a reflux condenser, HPMac (0.6 mol, 123.2 g), *p*-toluenesulphonic acid (0.05 mol 8.75 g), dimethylformamide (60 mL) and toluene (700 mL) were charged. The mixture was heated to reflux for about 8-10 h until the slurry turned into a clear solution and the stoichiometric amount of water was segregated. After removing toluene, the residue was poured into a large amount of water. The precipitate was collected with filtration, washed with 5% sodium bicarbonate solution, and with water. The crude product was recrystallized from a mixed solvent of water-isopropanol (1 : 1) to give brown crystalline needle product. Yield: 64%. Molecular formula C₁₀H₇NO₃. Elemental analysis: Found % (Calcd %) C: 63.50 (63.49), H: 3.66 (3.70), N: 7.45 (7.41). IR (KBr, cm⁻¹): 3416 (O-H), 1709 (-C=O), 1641 (C=C), and 1388 (C-N).

Synthesis of maleimide epoxy compounds (MIE). MIE was prepared by reacting B-13/B-11 epoxy resins and *N*-(4-hydroxy phenyl) maleimide (HPM). HPM (0.027 mol, 3.74 g) and B-13/B-11 (12.53 g) were dissolved in 20 mL of methylethylketone in a 150 mL round bottomed flask. TPP (0.05 g) was added to the solution as a reaction promoter. The reaction solution was then heated to reflux (at about 130-140 °C) for 4h and then cooled at room temperature. The solvent was removed out with rotary evaporator. The product was then heated at 70 °C under vacuum for 6 h to give a semisolid product.¹⁴ Yield 90%. Elemental analysis: Found % (Calcd %) C: 69.21 (69.87), H: 5.80 (5.72), N: 2.88 (2.96). IR (KBr, cm⁻¹): 3471 (O-H), 1636 (C=O), 1638 (C=C), 1367 (C-N), and 917 (oxirane ring). ¹H NMR (ppm,

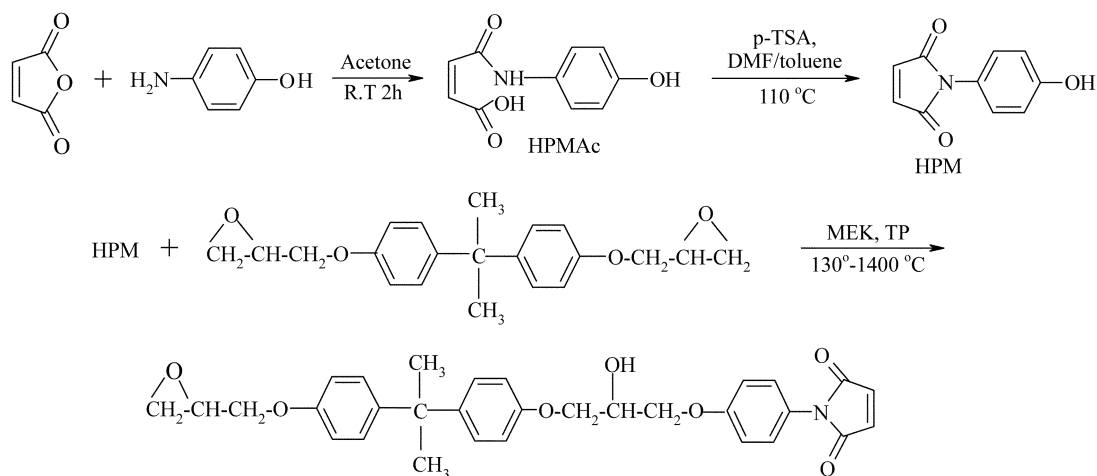
in DMSO-d₆): 1.54 (s, 6H), 2.64-2.66 (t, 1.2H), 2.77-2.81 (t, 1.2H), 3.25-3.28 (m, 1.2H), 3.43 (m, 0.8H), 3.71-3.77 (m, 1.2H), 3.95 (b, 3.2H), 4.20-4.25 (m, 1.2H), 5.39 (b, 0.8H), 6.71-7.29 (m, 12.8H). Softening point: 110-112 °C. Epoxy equivalent weight (MIEB-13) = 451 (calculated value 445). Epoxy equivalent weight (MIEB-11) = 369 (calculated value 362).

Preparation of cured epoxy resins. The cured epoxy resins were obtained from thermally curing of maleimide epoxy resin (MIE) with amines such as 1-(2-aminoethyl) piperazine (AEP) and 5-amino-1,3,3-trimethylcyclohexane methylamine isophoronediamine, IPDA (based on hydrogen equivalent weight) were mixed together in methylethylketone solution and cured in oven. The conditions of curing reactions for B-13MIE/AEP, B-13MIE/IPDA, B-11MIE/AEP, and B-11MIE/IPDA compositions were 80 °C (1 h).

Moisture absorption and chemical resistance measurements. The above cured maleimide epoxy resins were cut into small specimens of 25 × 25 mm and edges of specimens were coated with the same matrix system in order to avoid the moisture absorption through cut edges by capillary action. All the specimens were weighed bone dry in Sartorius balance. To start with, the initial weights were noted at room temperature.¹⁵ The samples were then immersed in water/alkali/solvent/acid for different intervals of time at room temperature. and then taken out, wiped, and dried with tissue paper, and weighed.

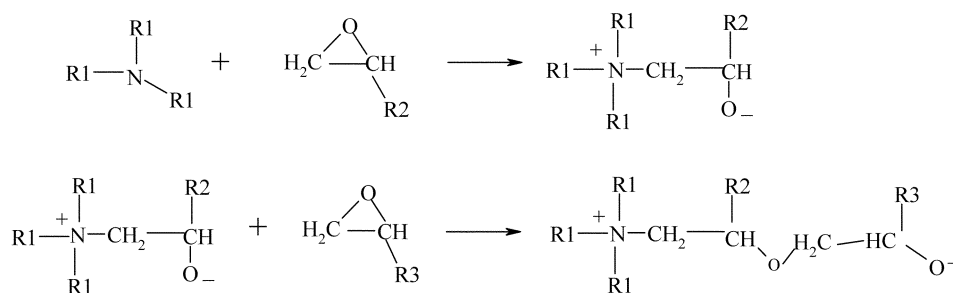
Results and Discussion

Preparation of MIE epoxy compounds. The preparation of the maleimide-epoxy compounds (MIE) were performed through by reacting HPM with a diglycidylether of bisphenol-A (B-13/B-11) via addition reactions between the phenol group and the oxirane group (Scheme 1). Owing to the high viscosity of the resulting products, a solution process was carried out for the above mentioned reactions with 500 ppm of triphenylphosphine as a catalyst and

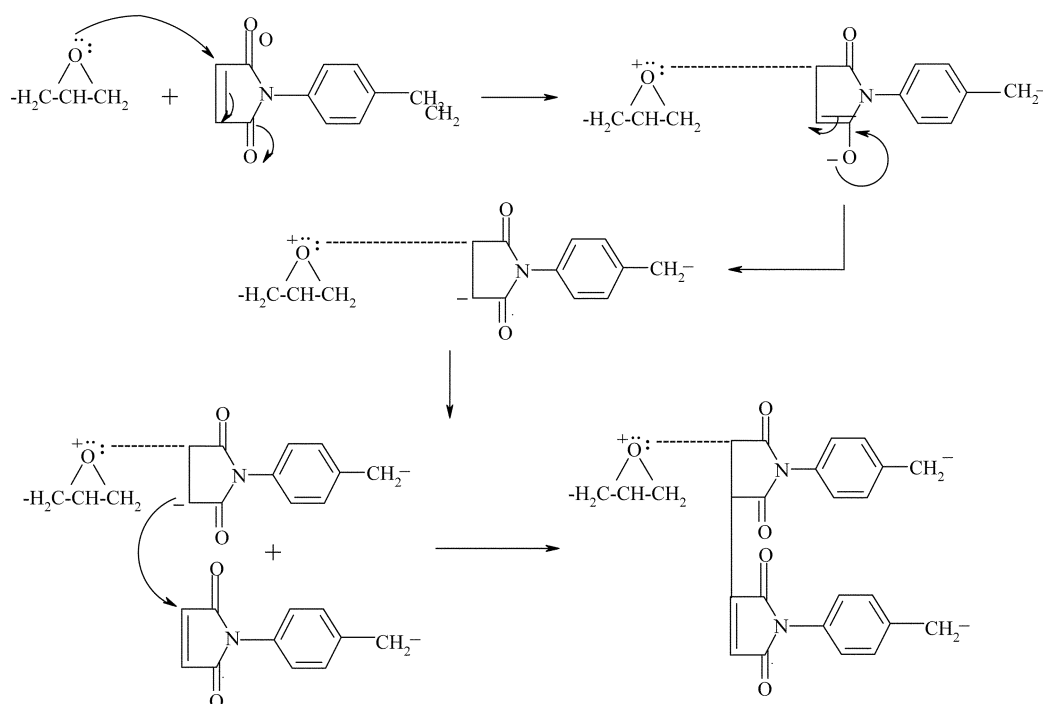


MIE

Scheme 1



Scheme 2



Scheme 3

methylethylketone as a solvent. The epoxy equivalent weight values of the maleimide-epoxy compounds calculated from reaction compositions were consistent with the values obtained from titration experiments. This result implies the high conversions of the reactions between phenol groups and oxirane rings. The above reaction was monitored by FTIR (Fig. 5). The decrease in the intensity of the absorption peak of the oxirane ring at 917 cm^{-1} clearly indicated the decrease in concentration of oxirane rings as the reaction proceeds. The chemical structure of the resulting maleimide epoxy compound obtained was confirmed by the presence of the following absorption peaks at 1367 cm^{-1} (C-N), 1711 , 1778 and 716 (imide group), and 1698 cm^{-1} (C=C). The authenticity of maleimide epoxy compounds was also confirmed by the elemental analysis. The maleimide epoxy compounds obtained were highly viscous liquid, and this may be due to incorporation of the heterocyclic hard imidophenyl groups, and increase of molecular weight.

In addition to IR and elemental analysis, the ^1H NMR analysis on the MIE compound also indicated the proposed chemical structure as shown in the (scheme 1) (Fig. 6). The

appearance of the absorption peaks at about 3.95 ppm (ring opened oxirane ring, $-\text{OCH}_2\text{CH}(\text{OH})-$) and 5.39 ppm ($-\text{COH}$) demonstrated the performance of the addition reaction between HPM and B-11/B-13. The peaks at about 2.64, 2.77, 3.25, 3.75, and 4.24 ppm showed the typical oxirane absorptions, and the peak at 1.54 ppm exhibited the absorption of the isopropyl group. Moreover, the HPM/B-11/B-13 unit ratios were directly calculated from the peak area ratios of the absorption at 6.71-7.29 ppm (aromatic proton and $\text{CH}=\text{CH}$), and the absorption peak at 1.54 ppm (isopropyl group), and the results were coincident with the feeding ratios of HPM/B-11/B-13 for every MIE compounds. Additionally, the chemical structures of MIE compounds were confirmed with the experimental results of elemental analysis. All the above evidences indicate that MIE obtained is MI-monobifunctional bisphenol-A epoxy compound.

Preparation of cured epoxy resins. The probable mechanism of curing of epoxy oxirane ring with amines and self addition of maleimide groups with curing agents is as shown in Scheme 2 and 3 respectively.^{17,18}

In this way a cross-linked structure can be built up.

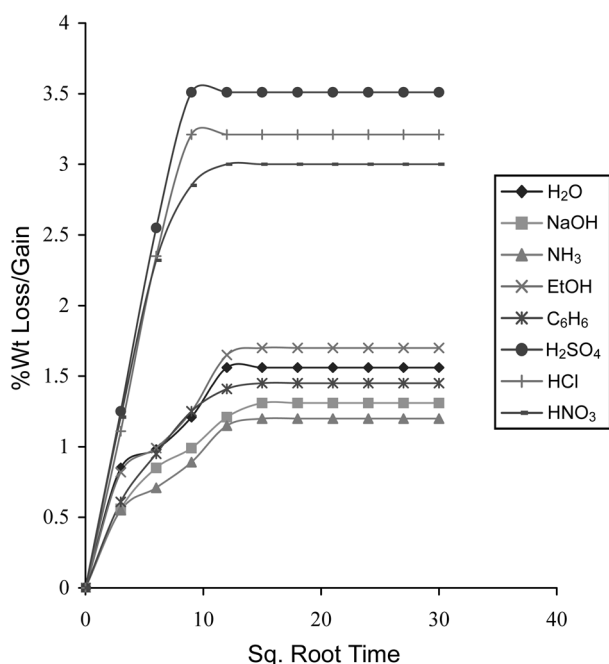


Figure 1. Moisture/Acid/Alkali/Solvent resistance of MIEB-13 with AEP at room temperature.

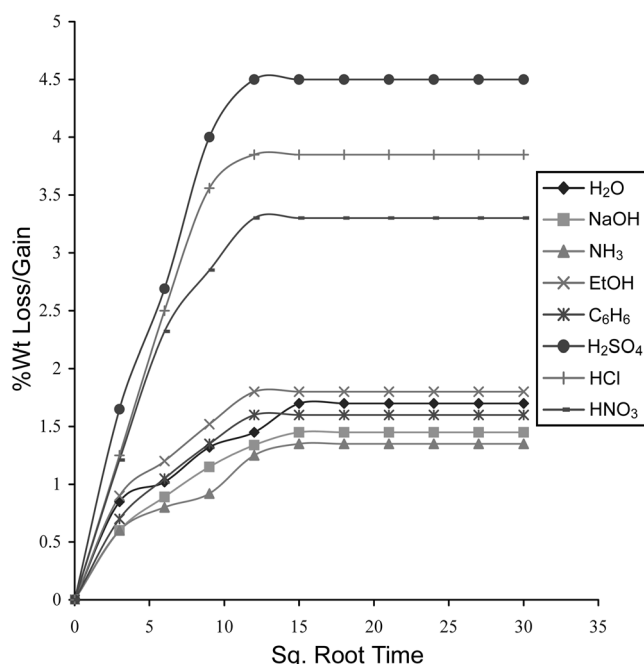


Figure 3. Moisture/Acid/Alkali/Solvent resistance MIEB-13 with IPDA at room temperature.

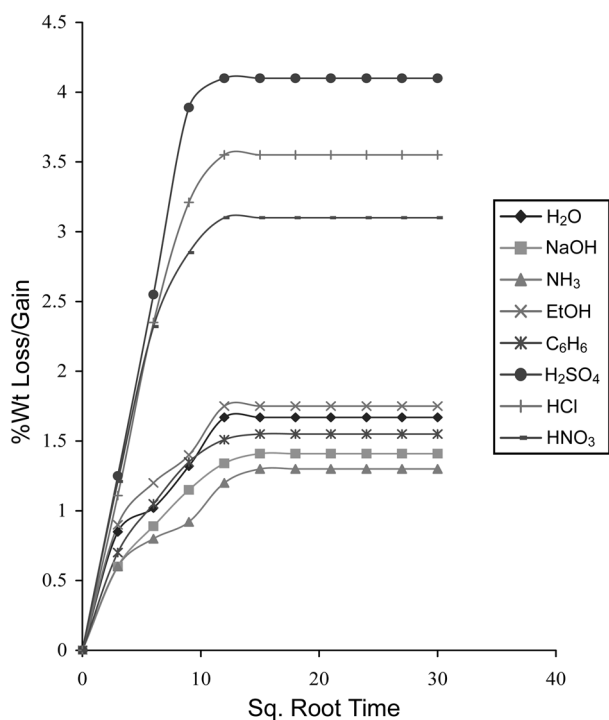


Figure 2. Moisture/Acid/Alkali/Solvent resistance MIEB-11 with AEP at room temperature.

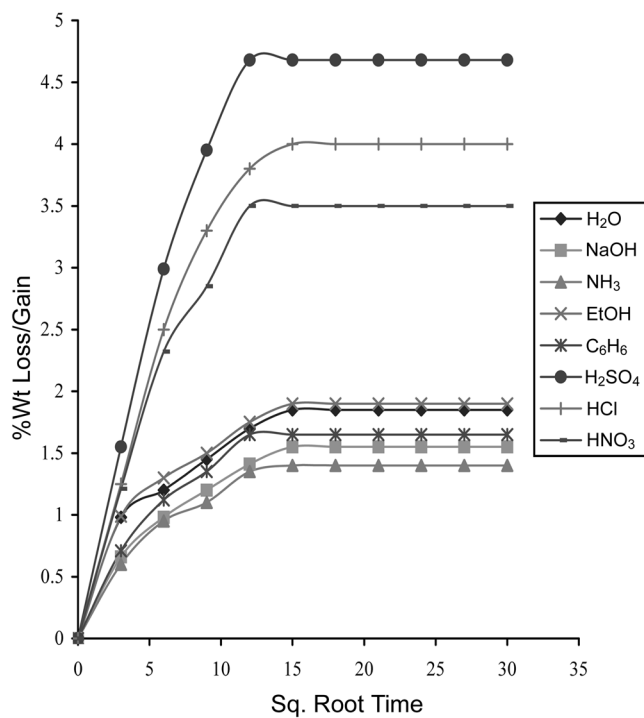


Figure 4. Moisture/Acid/Alkali/Solvent resistance MIEB-11 with IPDA at room temperature.

Moreover, the maleimide groups might also crosslink through self-addition reaction under heating during thermal curing. Since the curing compositions were based on the hydrogen equivalent weight of amines, most of the amine groups were expected to react with oxirane groups at low temperature region. Since almost no amino groups were left to react with maleimide group, only self-addition reactions

would have occurred for maleimide groups in the curing reaction. The resulting products were expected to possess high cross-linking densities.

Thermal properties of the cured epoxy resin. The thermal stability of the maleimide epoxy resins was investigated with thermo gravimetric (TGA/DTA) analysis in air atmosphere (Fig. 7-10). The thermograms of the cured

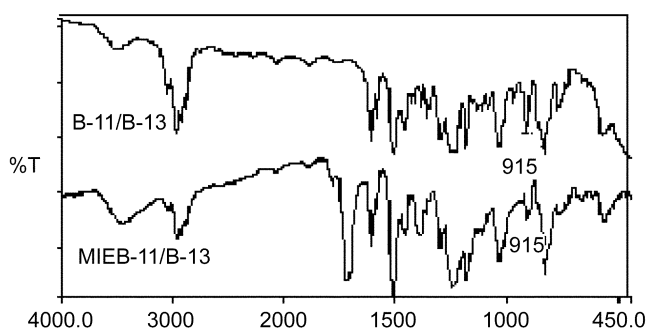


Figure 5. FT-IR Spectrum of MIE.

maleimide epoxy resins clearly indicate that the thermal stability of cured resins was improved with the incorporation of maleimide groups.^{17,18} With the incorporation of the maleimide groups, the IDT of the epoxy resin was increased (Table 1). The enhancement due to incorporation of maleimide groups on the thermal stability of epoxy resins was thus demonstrated. On the other hand, the IPDT also systematically increased with incorporation of maleimide groups. The high IPDT (Table 1) of the maleimide-modified epoxy resins indicates high thermal stability for the cured maleimide epoxy compounds.

Moisture absorption and chemical resistance measurements. The above cured maleimide epoxy resins were cut into small specimens of 25 × 25 mm and edges of specimens were coated with the same matrix system in order to avoid the moisture absorption through cut edges by capillary action. All the specimens were weighed bone dry in Sartorius balance. To start with, the initial weights were noted at room temperature.¹⁵ The samples were then immersed in water/alkali/solvent/acid for different intervals of time at room temperature, and then taken out, wiped, and

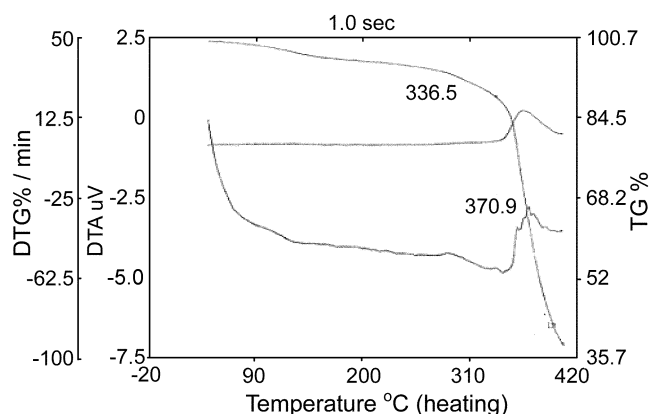


Figure 7. Thermogram Analysis of MIEB-13 with AEP

dried with tissue paper, and weighed.

The % moisture absorbed was calculated by measuring the weights of the specimen periodically using the following equation.

$$\% \text{ Moisture Abs} = \frac{(\text{Specimen weight at any time} - \text{Weight of the dry specimen})}{\text{Weight of the dry specimen}} \times 100$$

The plots of moisture absorption vs. square root of time were constructed (Figure 1-4) to note the saturation limits of the absorbed moisture. From the figures it is observed that initially the water uptake increased, and showed a flat profile exhibiting Fickian type behaviour.¹⁵ The maximum moisture absorption under a given condition of temperature and humidity in case of maleimide epoxy resins with our amine systems showed a decreasing trend. Further more, it was observed that in case of AEP/MIEB-13 and IPDA/MIEB-13

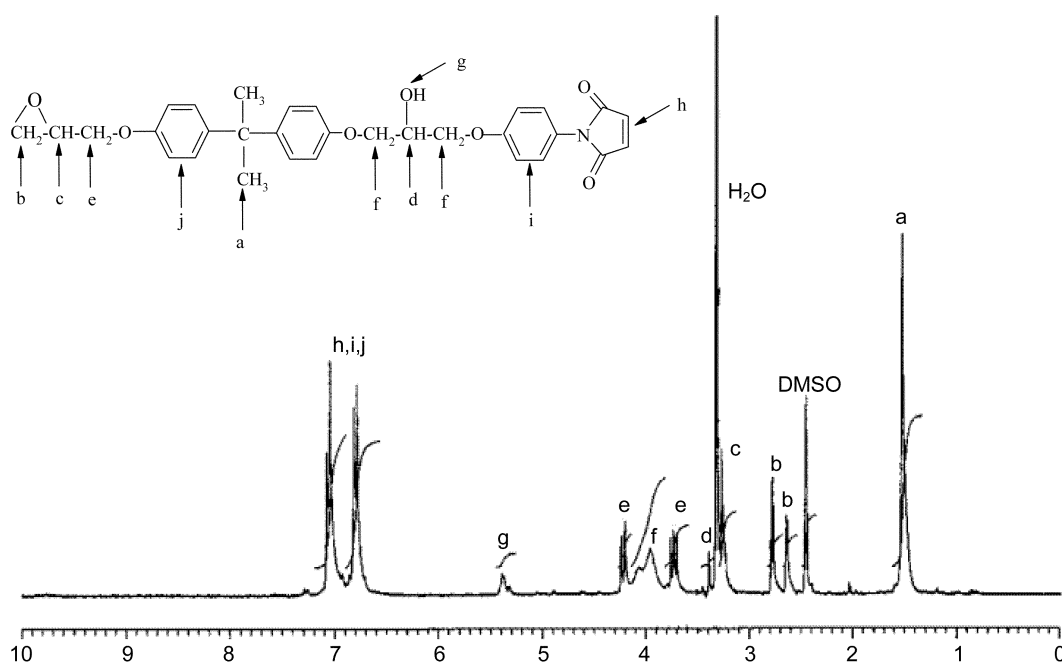


Figure 6. ¹H NMR Spectra of MIE.

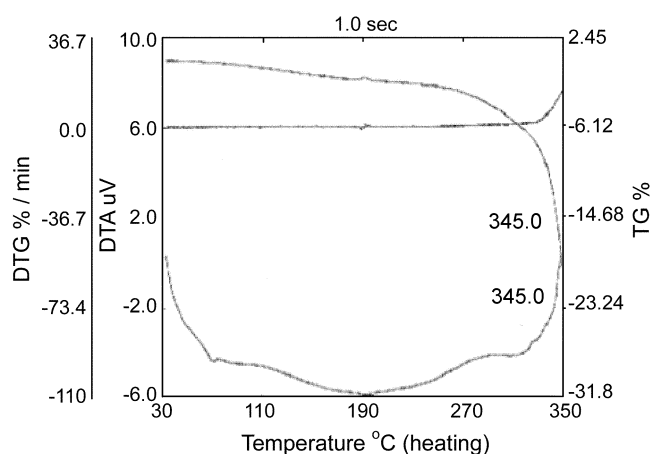


Figure 8. Thermogram Analysis of MIEB-11 with AEP.

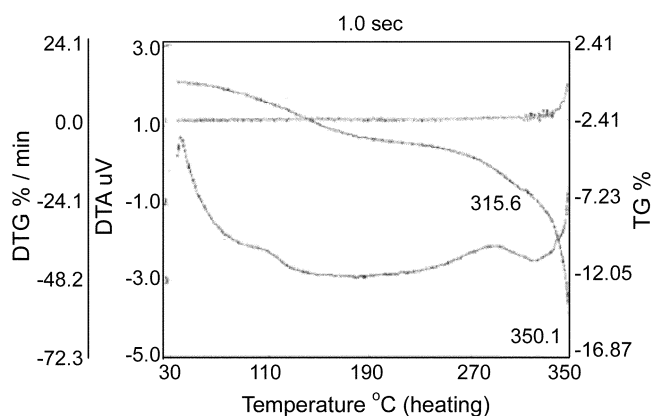


Figure 9. Thermogram Analysis of MIEB-13 with IPDA.

systems, AEP cured resin is more resistant towards moisture absorption than IPDA. This may be because of the presence of tertiary nitrogen atom in case of AEP¹⁹ (acts as catalyst), which accelerates the curing rate very much, compared to IPDA. This was the case too in the case of B-11.

Similar behaviour was observed in case of acid/solvent/alkali resistance measurements (Figures 1-4). The maximum moisture/acid/alkali/solvent resistance content under a given condition of temperature in case for maleimide epoxy resins with our amine (AEP and IPDA) systems are shown in the Table 2. These data clearly indicate that the cured maleimide epoxy resin with the curing agents (AEP and IPDA) shows more resistance to water absorption and other chemicals compared to the traditional epoxy cured resin with the same amines.

Table 2. The maximum moisture/acid/alkali/solvent resistance content under a given condition of temperature (25 °C).

Sl. No	System	% Weight Gain					% Weight loss		
		H ₂ O	10% NaOH	NH ₃	C ₂ H ₅ OH	C ₆ H ₆	H ₂ SO ₄	HCl	HNO ₃
1	MIEB-13 + AEP	1.56	1.31	1.20	1.70	1.45	3.51	3.21	3.00
2	MIEB-11 + AEP	1.67	1.41	1.30	1.75	1.55	4.1	3.55	3.10
3	MIEB-13 + IPDA	1.7	1.45	1.35	1.80	1.60	4.50	3.85	3.85
4	MIEB-11 + IPDA	1.85	1.55	1.40	1.90	1.65	4.68	4.00	3.50

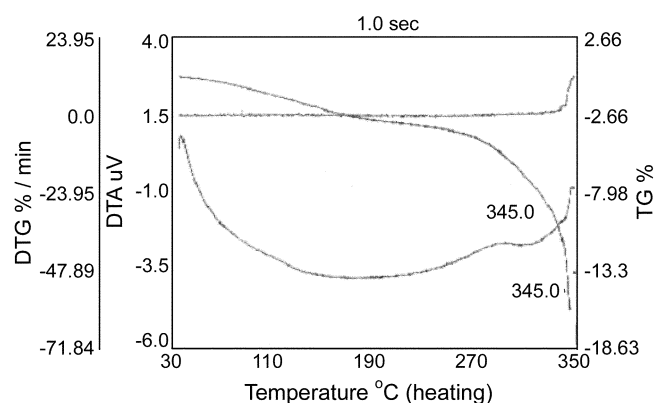


Figure 10. Thermogram Analysis of MIEB-11 with IPDA.

Table 1. Thermal Analysis of the cured epoxy resin: evaluation with TGA/DTA under air atmosphere

Sl. No	System	IDP (°C)	IPDT (°C)
1	MIEB-13 + AEP	336.5	370.9
2	MIEB-11 + AEP	350.0	350.0
3	MIEB-13 + IPDA	315.6	350.1
4	MIEB-11 + IPDA	345.0	345.0

Conclusion

Phenylmaleimido group was successfully incorporated into bisphenol-A type epoxy resins (B-13 and B-11) to result in compounds possessing both oxirane ring and maleimide reactive groups. The cured resins obtained by thermally curing of the maleimide epoxy (MIE) compounds with AEP and IPDA exhibited excellent thermal stability and good chemical (acid/alkali/solvent) and water absorption resistance.

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