# Synthesis and thermal studies of bisphenol-A based bismaleimide

## Effect of nanoclays

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**Abstract** The compound 2,2-bis[4-(4-maleimidophenoxy phenyl)]propane was prepared by the imidization of bisamic acid of 2,2-bis(4-aminophenoxy phenyl)propane. Various nanoclays were blended with this bismaleimide and thermally cured. The structural characterization of the synthesized materials and the thermal properties of the bismaleimide and their blends were investigated through FTIR, $^{1}$H and $^{13}$C NMR, differential scanning calorimetry and thermo gravimetric analysis. Among the various clays investigated, Cloisite 15A shows strong influence on the cure exotherm of bismaleimide. Introduction of clay mineral into bismaleimide shifts the onset of curing exotherm to higher temperature and is nearly 40 °C. The thermal stability of the clay loaded cured bismaleimide increases and the presence of clay particles in the cured bismaleimide matrix enhances the char formation.

**Keywords** Bismaleimide · Nanoclay · FTIR · NMR · DSC · TGA

## Introduction

Recently, polyimides especially aromatic polyimides have more and more applications in microelectronics, automotive, and aerospace sector because of their high thermal stability, mechanical strength, and excellent chemical resistance. It is classified into two types such as addition polyimides and condensation polyimides. Addition polyimides generally possess higher stiffness and dimensional stability than the condensation polyimides due to their high crosslinking network. These high performance polyimides are widely used as matrices for many advanced composites [1, 2]. Polyimide composites are very attractive for various applications due to their high strength to mass ratio and excellent thermal stability [3].

Among the addition polyimides, bismaleimides are the most important polyimide class because of their good thermal stability, low water absorption, and high mechanical properties at high temperature. Additionally, bismaleimides possess many desirable properties such as high tensile strength, corrosion and excellent chemical resistance and hot-wet performance [4]. The two maleimido groups present at the end of the molecule will undergo homo polymerization on heating without the addition of any free radical initiators to result in highly crosslinked and brittle thermosetting polyimides. Bismaleimides can be cured without the evolution of volatiles. One drawback arises from that unmodified bismaleimide resins suffer from brittleness due to their high crosslinking density. Micheal addition of primary or secondary diamines to bismaleimides was used to effect chain extension through thermal curing to reduce the high crosslinking density and brittleness of the polymers [5, 6].

Various processes have been made to improve the properties of polyimides [1, 2, 6–8]. The dispersion of clay particles is one of the method has been well established since 1960s [8]. Nanocomposites are first commercially focused on thermoplastics such as nylon 6 in Toyota R&D labs. By the success of thermoplastic-clay nanocomposites

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like polyethylene oxide/clay, polycaprolactone/clay, and polymethylmethacrylate/clay it has been focused to improve the properties of thermoset resins such as epoxy and polyimide by converting them into clay nanocomposites [9]. The polymer–clay nanocomposites can be formed in one of the three ways, i.e., solution dispersion, in situ polymerization, and intercalation method. In solution dispersion method the preformed polymer solution will mix into the clay layers. Nanocomposites are formed by dispersion and distribution of clay layers into the monomer followed by polymerization in in situ polymerization method. The intercalation method involves mixing of clay layers with polymer pellets while heating the mixture above the softening point of the polymer [10]. Introduction of small amount of nanoclay particles into the system will enhance the properties like mechanical, thermal barrier, optical, and flammable properties [11, 12]. The gas diffusivity of polymer matrix can be reduced by the dispersion of plate-like nanoparticles [8, 13]. The chemical substitution of the clay minerals will resolve the incompatibility between the organophilic polymer matrix and hydrophilic-layered silicates for an example the $Na^+$ montmorillonite clay has been modified to convert the surface from hydrophilic to organophilic [5, 14].

Hu et al. [8] studied the effect of organo silicate clay as filler material on bismaleimide/diallyl bisphenol-A resin system. They observed that when the clay concentration increases, the gelation and rheological behavior of the prepolymer differs. The fillers are also used as modifier to toughen the BMI resin. Jana et al. [15] studied the exfoliation of closite nanoclay in thermoset polyimide. The clay particles increase the thermal and mechanical properties compared to neat resin system.

The present investigation is focused on the synthesis of bisphenol-A based bismaleimide and is blended with various nanoclays such as Cloisite 15A, Bentonite, Nanoclay DK4, Nanoclay DK3, Micro Talc IT Extra, Calcined clay, and Natural clay. The pure bismaleimide and the nanomaterial blended materials are cured thermally. The thermal properties of these materials are investigated using DSC and TG technique and the results are discussed.

## Experimental

### Materials

Bisphenol-A was purchased from SISCO Research Laboratory Pvt. Ltd., Mumbai-400099. Maleic anhydride, p-chloronitrobenzene, and anhydrous sodium acetate were supplied by s.d. fine-chem Ltd., Mumbai-400025. The solvents $N,N'$-dimethyl formamide and acetone were purchased from MERCK Specialist Pvt. Ltd., Mumbai-400018. Palladium 10% on carbon was supplied by

Lancaster Clariant Group Company, Chennai-600017. Anhydrous potassium carbonate was obtained from RanBaxy Laboratories Ltd., New Delhi-160055. Ethyl alcohol and Hydrazine hydrate were purchased from Loba Chemie Pvt. Ltd., Mumbai-400002. All the chemicals were used as received.

### Preparation of 2,2-bis(4-nitrophenoxy phenyl)propane (DN-BPAPCNB)

Bisphenol-A (22.8 g), p-chloronitrobenzene (34.6 g), and anhydrous potassium carbonate (30.4 g) were taken in a round bottom flask containing 125 mL of $N,N'$-dimethyl-formamide. After few minutes, the orange colored reaction mixture changed its color to blood red and potassium chloride gets precipitated. The resultant reaction mixture was refluxed for 12 h. After this period, the precipitated potassium chloride was filtered off. The filtrate was poured into copious amount of crushed ice with effective stirring. The separated yellow colored 2,2-bis(4-nitrophenoxy phenyl)propane, DN-BPAPCNB, was filtered, washed with ice cold water, and dried at 50 °C for 24 h in a hot air oven. The yield was found to be 90%.

### Preparation of 2,2-bis(4-aminophenoxy phenyl)propane (DA-BPAPCNB)

Dinitro compound (DN-BPAPCNB) (28.2 g) and 0.15 g of 10% Pd/C dispersed in 180 mL of ethanol were taken in a round bottom flask. About 60 mL of hydrazine hydrate was added dropwise and the resultant reaction mixture was refluxed at 85 °C for 12.5 h. The hot black colored solution was filtered to remove palladized charcoal. The filtrate was poured into large amount of ice cold water with efficient stirring. A pale gray precipitate of 2,2-bis(4-aminophenoxy phenyl)propane, DA-BPAPCNB, was filtered, washed with ice cold water, and dried at room temperature. The yield of the diamino compound was 85%.

### Preparation of bisamic acid (BAA)

Exactly 12.3 g of diamine (DA-BPAPCNB) was dissolved in 155 mL of acetone with constant stirring at room temperature. To this solution, 6.5 g of powdered maleic anhydride was added in portions. Yellow precipitate was formed and it was stirred continuously for half an hour. It was filtered and washed with ice cold acetone to remove the acetone soluble materials and dried. The yield was 86%.

### Preparation of bismaleimide (BMIX)

The yellow BAA was dispersed in a 500 mL round bottom flask containing 160 mL of dry acetone. 3.44 g of

anhydrous sodium acetate and 40 mL of acetic anhydride were added into the reaction mixture and refluxed for 3 h. The brown color solution was poured into copious amount of crushed ice and 2,2-bis[4-(4-maleimidophenoxy phenyl)]propane (Scheme 1) was obtained as yellow precipitate. The material was filtered, washed with ice cold water, and dried in vacuum. The yield was 90%.

Purification of natural clay

About 100 g of natural clay was repeatedly treated with 4 N sodium hydroxide till the disappearance of red color. All the acid soluble impurities were removed by dispersing the clay in 1:1 hydrochloric acid–distilled water medium several times till the disappearance of yellow color. Finally washing with large amount of demineralised water gave acid and alkali-free natural clay. This purified clay was dried in an air oven at 130 °C for about 5 h and stored in a desiccator for further use.

Blending of nanoclays with bismaleimide (BMIX)

All the nanoclays were dried at 105 °C for 24 h in a hot air oven. The dry bismaleimide (BMIX) 97% and the moisture-free dry nanoclay 3% were taken in an agate mortar and with minimum quantities of dry acetone a paste was



Scheme 1 Preparation of bismaleimide (BMIX)

made and ground repeatedly to effect intimate mixing. The mixture was then dried in a vacuum oven and preserved for the polymerization. The materials BMIX, BMIX + 3% Cloisite 15A, BMIX + 3% Bentonite, BMIX + 3% Nanoclay DK4, BMIX + 3% Nanoclay DK3, BMIX + 3% Micro Talc IT Extra, BMIX + 3% Calcined clay, and BMIX+3% Natural clay were made.
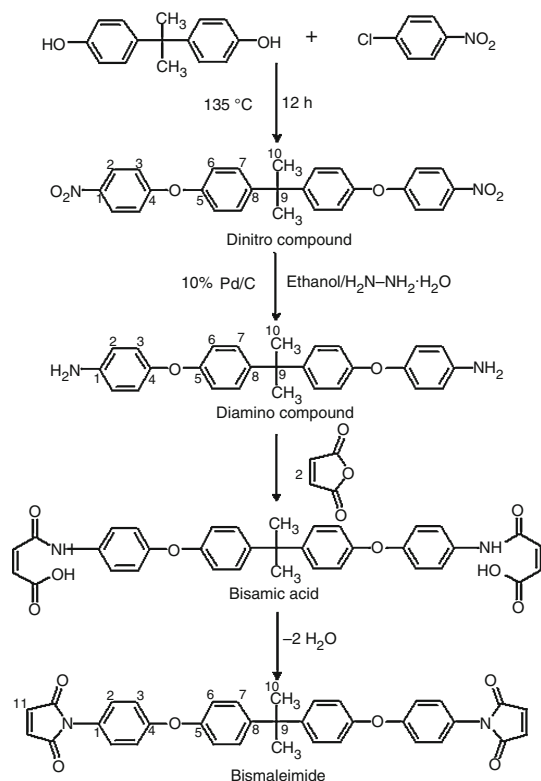
Thermal curing

The pure bismaleimide and the nanoclay blended bismaleimides were taken in separate micro test tubes and flushed with dry oxygen-free nitrogen and polymerized at 250 °C for 6 h. After the polymerization, the samples were removed from the micro test tubes, ground to coarse powder, packed, and stored for further analysis.

Methods

The FTIR spectra of the materials were recorded using Fourier Transform Infrared Spectrophotometer-8400S, Shimadzu, Japan by employing KBr disc technique. The $^1$H and $^{13}$C NMR spectral analysis were performed in a Bruker 300 MHz NMR spectrometer with tetramethylsilane (TMS) as the internal standard.

The differential scanning calorimetric (DSC) curves for pure BMIX and its blends with various nanoclays were recorded in a TA Instruments DSC Q10. Nearly 5 to 6 mg of the materials were taken in Tzero aluminum pan and heated from ambient to 400 °C by 10 °C min$^{-1}$. Dry nitrogen gas was used to provide the inert atmosphere. The thermogravimetric (TG) curve for all the thermally cured materials were recorded in a Mettler STAR TG system. The samples (nearly 6–7 mg) were taken in platinum pan and heated from ambient to 850 °C at 10 °C min$^{-1}$ in inert (nitrogen) atmosphere.

Results and discussion

FTIR and NMR studies

The peak seen at 1344 and 1340 cm$^{-1}$ in the dinitro and diamino compound, respectively, is attributed to the C–H deformation. The peak noted in the region 2970 cm$^{-1}$ for the dinitro, diamino, and bismaleimide is assigned to the C–H stretching vibration. The peaks noted at 1344 and 1521 cm$^{-1}$ in the FTIR spectrum of the dinitro compound is due to the N–O stretching. In the diamino compound, the N–H stretching was seen as doublet (3434 and 3406 cm$^{-1}$). The absence of N–O stretching peak in FTIR spectrum of the diamino compound proves the complete reduction of dinitro compound. The bismaleimide shows for the cyclic

**Table 1**  $^1$H NMR and $^{13}$C NMR study for the dinitro, diamino, and bismaleimide materials

| Code | $^1$H NMR | | | $^{13}$C NMR | | |
|------|-----------|-----------|-------|--------------|-----------|-------|
|      | DN-BPAPCNB | DA-BPAPCNB | BMIX | DN-BPAPCNB | DA-BPAPCNB | BMIX |
| 1    | –          | –          | –          | 147.5 | 156.6 | 130.5 |
| 2    | 8.17, 8.20 | 7.15, 7.12 | 7.26, 7.28 | 125.9 | 116.1 | 128.4 |
| 3    | 7.29, 7.31 | 6.89, 6.86 | 7.06, 7.09 | 120.0 | 116.4 | 117.0 |
| 4    | –          | –          | –          | 163.3 | 144.3 | 152.8 |
| 5    | –          | –          | –          | 152.5 | 148.6 | 153.4 |
| 6    | 7.25, 7.26 | 6.84, 9.81 | 6.95, 6.97 | 117.0 | 121.0 | 117.5 |
| 7    | 6.99, 7.02 | 6.68, 6.65 | 7.21, 7.24 | 128.6 | 127.7 | 128.0 |
| 8    | –          | –          | –          | 142.5 | 142.5 | 135.8 |
| 9    | –          | –          | –          | 30.9  | 41.8  | 41.7  |
| 10   | 1.73       | 3.57       | 1.69       | 42.5  | 31.0  | 31.1  |
| 11   | –          | –          | 6.84       | –     | –     | 136.4 |
| NH$_2$ | –        | 1.64       | –          | –     | –     | –     |

For numbering refer Scheme 1

CO–NR–CO imide unit a strong absorption at 1744 cm$^{-1}$. The absence of N–H stretching peak in the bismaleimide proves the complete imidization of BAA.

The chemical shift values for the peaks noted in the $^1$H and $^{13}$C NMR spectra of 2,2-bis(4-nitrophenoxy phenyl) propane, 2,2-bis(4-aminophenoxy phenyl)propane, and 2,2-bis[4-(4-maleimidophenoxy phenyl)]propane were presented in Table 1. The labeling of protons and carbons are shown in Scheme 1. The peak assignments confirmed the structure of dinitro, diamino, and bismaleimide.

## Thermal studies

### DSC studies

The DSC curves for pure BMIX and its blends with different nanoclays are shown in Fig. 1. For clarity, the curves are shifted in the ordinate by using a common factor for each curve. The pure BMIX shows the melting point at 74 °C and the cure exotherm starts at 227 °C, reaches the maximum at 305 °C and ends at 378 °C. Pure BMIX undergoes thermal curing with in a temperature region of 151 °C. The melting characteristic of the bismaleimide is not much altered by the incorporation of 3% of different nanoclays. But the Bentonite incorporated BMIX increases the melting point to 77 °C. Priya and Jog [16] studied the organically modified Bentonite clay interaction in the poly(vinylidene fluoride) (PVDF). They observed that the clay particle increases the melting point of the virgin polymer. This is attributed to the presence of β-form of PVDF. In our studies also, Bentonite clay increases the melting point of BMIX and this may be due to the interaction of the bentonite clay with the crystal structure of BMIX (Table 2).
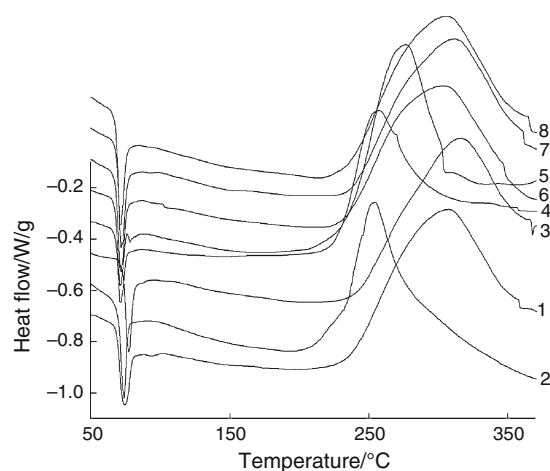


**Fig. 1** DSC curves for pure BMIX and its blends with 3% of various nanoclays. *1* BMIX, *2* BMIX + 3% Cloisite 15A, *3* BMIX + 3% Bentonite, *4* BMIX + 3% Nanoclay DK4, *5* BMIX + 3% Nanoclay DK3, *6* BMIX + 3% Micro Talc IT Extra, *7* BMIX + 3% Calcined clay, *8* BMIX + 3% Natural clay

The Micro Talc IT Extra incorporated BMIX shows much broader curing exotherm region covering 160 °C than the virgin BMIX (Table 2). Incorporation of Cloisite 15A and nanoclay DK4 in BMIX reduce the cure exotherm temperature region to 59 and 98 °C, respectively. There is no tremendous change in the curing exotherm region for all other nanoclays incorporated BMIX. Except Cloisite 15A and nanoclay DK4, all the other nanoclay incorporated BMIX showed very little influence on the $\Delta H_c$ value. Both Cloisite 15A and nanoclay DK4 particles are having interaction with the intermediates formed during the thermal curing of BMIX and this interaction causes reduction in the $\Delta H_c$ value.

**Table 2** DSC studies: melting and curing characteristics of BMIX and its blends with different clay materials

| Sample | $T_m/^\circ C$ | $T_S/^\circ C$ | $T_{max}/^\circ C$ | $T_E/^\circ C$ | $T_E - T_S/^\circ C$ | $\Delta H_c/\text{J g}^{-1}$ |
|---|---|---|---|---|---|---|
| BMIX | 74 | 227 | 305 | 378 | 151 | 186 |
| BMIX + 3% Cloisite 15A | 74 | 226 | 252 | 286 | 59 | 67 |
| BMIX + 3% Bentonite | 77 | 236 | 312 | 366 | 130 | 108 |
| BMIX + 3% Nanoclay DK4 | 71 | 215 | 256 | 313 | 98 | 111 |
| BMIX + 3% Nanoclay DK3 | 71 | 206 | 275 | 319 | 112 | 103 |
| BMIX + 3% Micro Talc IT Extra | 71 | 214 | 301 | 374 | 160 | 186 |
| BMIX + 3% Calcined clay | 72 | 234 | 309 | 376 | 141 | 174 |
| BMIX + 3% Natural clay | 71 | 226 | 303 | 377 | 152 | 178 |

The possibility of clay exfoliation in thermoset matrix can be predicted from the thermodynamic point of view. The free energy changes for the polymer or monomer matrix and clay blended polymer matrix are given below:

$$\Delta G_p = \Delta H_p - T\Delta S_p$$

for polymer or monomer matrix

$$\Delta G_c = \Delta H_c - T\Delta S_c$$

for clay blended polymer matrix

$$\Delta G_t = \Delta H_t - T\Delta S_t = (\Delta H_p + \Delta H_c) - T(\Delta S_p + \Delta S_c)$$

for the total free energy change.

From the above expression the possibility of clay exfoliation can be determined by the total free energy change, $\Delta G_t$. The most favorable case should be $\Delta H_t$ is negative and $\Delta S_t$ is positive. When the clay is blended with the monomer and polymerized, the blended system experiences a strain due to the penetration of the monomer molecules into the gallery resulting in an entropy loss, i.e., $\Delta S_p$ is negative. This causes the entropy gain in clay gallery, i.e., $\Delta S_c$ is positive and this will compensate the entropy loss experienced by the monomer matrix. So, the total enthalpy change will determine whether the clay exfoliation is possible or not. That means the larger the value of heat released, $\Delta H_p$ (negative) by intragallery polymerization, compared to the van der Waals attractive energy $\Delta H_c$, the higher the possibility of clay exfoliation [7].

Pure BMIX has the cure enthalpy as 186 J g$^{-1}$. The enthalpy of curing for the Micro Talc IT Extra, Calcined clay, and Natural clay blended BMIX matrix are more or less same as the pure BMIX. So, there is no possibility of reasonable interaction between the above said three clays and BMIX. Even though the heat release for other clays blended BMIX differ from pure BMIX, significant difference is noted in the case of Cloisite 15A blended BMIX (Table 2). So out of the different clays investigated, Cloisite 15A is having strong interaction with the molten BMIX matrix and influences the total heat release during polymerization reaction.
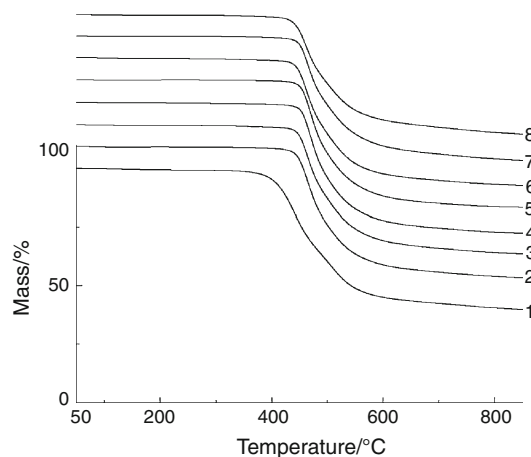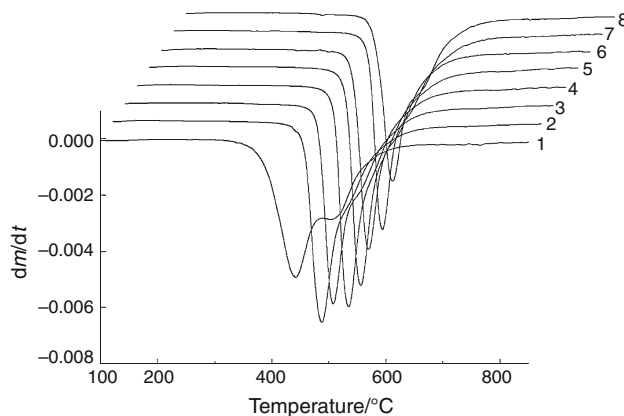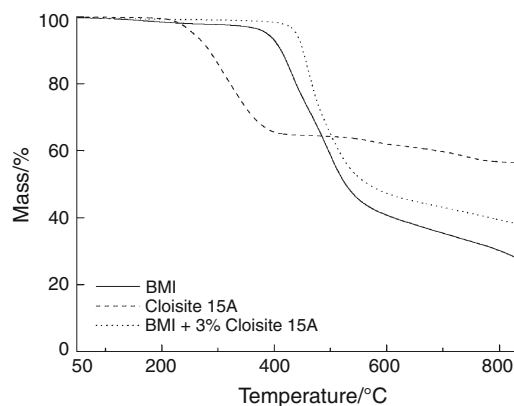


**Fig. 2** TG curves for thermally cured BMIX and its blends with 3% of various Nanoclays. *1* BMIX, *2* BMIX + 3% Cloisite 15A, *3* BMIX + 3% Bentonite, *4* BMIX + 3% Nanoclay DK4, *5* BMIX + 3% Nanoclay DK3, *6* BMIX + 3% Micro Talc IT Extra, *7* BMIX + 3% Calcined clay, *8* BMIX + 3% Natural clay



**Fig. 3** DTG curves for thermally cured BMIX and its blends with 3% of various Nanoclays. *1* BMIX, *2* BMIX + 3% Cloisite 15A, *3* BMIX + 3% Bentonite, *4* BMIX + 3% Nanoclay DK4, *5* BMIX + 3% Nanoclay DK3, *6* BMIX + 3% Micro Talc IT Extra, *7* BMIX + 3% Calcined clay, *8* BMIX + 3% Natural clay

**Table 3** TG studies: the degradation parameters for the thermally cured BMIX and different clay loaded BMIX cured thermally

| Sample | $T_S/°C$ | $T_{max}/°C$ | $T_E/°C$ | Char residue at 700 °C |
|---|---|---|---|---|
| BMIX | 404 | 445 | 552 | 42 |
| BMIX + 3% Cloisite 15A | 445 | 469 | 543 | 46 |
| BMIX + 3% Bentonite | 446 | 467 | 546 | 47 |
| BMIX + 3% Nanoclay DK4 | 452 | 474 | 552 | 46 |
| BMIX + 3% Nanoclay DK3 | 451 | 472 | 562 | 47 |
| BMIX + 3% Micro Talc IT Extra | 444 | 465 | 549 | 48 |
| BMIX + 3% Calcined clay | 449 | 468 | 553 | 50 |
| BMIX + 3% Natural clay | 441 | 465 | 544 | 52 |



**Fig. 4** TG curves for cured BMIX, pure Cloisite 15A, and the cured blend of 3% Cloisite 15A with BMIX

## TG studies

The TG and DTG curves for thermally cured BMIX and the nanoclay incorporated BMIX are shown in Figs. 2 and 3, respectively. For clarity, the TG curves were shifted in the mass axis uniformly. In the DTG curves (Fig. 3), the curves are shifted both in the X and Y axis direction uniformly. The thermally cured BMIX starts degrade around 404 °C and the degradation reaches maximum at 444 °C and the process is over at 553 °C. The incorporation of nanoclay shifts the degradation temperature to nearly 440 °C, i.e., 40 °C higher than the pure cured BMIX and the degradation is over approximately 10 °C earlier. The major degradation covering the temperature region 404–553 °C amounts to a weight loss of 46% in the case of thermally cured pure BMIX. The nanoclay incorporated systems show decreased mass loss in the degradation region and the amount of weight loss noted is around 38%. Among these nanoclays, the incorporated Natural clay reduces the mass loss of the pure BMIX to 36%. From this, it is evident that the interaction existing between the network structure of the thermally cured BMIX and the dispersed natural clay is maximum compared to other nanoclays. It is interesting to note that the amount of char value noted at 700 °C is roughly 10% higher than the cured pure BMIX in the case of natural clay and calcined clay loaded systems. The DTG curves (Fig. 3) shows that the $T_{max}$ value of the initial degradation shifts to higher temperatures roughly by 25 °C owing to the incorporation of the clay particles when compared to the thermally cured pure BMIX (444 °C). The DTG curve recorded for the thermally cured BMIX shows two major degradations, overlapping with one another. It shows that the initiation of the second degradation reaction is effected before the termination of the initial degradation process. Nearly in all the nanoclay incorporated thermally cured BMIX a single degradation is noted. Thus, the incorporation of the nanoclay in BMIX system increases the thermal stability of the system and is reflected in the char residue value (Table 3).

Using Cloisite 15A clay system, the interaction between the clay and the thermally cured BMIX matrix may be explained. The char residue at 800 °C for the pure thermally cured BMIX and pure Cloisite 15A clay are 30 and 57%, respectively (Fig. 4). For the thermally cured BMIX matrix (97%) and Cloisite 15A (3%) the theoretically expected char residue value at 800 °C is 31%. But the experimentally found value is 39%. Thus, the presence of 3% of Cloisite 15A in cured BMIX matrix enhances the char value by 8%. It is very clear from this fact clay like a Cloisite 15A is able to influence the primary degradation of the thermally cured BMIX and hence results in a comparatively higher char yield.

## Conclusions

From bisphenol-A and *p*-chloronitrobenzene, the aromatic dinitro compound was prepared and it was reduced to yield aromatic diamine using hydrazine hydrate. The imidization of bisamicacid prepared from aromatic diamine gives bismaleimide. Different types of nanoclays were incorporated into the bismaleimide and thermally cured. The complete reduction of nitro compound was confirmed by using FTIR. The DSC studies illustrate that the Cloisite 15A clay reduces the cure exotherm window and also the amount of heat liberated during the curing process. So, the physical blending of Cloisite 15A with BMIX matrix is efficient. The thermal stability and the char residue value are generally increased and this is certainly due to the incorporation of clay particles in the bismaleimide matrix. Among the different clays investigated using BMIX, the bentonite clay increases the melting point of pure BMIX whereas the Cloisite 15A and nanoclay DK4 reduces the

cure exotherm region. Presence of natural clay in the thermally cured BMIX increases the char residue indicating its strong influence over the primary thermal degradation of the thermally cure BMIX. Further investigation is under progress.

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