

TGA, DSC, DTG Properties of Epoxy Polymer Nanocomposites by Adding Hexagonal Boron Nitride Nanoparticles

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Abstract: In this study, the thermal analysis methods reported for the characterization of epoxy/h-BN nanocomposites were conducted using Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). A thermosetting epoxy resin was mixed with a different weight percent of hexagonal Boron Nitride Nanoparticles (BNNPs) to prepare epoxy nanocomposites. Study of non-isothermal kinetics decomposition of epoxy and epoxy/BNNPs nanocomposites were carried out by utilizing Thermogravimetric Analysis (TGA). The samples were heated from room temperature to 600°C at a constant heating rate of 10°C/min under oxidative atmosphere using air. TGA and DTG curves obtained from the decomposition were analyzed using the Coats-Redfern method. Kinetic parameters were determined for all specimens that show a good correlation with the linear correlation coefficient. Where Coats and Redfern procedure was the best to result in good estimates of the kinetic parameters.

Key words: Epoxy nanocomposites, boron nitride nanoparticles, thermal degradation and thermogravimetric analysis, DSC, DTA, epoxy/BNNPs

INTRODUCTION

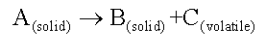
Nanocomposites, a high-performance material in which at least one of the phases shows dimensions in the nanometer range ($1 \text{ nm} = 10^{-9} \text{ m}$). Where exhibit unusual property combinations and unique design possibilities. Being environmentally friendly, applications of nanocomposites offer new technology and business opportunities for several sectors of the aerospace, automotive, electronics and biotechnology industries (Camargo *et al.*, 2009). The most common materials used as a matrix in nanocomposites are polymers (e.g., epoxy, nylon, polyepoxide, polyetherimide), ceramics, (e.g., alumina, glass, porcelain, boron nitride) and metals, (e.g., iron, titanium, magnesium) (Hu *et al.*, 2010). Nanoparticles are a microscopic particle with at least one dimension $<100 \text{ nm}$ (Naito *et al.*, 2018). Hexagonal Boron Nitride (h-BN) is also known as 'white graphite' has a similar (hexagonal) crystal structure as of graphite. This crystal structure high thermal conductivity and chemical stability and provides excellent lubricating properties (Xue *et al.*, 2014).

A very important process is thermal degradation which helps to know the polymer structure on the thermal stability, the optimum temperature of use, kinetic parameters and thermodynamic properties (Al-Bayat and Farhan, 2015). In this study, influences of different weight fraction of boron nitride nanoparticles on the

decomposition process of an epoxy polymer was investigated by Thermogravimetric Analysis (TGA), Derivative Thermo-Gravimetric (DTG) and Differential Scanning Calorimetry (DSC). The decomposition kinetic parameters of the mixtures were also determined according to the Coats-Redfern method. Several reports have been carried out about the investigated such properties as by Junwei *et al.* showed that the thermal conductivity of BN/EP composites exhibits a very high thermal conductivity and relatively good mechanical properties. The thermal conductivity of the composites increases with the increasing content of microparticle BN and also by TGA analysis showed that the thermal decomposition temperature increases with the increases concentration of BN (Gu *et al.*, 2012). Xiao *et al.* (2008) studied improving thermal properties Polyarylene Ether Nitrile (PEN) by the incorporation of Boron Nitride Nanosheet (BNNS), the results show a good thermal stability of BNNS/PEN nanocomposites, the glass transition temperatures and initial decomposition temperatures of them are higher than 200 and 4908 (Xiao *et al.*, 2008).

Kinetics theory: The application of dynamic TGA, DSC and DTGA methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during solid's degradation. In this study, method Cost-Redfern has been used to analyze the

non-isothermal kinetics. The pyrolysis process may be represented by the following reaction scheme (Al-Ayed).



Usually, the change in the extent of reaction (α) is used to study the solid state reactions kinetics:

$$\alpha = \frac{m_o - m_t}{m_o - m_\infty} \quad (1)$$

where, m_o , m_t and m_∞ are initial sample mass, sample mass at time t and sample mass at the end of reaction, respectively (Ebrahimi-Kahrizsangi and Abbasi, 2008).

In the non-isothermal TGA experiments, the mass of the sample is measured as a function of temperature while the reaction proceeds for a constant heating rates, β ($^{\circ}\text{C}/\text{min}$) (Uzun and Yaman, 2015).

The rate of conversion dx/dt for TGA experiment at constant heating rate of temperature change, $\beta = dT/dt$ may be expressed by Eq. 2:

$$\frac{dx}{dt} = \beta \frac{dx}{dT} = K(T)f(x) \quad (2)$$

Where:

x = The degree of advance
 $f(x)$ and $K(T)$ = Function of conversion and Temperature, respectively

$K(T)$, the temperature dependence of the rate of weight loss is often modeled successfully by Arrhenius equation (Eq. 3) (Aboukhas and El Harfi, 2008):

$$K(T) = A_o \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

Where:

E_a = The apparent activation Energy
 A_o = The pre-exponential factor
 R = The gas constant

Coats-Redfern is the most commonly used to find activation energy as follows:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{A_o R}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (4)$$

Plotting $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ against $1000/T$, to determine the activation energy from the slope of the linear

expression, the value of frequency factor (A_o) can be determined from the intercept on the y-axis and by substituting values of activation energy in Eq. 5 (Kim and Oh, 2005; Maitra *et al.*, 2007):

$$\text{Intercept} = \ln\left(\frac{A_o R}{\beta E}\right)\left\{1 - \frac{2RT}{E_a}\right\} \quad (5)$$

MATERIALS AND METHODS

Experimental: A commercial epoxy (EUXIT 50) is primarily low viscosity (highly fluid) special mixture with high capillary action. Mix ratio (by weight) of the epoxy resin to the hardener was 3:1, viscosity equal 1 (poise) at 20. The properties of the epoxy resin are specific density (g/cm^3) at 20 is 1.05 produced by Egyptian Swiss chemical industries company was used in this present investigation.

Samples of the epoxy and epoxy nanocomposites at a different weight percentage of hexagonal boron nitride nanoparticles (0.5, 0.7, 1.2 and 5%) are prepared by hand lay-up technique and mixing process. All content mixed thoroughly before casting, then the samples left at room temperature for one day and then for post curing, the sample sheets were left for 1 h in an oven at temperature 50.

The hexagonal boron nitride Nanoparticles (NPs) utilized in the present study have been procured from (US Research Nanomaterials inc. USA) (99.8+% purity as per suppliers data), Atomic Force Microscopy (AFM) was used (CSPM Scanning Probe Microscope) to measure the average particles size, surface roughness and Root Mean Square (RMS) of BN nanoparticles as shown in Table 1, Fig. 1 shows image (3D-AFM) of nanoparticles boron nitride and the particles size distribution.

The thermogravimetric measurement was carried out by a Linseis STA PT1000 TG-DSC (STA Simultaneous Thermal Analysis) analyzer in non-isothermal condition. This experiment was carried out at Ibn AL-Haitham Company (Central Service Laboratory). The sample weights were (21 mg). Decomposition profiles were obtained with a constant heating rate 10/min in the oxidative atmosphere using air.

Table 1: Average diameter, surface roughness and root mean square values of nanoparticles boron nitride

Material	Average diameter (nm)	Surface roughness (nm)	RMS (nm)	Peak-to-peak (nm)
Boron nitride	52.91	2.83	3.27	11.3

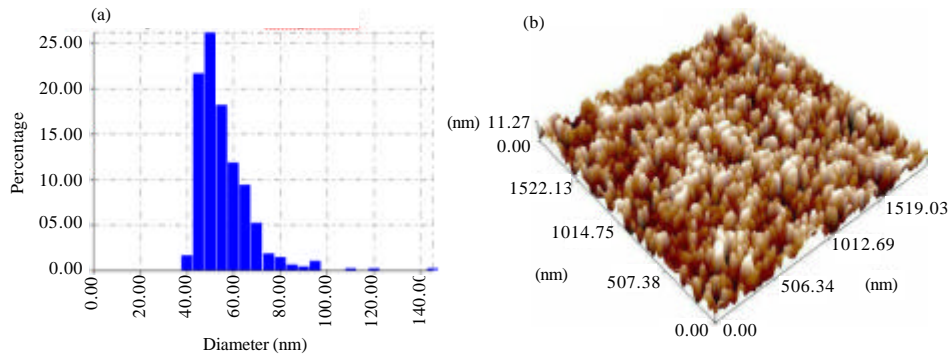


Fig. 1: AFM of nanoparticles boron nitride; a) Granularity distribution of nanoparticles; b) 3D image AFM

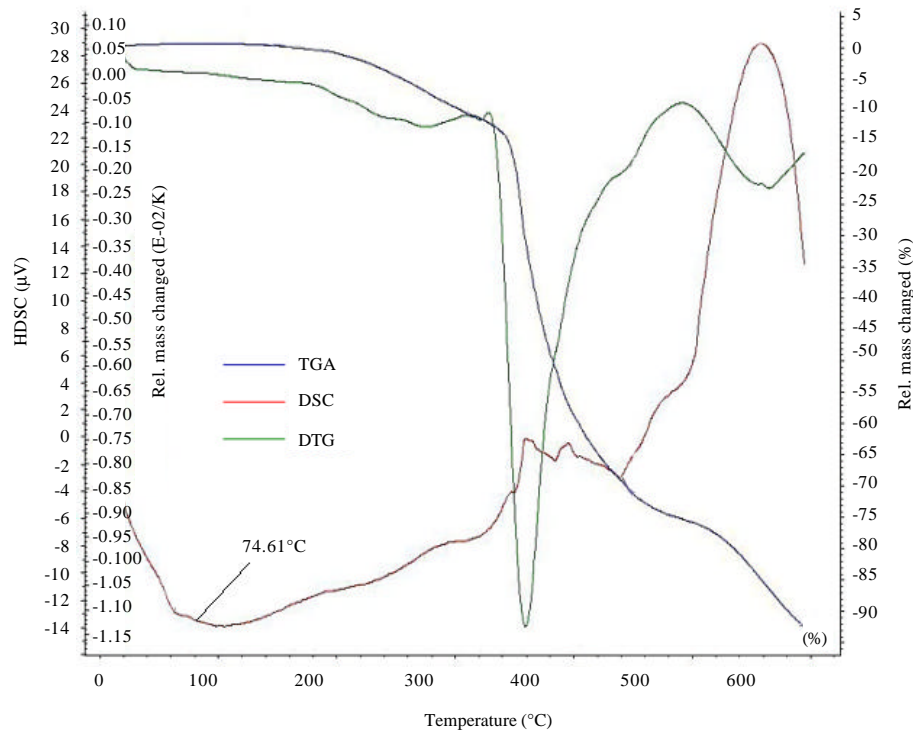


Fig. 2: TGA, DSC, DTG curves of pure epoxy resin at heating rate 10°C/min

RESULTS AND DISCUSSION

Thermogravimetric Analysis (TGA): Thermogravimetric Analysis (TGA) has been used as a means of determining pyrolysis characteristics and also to determine kinetic parameters (Uzun and Yaman, 2015) TGA and DTG for pure epoxy and epoxy/BNNPs nanocomposites are shown in Fig 2-7 at heating rate 10/min under oxidative atmosphere using air. Mass loss of degraded nanocomposites as a function of temperature was determined by a TGA technique and was an irreversible process. Table 2 shows the loss mass due to decomposition of the thermosetting epoxy resin and with various contents of BNNPs. From Fig. 2-6, it was showed

that the pure epoxy have a two stage mass loss while epoxy/BNNPs nanocomposites have a two stage in the 0.5, 0.7, 1 wt.% and 3 stages in 2, 5 wt.%. This means that when increasing the ratio of BNNPs in the epoxy resin will lead to increase the number stages of in the decomposition it was also noticed that the rate of mass loss during degradation at 592°C of nanocomposites is lower than pure epoxy, since, its thermal stability was increase and the degradation process shift to a higher temperature.

Differential Scanning Calorimetry (DSC): Differential Scanning Calorimetry (DSC) analysis was carried out to study the cure properties of the epoxy resin and

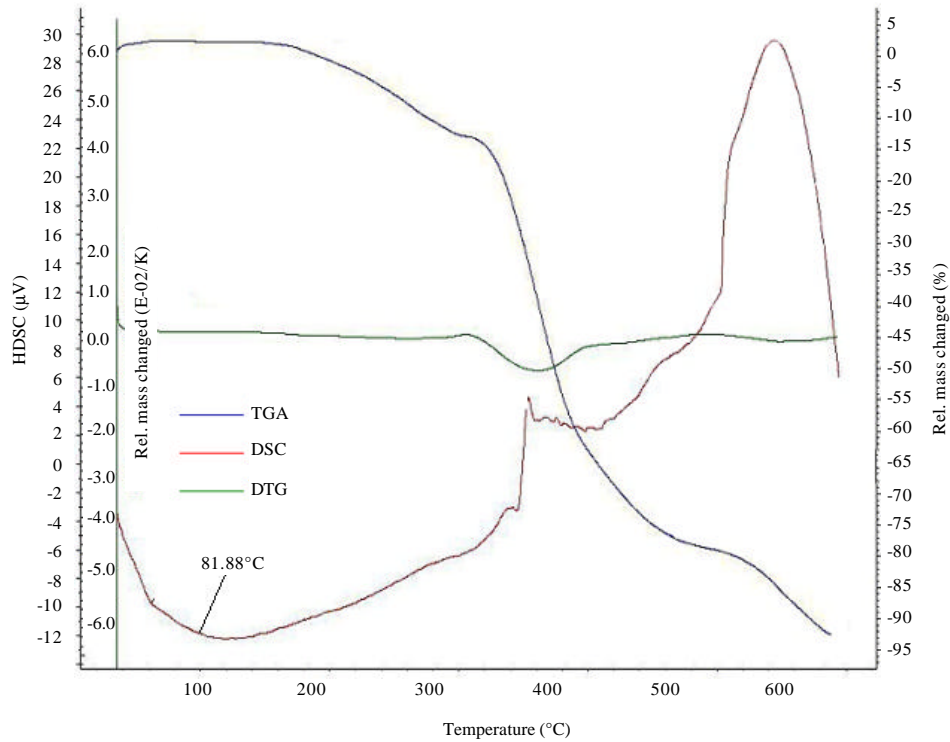


Fig. 3: TGA, DSC, DTG curves of epoxy/BNNPs 0.5 wt. % at heating rate 10°C/min

Table 2: The mass loss of the epoxy resin with various contents of BNNPs

Samples	First stage mass loss (%)	Second stage mass loss (%)	Third stage mass loss (%)	Total mass loss (%) at 592°C
Epoxy pure	448.56°C, -71.26	594.5°C, -21.2	-	-92.46
Epoxy+0.5 BN	463.9°C, -79.02	593.57°C, -16.4	-	-95.42
Epoxy+0.7 BN	428.51°C, -73.84	594.10°C, -26.42	-	-100.26
Epoxy+1 BN	454.01°C, -70.18	594.16°C, -22.73	-	-92.91
Epoxy+2 BN	314.81°C, -20.89	443.32°C, -53.83	591.35°C, -26.29	-101.07
Epoxy+5 BN	325.57°C, -14.26	442.62°C, -49.65	594.09°C, 24.3	-88.21

Table 3: The glass transition temperature

BNNPs (wt.%)	TGA (°C)
0.0	74.61
0.5	81.88
0.7	102.73
1.0	123.72
2.0	123.82
5.0	110.01

epoxy/BNNPs nanocomposites as shown in Fig. 2-6. Dynamic scans were made from room temperature to 600°C at a constant heating rate 10°C/min under oxidative atmosphere using air. The value of glass transition temperature was determined from Fig. 2-6. It was noticed that the glass transition temperature increased with the increase in the weight fraction of boron nitride nanoparticles as shown in Table 3. Where the addition of nanoparticles in epoxy matrix lead to reduce the mobility of the epoxy chains due to formation high immobility monolayer around each nanoparticle while the matrix chains (epoxy chains not bonded to nanoparticles)

bonded to that monolayer constrained the non-contact matrix chains, so, the network of nanoparticles reduce the overall mobility of the nanocomposites system. Due to reducing free volume space occupied by the spaces at the end of chains.

Kinetics of thermal decomposition: The Coast-Redfern integral kinetic method was applied to calculate the kinetic parameters. This method can determine the decomposition activation energy by specifying a heating rate. In this study, the TGA curves at a heating rate of 10°C/min were used to calculate the degradation kinetics for all samples using Eq. 4. The results are given in Table 4.

The activation energy increased gradually when boron nitride nanoparticles were added to epoxy from 59.323 kJ/mol for the pure epoxy to 105.311 kJ/mol at ratio 5 wt.% of BNNPs. The increasing in the value of activation energy is due to the increase in the decomposition temperature of all examined samples in turn

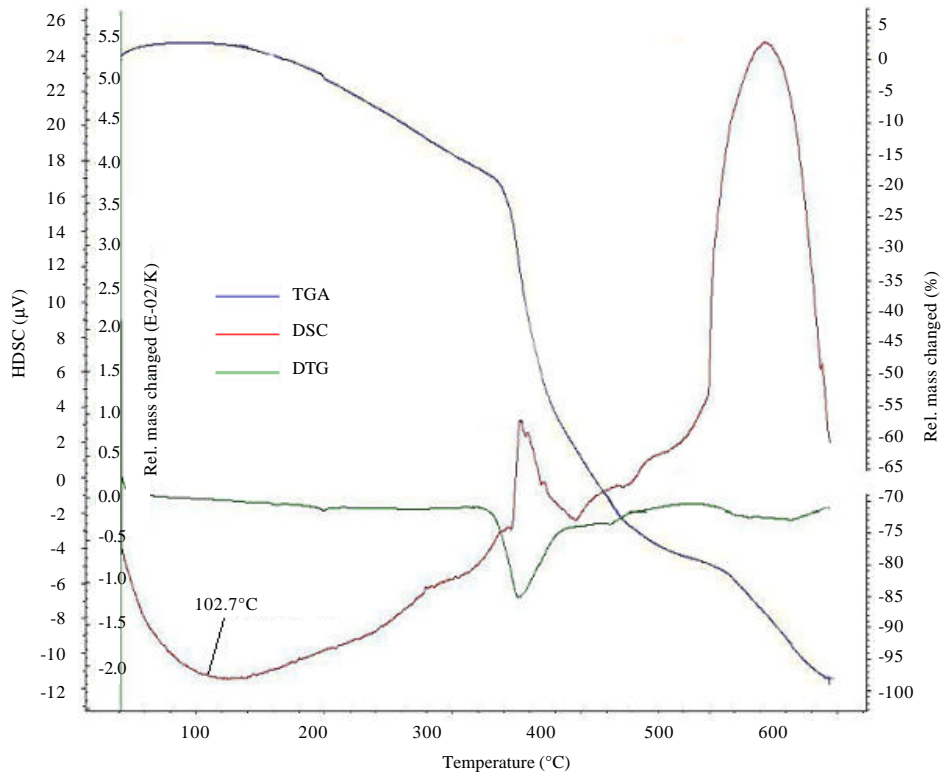


Fig. 4: TGA, DSC, DTG curves of epoxy/BNNPs 0.7 wt.% at hating rate 10°C/min

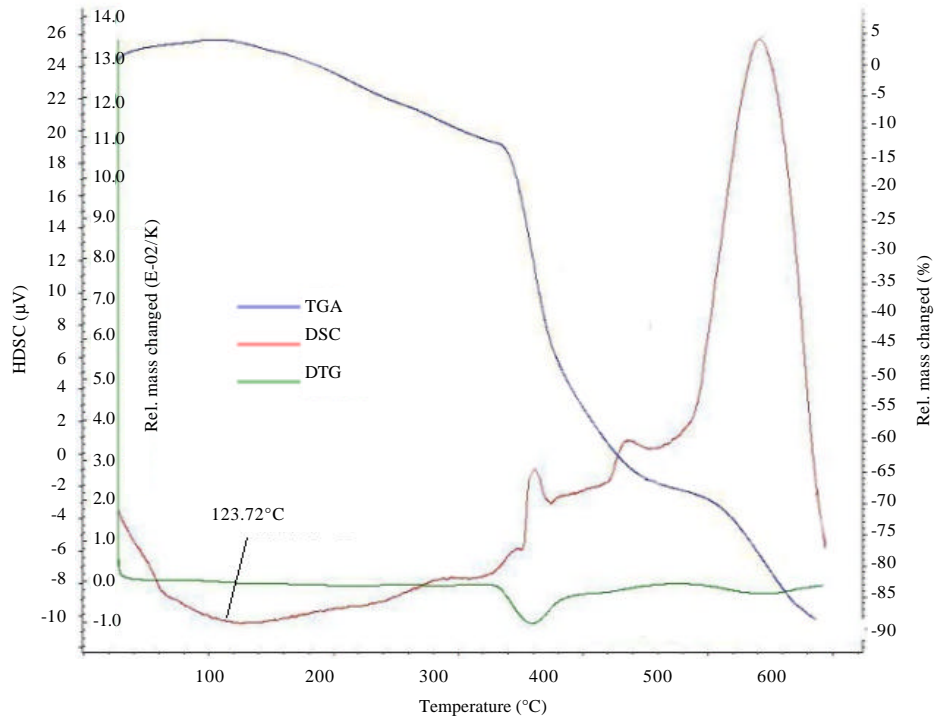


Fig. 5: TGA, DSC, DTG curves of epoxy/BNNPs 1 wt.% at hating rate 10°C/min

thermal stability will increases as shown in Table 4. Figure 8 shows Coast-Redfern plot of epoxy/BNNPs

of different weight fraction and at constant heating rates. The results obtained are shown in the Table 4.

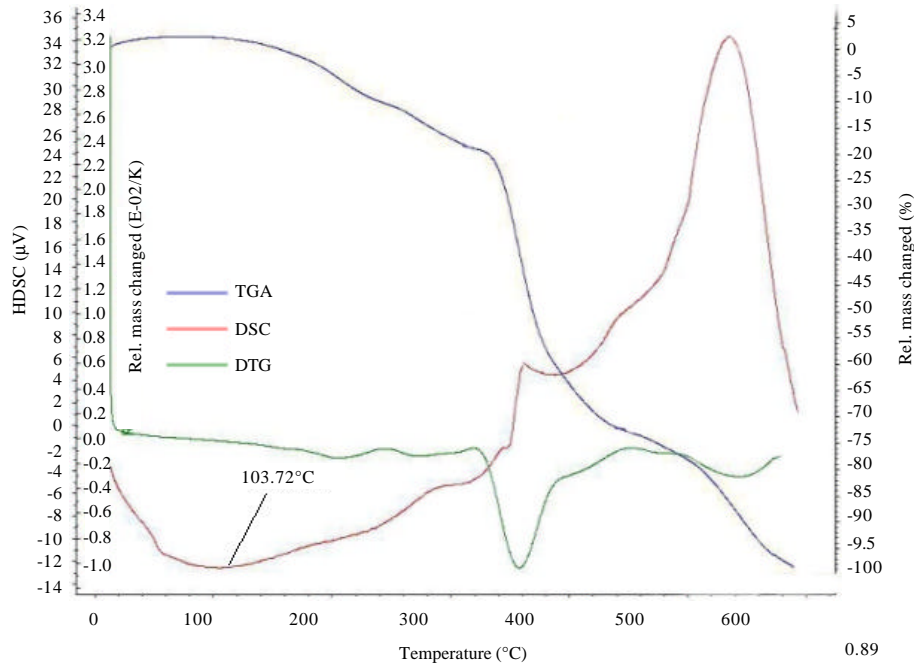


Fig. 6: TGA, DSC, DTG curves of epoxy/BNNPs 2 wt.% at hating rate 10°C/min

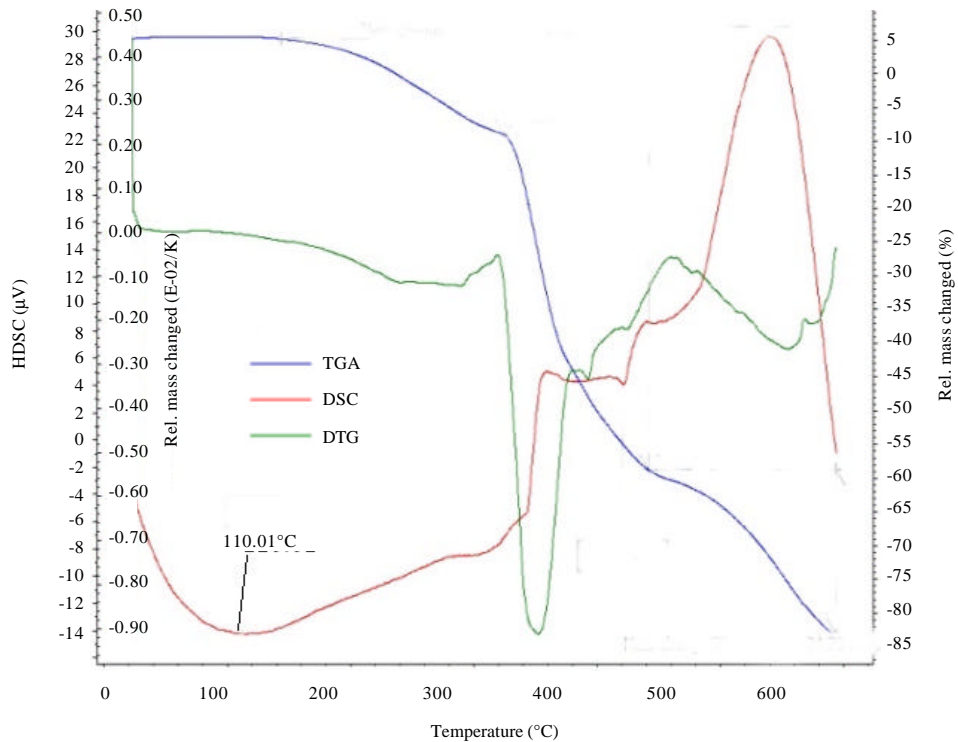


Fig. 7: TGA, DSC, DTG curves of epoxy/BNNPs 5 wt.% at hating rate 10°C/min

It was noticed there is a linear dependence between $\ln A_0$ and E_a (Fig. 9) which gives a proof that the mechanistic kinetic equations employed adequately reflect the specific kinetic parameters, it means that the

most probable kinetic equations found describe correctly the mechanism of thermal destruction of the samples (Al-Bayaty and Farhan, 2015; Turmanova *et al.*, 2008).

Table 4: Results of the non-isothermal kinetic analysis for epoxy/BNNPs nanocomposites using coast-redfern method

BNNPs (wt.%)	Peak temperature (K)	Activation energy E _a (kJ/mol)	Reaction rate (S ⁻¹)	R ²
0.0	632.391	59.323	4.62E+05	0.999
0.5	629.576	60.695	7.27E+05	0.994
0.7	619.154	62.557	1.10E+06	0.999
1.0	632.255	69.361	2.81E+06	0.999
2.0	630.707	82.214	2.70E+07	0.990
5.0	624.100	105.311	5.13E+09	0.998

Table 5: Thermodynamics parameter for pure epoxy and epoxy/BNNPs nanocomposites

BNNPs (wt.%)	Activation energy (E) (kJ/mol)	Reaction rate constant, A _o (S ⁻¹)	ΔH (kJ/mol)	-ΔS (J/mol)	ΔG (kJ/mol)
0.0	59.323	4.62E+05	54.065	151.044	95.573
0.5	60.695	7.27E+05	55.460	147.239	92.753
0.7	62.557	1.10E+06	57.409	143.681	89.018
1.0	69.361	2.81E+06	64.105	136.029	86.069
2.0	82.214	2.70E+07	76.970	117.191	73.990
5.0	105.311	5.13E+09	100.750	73.432	146.038

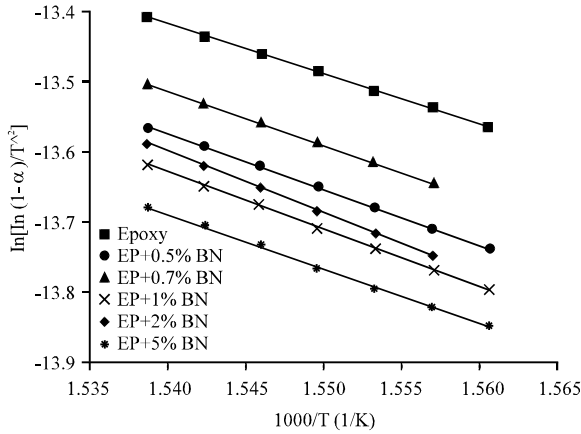


Fig. 8: Coast-Redfern plot for thermal degradation of Ep/BNNPs nanocomposites at constant heating rate 10°C/min

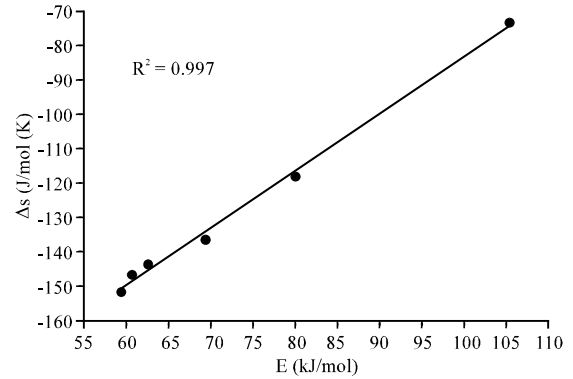


Fig. 10: Plot activation energy kJ/mol versus ΔS (J/mol K)

$$\Delta G = \Delta H - T_{peak} \Delta S \quad (8)$$

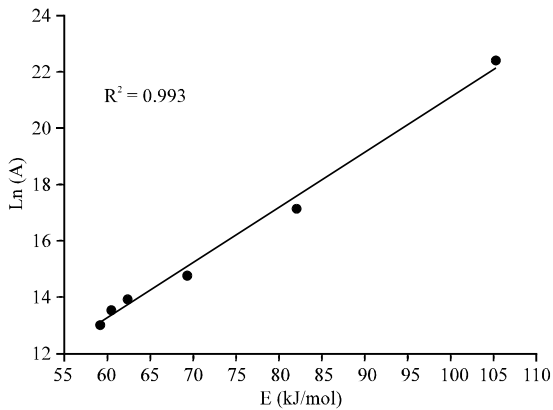


Fig. 9: Plot of activation energy versus ln A_o for the thermal decomposition of Ep/BNNPs

Thermodynamic parameters: Thermodynamic functions were calculated according to the following relationships (Low *et al.*, 1973; Ramakutty and Ramachandran, 2014):

$$\Delta H = E - RT_{peak} \quad (6)$$

$$\Delta S = R \left[\ln \left(\frac{h A_o}{K_b T_{peak}} \right) - 1 \right] \quad (7)$$

The thermodynamic parameters of: entropy of activation ΔS, enthalpy of activation ΔH and free energy of decomposition ΔG and T_{peak} is the maximum peak temperature, h plank constant and kb is Boltzmann constant, Table 5 shows the thermodynamics parameter of pure epoxy and epoxy/BNNPs nanocomposites. It is observed that the entropy of activation increases with the increase of activation energy the positive value of ΔG shows that the reaction involved in the decomposition of BNNPs nanocomposites is not spontaneous. However, there is a linear dependence between the entropy ΔS and the activation energy E_a as shown in Fig. 10.

CONCLUSION

TGA, DTG and DSC analysis of nanocomposites shows enhancement in the thermal stability of nanocomposites, the TG will increased when increased the weight fraction of boron nitride nanoparticles and the activation energy, activation entropy show the linear relationship between them that's mean the composites BNNPs has a high thermal stability.

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