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Curing and thermal behavior of epoxy resins of hexafluoro - bisphenol –A and bisphenol-A

Vaishnav Kiran[1] and Bharti Gaur[1]*

[1]Research and Development Laboratory, Department of Chemistry, National Institute of Technology Hamirpur, Himachal Pradesh, India

*bhartigaur@gmail.com

Abstract

This paper describes the synthesis and characterization of epoxy resins based on (hexafluoroisopropylidene)diphenol (EFN) and p,p'-isopropylidenebisphenol (EBN), respectively and 4, 4'- (hexafluoroisopropylidene)dipthalic-imideamine (IMAM), a curing agent. The synthesized epoxy resins and IMAM curing agent were characterized by Fourier Transform Infrared (FTIR) and [1]H Nuclear Magnetic Resonance (NMR) spectroscopy.^{13}C NMR technique was also used to characterize IMAM. Study of curing behavior of EFN and EBN with stoichiometric amount of aromatic 4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenylsulfone (DDS) and IMAM by using Differential Scanning Calorimetery (DSC) indicated that IMAM was least reactive curing agent towards both epoxy resins as compared to DDS and DDM. The investigation of thermal decomposition of the cured compounds by thermogravimetric analyzer (TGA) indicated the higher thermal stability of EFN and EBN resins initially with DDS and at elevated temperatures with IMAM. It was also observed that EFN resins were thermally more stable than EBN resins cured with corresponding curing agents.

Keywords: *aromatic diamines, curing behavior, epoxy resins, imide amine, thermal properties.*

1. Introduction

Epoxy resins are one of the most important thermosetting resins known to possess good mechanical properties, high chemical resistance and excellent adhesive properties. These desirable properties make them widely applicable materials viz for surface coatings, adhesives, corrosion protectants, composites and laminates, encapsulants for semiconductors, insulating materials for electronic devices etc[1-10]. However the conventional epoxy resins do not exhibit very high thermal resistance, which is a prerequisite for advanced materials. Over the years multifunctional epoxy resins have been synthesized by many researchers to improve the thermal stability of these resins, either by incorporating aromatic ring as in case of phenolic based resins or introducing phosphorus in the epoxy backbone[11-13]. Attempts have also been made to introduce fluorinated substituents into the polymer backbone in order to improve electrical properties such as dielectric constant. These fluorinated substituents are also reported to reduce the moisture absorption due to the nonpolar character of fluorocarbons[14]. Some typical structures of multifunctional epoxy resin are shown in Figure 1. These resins are reported to be used as matrix material for high performance fiber-reinforced composites in the aerospace industry and as encapsulant for electronic components.

Outstanding properties and performance of epoxy resins are obtained by crosslinking these into a three-dimensional, insoluble and infusible network by reacting with suitable curing agents. The crosslinking occurs through reaction of the epoxide or oxirane group. In the recent years attention has also been focused by the researchers on the development of novel curing agents that will help to improve the performance of epoxy resins at elevated temperatures. This article reports the introduction of pendant fluoro groups on the epoxy backbone in order to increase the thermal stability of the

epoxy resin. An attempt has also been made to host these fluorinated substituents as well as the aromatic rings on the backbone of the curing agent, an Imide-amine, in order to obtain matrix which could show even better heat stability. Curing and decomposition behavior of fluorine containing epoxy resin (EFN) was compared with bisphenol-A novolac based (EBN) epoxy resin by using aromatic DDM, DDS and IMAM as curing agents.

2. Materials and Methods

2.1 Materials

4,4'-diaminodiphenlymethane, 4,4'-diaminodiphenyl sulfone, p,p'-isopropylidenebisphenol (bisphenol-A/BPA) and 4,4'- (hexafluoroisopropylidene) dipthalicanhydride were purchased from Alfa Aesar. Formaldehyde, tetrahydrofuran (THF) and glacial acetic acid were received from Fisher Scientific, Epichlorohydrin (ECH) and sodium hydroxide were obtained from Loba Chemie. Isopropanol and methyl isobutyl ketone (MIBK) were purchased from Merck, 4,4'-(hexafluoroisopropylidene)diphenol (hexafluoro/6F-bisphenol-A/6F-BPA) was obtained from Sigma Aldrich and paratoluene sulfonic acid (PTSA) from laboratory reagents, sodium bicarbonate was of analytical grade.

2.2 Synthesis and Characterization

2.2.1 Synthesis of 4, 4'-(hexafluoro-isopropylidene) - diphenol (6F-BPA) and p,p'-isopropylidenebisphenol (BPA) based novolac resins (Scheme 1 and 2)

A 40ml methyl isobutyl ketone (MIBK) solution containing 6F-BPA (0.05 mol) and PTSA (0.0014 mol) was added to a 250ml three- necked round bottom flask equipped with
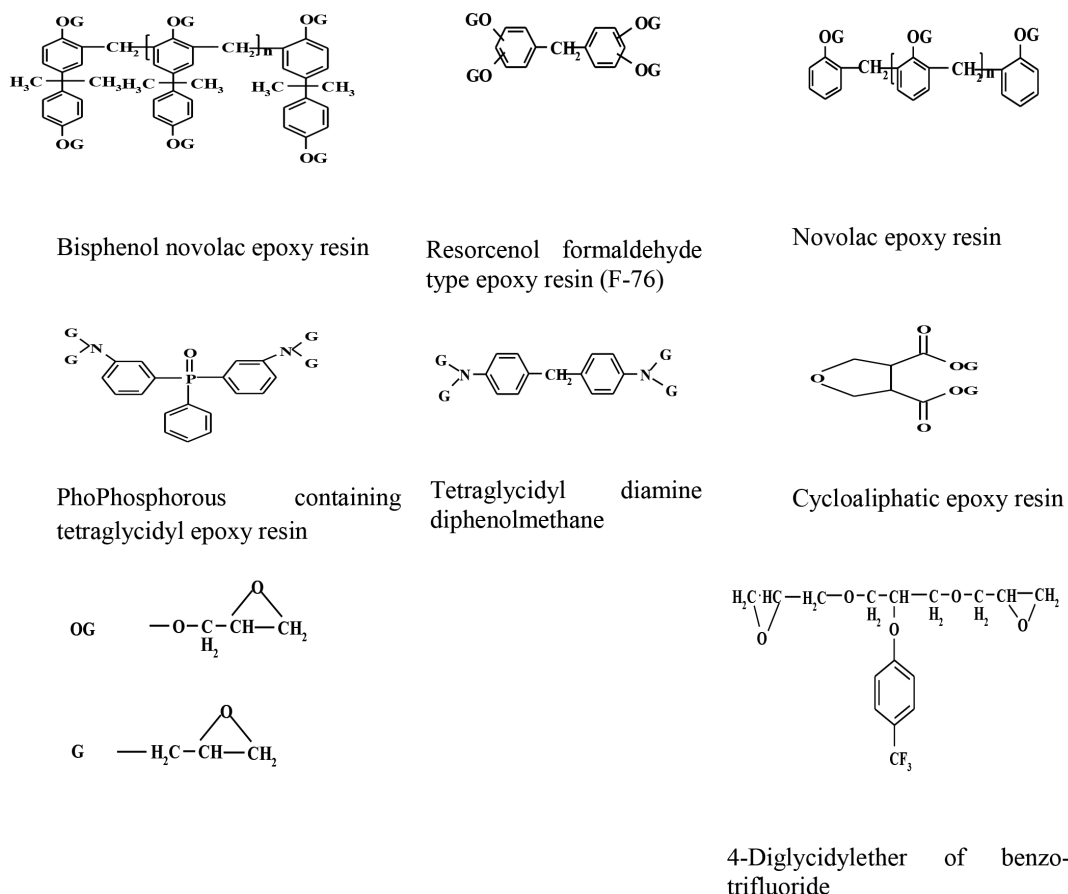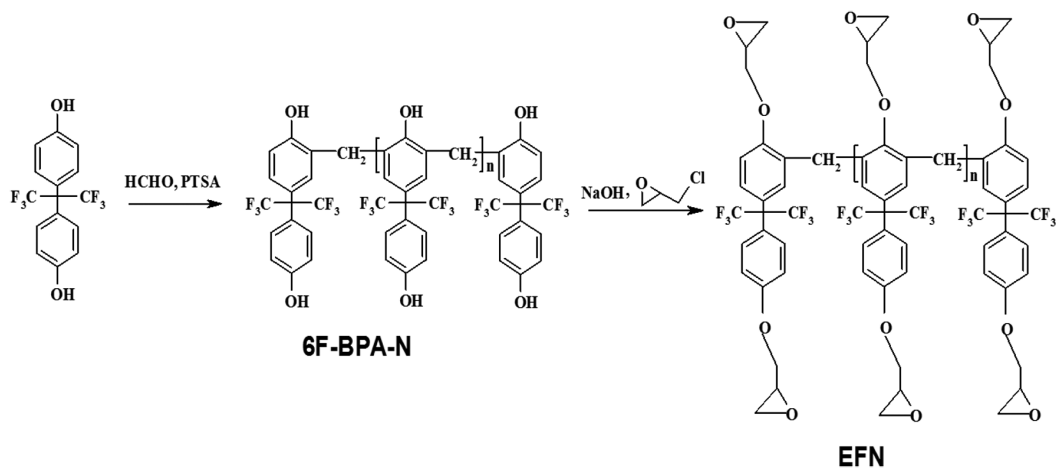
Bisphenol novolac epoxy resin

Resorcenol formaldehyde type epoxy resin (F-76)

Novolac epoxy resin

PhoPhosphorous containing tetraglycidyl epoxy resin

Tetraglycidyl diamine diphenolmethane

Cycloaliphatic epoxy resin

4-Diglycidylether of benzo-trifluoride

Figure 1. Some typical structures of multifunctional epoxy resins[11-13].

Scheme 1. Synthesis of hexafluorobisphenol-A novolac epoxy resin (EFN).

mechanical stirrer and dean and stark trap with a reflux condenser. Nitrogen gas was purged for 30 minutes and the reaction solution was heated to 100°C with stirring. 0.08 mol of formaldehyde solution (37-41%) was added to the reaction mixture drop wise. Then, the reaction mixture was heated to 120°C with constant stirring and maintained at this temperature for five hours. The condensation of novolac

resin is a reversible process; therefore (0.13 mol) of water generated during the reaction was removed as azeotropic mixture with MIBK. The reaction mixture was cooled to room temperature and washed with deionised water several times until it became neutral. The solution was then distilled at 120°C in order to remove the MIBK solvent. The product was then washed with a mixture of water/methanol (2:1 v/v)

several times to remove the unreacted 6F-BPA. A red brown solid product was obtained after vacuum drying at 60°C for 48 h. Similar procedure was followed for the synthesis of BPA based novolac resin.

2.2.2 Synthesis of novolac epoxy resins of 4, 4'-(hexafluoro-isopropylidene) - diphenol (EFN) and p,p' - isopropylidenebisphenol (EBN) (Scheme 1 and 2)

To the above dried product of 6F-BPA novolac 8 mol of epichlorohydrin for every phenolic group of novolac resin and isopropyl alcohol (0.83mol) was added to 250ml three necked round bottom flask equipped with mechanical stirrer and condenser. After increasing the reaction temperature to 70°C with constant stirring, 0.078 mol of 20 wt% aqueous solution of sodium hydroxide was added drop wise into the reaction solution within one hour. The system was maintained at 70°C for another four hours with constant stirring. The reaction product in the flask was washed several times with deionized water to remove the sodium chloride. The product was dissolved in toluene and filtered in order to remove residual salt. Toluene and excess of ECH were distilled off under reduced pressure. Finally the product obtained was dried at 60-70°C under vacuum for 48 hours. BPA based novolac epoxy resin (EBN) was also synthesized by adopting a similar procedure.

2.2.3 Synthesis of 4, 4'- (hexafluoroisopropylidene)diphthalic-imideamine (IMAM) curing agent (Scheme 3)

0.011 mol of DDM was dissolved in 40 ml glacial acetic acid in a round bottom flask equipped with condenser. To this 0.005mol of 4, 4'- (hexafluoroisopropylidene)diphthalic anhydride was added. The reaction mixture was heated at 120°C for ten hours with constant stirring. The prepared 4, 4'-(hexafluoroisopropylidene)diphthalic imideamine (IMAM) was precipitated in ice-cold water, filtered and washed several times with distilled water followed by washings with sodium bicarbonate solution. The product was again washed with distilled water several times before drying it in vacuum oven at 50-60°C.

## 2.3 Characterization

2.3.1 Structural characterization

FTIR spectra of the samples were recorded by using Perkin Elmer 1600 FTIR spectrophotometer in the range of 4000-400cm^{-1} on the KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCE II 400 NMR spectrometer using deuterated Dimethylsulfoxide as solvent, and tetramethylsilane as the internal standard.

2.3.2 Curing and decomposition behavior

The samples for curing studies were freshly prepared at 25°C by mixing the novolac epoxy resins EFN and EBN with three different curing agents DDM/DDS/IMAM, dissolved in appropriate solvents respectively, in the molar ratio of 1:2 in small glass vial with vigorous stirring using a glass rod until the samples became homogeneous in nature. DDM and DDS were dissolved in minimum amount of acetone whereas IMAM in minimum amount of THF. The solvents were then removed by vacuum stripping before recording the DSC scans. DSC scans for all these samples under dynamic conditions were obtained on Mettler Differential Scaning Calorimetery with programmed heating rate of 10°C min^{-1}
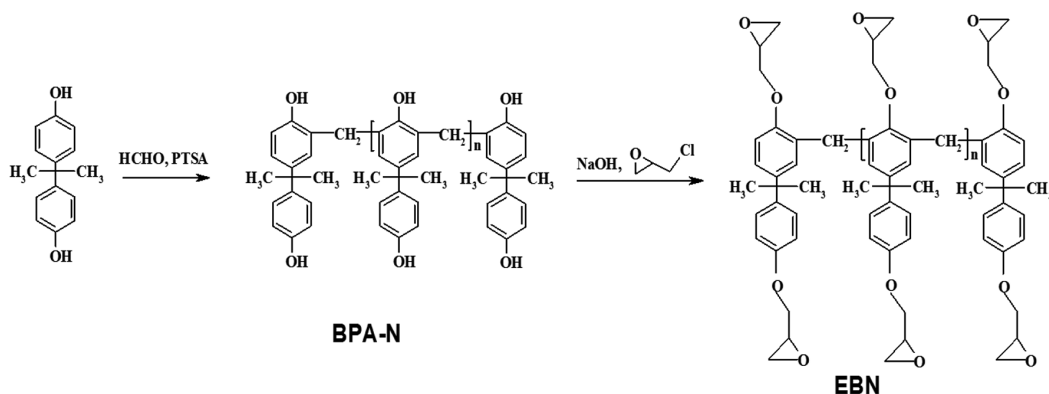
Scheme 2. Synthesis of bisphenol-A novolac epoxy resin (EBN).
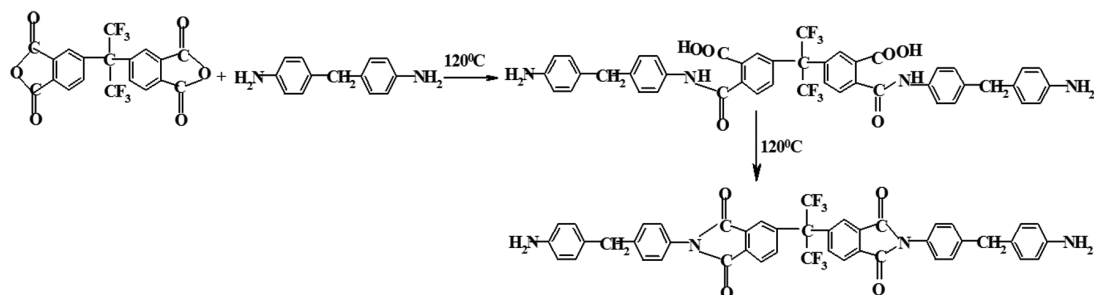
Scheme 3. Synthesis of 4, 4'- (hexafluoroisopropylidene)diphthalic-imideamine (IMAM).

from 35°C to the temperature at which exothermic reactions were completed.

Thermal stability of the samples cured isothermally at 250±10 °C in hot air oven was evaluated by thermogravimetry in nitrogen atmosphere (flow rate=200ml/min). EXSTAR TG/DTA 6300 was used to record TG/DTG/DTA traces at heating rate of 10°C min⁻¹ with sample size of 10±1 mg. The relative thermal stabilities of the different cured resins were quantitatively estimated by comparing the temperature at which maximum degree of weight loss occurred and by determining the activation energy of the thermal decomposition reaction.

2.3.3 Epoxide equivqlent weight

Epoxide equivalent weights (EEWs) of synthesized epoxy resins EFN and EBN were determined by the pyridinium chloride method[15] were found to be 354 and 377 respectively.

3. Results and Discussions

3.1 Characterization of 6F-BPA and BPA novolacs and their epoxy resins

The FTIR spectra of 6F-Bisphenol-A novolac (6F-BPA-N) (Figure 2a) and Bisphenol-A novolac (BPA-N) resins showed the –CH$_2$- stretching vibration due to bridging
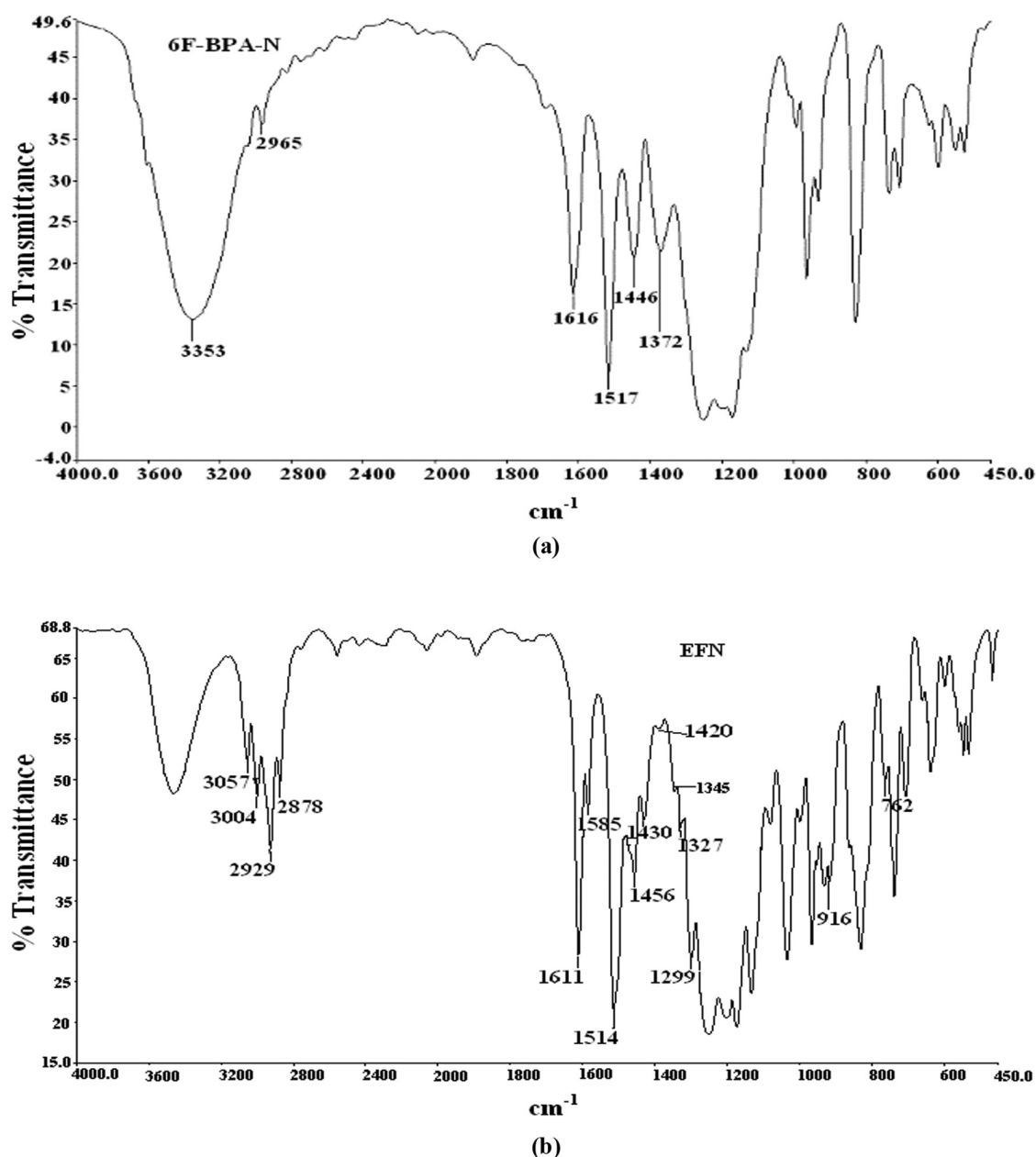

(a)

(b)

Figure 2. FTIR spectra of (a) 6F-BPA novolac; (b) EFN novolac epoxy resin.

methyene groups at 2965 cm^{-1} . A broad band was observed at 3353 cm^{-1}due to the hydroxyl group. Apart from the other peaks appearing for the aromatic C-H stretching, C=C stretching, -CH$_2$- bending, as in case of BPA-N resin. IR spectrum of 6F-BPA-N resin showed peaks in the region of 1372-1446 cm^{-1}, which indicated the presence of C-F bonds.

The FTIR spectra of EFN (Figure 2b) and EBN novolac epoxy resins showed characteristic absorptions at 3057 and 2929cm^{-1} due to streching vibrations of aromatic rings and bridging methylene groups, respectively. A characteristic absorption band at 1299 cm^{-1} depicted the ring breathing frequency of epoxy ring, the appearance of band at 916 cm^{-1} proved the asymmetric ring deformation and band at 762 cm^{-1} showed the symmetric ring deformation of epoxy ring. The spectrum of EFN (Figure 2b) also showed peaks in between 1372-1446 cm^{-1} due to the presence C-F bonds.

Figure 3 shows the ^{1}H NMR spectra of 6F-BPA-N, BPA-N novolac resins and EFN, EBN novolac epoxy resins. Figures 3a and c showed characteristic proton resonance signal at 3.7 ppm due to methylene (–CH$_2$) bridging protons and multiplet for aromatic protons at 6.6-7.1 ppm. A singlet due to -OH protons of phenol appeared at 9.5 ppm in the spectrum of 6F-BPA-N (Figure 3a) and at 8.7 ppm in the spectrum of BPA-N (Figure 3c). BPA-N resin also showed a characteristic singlet due to –CH$_3$ protons at 1.5 ppm (Figure 3c). ^{1}HNMR spectra (Figures 3b and 3d) of EFN and EBN showed proton resonance signals at 3.6-3.8 and 6.7-7.3 ppm due to –CH$_2$ bridging and aromatic protons respectively. Characteristic proton resonance signals at

2.7-2.9, 3.3 and 3.9-4.2 ppm due to –O-CH$_2$, -CH and -CH$_2$ protons of epoxy ring were also observed, respectively.

3.1.1 Characterization of IMAM curing agent

The FTIR spectrum of IMAM curing agent in Figure 4a showed characteristic absorption bands at 1783 and 1725 cm^{-1} due to asymmetric and symmetric stretching vibration of imide group and a band was observed at 722 cm^{-1} due to five-membered ring deformation of the cyclic imide. –NH$_2$ stretching bands appeared at 3260 ± 30 cm^{-1}. Absorption bands for C-N and C=C stretching of aromatic rings were observed at 1409-1435 cm^{-1} and 1602-1672 cm^{-1}, respectively. ^{1}H NMR spectrum Figure 4b of IMAM curing agent showed proton resonance signal at 3.9 ppm for –NH$_2$ protons and 7.0-8.1 ppm for aromatic protons. A resonance signal appeared at 2.0 ppm due to methylene protons.^{13}C NMR spectrum (Figure 4c) was recorded in order to confirm the cyclization of the amic acid which is an intermediate in the reaction represented by the Scheme 3. The characteristic signal at 168 ppm due to cyclic imide carbon was observed. Carbons of Ar-CH$_2$ and Ar-NH$_2$ appeared at 132 and 141 ppm respectively. Peaks due to aromatic carbons were observed at 119-137 ppm.

3.2 Thermal curing behavior

The curing behavior of EFN and EBN novolac epoxy resins with three different curing agents were studied by DSC. The reactivity of the curing agents towards epoxy resins can be examined from the onset exothermic temperature. The onset exothermic temperature was obtained by extrapolating the steepest portion of the curve to the base line. A curing agent
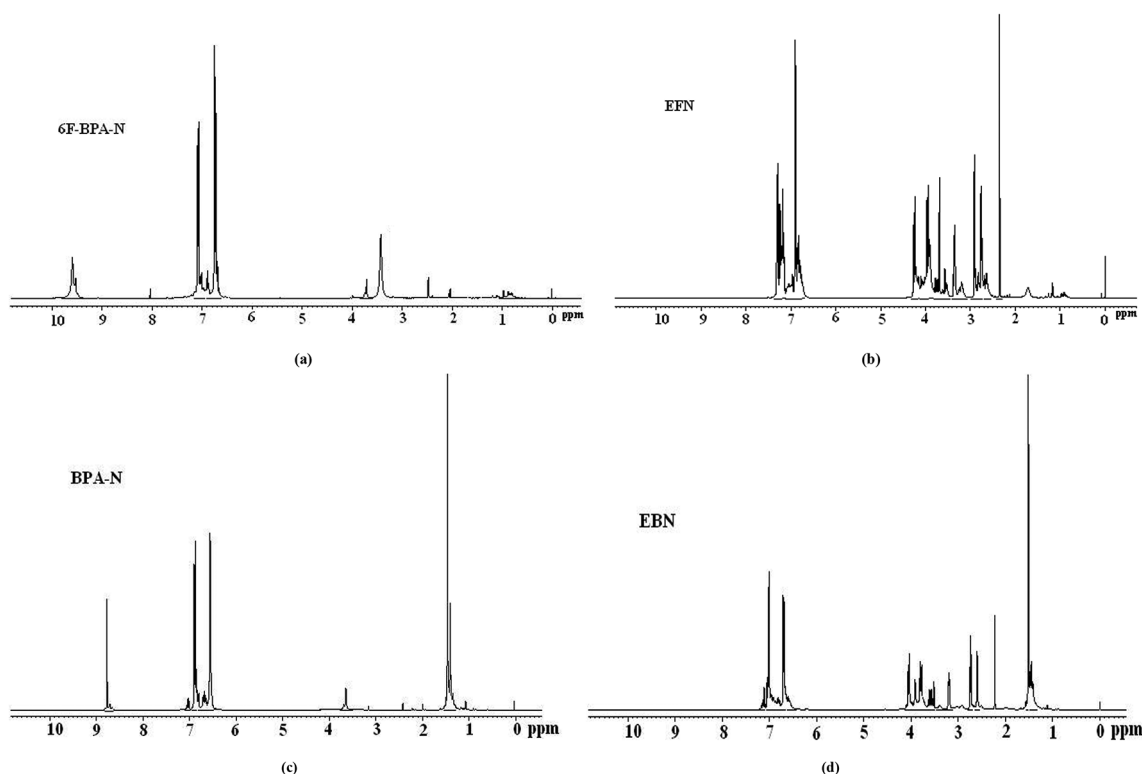

Figure 3. ^{1}HNMR of (a) 6F-BPA novolac; (b) EFN novolac epoxy resin; (c) BPA novolac; (d) EBN novolac epoxy resin.

that exhibits lower onset exothermic temperature is more reactive towards the epoxy resin. Figures 5 and 6 show the typical DSC scans for curing of EFN and EBN epoxies with DDS and IMAM curing agents respectively. The exothermic temperatures, onset, peak and endset temperatures have been given in Table 1. The enthalpy change (ΔH) which can be used to determine the extent of curing of resin[16,17] have been calculated by measuring the area under the

exothermic transition and are also summarized in Table 1. The onset curing exothermic temperature of EFN with DDM/DDS/IMAM were observed at 118, 184, 240°C, respectively. Curing exotherms of EBN with DDM/DDS/ IMAM showed the onset curing temperatures at 126, 147, 256°C respectively. The reaction of the amine with an oxirane ring is a nucleophilic addition reaction. From the results of thermal curing it was observed that despite the presence of
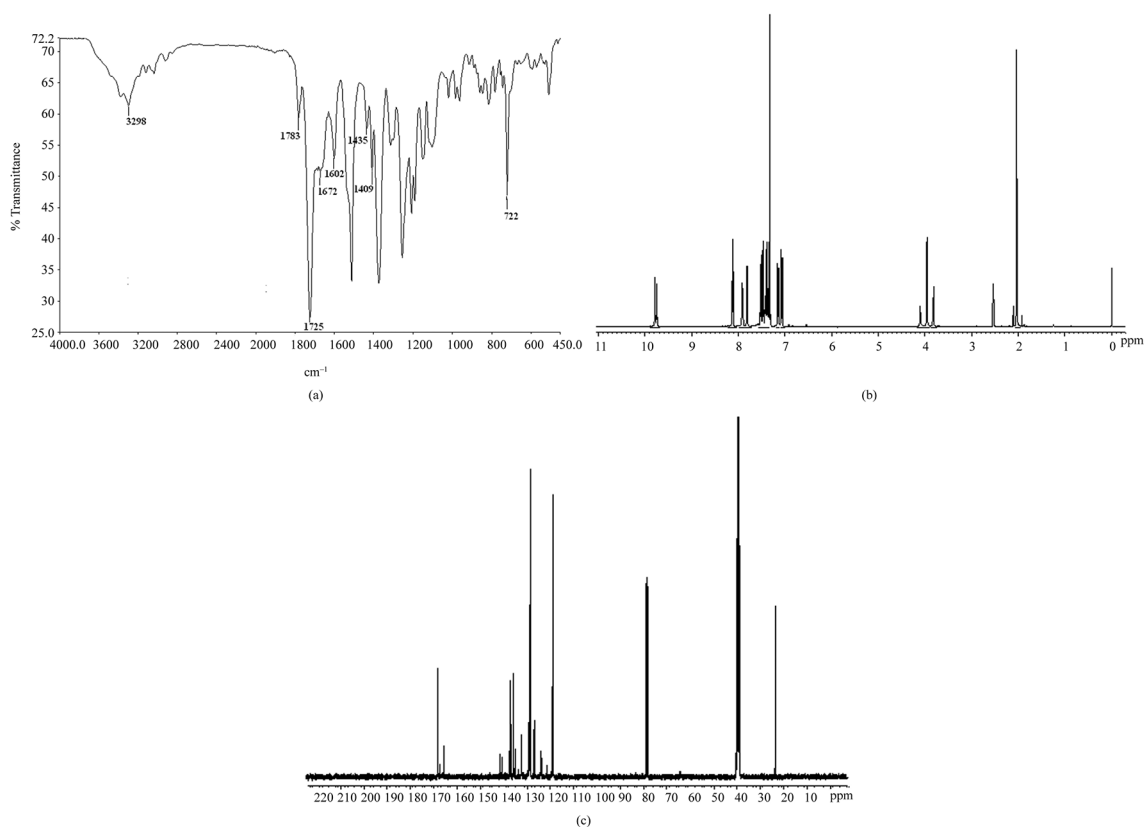

Figure 4. (a) FTIR; (b) ¹H NMR of IMAM curing agent; (c) ¹³ C NMR of IMAM curing agent.
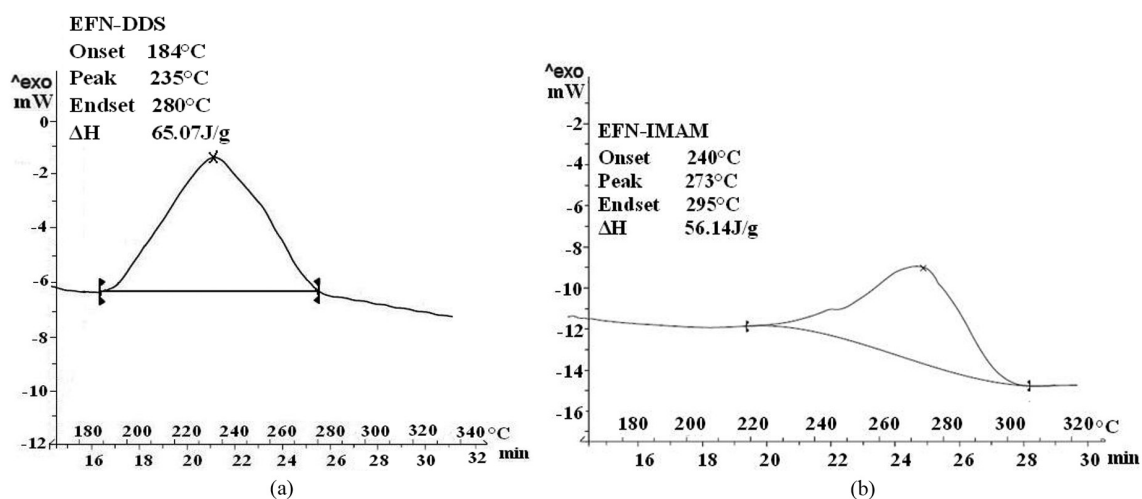

Figure 5. DSC scans of novolac based epoxy resins of (a) EFN/DDS; (b) EFN/IMAM.
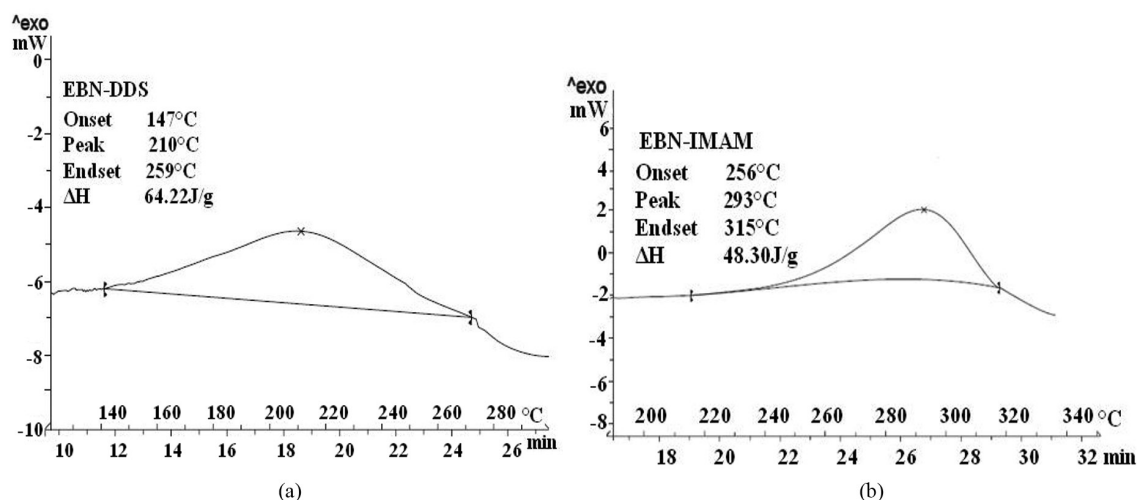
Figure 6. DSC scans of novolac based epoxy resins of (a) EBN/DDS; (b) EBN/IMAM.

Table 1. DSC results of cured epoxy resins.

Sample Designation	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	ΔH (J/g)
EFN- DDM	118	144	194	99.81
EFN- DDS	184	235	280	65.07
EFN-IMAM	240	273	295	56.14
EBN- DDM	126	134	154	73.88
EBN- DDS	147	210	259	64.22
EBN- IMAM	256	293	315	48.30

electron donating methyl group in IMAM it was found to be the least reactive. The reason for this may be attributed to the presence of electron withdrawing CF_3 and carbonyl groups in the main chain as well as the steric hinderance caused due to the bulkiness of the groups. This reduced the basicity of amine and consequently the reactivity of the IMAM curing agent decreased. Whereas in DDS only electronic factor dominated and owing to the electron withdrawing nature of sulfone group the reactivity of DDS was found to be higher than IMAM. The highest reactivity of DDM towards both the epoxy resins was in good agreement with electronic donating effects of methane moiety[1,10,18]. Thus the order of basicity of amine groups in the three curing agents will be DDM>DDS>IMAM. Furthermore, the melting point of DDS (175°C) and IMAM (195°C) is very high as compared to DDM (90°C), which may also have a negative effect on their reactivity. The EFN epoxy resin was observed to be more reactive towards the curing agents as compared to that EBN which may be probably due to electronic factors. The presence of electron withdrawing groups CF_3 may facilitate the oxirane ring opening during the reaction with the amine group.

3.3 Thermal properties of cured resins

EFN and EBN epoxy resin samples were isothermally cured at 250±10 °C for twelve hours with stoichiometric amount of diamines or imide-amine curing agents. DSC scans were recorded for these samples and absence of any residual exothermic peak in their scans confirmed complete curing of the samples. TGA technique considered to be the most

favorable technique for rapid estimation in comparing and ranking the thermal stability of samples, was employed for determining the thermal stability of these isothermally cured samples. The relative thermal stability of the cured samples was compared by observing the initial degradation temperatures (IDT), temperature of maximum degradation (T_{max}), final degradation temperature (FDT) and residual weight retention (R_w) at 900°C. The results have been summarized in Table 2.

The TG curves of cured epoxy resins EFN/DDM, EFN/DDS, EFN/IMAM are shown in Figure 7. It can be seen that the samples did not show initial weight loss till 345°C which implied that the cured samples of EFN resin were thermally stable till this temperature. As the temperature reached 350±5°C these samples showed a slight weight loss and it was observed that the EFN/DDS sample showed better thermal stability as compared to EFN/DDM and was found to be thermally less stable than that of EFN/IMAM. However as the scanning temperature reached 415±5°C rapid thermal degradation occurred and EFN/DDS found to be less stable as compared to corresponding EFN/DDM and EFN/IMAM respectively and the final decomposition temperatures of all the samples were found to be almost identical.

Figure 8a shows typical TG/DTG/DTA scans of cured epoxy resin of EBN with IMAM and Figure 8b shows the TG curves for cured EBN/DDM, EBN/DDS and EBN/IMAM, respectively. From the Figure 8b and Table 2 it can be observed that the cured EBN resins containing DDM/DDS/IMAM, respectively, were thermally stable till the scanning temperature reached up to 330±5°C. As the

**Table 2.** Thermal properties of cured epoxy resins.

Sample Designation	IDT (°C)	T$_{max}$ (°C)	FDT (°C)	Residual weight retention (R$_w$) %	Activation energy of decomposition reaction (E$_a$)	
					Temperature Range (°C)	E$_a$ (KJ/mol)
EFN-DDM	354	422	540	26.46	290-690	62.825
EFN-DDS	359	417	542	22.48	290-625	48.742
EFN-IMAM	369	456	544	29.08	280-670	74.208
EBN-DDM	339	409	465	22.83	265-560	63.836
EBN-DDS	350	407	470	17.65	280-560	59.773
EBN-IMAM	356	453	490	30.80	270-570	96.365
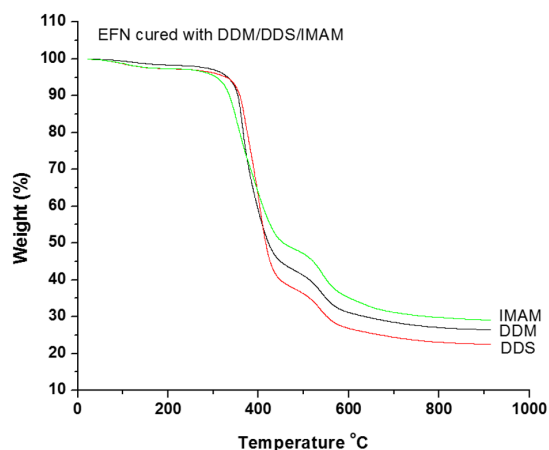
Figure 7. TG curves for EFN cured with DDM/DDS/IMAM.

scanning temperature rose above 340°C, the cured EBN/DDS sample showed the values of IDT, Tmax, FDT as 350, 407, and 470°C respectively. However the FDT for the sample EBN/IMAM was found to be higher as compared EBN cured with DDM and DDS respectively.

From the values of IDT and FDT it was observed that initially better thermal stability of EFN and EBN resins with DDS may be due to the rigidity provided by high functionality and rigid structure of DDS as compared to that cured with DDM[19]. For the superior thermal stability of EFN and EBN resins cured with IMAM, It is assumed that the solid state aromatization reaction in the case of IMAM are promoted by the formation of the crosslinks which may develop between the carbonyl and trapped or unreacted amino groups at elevated temperatures and thus may have increased the thermal stability of the sample. It was also seen that the cured EFN and EBN resins with IMAM showed highest residual weight retentions (R$_w$) at 900°C. This was probably due to the presence of thermally oxidative resistant CF$_3$ groups in the main chain of IMAM. Furthermore the cured EFN resins were found to be thermally more stable as compared to cured EBN resins. The enhanced thermal properties of cured EFN samples were probably due to the presence of fluorinated groups in the EFN network structure.
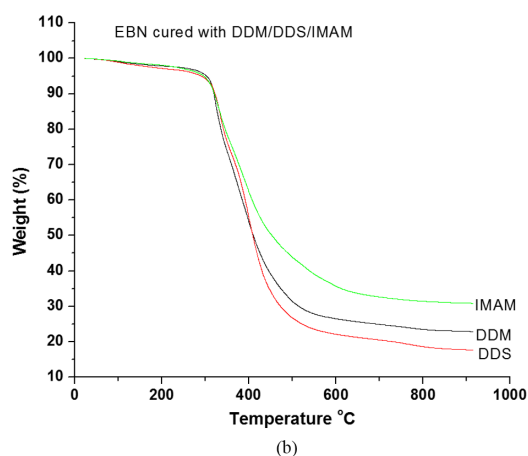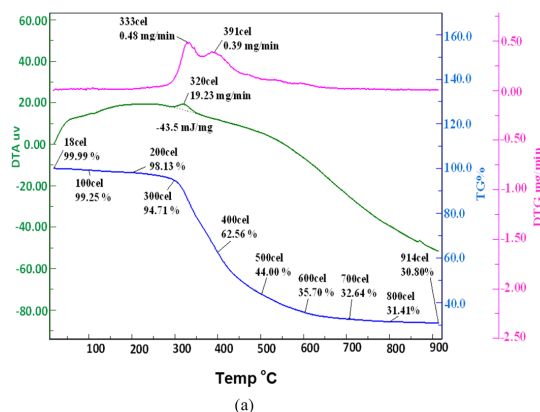
Figure 8. (a) Typical TG/DTG/DTA scans for cured sample of EBN/IMAM; (b) TG curves for EBN cured with DDM/DDS/IMAM.

3.3.1 Activation energy of decomposition (E$_a$)

Activation energy of decomposition (E$_a$) can also be used as a decisive factor for evaluating the thermal stability of the polymers, higher the value of activation energy higher will be the stability of the compounds. Because the rate constant of reaction depends upon energy difference between initial and transision states of the reaction. If higher is the value of the energy difference higher will be the activation energy and more will be the stability of the compound. Calculation of activation energy from the TG curves has

been reported in the literature by several methods[20-24]. But the expression used by Dharwadkar and Kharkhanawala for the calculation of activation energy is independent of sample size and heating rate.

$$\ln\left[\ln\left(1-\alpha\right)^{-1}\right] = \frac{E_a 100\theta}{RT_i^2(T_f - T_i)} + C \qquad (1)$$

where α, fraction reacted; T_i, the temperature of inception of reaction; T_f, temperature at the point of inflection on the thermogram; $\theta = (T-T_s)$ (where T is the temperature under consideration and T_s is the maximum temperature); C, constant; R, gas constant. A plot of $\ln\left[\ln\left(1-\alpha\right)^{-1}\right]$ versus θ gave a straight line was equal to

$$m = \frac{100E_a}{RT_I^2(T_f - T_i)} \qquad (2)$$

From this equation, E_a was calculated.

Activation energies of decomposition (E_a) were calculated by using Equations 1 and 2 and the values of E have been summarized in Table 2. On comparing the activation energies of decomposition reaction of EFN and EBN novolac epoxy resins cured with DDM/ DDS/ IMAM curing agents respectively, the following trend was observed for activation energies [(EFN / EBN) + IMAM] > [(EFN / EBN) + DDM] > [(EFN / EBN) + DDS].

These results also substantiate the fact that the presence of fluorinated groups in the curing agent IMAM have also contributed towards the improvement of thermal stability of both the cured epoxy resins. From Table 2 it was also observed that the cured samples having high Rw value showed higher activation energy which led to the increase in their thermal stability.

4. Conclusions

EFN and EBN novolac epoxy resins were synthesized, which were then thermally cured with aromatic amines (DDM, DDS) and synthesized aromatic imide-amine (IMAM) curing agents. The investigation of curing behavior of cured epoxy resins revealed that IMAM was found to be the least reactive curing agent towards both EFN and EBN as compared to their counterparts DDM and DDS. This was attributed to the electronic effects, high molecular weight and physical properties of IMAM curing agent. The experimental results for the thermal degradation demonstrated that the major weight loss for all the samples occurred in the temperature range of 300-600°C. Both the EFN and EBN samples cured with IMAM exhibited higher thermal stability probably due to the solid state aromatization reactions which may lead to the formation of cross-links between the carbonyl and trapped or unreacted amino groups. The presence of CF_3 groups in IMAM may also have played its role in the enhancement of thermal stability of such cured resins. The EFN cured resins were found to be more heat resistant as compared to their corresponding EBN resins. This was owing to the ease of oxirane ring opening due to the presence of CF_3 groups in EFN that might have been a good ignition for

the formation of better crosslinked network structure than EBN cured resins.

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