

Synthesis, Characterization, Curing And Thermal Decomposition Kinetics Of Bisphenol-A Based Polybenzoxazine

D. L Jayamohan Das, DR R Rajeev, DR R. S Rajeev, DR K. S Santhosh kumar

ABSTRACT: A bisphenol-A-aniline based Polybenzoxazine was synthesized by reacting bisphenol-A with formaldehyde and aniline. The chemical structure was characterized by FT-IR analysis. The polymerization behavior of the monomer was monitored by differential scanning calorimetry (DSC) and FT-IR. The curing kinetics was studied by non-isothermal DSC and kinetic parameters were determined at heating rate (5, 10, 15 and 20 °C/min) from RT - 400 °C. The kinetic of thermal decomposition was investigated with thermogravimetric analysis by conducting the measurements at four different heating rates (5, 10, 15 and 20 °C/min) from RT - 900 °C/min. Different kinetic models such as, Flynn-wall-Ozawa method, Kissinger method were adopted for both non-isothermal curing kinetics and decomposition kinetics.

Index Terms: Activation energy (Ea), Aniline, Bisphenol-A-based benzoxazine, Chloroform, Curing kinetics, Differential scanning calorimetry(DSC), Nano Clay(NC), para-formaldehyde, Thermal properties, Thermogravimetric analysis(TGA).

1 INTRODUCTION

Polybenzoxazine, is a class of an thermosetting phenolic resins formed by the thermal ring-opening benzoxazine monomer without any catalyst, have demonstrated various attractive properties such as high thermal stability, high char yields, high glass transition temperature (Tg), near-zero volumetric change upon curing, good mechanical and dielectric properties, low water absorptions, and low flammability [1], [2], [3], [4], [5], [6], [7]. These unique characteristics make the polybenzoxazine a better candidate over epoxies and traditional phenolic resins in the electronics, aerospace, and other industries. Benzoxazine monomers as the polybenzoxazine precursors can be easily prepared from phenols or amines, formaldehyde, and primary amines or phenols. The benzoxazine monomer was synthesized from bisphenol-A, formaldehyde and aniline by mannich condensation reaction. polybenzoxazine is an addition polymerized phenolic system, having the capability to overcome several shortcomings associated with conventional novolac and resole type phenolic resins while retaining their benefits. It exhibits the thermal properties of phenolic and mechanical stability of epoxy system concomitantly. They possess excellent resistance to chemicals and uv light and amazingly high Tg. The lowest heat release during combustion surpassing that of phenolics and polyether imides renders benzoxazine as the future aerospace matrices of choice. The polymeric features are truly amazing that they are cured usually in the temperature window of 160-220 °C and display higher Tg than the cure temperature. The curing occurs with either near zero shrinkage or even with slight expansion upon cure. No acid catalyst is required for the oxazine polymerization and releases no toxic by-product during cure. They possess high mechanical strength and module which facilitates their use as potential candidate for composite application.

Long-term immersion studies indicate that they have a lower rate of water absorptions. char-yield as high as 82% has also been claimed [8], [9], [10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20], implying their potentially in ablative compositions. The introduction of cloisite-30B (Nano-clay) to Bisphenol-A based polybenzoxazine is expected to improve the mechanical and thermal properties of the polymers. In this study, polybenzoxazine (BA-A) was synthesized and characterized by FT-IR. The polymerization behavior, network structure, and thermal properties of the monomers and cured polymers were investigated by DSC, FT-IR and TGA. Non-isothermal DSC was used to study the curing kinetics of BA-A by Kissinger method while TGA was used to study the thermal decomposition or degradation by Flynn-wall-ozawa method.

2. EXPERIMENTAL

2.1 MATERIALS

Bisphenol-A (97%, Alfa Biochem), Aniline (99.5%, Ranbaxy fine chemical limited), P-formaldehyde (97%, Otto Kemi), Chloroform extra pure A.R (99.5%, Sisco research laboratories pvt.ltd), Sodium hydroxides pellets A.R (98%, SD fine-chem limited), respectively where used. Aniline was used after vacuum distillation. All other chemicals and solvents where used without further purification.

2.2 SYNTHESIS OF BENZOXAZINE MONOMER (BA-A)

Benzoxazine monomer was prepared using Bisphenol-A, p-Formaldehyde and Aniline.

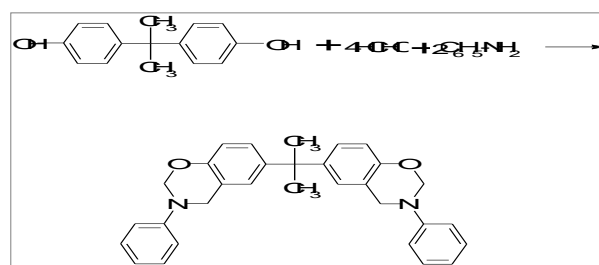


Fig 1. Synthesis of benzoxazine monomer

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A solution of aniline and bisphenol-A was added in a reaction vessel and stirred for 30 min at room temperature. The mixture was cooled down to below 5⁰ C in an ice bath and p-formaldehyde was added and heated at 60⁰ C for an 1h and the temperature was raised gradually to 120⁰ C and reaction continue for 4h with constant stirring. Then the resulting orange coloured, residue was dissolved in chloroform, washed three times with 1N NaOH aqueous solution and twice with distilled water. The solvent were removed by rotary evaporation at 50⁰C followed by vacuum drying to afford light-yellow crystal with 79% yield. FT-IR (KBr, cm⁻¹) the characteristic absorption peak of oxazine ring was observed at 946cm⁻¹ [21]. Also the asymmetric and symmetric stretching vibrations of C-O-C located at 1231 cm⁻¹, 1248 cm⁻¹ and 1030 cm⁻¹ respectively. The asymmetric and symmetric stretching vibration of C-N-C located at 1120-1159 cm⁻¹ and around 824 cm⁻¹ confirmed the formation of benzoxazine ring structure. The very strong and sharp bands at 1496 cm⁻¹ and the medium intensity bands at 1599 cm⁻¹ are corresponded to C-H in-plane and out-of-plane bending mode of the tri-substituted benzene ring. There is an OH peak at 3421 cm⁻¹ and it may due to ring-opening benzoxazine monomer structure in smaller quantity. The absorption bands at 755 and 694 cm⁻¹ are assigned to the mode of mono-substituted benzene in the bisphenol-A skeleton.

2.3 CURING OF BENZOXAZINE MONOMER (BA-A)

Benzoxazine monomer was polymerized without catalyst according to the following schedule: 50⁰ C /30min, 100⁰ C /1h, 140⁰ C /1h, 180⁰ C /1h and 200⁰ C /4h in an air-circulating oven.

2.4 CHARACTERIZATION

FT-IR spectre were recorded in the range of 4000-500 cm⁻¹ on a perkin Elmer100 spectrometer, equipped with deuterated triglycine sulfate (DTGS) detector and KBr optics. Transmission spectra were obtained at a resolution of 4 cm⁻¹ after averaging two scans by casting a thin film on a KBr plate for monomers and cured samples. DSC measurements were carried on a TA Q-20 differential scanning calorimeter under a nitrogen flow and the instrument was calibrated with a high-purity indium standard. α -Al₂O₃ was used as a reference material. About 3mg of sample was weighted into a hermetic aluminium sample pan which was sealed and tested immediately. This study was performed with a sealed aluminium capsule pan, under a nitrogen atmosphere at four different heating rates (5,10,15 and 20⁰ C /min) between RT-400⁰ C. Thermogravimetric analysis was done with a TA instrument (SDT 2960 simultaneous TGA-DTA) in a nitrogen atmosphere at five different heating rates (5,10,15 and 20⁰ C /min) between RT-900⁰ C with a thermogravimetric analyzer.

3. RESULTS AND DISCUSSIONS

3.1 STRUCTURAL CHARACTERIZATION OF THE BENZOXAZINE MONOMER (BA-A)

The structure of benzoxazine monomer was confirmed by FT-IR analysis. The FT-IR of benzoxazine monomer was shown in Fig 1(b) as shown below.

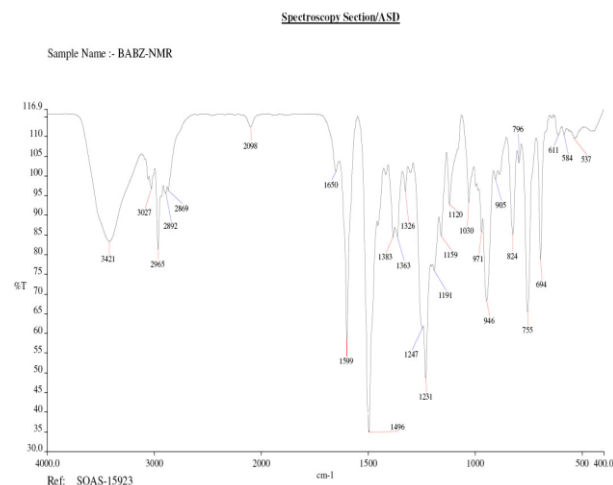


Fig 2(a) FT-IR of benzoxazine monomer

The characteristic absorption peak of oxazine ring was observed at 946 cm⁻¹ [22]. Also the asymmetric and symmetric stretching vibrations of C-O-C located at 1231 cm⁻¹, 1248 cm⁻¹ and 1030 cm⁻¹ respectively. The asymmetric and symmetric stretching vibration of C-N-C located at 1120-1159 cm⁻¹ and around 824 cm⁻¹ confirmed the formation of benzoxazine ring structure. The very strong and sharp bands at 1496 cm⁻¹ and the medium intensity bands at 1599 cm⁻¹ are corresponded to C-H in-plane and out-of-plane bending mode of the tri-substituted benzene ring. There is an OH peak at 3421 cm⁻¹ and it may due to ring-opening benzoxazine monomer structure in smaller quantity. The absorption bands at 755 and 694 cm⁻¹ are assigned to the mode of mono-substituted benzene in the bisphenol-A skeleton

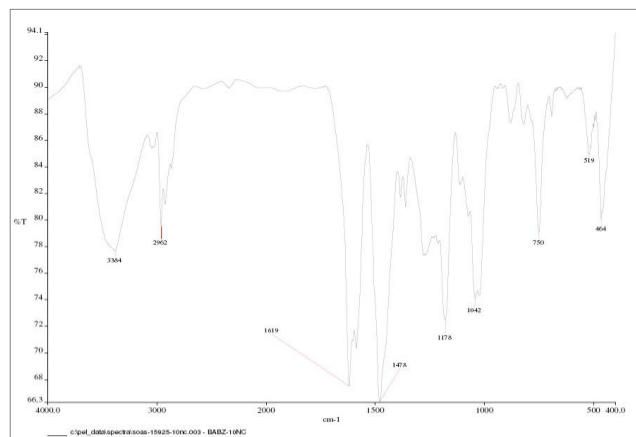


Fig 2(b). bebenzoxazine + 10wt% Nano-clay (cured sample)

The curing behavior of benzoxazine monomer was studied by FT-IR analysis. The characteristic absorption bands due to the benzoxazine structure at 946 cm^{-1} (vibrational mode of cyclic C-O-C), and the asymmetric and symmetric stretching mode of C-O-C, CH₂ wagging at 1326 cm^{-1} and tri-substituted benzoxazine ring around 1496 and 824 cm^{-1} completely disappear, indicating the completion of ring-opening at this stage. Meanwhile, the very strong bands assigned to the asymmetric stretching mode of C-N-C shift around 1178 cm^{-1} . The new absorption band appears around 1478 and 1619 cm^{-1} , which are ascribed to tetra-substituted benzoxazine ring and intermolecular hydrogen, bonded phenolic OH [23], [24]. These indicate that the mannich bridge linkage and phenolic hydroxyl groups were produced by the ring-opening polymerization of the Bisphenol-A based benzoxazine.

3.2 CURING KINETICS

The curing behavior of benzoxazine (BA-A) was studied by DSC analysis, which is one of the widely used techniques for cure kinetic studies of thermoset materials. DSC has an advantage of being on the same assumption as the heat equation, which is the proportionality between the rate of heat generation and the rate of the reaction. The Kissinger method [25], curing kinetics analysis is based on the rate Eq.(1)

$$-\ln(\beta T_p) = -\ln(A/E_a) + (1/T_p)(E_a/R) \dots\dots\dots (1)$$

A and E_a were obtained by the plotting of $-\ln(\beta T_p)$ versus $1/T_p$, where T_p is the peak temperature. The curing kinetics from DSC at different heating rates, required to obtain the fundamental kinetic constants of the activation energy (E_a), were obtained from the plotting of $-\ln(\beta T_p)$ against $1/T_p$.

3.2.1 DSC THERMOGRAM OF SAME COMPOSITE AT DIFFERENT HEATING RATE

The DSC thermogram of neat, 3wt% nanoclay filled and 10wt% nanoclay filled compositions at heating rate 5, 10, 15, 20° C /min are given in the fig: 3, 4, 5 respectively, in all the cases as heating rate increase area under the curve increase.

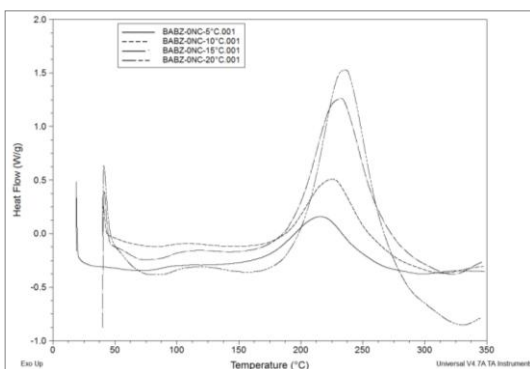


Fig 3: DSC curve of benzoxazine (BA-A) and 0% Nano clay (NC)

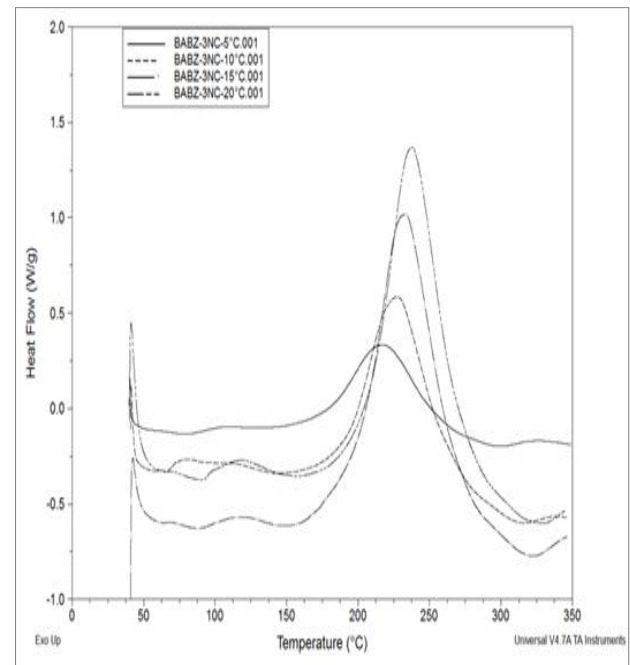


Fig 4: DSC curve of benzoxazine (BA-A) and 3% Nano clay (NC)

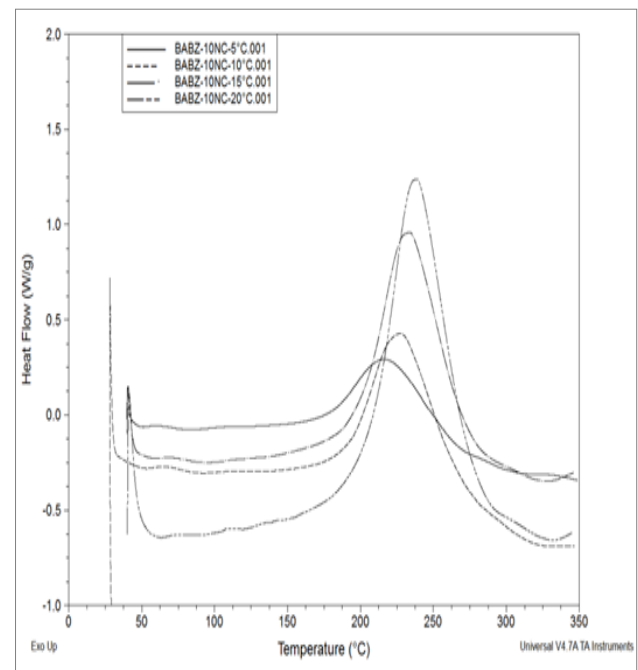


Fig 5: DSC curve of benzoxazine (BA-A) and 10% Nano clay (NC)

Table-I DSC heat flow maximum

Benzoxazine Composite (BA-A+NC)	Temperature(°C/min)	Temperature corresponding to maximum heat flow (°C)
BA-A+0NC	5	215.43
	10	226.4
	15	231.83
	20	237.01
BA-A+3NC	5	216.15
	10	226.85
	15	232.66
	20	238.6
BA-A+10NC	5	214.72
	10	228.22
	15	233.27
	20	238.98

As heating rate increase, the maximum temperature of the curve increase (as shown in the Table-iii) because at lower heating rate enough time is given for uniform temperature distribution across the material so then curing takes place early.

3.2.2 DSC THERMOGRAM OF DIFFERENT COMPOSITIONS AT HEATING RATE

The DSC thermogram of different compositions at heating rate of neat, 3wt% nanoclay filled and 10wt% nanoclay filled compositions at heating rate 5, 10, 15, 20° C /min are given in the fig:6, 7, 8& 9 respectively.

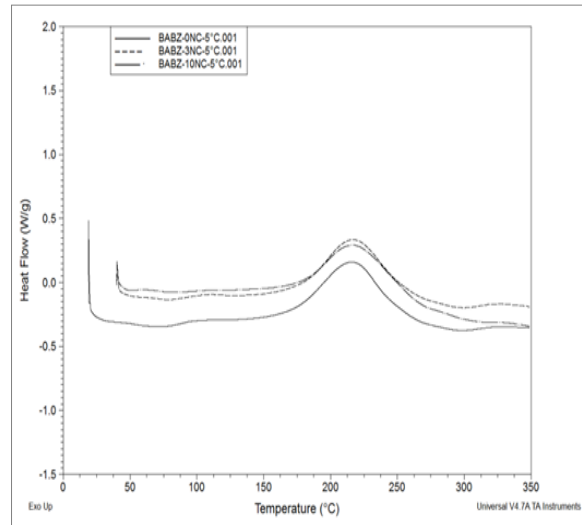


Fig 6: Shows the heating rate of different composite at 5° C

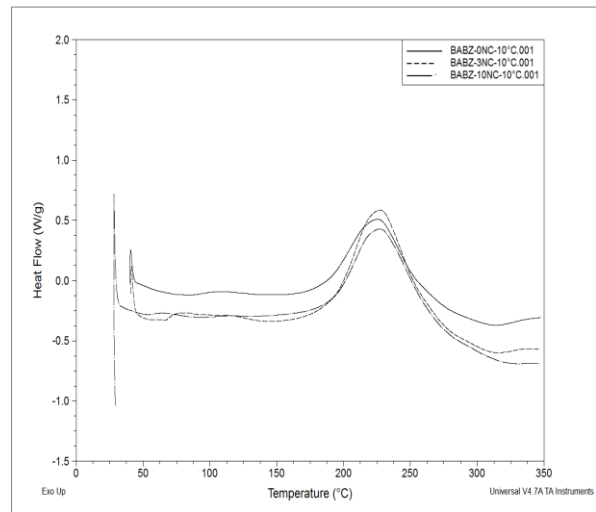


Fig 7: Shows the heating rate of different composite at 5° C

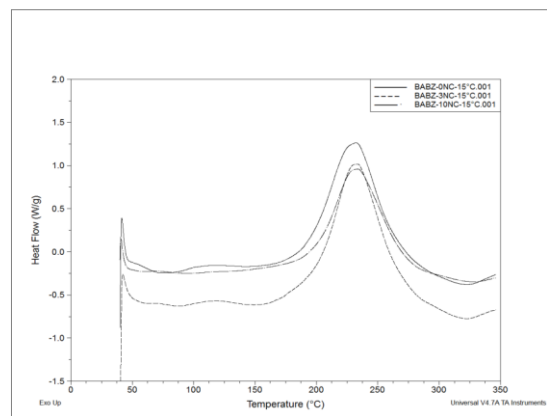


Fig 8: Shows the heating rate of different composite at 15° C

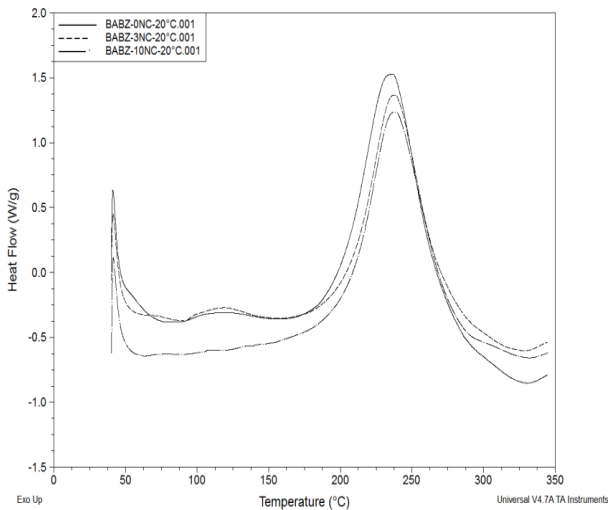


Fig 9: Shows the heating rate of different composite at 20⁰C

The DSC thermogram of neat, 3wt% nanoclay filled and 10wt% nanoclay filled compositions at the heating rate 5, 10, 15 and 20⁰ C /min are given in the fig: 6, 7, 8 and 9 respectively. The exotherm shows different trends at different heating rate at 5⁰ C /min the heat flow of neat benzoxazine is lower than the nanoclay filled composites; even though as 15 & 20⁰ C /min the heat flow for neat is higher than that of nanoclay filled composites. The change starts at 10⁰ C /min.

3.2.3 ACTIVATION ENERGY OF BA-A AND BA-A+NC BY DSC

The plot of $-\ln(\beta/T_p^2)$ against $1/T_p$, for benzoxazine and benzoxazine filled nanocomposite are shown in Fig 10: The curing kinetics with DSC at different heating rates, used to obtain the fundamental kinetic constant of the activation energy (Ea), were obtained from the plotting of $-\ln(\beta/T_p^2)$ against $1/T_p$ as shown below.

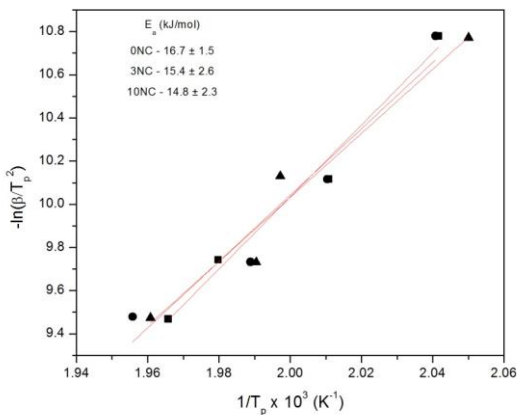


Fig 10: plot of $-\ln(\beta/T_p^2)$ versus $1/T_p$ for benzoxazine and benzoxazine composite.

From the graph it shows that benzoxazine has high activation energy(Ea) of 16.7 and benzoxazine + 3wt% nano clay has activation energy(Ea) of 15.4 while benzoxazine + 10wt% nano clay has activation energy(Ea) of 14.8. It shows that benzoxazine has higher activation energy than the benzoxazine nanocomposite, thus it require less energy to attain the rate of the reaction. The kinetic parameters of benzoxazine composite obtained by kissinger analysis are given in the Table-IV. From the table it is evident that the energy of uncured benzoxazine has high activation energy while compared to benzoxazine nanocomposite due to the incorporation of nanoclay present .It is also assumed that the modifier in the nanoclay catalysis the cure reaction thus reduces the activation energy (Ea).

Table-2 Kinetic parameters of Benzoxazine composite : Obtained by Kissinger's Analysis

Benzoxazine Composite	β (°C/min)	Tp (°C)	Ea (KJ/mol)
BA-A + 0wt% NC	5	216.8	16.7±1.5
	10	224.3	
	15	232.1	
	20	235.7	
BA-A + 3wt% NC	5	217	15.4±2.6
	10	224.4	
	15	229.8	
	20	238.3	
BA-A + 10wt% NC	5	214.8	14.8±2.3
	10	227.7	
	15	229.4	
	20	237	

3.3 THERMAL DECOMPOSITION

In the polymer degradation that the rate of conversion are proportional to the concentration of reacted material. The flynn-wall-ozawa method [26] rate of conversion can be expressed by the following basic rate Eq (2)

$$\log \beta = \log A Ea/g(\alpha)R - 2.315 - 0.457 Ea/RT \dots\dots\dots (2)$$

The Ea of the thermal degradation process of the alloy was

determined from the slop of the straight line $\log\beta$ versus $1/T$. The thermograms of the neat benzoxazine and nanoclay filled benzoxazine composites are shown in following Fig: 11, 12, and 13.

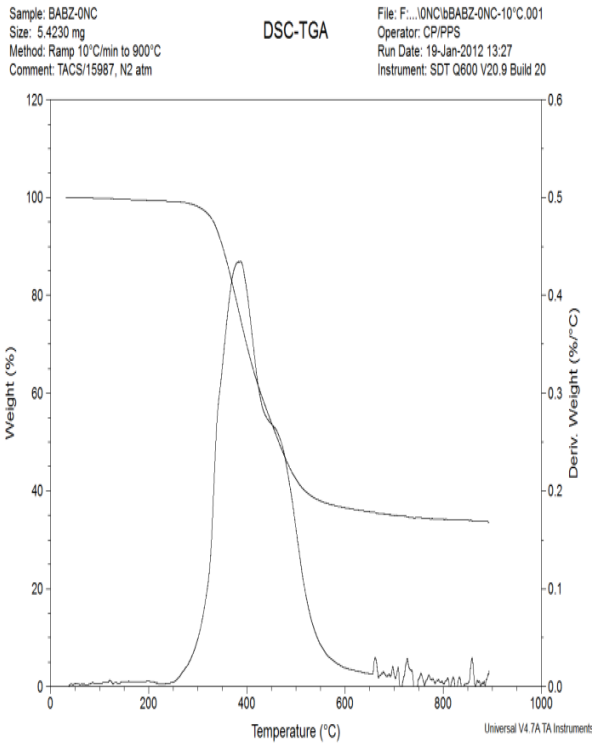


Fig11: TGA thermograms of the benzoxazine under nitrogen at 10⁰C.

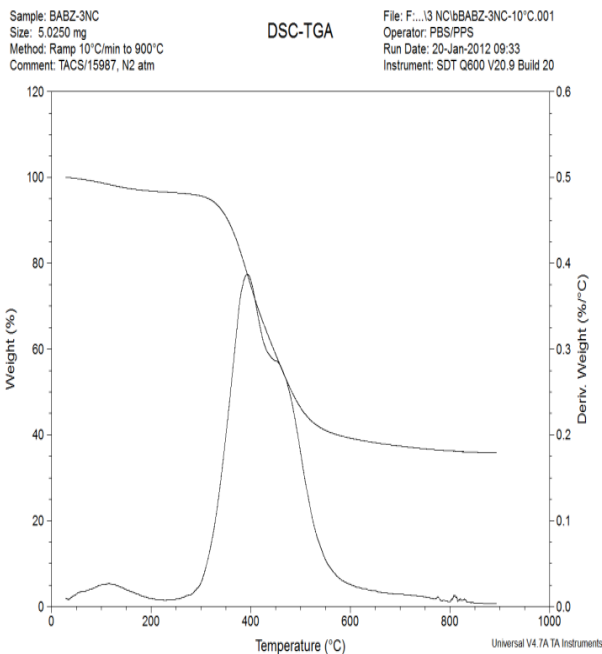


Fig12: TGA thermograms of the BA-A +3wt% NC under nitrogen at 10⁰C.

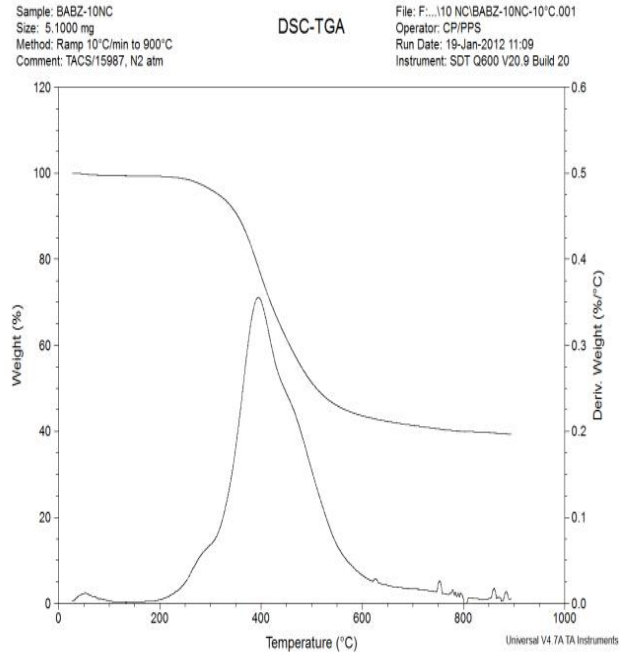


Fig13: TGA thermograms of the BA-A +10wt% NC under nitrogen at 10⁰C.

The TGA thermogram of neat, 3wt% nanoclay filled and 10wt% nanoclay filled under nitrogen at 10⁰ C is shown in the fig: 11, 12 &13 respectively. The onset degradation of BA-A+0NC is 323⁰ C, BA+3NC is 346⁰ C and BA-A+10NC is 346⁰ C and there is a difference of 23⁰ C in onset degradation compared to BA-A & BA-A+NC. The residue at 900⁰ C for BA-A+0NC is 33.7%, BA-A+3NC is 35.8% and BA-A+10NC is 39.4% and the derivative peak maximum of BA-A+0NC is 379⁰ C, BA-A+3NC is 396⁰ C and BA-A+10NC is 395⁰ C and there is a difference 17⁰ C in derivative peak maximum while comparing BA-A & BA-A+NC. (As shown in Table-3)

Table-3 Analysis of thermograms at 10⁰C/min

Benzoxazine composite	Onset of degradation (° C)	Residue at 900° C (%)	Derivative peak max (° C)
BA-A + 0NC	323	33.7	379
BA-A + 3 NC	346	35.8	396
BA-A + 10NC	346	39.4	395

The thermogram of the three different composites are compared in Fig 14.

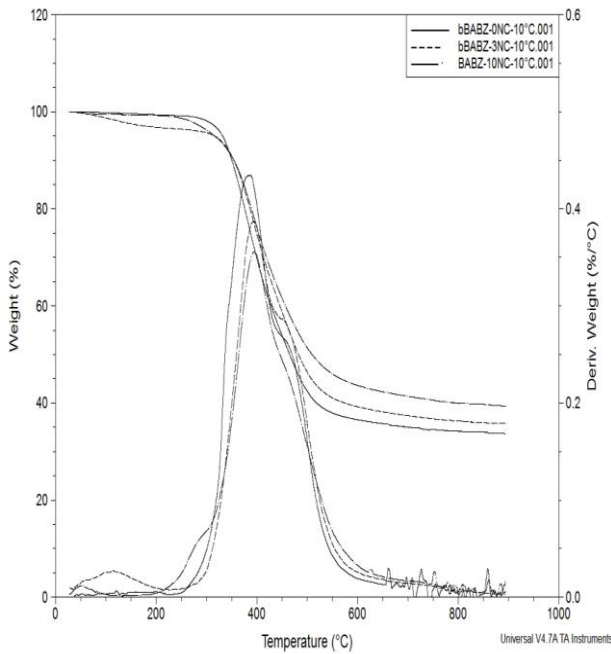


Fig 14: Comparison of BA-A+0NC, BA-A+ 3NC and BA-A + 10NC under nitrogen at 10°C.

3.3.1 TGA kinetic degradation

In order to study the kinetics of decomposition of neat and nanoclay filled benzoxazine, TGA was done at four different heating rate that is, 5, 10, 15 & 20⁰ C /min. The thermograms are given in Fig 15, 16, 17 respectively for neat, 3wt% & 10wt% nanoclay filled composite.

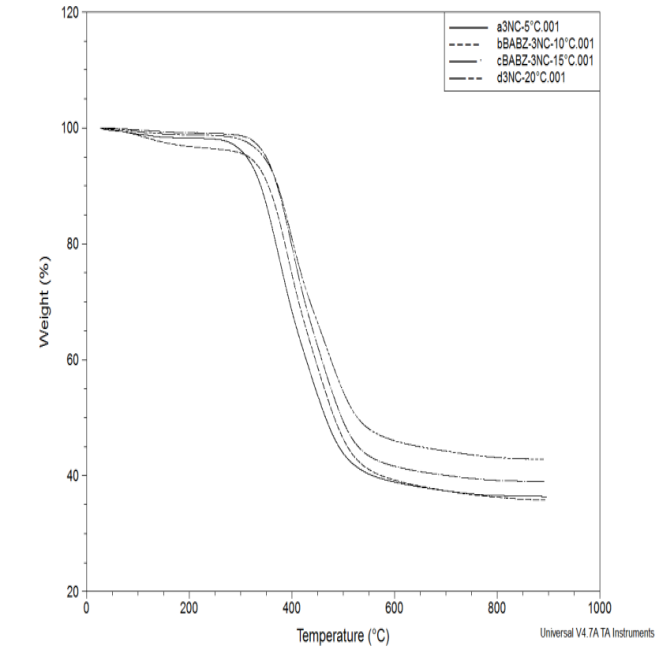


Fig 16: Kinetic degradation of BA-A + 3NC at different heating rate

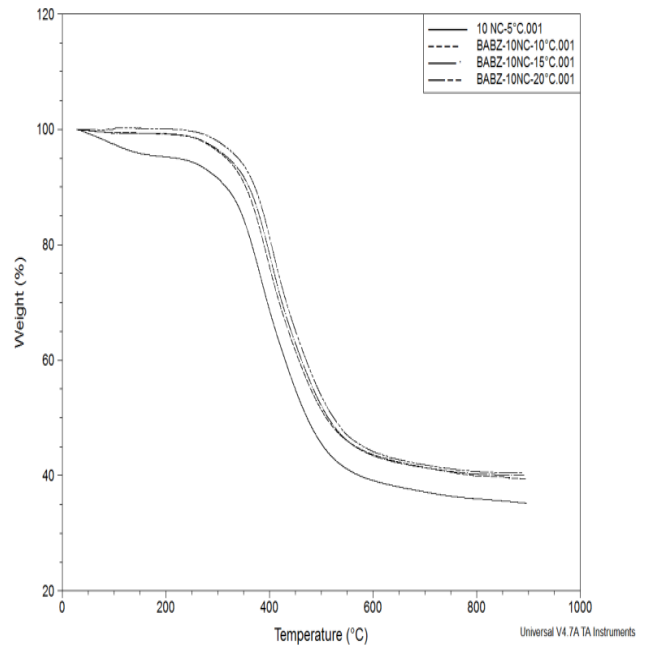


Fig 17: Kinetic degradation of BA-A + 10NC at different heating rate

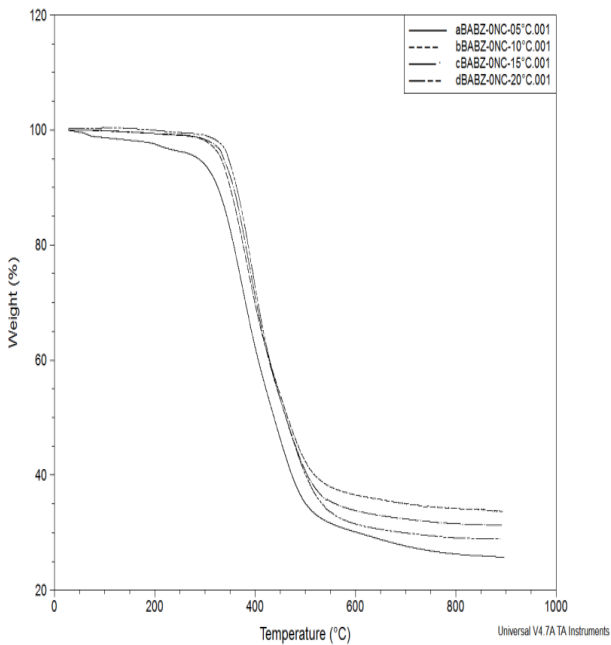


Fig 15: Kinetic degradation of BA-A + 0NC at different heating rate

The kinetic degradation of benzoxazine and benzoxazine nanocomposite at different heating rate are shown in above fig: 15, 16, and 17. The above fig: shows the benzoxazine and benzoxazine nanocomposite kinetic degradation takes place in two or more stages. The curve shows the broadening of the derivative peaks, indicating a slower decomposition rate over a wider temperature range.

3.3.2 DEGRADATION CONVERSION OF 10, 30, 50, 70 % AT 300-800° C

In order to study the degradation in activation energy of benzoxazine and benzoxazine nanocomposite. The degradation conversion of 10, 30, 50, 70% at 300-800° C were obtained for benzoxazine and benzoxazine nanocomposite, as shown in fig: 18, 19 & 20 respectively.

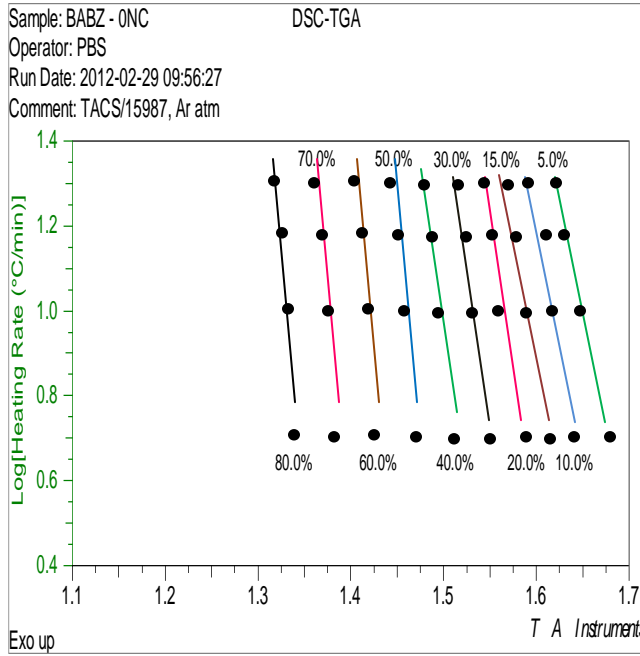


Fig 18 : plot of log β versus 1000/T degradation conversion of BA-A+0NC

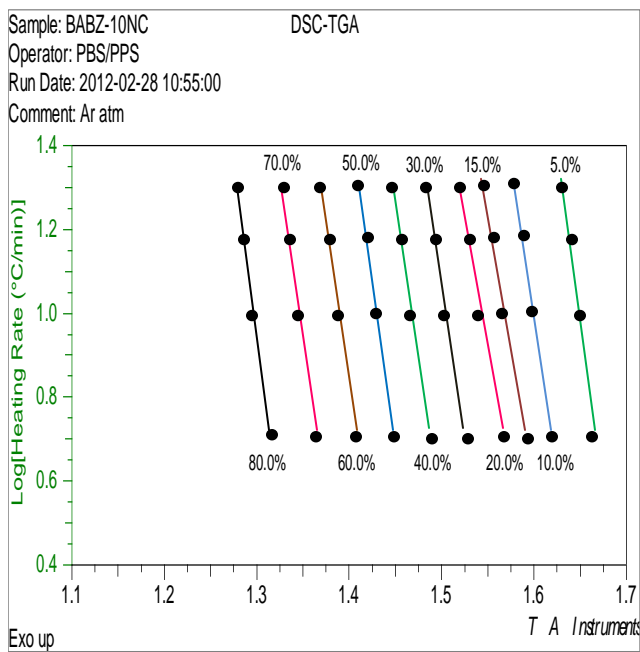


Fig 19: plot of log β versus 1000/T degradation conversion of BA-A+3NC

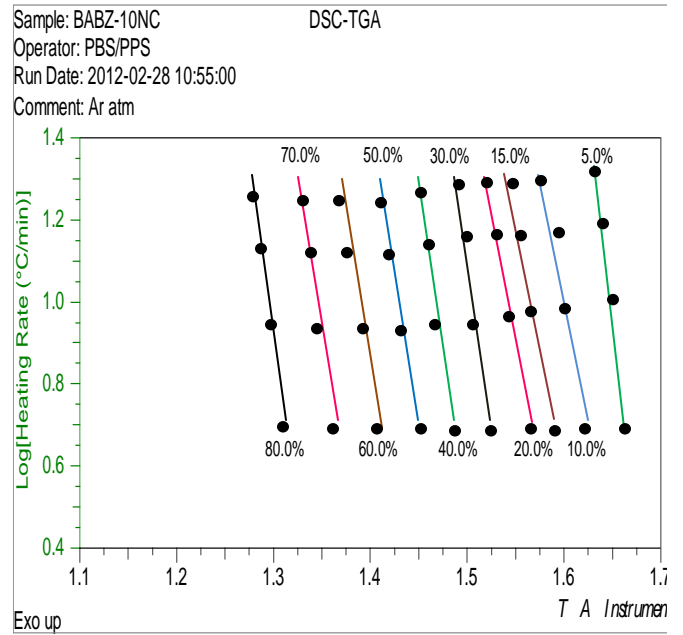


Fig 20: plot of log β versus 1000/T degradation conversion of BA-A+10NC

Table-4 Activation energy obtained by flynn-Wall-Ozawa of BA-A and BA-A+NC

Conversion (%) at 300-800°C.	E _a of BA-A+ 0NC (KJ/mol)	E _a of BA-A+ 3NC (KJ/mol)	E _a of BA-A+ 10NC (KJ/mol)
10	187.4	178.2	234.5
30	242.9	187.1	236.2
50	357.4	203.3	282.3
70	434.7	208.9	303
Average	305.6±111.45	194.4±14.21	264.0±34.16

The activation energy obtained by Flynn-Wall-Ozawa of BA-A & BA-A+NC is shown in the Table-iv. The average activation energy of BA-A+0NC is 305.6±111.45, BA-A+3NC

is 194.4 ± 14.21 and BA-A+10NC is 264.0 ± 34.16 . While comparing the activation energy BA-A+0NC has high activation energy than BA-A+3NC & BA-A+10NC.

4. CONCLUSION

The benzoxazine monomer based on bisphenol-A was prepared and the structure was characterized by FT-IR. The polymerization behavior, network structure and thermal properties were studied by DSC, FT-IR and TGA. The structure of benzoxazine was confirmed by FT-IR analysis. From FT-IR the characteristic absorption peak of oxazine ring was observed at 946 cm^{-1} and also the asymmetric and symmetric stretching vibration of C-O-C located at 1231 , 1248 cm^{-1} and 1030 cm^{-1} respectively. The asymmetric and symmetric stretching vibration of C-N-C located at 1120 , 1159 cm^{-1} and 824 cm^{-1} confirmed the formation of benzoxazine ring structure. There is an OH peak at 3421 cm^{-1} it may be due to ring-opening of benzoxazine structure in smaller quantity. The absorption bands at 755 and 694 cm^{-1} are assigned to the mode of mono-substituted benzene in the bisphenol-A skeleton. From the DSC analysis the activation energy (E_a) of benzoxazine and benzoxazine nanocomposite were determined using Kissinger method. The benzoxazine has high activation energy while benzoxazine nanocomposite has low activation energy (E_a), the value of activation energy (E_a) of the benzoxazine composites as follows; BA-A+0NC 16.7 ± 1.5 , BA-A+3N 15.4 ± 2.6 and BA-A+10NC 14.8 ± 2.3 respectively. The decrease in activation energy (E_a) with increase in nanoclay content may be due to the presence of aliphatic and quaternary ammonium salt present in the nanoclay, which act as a catalyst and decreases the activation energy. From the TGA analysis, the char yield, thermal degradation and derivative peak were determined. The activation energy of decomposition was determined using Flynn-Wall-Ozawa method. The benzoxazine nanocomposite has high char yield while compared to benzoxazine, the values are as follows BA-A+0NC 33.7%, BA-A+3NC 35.8% and BA-A+10NC 39.4 % respectively. The onset thermal degradation of BA-A+0NC is 323°C , BA-A+3NC is 346°C and BA-A+10NC is 346°C respectively. It is evident from the studies that the presence of nanoclay improves the thermal stability of Polybenzoxazine as the onset of degradation increases with the presence of nanoclay. However no conclusive assumption could be made from the kinetic analysis of decomposition. This may be due to the multiple decomposition steps in the degradation of Polybenzoxazine in the temperature range from 300 - 800°C .

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