

## PREPARATION AND REACTIVITY STUDIES OF MALEIMIDOPHENYL GLYCIDYLETHER WITH AMINES

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**ABSTRACT.** The hybrid thermosetting maleimido epoxy compound 4-(N-maleimidophenyl) glycidylether (N-MPGE) was prepared by reacting N-(4-hydroxyphenyl) maleimide (HPM) with epichlorohydrin by using benzyltrimethylammonium chloride as a catalyst. The resulting compound possessed both the oxirane ring and maleimide group. The curing reaction of N-MPGE with amines as curing agents such as tetraethylenepentamine (TEPA), bishexamethylenetriamine (BHMT), 2-methyl pentamethylenediamine (2-MPMDA) and 2,2,4-trimethyldiamines (2,2,4-TMDA) was studied. The cured samples exhibited good thermal stability and excellent chemical (acid/alkali/solvent) and water absorption resistance. Morphological studies by the SEM technique further confirmed the phase homogeneity network of the cured systems.

**KEY WORDS:** Amine, Epoxy resin, Maleimide, Curing, Epichlorohydrin

### 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. Other major applications of epoxy resins include the manufacture of printed circuit boards, composites, tooling and casting, adhesives and putties. Civil engineering uses include flooring, crack injection, grouts and sealants, paving and concrete flooring application. Epoxies can be employed in two-pack, ambient cured maintenance coatings. People have used amines, anhydrides, fatty acids, acrylics, polyesters, polyisocyanides and amides as curing agents to study the effect on the curing rate and related 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 compounds [3] provide a convenient approach of enhancing the thermal stability of epoxy resins. Therefore, epoxy resins were cured with reactive polyimides [4], polyamic acid [5], and imido-modified curing agents [6] to introduce imide structure into epoxy resin. The thermal stability of the above mentioned imido epoxy resins was significantly levelled 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 also received attractive attentions, due to the similar curing conditions and processing properties of the epoxy resins and maleimides. Maleimide-epoxy resins usually showed appropriate properties between epoxy and maleimide resins. Thus, both the intercrossed and the interpenetrating systems (IPN) based on bismaleimides and epoxy resins were prepared and exhibited good thermal and

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mechanical properties. Additionally [8, 9], since imide groups could provide char formation in the condensed phase to improve polymers flame retardant properties, epoxy resins modified with imide compounds through chemical reactions or physical blending have been reported to show good flame retardant properties [10-12].

In the present work a maleimide compound with hydroxyl group was first synthesized. Maleimidophenyl glycidylether epoxy compounds were consequently obtained through a simple addition reaction between the oxirane group of epichlorohydrin and hydroxyl group of maleimide. The resulting maleimidophenyl glycidylether epoxy compound 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 maleimidophenyl glycidylether epoxy compounds with different amines and to study properties of the cured resin systems. The cured samples were found to have good thermal stability, chemical resistance and water absorption resistance. The cured samples exhibited homogeneity with no phase separation which was confirmed by scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

Maleic anhydride and 4-amino phenol were purchased from s.d. Fine-chemicals (India). Tetraethylenepentamine (TEPA), bishexamethylenetriamine (BHMT), 2-methyl pentamethylenediamine (2-MPMDA) and 2,2,4-trimethyl diamines (2,2,4-TMDA) and benzyltrimethyl ammonium chloride (BTAC) were supplied by Aldrich Chemicals (Germany). Dimethylformamide (DMF), *p*-toluenesulphonic acid, toluene, sodium bicarbonate, ethyl acetate, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCl, C<sub>6</sub>H<sub>6</sub>, CH<sub>3</sub>CH<sub>2</sub>OH, NH<sub>3</sub> and NaOH were obtained from s.d. Fine-chemicals (India).

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

Experimental procedure for the synthesis and characterization of *N*-(4-hydroxy phenyl) maleimide (HPM) was according to literature protocol [20-22].

### Synthesis of 4-(*N*-maleimidophenyl) glycidylether (*N*-MPGE)

HPM (0.1 mol, 18.7 g) was mixed with 100 g of epichlorohydrin (ECH) in a 500 mL 3-necked flask equipped with a stirrer, condenser, and a nitrogen inlet. After adding BTAC (1.8 g, 0.01 mol) to the solution, the mixture was stirred under nitrogen for 24 h at 60 °C. Excess ECH was removed under reduced pressure and the solid residue was dissolved in ethyl acetate, washed with water and dried over MgSO<sub>4</sub>. The product was purified by chromatography using a silica column and ethyl acetate/toluene (1:1 in vol.) to give MPGE product (yield 55%; melting point, 45–50 °C, epoxy equivalent weight = 254). IR (KBr, cm<sup>-1</sup>): 715 (C=O bending), 912 (oxirane-ring), 1248, 1037 (Ph–O–CH<sub>2</sub>), 1375 (C–N stretching), 1609 (C=C), 1715 (C=O symmetric stretching), 1781 (C=O asymmetric stretching), 3070 (C–H, imide group). <sup>1</sup>H NMR (300 MHz, DMSO-D<sub>6</sub>, ppm): 2.72 and 2.87 (2H, –(O)CH<sub>2</sub>); 3.68 (1H, –CH<sub>2</sub>CH(O)–); 4.13–4.26 (2H, –Ph–OCH<sub>2</sub>–); 6.87 (2H, –CH=CH–); 7.03–7.54 (4H, aromatic protons).

### Preparation of cured epoxy resins

The cured epoxy resins were obtained by thermally curing of epoxy resin (*N*-MPGE) with amines such as tetraethylenepentamine (TEPA), bishexamethylenetriamine (BHMT), 2-methyl pentamethylenediamine (2-MPMDA) and 2,2,4-trimethyl diamines (2,2,4-TMDA) as curing

agents. Epoxy resin (N-MPGE) and the amines were dissolved in methylethylketone to form a homogeneous solution. After evaporating the solvent at ambient temperature the mixture was cured with specific curing condition to result in cured resins. The curing conditions are listed in Table 1.

Table 1. Preparation and curing conditions and thermal stability of cured systems evaluation with TGA and DSC under air atmosphere.

S. No	System	Curing conditions	Thermal stability		DSC data	
			IDT ( $^{\circ}\text{C}$ )	IPDT ( $^{\circ}\text{C}$ )	T <sub>endo</sub> ( $^{\circ}\text{C}$ )	T <sub>exo</sub> ( $^{\circ}\text{C}$ )
1	N-MPGE + TEPA	50 $^{\circ}\text{C}$ (5 h), 110 $^{\circ}\text{C}$ (5 h)	380	410	75	330
2	N-MPGE + BHMT	50 $^{\circ}\text{C}$ (5 h), 110 $^{\circ}\text{C}$ (5 h)	375	415	77	340
3	N-MPGE + 2-MPMDA	50 $^{\circ}\text{C}$ (5 h), 110 $^{\circ}\text{C}$ (5 h)	350	400	78	365
4	N-MPGE + 2,2,4-TMDA	50 $^{\circ}\text{C}$ (5 h), 110 $^{\circ}\text{C}$ (5 h)	330	400	80	369

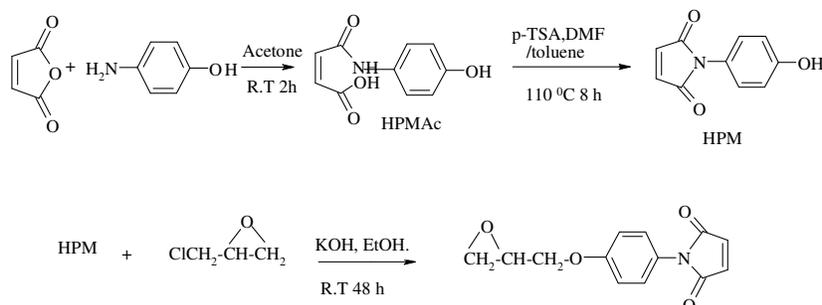
#### *Moisture absorption and chemical resistance measurements*

Water absorption and chemical resistance tests were conducted as explained in literature [21, 22]. The chemical resistance tests were carried out in acetone, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCl, C<sub>6</sub>H<sub>6</sub>, CH<sub>3</sub>CH<sub>2</sub>OH, NH<sub>3</sub> and NaOH solutions. We used the same thickness samples for the tests and an average of three sample readings was recorded at room temperature.

## RESULTS AND DISCUSSION

#### *Preparation of N-MPGE epoxy compounds*

4-(N-maleimidophenyl)glycidylether (N-MPGE) was prepared from reacting epichlorohydrin with N-(4-hydroxyphenyl)maleimide (HPM) which was synthesized according to the Scheme 1. The first attempt of synthesizing N-MPGE was performed under basic conditions by employing KOH as a catalyst. The crude product was analyzed with thin layer chromatography and showed complicated compositions containing various by-products. The pure N-MPGE was obtained by means of column chromatography with a low yield of less than 25%. The strong basic condition of the reaction might cause the hydrolysis of the imide groups of HPM and N-MPGE, therefore, to result in mixed by-products. To compensate this flaw, benzyltrimethyl ammonium chloride (BTAC), which was reported being useful in the synthesis of glycidyl phosphinate compounds without causing hydrolysis of the phosphinate compounds [23-28], was utilized in the synthesis of N-MPGE. The product yield was significantly raised to about 75%. The chemical structure of N-MPGE compound was assigned on the basis of FT-IR, elemental analysis and <sup>1</sup>H NMR studies. The absorption peak at around 915 cm<sup>-1</sup> which was observed in the FT-IR spectrum of N-MPGE, which conforms the oxirane group. The absorption peaks deriving from the cyclic maleimide group were also observed at 1781 cm<sup>-1</sup> (C=O asymmetric stretching), 1718 cm<sup>-1</sup> (C=O symmetric stretching), 1375 cm<sup>-1</sup> (C-N stretching), and 1610 cm<sup>-1</sup> (C=C). Other specific absorption bands at 3070 cm<sup>-1</sup> (C=C-H), 1245 cm<sup>-1</sup> and 1037 cm<sup>-1</sup> (Ph-O-CH<sub>2</sub>), and 1513 cm<sup>-1</sup> (phenyl) gave more evidence to the obtained compound having the expected chemical structure. The <sup>1</sup>H NMR signals observed are assigned as: 2.89 ppm and 2.68 ppm (2H, - (O) CH<sub>2</sub>); 3.24 ppm (1H, -CH<sub>2</sub>CH(O)-); 3.58 ppm (2H, -Ph-OCH<sub>2</sub>-); 6.87 ppm (2H, -CH=CH-); and 7.03-7.54 ppm (4H, aromatic protons). The chemical shifts of the absorption peaks and the area ratios of the peak integration were found to be consistent with the expected chemical structure. Moreover, the experimental results of titration of epoxy equivalent weight also demonstrated the successful of synthesis of N-MPGE compound.



Scheme 1. Preparation of N-maleimidophenyl glycidyl ether of epoxy compound.

N-MPGE is soluble in most of the industrially solvents, such as acetone, methylethylketone, tetrahydrofuran, N,N-dimethylacetamide, dimethylsulfoxide, ethyl acetate, methanol, ethanol, 1-methyl-2-pyrrolidone and dimethylformamide. The good organo-solubility of N-MPGE suggests its good processability associate with the current industrial processes.

#### *Curing reaction of N-MPGE with amines*

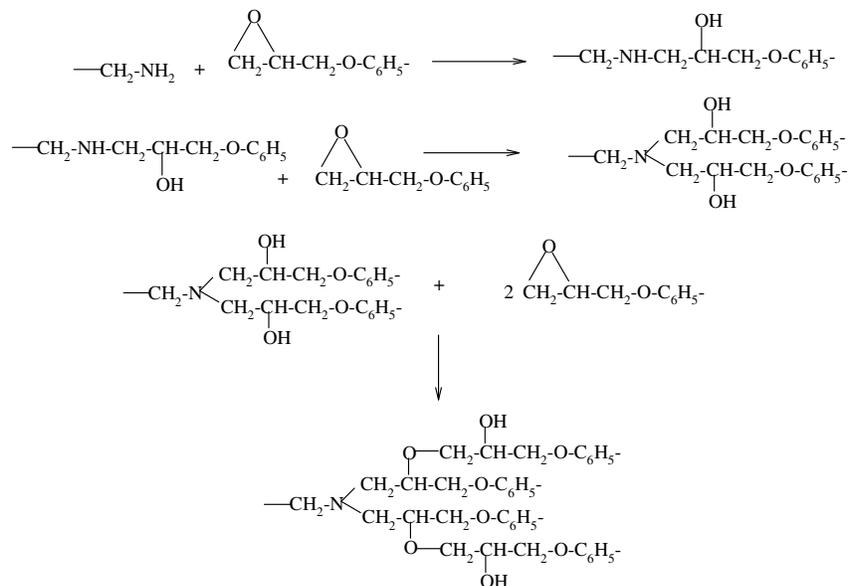
The curing reaction of the above resin (N-MPGE) was carried out with different amines such as tetraethylenepentamine, bishexamethylenetriamine, 2-methyl pentamethylene- diamine and 2,2,4-trimethy diamines, based on their hydrogen equivalent weights. N-MPGE resin was taken on a aluminum foil of about 5 cm diameter and the amine was added and mixed thoroughly for a minute using a thin wooden stick. In all the cases, the temperature of the reaction mixture at different intervals of time were measured using an infrared gun and the completion of the curing process is indicated when the reaction mixture became nonsticky to a wooden stick. The results are listed in Table 2.

Table 2. Reactivity studies data of N-maleimidophenyl glycidyl ether of epoxy compound with amines.

S. No	System	Wight of N-M-PGE (g)	Weight of amine (g)	Curing time (min)	Exotherm ( $^{\circ}$ C)
1	N-MPGE + TEPA	5	0.25	40	65
2	N-MPGE + BHMT	5	0.35	45	60
3	N-MPGE + 2-MPMDA	5	0.46	55	45
4	N-MPGE + 2,2,4-TMDA	5	0.67	55	45

The epoxide groups in epoxy resin react with the amine to form a highly cross-linked, three dimensional network. The curing process converts the epoxy resins into a hard, infusible and rigid material. All the curing reactions were carried out at room temperature ( $26^{\circ}$ C). The mechanism of curing reaction is given in Scheme 2.

The high reactivity of tetraethylenepentamine (TEPA) in these series of amines studied is due to the presence of five amine groups. Bishexamethylenetriamine (BHMT) which contains three amine groups showed slightly less reactivity with epoxy compared tetraethylenepentamine (TEPA). The other two curing agents such as pentamethylenediamine (2-MPMDA) and 2,2,4-trimethy diamines (2,2,4-TMDA) having only two amino groups are present. May be because of this these two curing agents are least reactive compared to other two amines. This is because of the increase in electron density of the chain as the number of amino groups increase and thereby enhances the rate of polymerization. Hence, the overall reactivity was found to be in the order: TEPA > BHMT > 2-MPMDA and 2,2,4-TMDA.

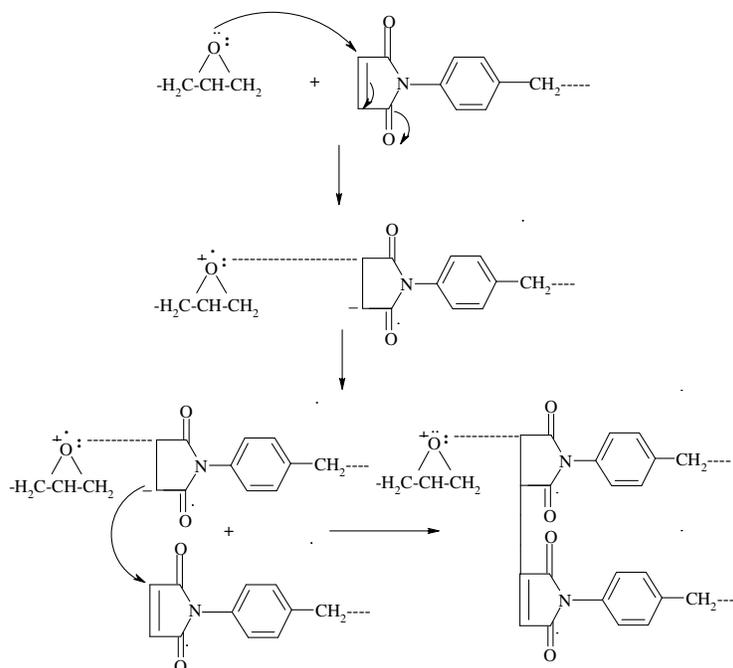


Scheme 2. The reaction mechanism of amine with oxirane ring.

It is also well known that the oxirane group of N-MPGE reacts with amines during the polymerization. Moreover, the maleimide groups might crosslink through self-addition reaction (Scheme 3) under heating [19]. Therefore, while curing N-MPGE with curing agents, all the three above-mentioned reactions might occur. In this work, the curing compositions were taken with the same stoichiometric amounts of the amine curing agent and oxirane groups. Therefore, most of the amine groups are expected to react with oxirane groups at low temperature region. Since almost no amino group was left to react with maleimide group, only self-addition reaction occurred for maleimido groups in the curing reaction. The resulting products obtained were therefore supposed to have high cross-linking densities.

#### Differential scanning calorimetric studies of cured systems

Dynamic DSC thermograms of the systems N-MPGE + TEPA, N-MPGE + BHMT, N-MPGE + 2-MPMDA and N-MPGE + 2,2,4-TMDA are represented in Figure 1. The dynamic scans were performed at a heating rate of 10 °C/min and the data are summarized in the Table 1. From the figure it is clear that all the cured systems exhibit similar behaviour. The peak at 75 to 80 °C corresponds to the melting point of the cured epoxy systems. The peak at around 300 to 315 °C is attributed to the exothermic curing reactions of the above mentioned epoxy and amines systems and the maximum of the exothermic peak obtained at around 330-360 °C. At about 400 °C, the completion of curing process indicates the absence of exotherm peaks in the post cure in epoxy amine systems.



Scheme 3. Self-addition reaction of maleimide groups of N-MPGE compound.

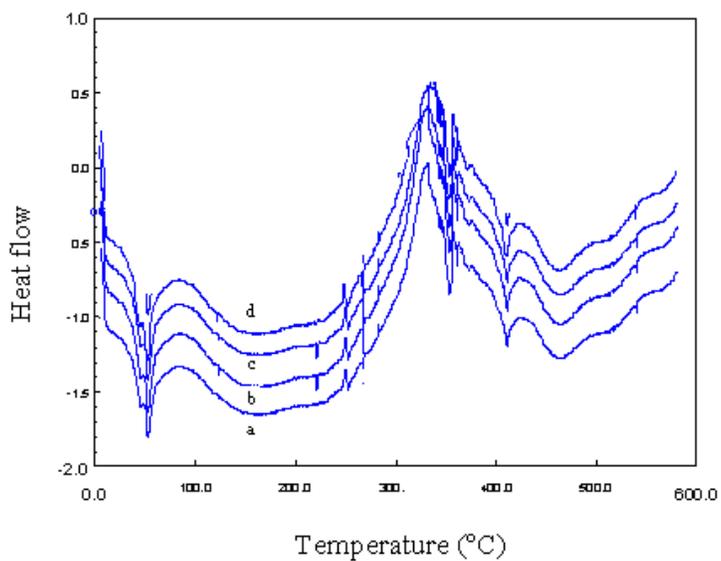


Figure 1. Dynamic DSC thermograms of the five systems: A) N-MPGE + TEPA, B N-MPGE + BHMT, C) N-MPGE + 2-MPMDA D) N-MPGE + 2,2,4-TMDA.

*Thermal properties of the cured systems*

The thermal stability of the maleimidophenyl glycidylether epoxy resins was investigated with thermogravimetric analysis (TGA) in air atmosphere (Figure 2). The thermograms of these cured systems clearly indicate that the thermal stability of cured resins was improved with the incorporation of maleimide groups into the epichlorohydrin [16-18]. With the incorporation of the maleimide groups, the initial decomposition temperature (IDT) of the maleimidophenyl glycidylether epoxy resin was increased (Table 1). The enhancement of the thermal stability due to incorporation of maleimide groups on maleimidophenyl glycidylether epoxy resins was thus demonstrated. On the other hand, the integral procedural decomposition temperature (IPDN) also systematically increased with incorporation of maleimide groups. The high IPDN indicates that the cured maleimidophenyl glycidyl epoxy compound with our chosen amines such as TEPA, BHMT, 2-MPMDA and 2,2,4-TMDA shows good thermal stability.

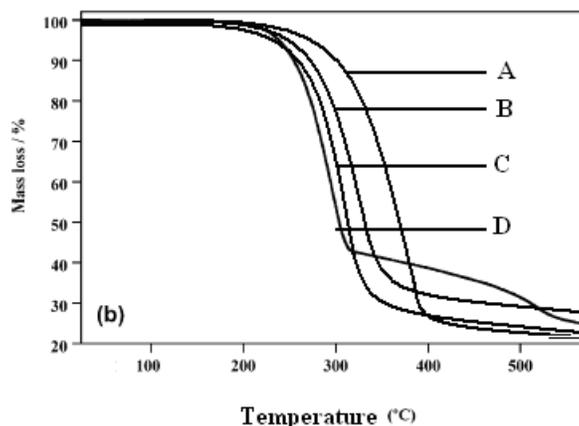


Figure 2. TGA curves for cured systems: A) N-MPGE + TEPA, B) N-MPGE + BHMT, C) N-MPGE + 2-MPMDA, and D) N-MPGE + 2,2,4-TMDA under air atmosphere.

*Moisture and chemical resistance measurements of cured systems*

The data of chemical and water absorption curves of the cured N-MPGE + TEPA, N-MPGE + BHMT, N-MPGE + 2-MPMDA and N-MPGE + 2,2,4-TMDA systems are shown in Table 3 and Figure 3. The goal of this study was to describe the interactions between the absorbed moisture and epoxy network. The transport of moisture through the epoxy network involves cooperative motion of water molecules and 3-dimensional resin network. The equilibrium water absorption of both systems was almost 1.71% by weight. One of the major factors affecting water absorption is the presence or absence of hydrophilic groups in the cross-linked network. There are the same types of hydrophilic groups in the present systems. There are also other relevant factors to consider, notably free volumes, which generally increases with cross-link density because of the development of a rigid macromolecular framework. It can be seen in Figure 4, that there is a sharp increase in water absorption, initially which can be due to water penetration into structural defects and cavities on the surface of samples, and a slow process of water absorption which reaches to its equilibrium values of 1.7% immersion in the distilled water at room temperature. Figure 3 shows that initially there is a sharp increase in water absorption due to water penetration into structural defects and cavities on the surface of samples. After some time a slow process of water absorption reaches its equilibrium at room temperature.

Table 3. The maximum moisture/acid/alkali/solvent resistance content under a given condition of temperature (25 °C).

S. No	System	% Weight gain					% Weight loss		
		H <sub>2</sub> O	10% NaOH	NH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl	HNO <sub>3</sub>
1	N-MPGE+TEPA	1.79	1.59	1.30	1.79	1.70	4.35	4.25	3.50
2	N-MPGE+BHMT	1.80	1.63	1.31	1.90	1.74	4.41	4.30	3.50
3	N-MPGE+2-MPMDA	1.89	1.72	1.52	1.98	1.80	4.75	4.70	3.80
4	N-MPGE+2,2,4-TMDA	1.90	1.72	1.51	1.98	1.88	4.80	4.80	4.00

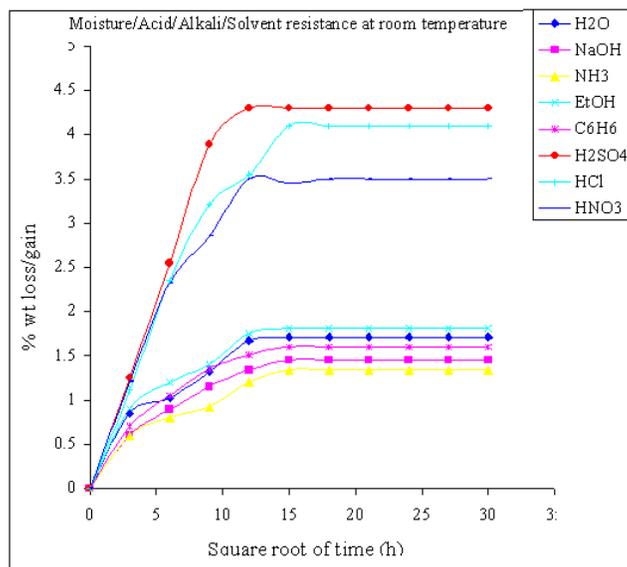


Figure 3. Chemical/moisture absorption resistance of N-MPGE with TEPA at room temperature.

In the case of chemical resistance measurements the cured systems were studied with ammonia. The more complex the network is, the longer it takes for ammonia to diffuse in to the system to reach to equilibrium. The weight reduction in ammonia reached to its equilibrium value of about 1.4% after 110 h immersion. The acid resistance of the cured systems was tested in the concentrated H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCl. In these cases, all the cured systems show similar trend and the almost same weight reduction magnitude. As it is seen from in Figures 3, there is almost a total of 4-4.3% weight loss which can probably be related to epoxy resins that are not contributed in the network formation. This is because; in the present study we used low concentration of amines as curing agent.

The plots of moisture absorption *vs* square root of time were constructed (Figure 3) to note the saturation limits of the absorbed moisture. From the figures it is observed that initially the water uptake increases, and shows a flat profile exhibiting Fickian type behavior [21-23]. The maximum moisture absorbed under a given condition of temperature and humidity in case of maleimidophenyl glycidyl epoxy compound with our amines showed a decreasing trend. The cured samples were found to have good chemical resistance (acid/alkali/solvent) and water absorption resistance compared to traditional epoxy amine cured systems [18, 21, 22]. This may be because of the incorporation of maleimide groups into the epichlorohydrin, which provides a cyclic imide structure and high cross-linking density to the cured resins.

The maximum moisture/acid/alkali/solvent resistance contents under a given condition of temperature in case of N-MPGE with amines systems are given in Table 3. These data clearly indicate that the cured maleimidophenyl glycidylether epoxy compound with the curing agents such as TEPA, BHMT, 2-MPMDA and 2,2,4-TMDA shows more resistance to water absorption and other chemicals resistance, when compared to traditional epoxy with amine systems [18, 22]. The TEPA and BHMT cured system exhibited slightly high resistant towards moisture/acid/alkali/solvent absorption than other amine cured systems. This may be due to the presence of more number of amine groups. This can possibly be credited to the presence of more number of amine groups, and which accelerates the curing rate very much, resulting in the high cross-link density network when compared to other amines [24, 25].

#### *Morphology studies of cured systems*

The morphologies of fracture surfaces of cured maleimidophenyl glycidyl epoxy with amines (TEPA, BHMT, 2-MPMDA and 2,2,4-TMDA) were examined using scanning electron microscope. All the above mentioned five systems exhibit similar morphology. From the Figure 4 it is clear that the fracture surfaces of the neat maleimidophenyl glycidylether epoxy compound with amine exhibit a homogenous pattern. All the cured samples show no formation of distinct domains, confirming the formation of a homogeneous network in all the maleimidophenyl glycidylether epoxy cured systems.

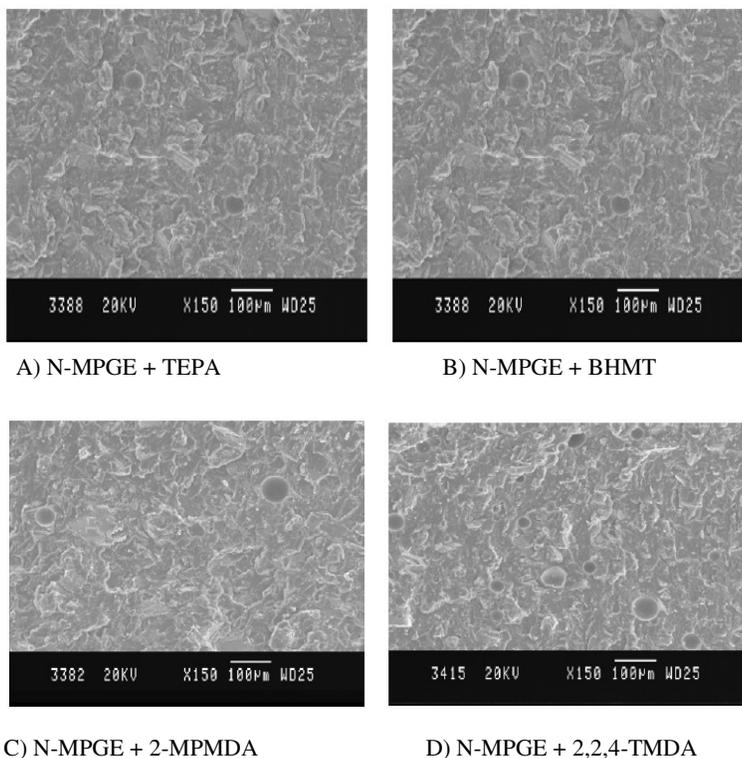


Figure 4. Fractured morphology analysis of cured maleimidophenyl glycidylether with different amines. A) N-MPGE + TEPA, B) N-MPGE + BHMT, C) N-MPGE + 2-MPMDA D) N-MPGE + 2,2,4-TMDA.

## CONCLUSIONS

Phenylmaleimido group was successfully incorporated into epichlorohydrin, the resulting compound possessing both oxirane ring and maleimido reactive groups. Amines act as very good curing agents in the case of maleimidophenyl glycidylether epoxy compound. The cured samples exhibited good thermal stability and excellent chemical (acid/alkali/solvent) and water absorption resistance. Morphological studies by the SEM technique further confirmed the phase homogeneity of the cured systems.

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