# Curing and Thermal Behaviour of Epoxy Resin in the Presence of Pyromellitic Dianhydride and Imidazole

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**ABSTRACT:** The curing behaviour of DGEBA was investigated by differential scanning calorimetry in the presence of varying amounts of PMDA. The molar ratio of DGEBA : PMDA was varied as 1 : 0.8, 1 : 1, 1 : 1.5, 1 : 2.0, and 1 : 2.5. The heat of polymerization ($\Delta H$) was found to be maximum at a molar ratio of 1 : 0.8 (DGEBA : PMDA). To study the effect of imidazole content on the curing behaviour, varying amounts of imidazole, i.e., 0.1, 0.15, 0.2, and 0.3% (w/w) were used keeping the ratio of DGEBA : PMDA (1 : 0.8) constant. A broad exotherm was observed in all the samples. A significant decrease in the peak exotherm was observed when 0.1% imidazole was used. Further increase in the imidazole concentration up to 0.2% resulted in a marginal decrease in the peak exotherm temperature. Thermal stability of epoxy resin, cured isothermally, was evaluated by recording thermogravimetric traces in nitrogen atmosphere. The percent char yield was highest in case of resin sample, IP1-30 (i.e., DGEBA (1 mole) cured using 0.8 mole of PMDA in the presence of 0.3 (w/w) of imidazole). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2593–2598, 2007

**Key words:** diglycidyl ether of bisphenol–A (DGEBA); pyromellitic dianhydride (PMDA); imidazole; curing; thermal stability

## INTRODUCTION

Epoxy resins have been used in many industrial applications, such as in surface coatings, adhesives, structural composites, printed circuit boards, and insulating materials, for electronic devices because of their good heat and chemical resistance and superior mechanical and electrical properties.[1,2] However, the conventional epoxy resins are inefficient to satisfy the required properties in the field of advanced materials, which require high thermal and flame resistance.[3–5] Several approaches were used in the past to improve thermal stability and flame retardancy of epoxy resins.[6,7] The properties can be varied by the modification of epoxy backbone, i.e., either during synthesis or cure using curing agents of different structures.

The Curing of epoxy resin has been extensively investigated using amines of varying structures and of varying molecular weight[8,9] however, very few reports are available using acids/anhydride as curing agents. Anhydride curing agents find use in most of the important application of epoxy resins particularly in casting and laminates. Chemical reactions that take place during cure determine the resin morphology, which, in turn, determines the properties of the cured thermoset. On the other hand, aromatic primary amines are known to impart high glass transition temperature ($T_g$) to cured resins. Recent studies[10,11] demonstrated that epoxy resins cured with imidazoles have superior physical properties when compared with those with amines. Imidazole-cured resins are widely used in the electronic industry as molding and sealing compounds because they exhibit better heat resistance, lower tensile elongation, higher modulus, and wider range of cure temperatures than amine cured systems.

Imidazoles have been used to cure epoxy resins catalytically, i.e., homopolymerisation of epoxide groups or by initiating the esterification reaction in epoxy phenol groups. The mixture of imidazole and bis (4-carboxyphenyl) dimethyl silane (CPA) was investigated in our laboratories.[12] The reaction between phenyl glycidyl ether and imidazoles is well documented in the literature.[13–18] Barton et al.[14,15] concluded that both 1 : 1 and 2 : 1 adducts were formed from the epoxide ring opening by "pyridine type" nitrogens. These adducts were assumed to be the catalysts that initiated the polymerization process, and therefore imidazole became permanently incorporated in to the epoxy networks. Although extensive work has been done using imidazoles but nobody has investigated the use of mixture of dianhydrides, diamines, and imidazole. It was therefore considered of interest to investigate

systematically the effect of incorporation of mixture of curing agents.

In the present work, the curing behaviour of DGEBA with stoichiometric or nonstoichiometric amounts of pyromellitic dianhydride (PMDA) in the presence or absence of varying concentration of imidazole (0.1–0.3% w/w) was investigated by differential scanning calorimetry (DSC). The Curing behaviour of DGEBA in the presence of 4,4′-diaminodiphenyl sulfone : pyromellitic dianhydride (DDS:PMDA) mixtures in the ratio 1 : 0, 0.75 : 0.25, 0.5 : 0.5, and 0.25 : 0.75 were also investigated.[19] Thermal stability of the epoxy resins cured isothermally was analyzed using dynamic thermogravimetry (DTG).

## EXPERIMENTAL

### Materials

Diglycidyl ether of bisphenol-A (DGEBA, Grade LY556; epoxy equivalent 177) was procured from Hindustan Ciba Geigy (Delhi, India) Imidazole (Loba Chemie, Mumbai, India), and PMDA (Merck, Mumbai, India), ethyl methyl ketone were used as received.

### Sample preparation

The samples were obtained by mixing DGEBA:PMDA in the ratio of 1 : 0.8, 1 : 1, 1 : 1.33, 1 : 1.5, 1 : 2.0, and 1 : 2.5 using minimum amount of methyl ethyl ketone (MEK) as a solvent and have been designated as P1, P2, P3, P4, P5, and P6, respectively. MEK was used to facilitate uniform mixing of curing agents with DGEBA. The solvent was then removed by vacuum stripping. Freshly prepared samples were used for monitoring the curing behaviour of DGEBA in the presence of stoichiometric/nonstoichiometric amounts of PMDA.

To evaluate the effect of imidazole content on the curing behaviour, fresh samples were obtained by mixing 1 mole of DGEBA with 0.8 mole of PMDA using MEK as solvent and varying amounts of imidazole, i.e., 0.1, 0.15, 0.2, and 0.3% (w/w) and the samples have been designated as IP1-10, IP1-15, IP1-20, and IP1-30, respectively. In the sample designation, I stand for imidazole, P1 for DGEBA:PMDA mixture in the ratio of 1:0.8 and numerical suffix 10, 15, 20, and 30 represent the percentage of imidazole multiplied by 100.

### Equipments

#### Curing studies

For curing studies, TA 2100 thermal analyzer having 910 DSC module was used for recording DSC scans
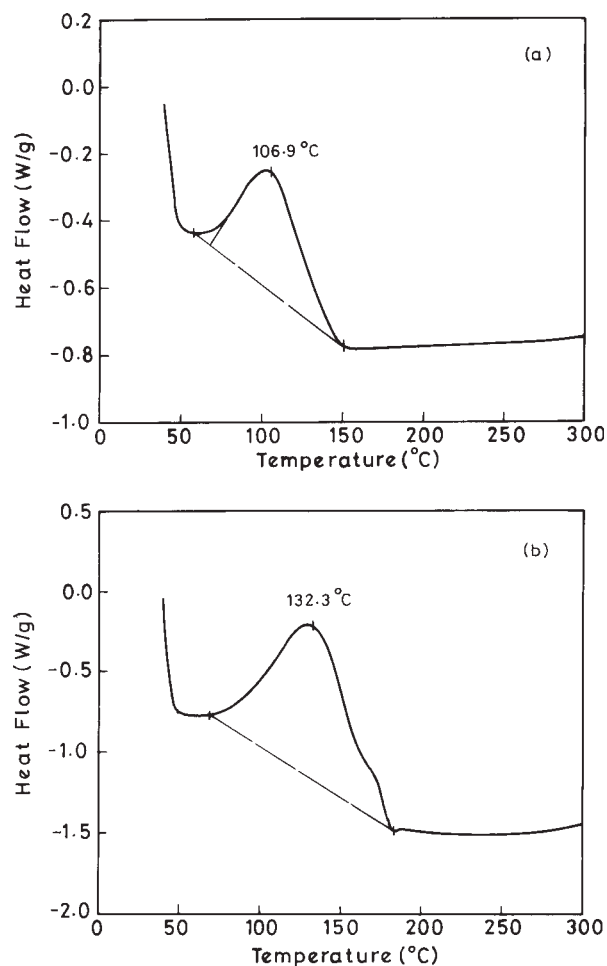
**Figure 1** DSC scans of epoxy resin with varying molar ratios of PMDA at heating rate of 10°C/min. (a) P1, (b) P2.

in static air atmosphere. DSC traces were recorded at a heating rate of 10°C/min using 5 ± 2 mg of sample.

Isothermal curing of DGEBA in the presence of varying amounts of PMDA or a mixture of PMDA and imidazole was done by heating in an air oven at 180°C for 3 h and the DSC scans of cured samples were recorded at a heating rate of 10°C/min. Powdered samples were used for recording DSC traces by taking 5 ± 2 mg of sample.

#### Thermal stability

Thermal stability of the isothermally cured samples [curing done by heating mixture of DGEBA and PMDA/or PMDA + imidazole in the hot air oven at (180 ± 10)°C for 3 h] was evaluated by recording TG/DTG traces in nitrogen atmosphere (flow rate 60 cm³/min). Rheometric Scientific thermal analyzer having TG 1500+ module was used for recording TG/DTG traces. A sample size of 10 ± 2 mg and a heating rate of 20°C were used in each experiment.

| Sample designation | Moles of PMDA | $T_i$ (°C) | $T_{onset}$ (°C) | $T_p$ (°C) | $T_f$ (°C) | $\Delta H$ (J/g) | $T_g$ (°C) |
|---|---|---|---|---|---|---|---|
| P1 | 0.8 | 92.0 | 110.5 | 185.0 | 267.9 | 248.3 | 226.8 |
| P2 | 1.0 | 92.9 | 113.0 | 173.6 | 255.0 | 246.6 | 227.9 |
| P3 | 1.33 | 101.6 | 115.1 | 168.2 | 250.5 | 188.2 | 228.1 |
| P4 | 1.5 | 103.6 | 131.0 | 177.3 | 230.1 | 143.0 | 238.1 |
| P5 | 2.0 | 107.4 | 114.3 | 175.3 | 239.3 | 237.8 | 232.6 |
| P6 | 2.5 | 107.0 | 116.4 | 140.8 | 233.9 | 179.8 | 231.1 |

## RESULTS AND DISCUSSION

### Curing studies

Curing of epoxy resin depends on the nature of the curing agent as well as on the stoichiometry. A broad curing exotherm was observed in all the DSC scans. To evaluate the curing behaviour of DGEBA in the presence of PMDA, DSC scans were recorded, using stoichiometric and nonstoichiometric amounts of PMDA, in the presence or absence of imidazole. The exothermic transitions associated with curing were characterized by noting the following parameters:

$T_i$ = kick-off temperature, where the curing starts.

$T_{onset}$ = temperature where the first detectable heat is released. It was obtained by extrapolation of the steepest portion of curve.

$T_p$ = temperature of peak position of exotherm.

$T_f$ = temperature of the end of curing exotherm.

$\Delta H$ = heat of curing, calculated by measuring the area under the exothermic transition.

Typical DSC scans of DGEBA cured using 0.8 and 1.0 mole of PMDA obtained at a heating rate of 10°C/min are shown in Figure 1(a,b). The results of DSC scans are summarized in Table I. A broad exothermic transition was observed in the temperature range of 92–268°C. $T_p$, $T_i$, $T_{onset}$, and $T_f$ did not show any definite trend with increasing PMDA content whereas $\Delta H$ was found to decrease with increasing amounts of PMDA except in sample P5, which showed higher value of $\Delta H$ as compared with P4 or P6. On the basis of $\Delta H$ value, the optimum concentration of PMDA required to cure DGEBA (1 mole) was found to be 0.8 moles. DGEBA has a functionality of two whereas PMDA has a functionality of four. If all the groups are participating in the polymerization then one would have expected an optimum concentration of DGEBA : PMDA as 1 : 0.5, whereas optimum was observed at a ratio of 1 : 0.8. This could be due to the increased viscosity of the cured system, which hinders the access of the functional group for curing. In case of DGEBA : CPA, optimum concentration was observed as 1 : 1.75.

Mixtures of diaminodiphenyl sulfone (DDS and CPA or phthalic anhydride (PA) and CPA in ratios of 1 : 0, 0.25 : 0.75, 0.5 : 0.5, 0.75 : 0.25) were also used to investigate the curing behaviour of DGEBA.[12]

Absence of exothermic transition in the DSC scans of isothermally cured resins showed that the curing was complete. A shift in the base line was observed from which the glass transition temperature ($T_g$) was noted as a midpoint inflexion temperature. Figure 2 shows DSC scans of isothermally cured epoxy resin samples (a) P1, (b) P2, (c) P3, (d) P4, (e) P5, and (f) P6. $T_g$ increased as the PMDA content was increased from 0.8 to 1.5 moles (Table I). Further increase in PMDA content resulted in a decrease in $T_g$. Glass transition temperature, which is a measure of segmental mobility, depends on the rigidity of the polymer backbone as well as on the crosslink density. Increase in $T_g$ with increasing amount of PMDA could be due to the formation of more compact net-
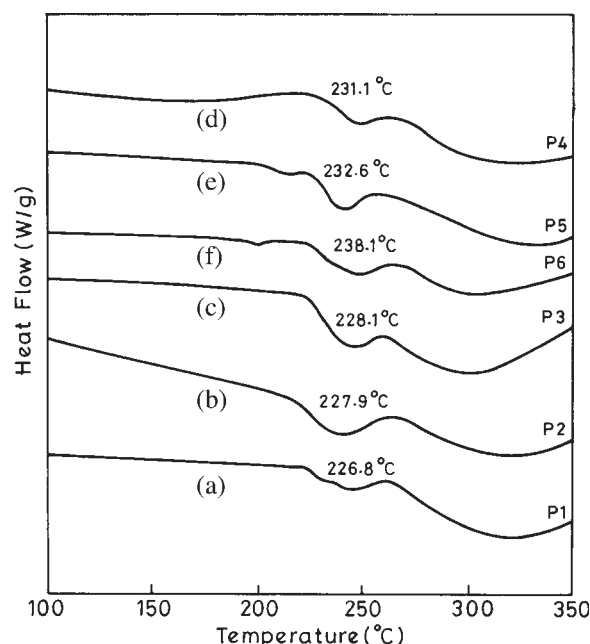


**Figure 2** DSC scans of isothermally cured epoxy resin samples: (a) P1, (b) P2, (c) P3, (d) P4, (e) P5, (f) P6.

work structure, which might decrease with increasing amount of PMDA content. Higher amounts of curing agents lead to the formation of linear structures and a decrease in the crosslink density. Therefore a decrease in $T_g$ observed with increasing amounts of PMDA could be explained on the basis of this theory. Similar observations have been made by authors who have investigated curing behaviour of DGEBA with varying amounts curing agent.[20]

To investigate the effect of imidazole content on the curing behaviour of DGEBA in the presence of PMDA, the ratio of DGEBA : PMDA was kept constant as 1 : 0.8 and the DSC scans were recorded in the presence of varying amounts of imidazole ranging from 0.1 to 0.3. Figure 3 show the DSC scans of epoxy resin with PMDA containing different amounts of imidazole and the results are summarized in Table II. Incorporation of 0.1% (w/w) of imidazole resulted in a significant decrease ($\sim 20°C$) in the peak exotherm temperature ($T_p$). Further increase in the amount of imidazole (i.e., up to 0.2%) resulted

**TABLE II**
**Results of DSC Scans of DGEBA with 0.8 Mole PMDA Containing Different Amounts of Imidazole (Heating Rate = 10°C/min)**

| Sample designation | Imidazole % (w/w) | $T_i$ (°C) | $T_{onset}$ (°C) | $T_p$ (°C) | $T_f$ (°C) | $\Delta H$ (J/g) |
|---|---|---|---|---|---|---|
| P1 | 0 | 92.0 | 110.5 | 185.0 | 267.9 | 248.3 |
| IP1-10 | 0.1 | 94.9 | 135.7 | 165.6 | 233.4 | 167.6 |
| IP1-15 | 0.15 | 100.3 | 140.3 | 160.1 | 209.8 | 162.8 |
| IP1-20 | 0.2 | 92.0 | 123.9 | 158.3 | 250.9 | 221.9 |
| IP1-30 | 0.3 | 95.4 | 109.8 | 137.5 | 172.1 | 212.9 |

in a marginal decrease in $T_p$ followed by a substantial decrease, i.e., $\sim 21°C$ as the imidazole concentration was increased further to 0.3%. $\Delta H$ for curing was significantly lower in the presence of imidazole. Imidazoles are the catalytic curing agents for DGEBA, which results in the formation of hydroxyl groups, which might undergo reaction with anhydride leading to the formation of ester linkages. Heat evolved would be much higher in the opening of epoxy ring as compared with esterification reaction.
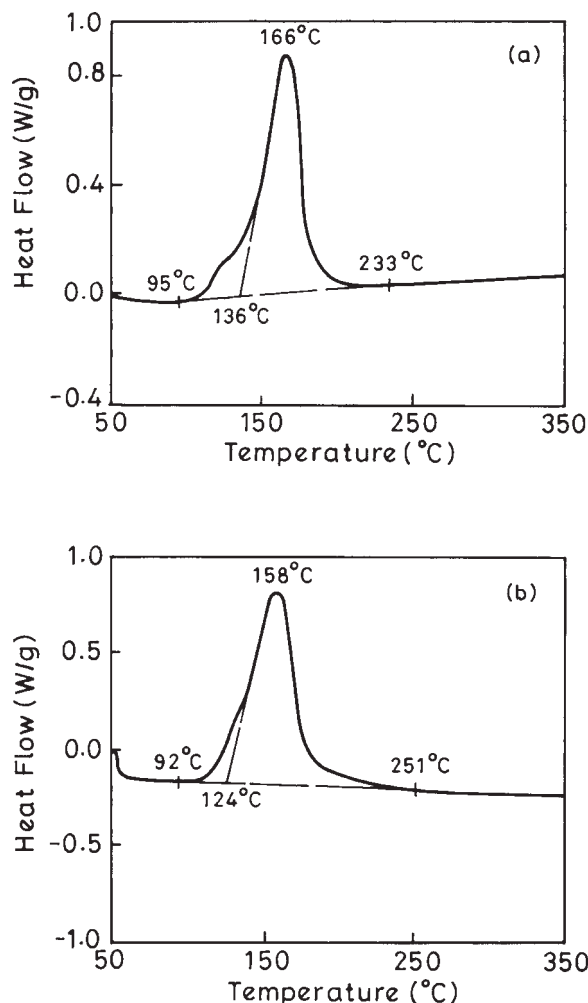


**Figure 3** DSC scans of epoxy resin with 0.8 mole of PMDA and varying concentrations of imidazole at heating rate of 10°C/min. (a) IP1-10, (b) IP1-20.



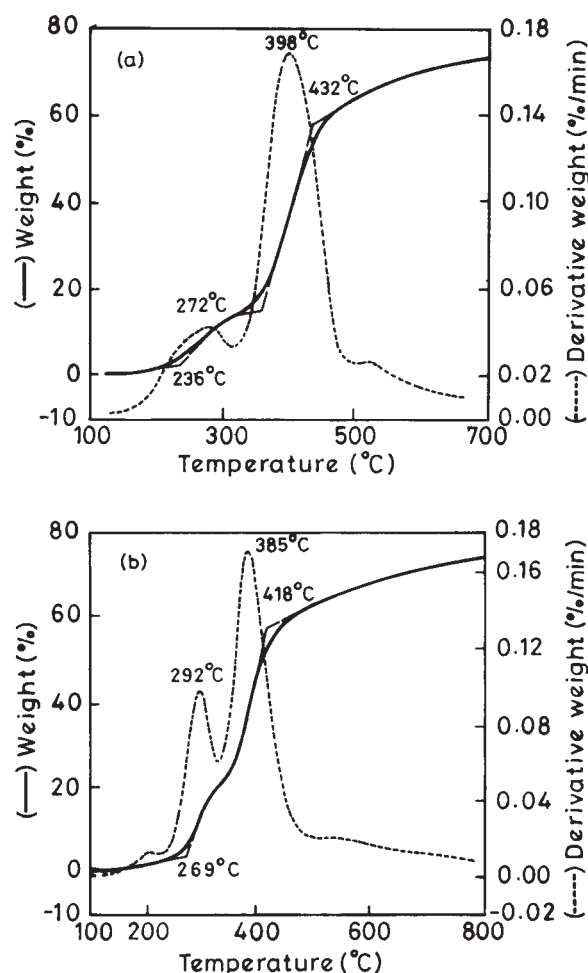**Figure 4** TG/DTG traces of epoxy resins cured isothermally with different molar ratios of PMDA in nitrogen atmosphere at heating rate 20°C/min. (a) P1, (b) P2.
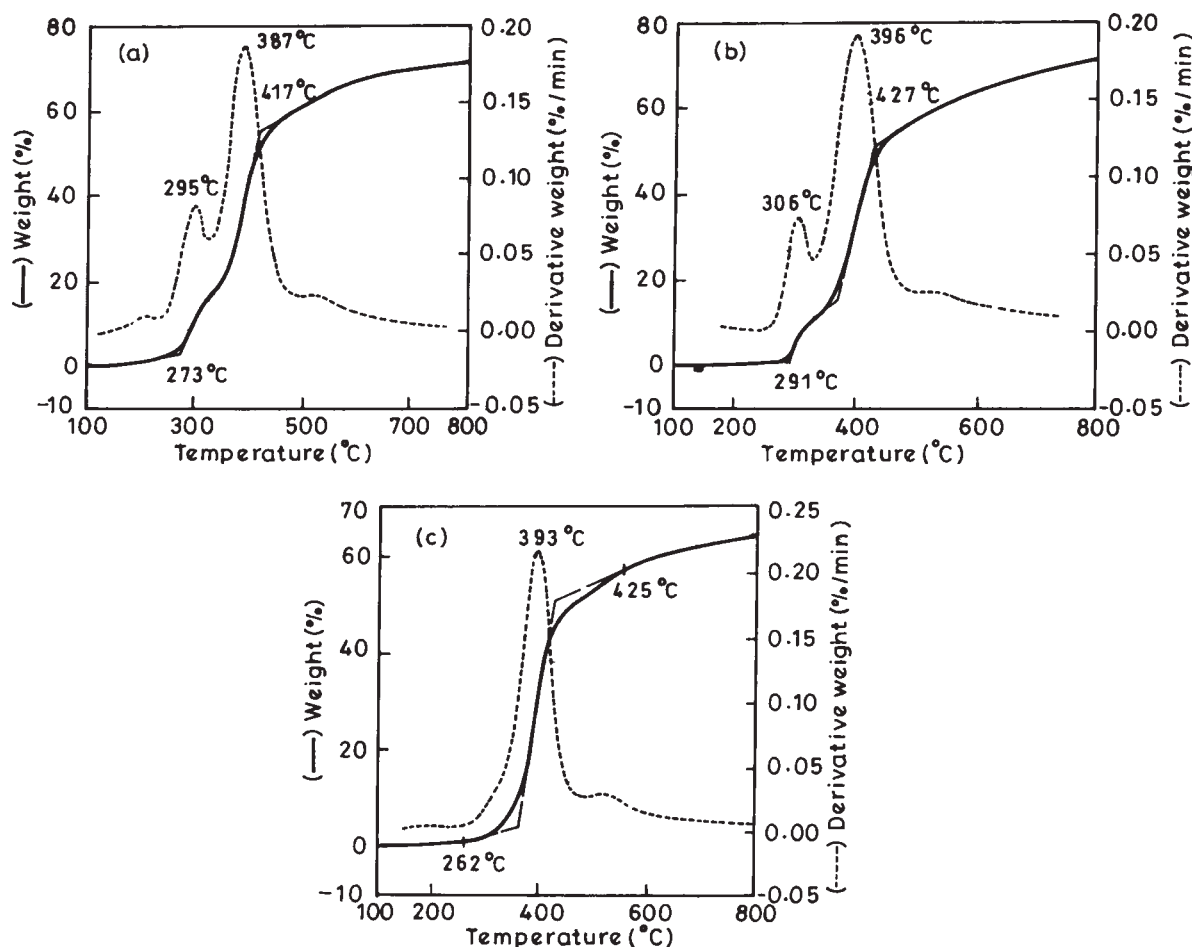
**Figure 5** TG/DTG traces of epoxy resins cured isothermally with 0.8 moles of PMDA in presence of varying amounts of imidazole in nitrogen atmosphere (heating rate 20°C/min). (a) IP1-15, (b) IP1-20, (c) IP1-30.

The lower heat evolved during curing in the presence of imidazole and PMDA could be explained on the basis of catalytic effect of imidazole.

DSC scans of isothermally cured DGEBA : PMDA (1 : 0.8) in the presence of varying amounts of imidazole were recorded. Absence of exothermic transition showed that curing was complete, however shift in the baseline corresponding to $T_g$ was not observed in the temperature range, in which DSC scans were recorded.

**TABLE III**
**Results of TG/DTG Traces of DGEBA Cured Isothermally with Different Concentrations of PMDA at 20°C/min Heating Rate in Nitrogen Atmosphere**

| Sample designation | Moles of PMDA | Degradation step | IDT (°C) | $T_{max}$ (°C) | FDT (°C) | % Char yield at 800°C | LOI (%) |
|---|---|---|---|---|---|---|---|
| P1 | 0.8 | I | 236.2 | 271.9 | 289.7 | 27.1 | 28.3 |
|  |  | II | 294.1 | 397.7 | 431.6 |  |  |
| P2 | 1.0 | I | 269.5 | 291.9 | 360.9 | 26.0 | 27.9 |
|  |  | II | 315.4 | 385.4 | 417.9 |  |  |
| P3 | 1.33 | I | 247.7 | 285.9 | 366.6 | 25.0 | 27.5 |
|  |  | II | 369.4 | 387.0 | 428.5 |  |  |
| P4 | 1.5 | I | 334.1 | 350.2 | 380.3 | 26.8 | 28.2 |
|  |  | II | 334.2 | 388.a9 | 431.2 |  |  |
| P5 | 2.0 | I | 248.6 | 285.2 | 360.0 | 16.2 | 24.0 |
|  |  | II | 362.2 | 381.2 | 397.7 |  |  |
| P6 | 2.5 | I | 251.8 | 293.8 | 361.8 | 21.7 | 26.2 |
|  |  | II | 364.4 | 384.4 | 418.6 |  |  |

**TABLE IV**
**Results of TG/DTG Traces of DGEBA Cured Isothermally with 0.8 Mole PMDA and**
**Different Concentrations of Imidazole at 20°C/min Heating Rate in**
**Nitrogen Atmosphere**

| Sample designation | Imidazole % (w/w) | Degradation step | IDT (°C) | $T_{max}$ (°C) | FDT (°C) | % Char yield at 800°C | LOI (%) |
|---|---|---|---|---|---|---|---|
| IP1-10 | 0.1 | I | 278.1 | 304.5 | 356.1 | 27.3 | 28.4 |
|  |  | II | 359.4 | 391.4 | 432.5 |  |  |
| IP1-15 | 0.15 | I | 273.0 | 295.0 | 364.2 | 28.1 | 28.7 |
|  |  | II | 368.1 | 387.1 | 417.4 |  |  |
| IP1-20 | 0.2 | I | 290.8 | 306.2 | 371.9 | 29.1 | 29.1 |
|  |  | II | 374.4 | 395.8 | 427.3 |  |  |
| IP1-30 | 0.3 | I | 361.8 | 293.1 | 424.8 | 35.7 | 31.8 |

## Thermal stability

Thermal stability of the isothermally cured epoxy resins in presence of varying molar ratios of PMDA/ and PMDA + varying amounts of imidazole (0.1–0.3%) (w/w) was evaluated by recording TG/DTG traces in nitrogen atmosphere. Figures 4 and 5 show the TG/DTG traces of samples (a) P1, (b) P2 and (a) IP1-15, (b) IP1-20, (c) IP1-30, respectively. In all the samples, two-step decomposition was observed except in IP1-30, where it showed single step decomposition. The relative thermal stability of the cured resins was evaluated by comparing initial decomposition temperature (IDT), the temperature of maximum rate of weight loss ($T_{max}$), the final decomposition temperature (FDT), and the percent char yield at 800°C. The results of TG/DTG traces are summarized in Tables III and IV. All the samples were stable up to $(250 \pm 15)$°C.

IDT, $T_{max}$ and FDT increased as the amount of PMDA increased from 0.8 to 1.5. All the resins had a char yield of $26 \pm 1$%. Further increase in PMDA content resulted in a significant decrease in the char yield. IDT, FDT, and $T_{max}$ also showed a decrease. ncorporation of imidazole to DGEBA : PMDA (1 : 0.8) system resulted in an increase in the degradation temperature, whereas char yield changed marginally up to imidazole content of 0.2% (IP1-20). Further increase in imidazole content showed single step degradation with a much higher char yield. This shows that the formation of network structures is dependent on the nature and amount of hardener.

Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resins in accordance to Van Krevelen and Hoftyzer equation.[21]

$$LOI = 17.5 + 0.4 \ CR \qquad (1)$$

where, CR = char yield.

All the samples had LOI values calculated based on their char yield was higher than 28. On the basis of LOI values, such materials can be classified as self-extinguishing resin.

## CONCLUSIONS

From these studies, it can be concluded that the curing behaviour of DGEBA was dependent on the amount of PMDA and heat of curing was maximum when the molar ratio of DGEBA : PMDA was 1 : 0.8. The thermal stability of epoxy resin depends on the structure of the cured network. Thermal stability of epoxy resin cured using mixture of DGEBA : PMDA (1 : 0.8) with 0.3% (w/w) was higher as compared with DGEBA : PMDA without imidazole.

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