Thermal Degradation Kinetics Epoxy (DGEBA) and Epoxy Reinforcement by Toner Carbon Nano Powder Composites

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ABSTRACT

In the present investigation epoxy resin (EP) mixed with different weight percent 2, 4, and 6% of toner carbon nano powder (TCNP) were used to prepare epoxy composite . The molding method was used to prepare EP and EP/TCNP composites specimens. Study of non isothermal degradation kinetics of EP and EP/TCNP composites were carried out by using thermo gravimetric analysis (TGA). The samples were heated from ambient temperature to 800 °C at different heating rates 5, 10, 15, and 20 C^{o}/min under helium as inert gas was used with flow rate 20 ml/min to yield gases and solid char. TG and DTG curves obtained from the decomposition were analyzed using iso-conversional method of Kissinger- Akahira-Sounose, and Coast-Redfern methods. Kinetic parameters were determined for all specimens were satisfactory presenting good correlation with linear correlation coefficient close to unit using SPSS package and was in a good agreement with published data. The experimental results show the decomposition of EP/TCNP composites obtained from thermal gravimetric analysis is faster comparing with those EP specimens. This enhancement is attributed to iron content in TCNP. The aim of this work is to characterize the thermal decomposition process in the relation to its kinetics.

Keywords: - Thermal degradation, Thermo gravimetric analysis, Epoxy composites, Toner carbon nano powder

1. INTRODUCTION

 Thermosetting polymer commonly used in engineering purpose as a modified with carbon particles, TiO_2, SiO_2, Al_2O_3, MgO, Clays, glass powders. However these particles and its particle size, surface area and interfacial adhesion have a great influence on mechanical property (1).The practical employment of epoxy and its composites required a great knowledge of its thermal stability which is useful in predicting the life time and study the kinetic parameters. Commonly polymeric material under degradation liberates gaseous compounds which can be studied by using TG/DTG, DTA, and DSC with FTIR (2). Thermal stability improved by using TGA for modifying epoxy by rubber powders since it have four benzene ring and resonance structure and decomposition occurred in one stage(2).Azeem M. et al(3) studied the kinetics of thermal degradation of epoxy/Al composite and the comparison of pure epoxy and found Al powder affects the thermal decomposition of the composite since Al catalyzing the process at relatively low temperatures while at higher temperature the catalytic activity reduced leads to increase its thermal stability. Other investigators found there a decrease in activation energy of thermal decompostion epoxy hardened with amine mixed with metal powders Al,Cu, Zn comparing with non filled system(5). Thermal stability of Epoxy/ Clay nanocomposites using TGA studied by Dzuhri S. et al (6) found that different type of montmorillonite can change the thermal stability by several factors related to polymer chain and other related to method of preparation of samples (the dispersion structure). Jiangbo Wang et al (7) reported that thermal decomposition of epoxy containing polyepoxyphenylsilsesquioxane (PEPSQ) found the increase in activation energy in the final stages which is attributed to PEPSQ stabilizing the char layer and improving the flame retardant of epoxy. Chen K. S. et al (8) studied thermal of oxidative degradation of Epoxy using Nitrogen gas, however they observed one stage reaction in inert atmosphere and two stage reactions in oxidative atmosphere, kinetic parameters are studied by using Friedman's method. Activation energy varied 129-151.9 Kj/mole in the first stage while in the second stage 103-117 Kj/mol. Thermal decomposition of high density poly ethylene HDPE short fibers reinforced epoxy composites, the fiber used as a retardants using

Horowitz Metzger method for analyzing thermograme showed addition 10% HDPE to fill the epoxy gave better thermal stability than other percentages used (9). Subhi A. Al-bayaty et al (12) studied thermal decomposition of un saturated polyester and unsaturated polyester/TCNP composite by TGA, however the results showed that TCNP contains metals of Fe, Mn, Cu which are reducing the activation energy by catalyzing effect.

2. KINETICS THEORY

The degradation process of solid state reaction may be presented as follow (10):

$A_{solid} \rightarrow B_{solid} + C_{volatile}$

The extent of reaction is described by a term degree of conversion α as follow

$\alpha = (m_o - m_t) / (m_o - m_\infty)$

Where m_o is initial mass of reactant, m_t is the mass at certain time during the reaction and m_∞ is the mass at the end of reaction.

The rate conversion may be expressed as:

$(d\alpha/dt) = \beta (d\alpha/dT) = K(T) . f(\alpha)$

Where α is the conversion, β is the heating rate, $f(\alpha)$ and $K(T)$ are function of conversion and temperature respectively . $K(T)$ is temperature dependence of Arrhenius equation expressed as follow

$K(T) = A_o \exp (-E_a/ R T)$

Where E_a is apparent activation energy, A_o the pre exponential factor and R is gas constant.

The Coats-Redfern method is a multi-heating rate application of the Coats-Redfern equation [11,12,13].

$\ln [\{-\ln (1-\alpha) / T^2 \}] = \ln (A_o R / \beta_i.E_a) \{1-(2R.T / E_a)\} - (E_a / R.T)$ -----   (1)

By plotting $\ln[\{-\ln(1-\alpha)/T^2 \}]$ against $1/T_i$ for each heating rate gives a family of straight lines of slope – E_a/R. Frequency factor directly determined from Y axsis intercept by substituting values of activation energies :

Intercept $= \ln (A_o R / \beta E_a) \{1-(2R T / E_a)\}$

For first order reaction Kissinger-Akahira-Sunose (KAS) method, the relation between the temperature $T_{\alpha i}$ and the heating rate β_i is given, (14)

$\ln(\beta_i/ T_{\alpha i}^2) = \ln(A_o R / E_a g(x)) - E_a/R T_{\alpha i}$ ---- (2)

By plotting $\ln(\beta_i/ T_{\alpha i}^2)$ against $1/T_{\alpha i}$ for constant of α gives a set of straight lines whose slope can be used to evaluate the activation energy .

3. EXPERIMENTAL AND DISCUSSION

3.1 RAW MATERIAL AND COMPOSITES PREPARATION

The materials used to prepare the nano composites are epoxy resin, diglycidyl ether of bisphenol A, (type conbextra EP10) which was supplied from Saudia industrial resin, it is a liquid with moderate viscosity and capable to be converted to solid state by adding the solution (Metaphenylene Diamine, MPDA) as a hardener a light liquid with yellowish color, the ratio of this hardener to the epoxy is about (1:3) . Toner carbon nanoparticles (TCNP) with particle size of (89.77 nm) were used in this work as filler. Table (1) shows the chemical composition of TCNP.

Table (1): Chemical composition for toner carbon nanoparticles (TCNP)

Component	C	Fe	Mn	Cu
Weight %	75.200	19.720	0.0610	0.0001

Samples of the polymer and nano composites at different weight percentage (2, 4, and 6 %) are prepared by cast molding. All content mixed thoroughly, firstly using an electrical mixer at 800 rpm for 15 minutes in order to have the homogeneity. Secondly, for better homogeneity ultrasonic homogenizer was employed for 4 minutes , finally vacuum system was used to remove the bubbles prior to molding the mixture, then poured in the desired mould, the samples left at room temperature about 24 hours, and then for post curing, the sample sheets were left for 2 hours in an oven at temperature 60 C^o .

3.2 THERMOGRAVIMETRIC ANALYSIS

Thermal decomposition by TGA and DTG is very useful process, where it helps us know the kinetic, thermodynamic parameters, optimum temperature of the process, and characterization and thermal stability .The thermo gravimetric measurement were carried out by a Perkin Elmer TGA analyzer, in non-isothermal condition. These experiments were carried out at Ibin Sina Company (Ministry of Industry). Decomposition profiles were obtained while heating rates at 5, 10, 15, and 20 C^o/min in Helium atmosphere with a flow rate of 20 ml/min between 30-800 C^o. The sample mass was heated in a standard ceramic pan.

In order to determine the kinetic to thermal degradation of epoxy (DGEBA) and its composites TGA profiles have been recorded for these samples as shown in Fig. (1) at different heating rate, it can be seen with increasing heating rate the TG curves displaces to the right because of   when the heating rate increases the initial and final temperature of degradation experiments also increased due to that epoxy molecules does not have enough time to exhaust the heat with increases heating, therefore leading to slower degradation rate at higher degradation temperature due to solw diffusion of heat (21) . It obvious from Table (2) it can be seen at the level of residual fraction 0.9 the temperatures for heating rate 5,10,15,20 K/min are 590.5 K, 605,5 K, 614 K,622 K respectively. However it can be seen the mass loss of epoxy is smooth between 300 - 450 C^o . Table(3) shows the residuals as function of peak temperature at various heating rates, whoever it can be seen the maximum loss in polymer weight occurs at higher heating rate, and the results indicates that DTG curves also shift toward due to the heat transfer enlarging with increasing heating rate (22) . The mechanism of epoxy thermal degradation could be attributed to the random chain scission reaction over temperature range 380-480 C^o. However when using amine hardener which consist of Nitrogen linkages with small dissociation energy comparing with other linkages, therefore scission occurs at especially at C-N bonds also OH groups are weak at higher temperature. Therefore the polymer losses its major weight about 90% according this reaction mechanism converting to volatiles and flammable organic compounds in turn these compounds catalysis the degradation process, then about 10-20% of original polymer weight convert to highly porous char (15) and this provide sufficient insulation to prevent decomposition consequently thermal stability increases (16,17) .
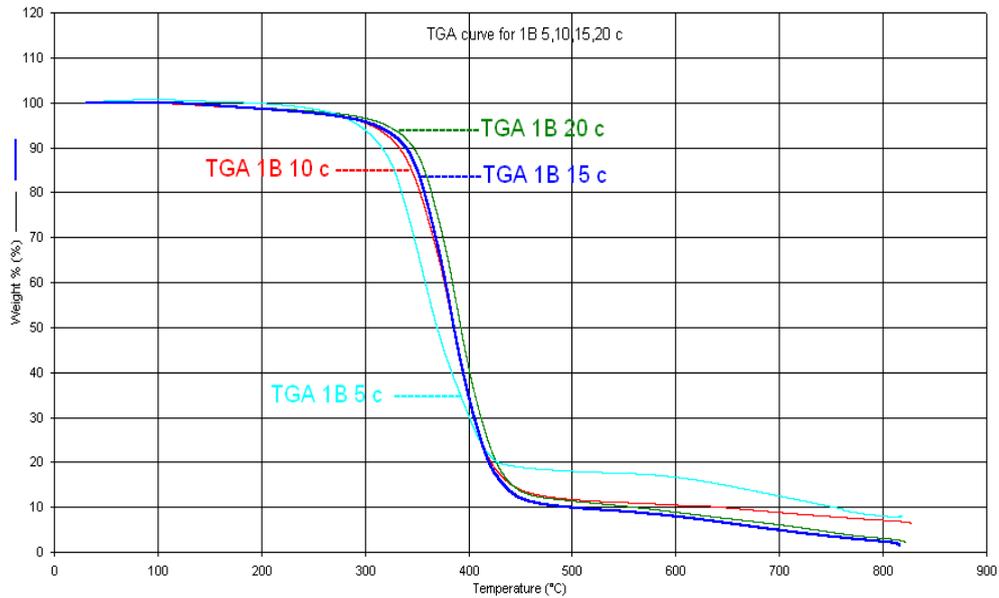
Fig (1) TGA curves recorded at different heating rates for EP

Table (2) Numerical data of thermal degradation at different heating rates of EP

Heating rate C^o/min	(1-α)							
	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2
5.0	590.5	607.0	620.5	630.1	641.0	655.5	673.0	689.5
10	605.5	627.0	640.0	650.0	658.0	669.0	680.0	697.0
15	614.0	630.5	643.0	651.0	659.0	669.0	680.5	693.0
20	622.0	638.0	647.0	657.0	665.0	673.0	686.0	700.5

Table (3) Peak temperature vs. amount of residual for EP

B C^o/min	derivative peak temperature, K	Percent Residual
5.0	628.14	13.31
10	655.42	7.20
15	655.59	4.25
20	661.65	3.33

Fig. (2) Shows the effect of TCNP content on decomposition process; however the curves of composites are shifted to the left since degrading much faster as comparing with pure epoxy. Table (4) shows the data extracted from Fig (2)   which shows the peak temperature . The high speed decomposition attributed to the enhancement effect of iron, consequently reducing activation energies of decomposition at levels of 4% of TCNP then thermal stability increases due to char formation at final stages. Table (4) shows that 4% TCNP degrades fairly lower temperatures than pure epoxy. The TCNP content in epoxy tends to accelerate the degradation of epoxy at relatively lower temperatures due to iron content.
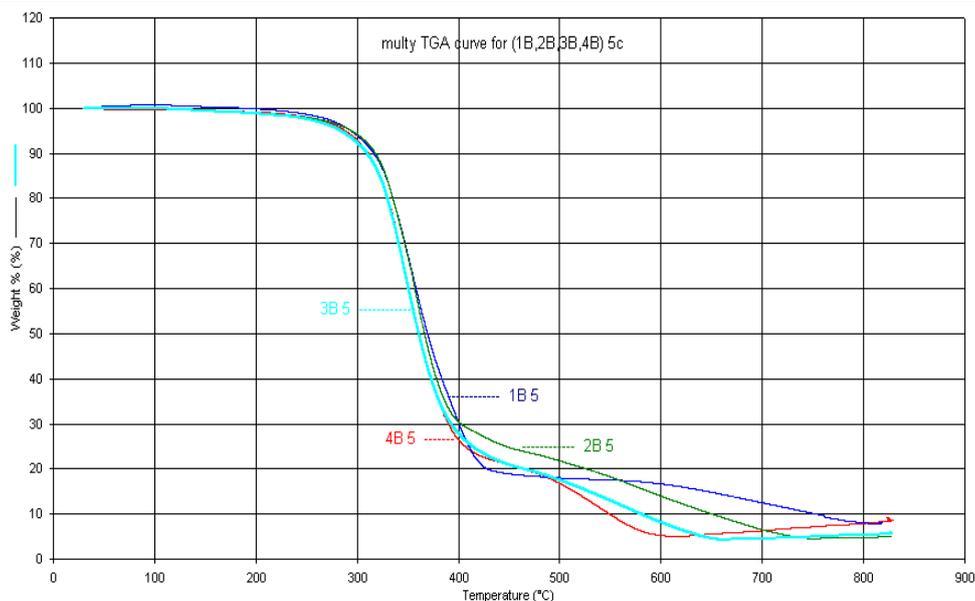
Fig (2) TGA curves at different % TCNP for EP/TCNP composite at $\beta=5C^o$/min

Table (4) Numerical data of thermal degradation at different %TCNP , $\beta=5 \ C^o$/min

Wt% TCNP	Residual level, (1-α)						
	0.9	0.8	0.7	0.6	0.5	0.4	0.3
	Temperature, K						
0.0	590.5	607.0	620.5	630.0	641.0	655.5	673.0
2.0	584.0	605.5	617	625.8	634.0	645.0	663.0
4.0	583.0	603.0	615.0	627.0	634.5	647.0	667.0
6.0	593.0	607.0	620.0	630.0	639.0	650.5	673.0

However it is obvious from Fig. (3), (4) shows typical thermogram for pure epoxy and epoxy / 4%TCNP the degradation region lies between 300 – 450 C which could be assigned to breakage of thee dimensional cross linked network and linear C-C chains in the backbone polymer chain via random scission . Phenol and bisphenol A and hydroxyl groups are also vulnerable to degradation in this range and also occur at C–N bonds (15). However the degradation much faster in case the composite Fig (4) comparing with pure epoxy since iron are fostering the degradation process of heating rate 5 C^o/min, it can be seen the residual at peak temperature for 4%TCNP is higher than EP.

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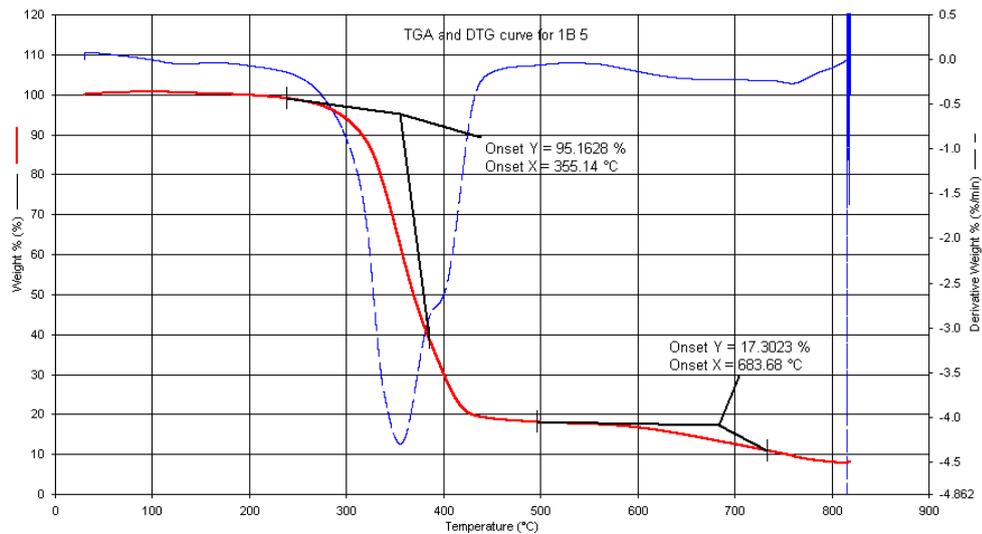
Fig (3) TG and DTG curve of pure EP at β=5 C^o/min
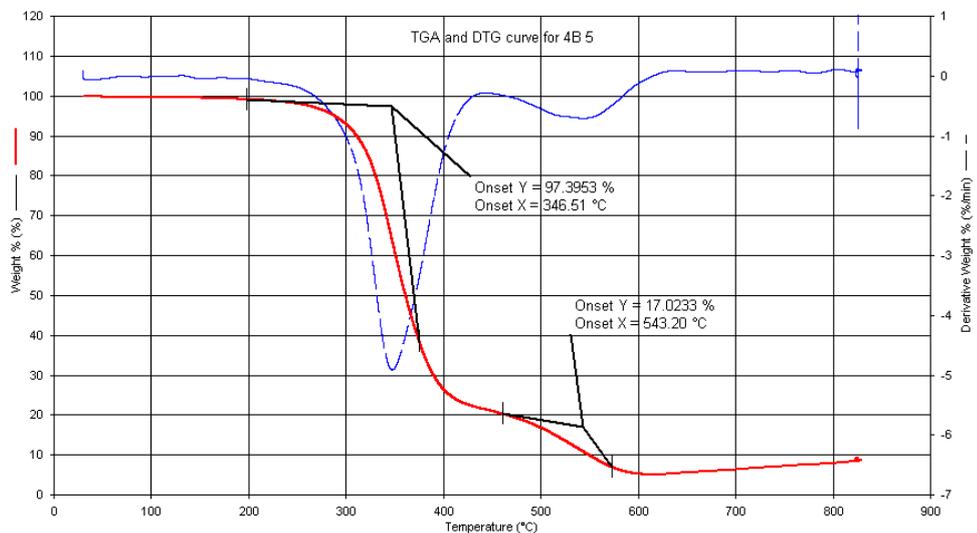
Fig (4) TG and DTG of EP/TCNP composite at 4%TCNP at β=5 C^o/min

There are several methods to determine the kinetic parameters of degradation process. However two type of model have been employed Coast-Radfern, and Kissinger-Akahira-Sunose (KAS) method . The estimated kinetic parameters by these models does not differ significantly . Fig (5) shows typical plot of $\ln(-\ln(1-\alpha)/T^2)$ against (1/T) at different heating rates which describe thermal decomposition very strongly, and the data fits reasonably to straight lines in the plot and indicate that the assumption of first order kinetics for thermal degradation is acceptable. Table(5) shows the kinetics parameter obtained from Fig(5). However it can be seen the activation energy increases with increasing heating this is because of very low thermal conductivity of EP used and hence the temperature distribution will be very significant at higher heating rates (19).These results agree very well with published research (20).
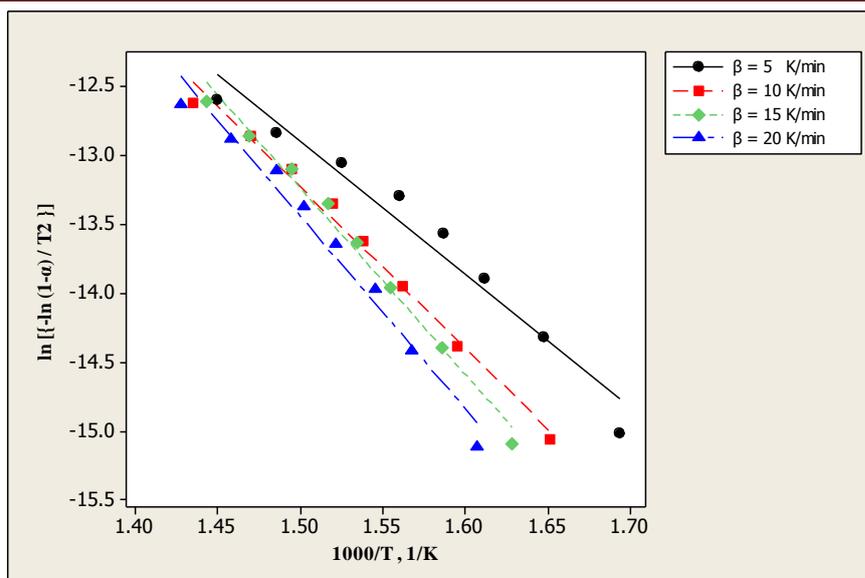
Fig (5) Coast-Radfern plot for thermal degradation of pure EP at different β

Table (5) Kinetic parameter obtained by Coast-Radfern of pure EP at different β

B	Activation Energy (Kj/mol)	Frequency Factor, A_o ,(S^{-1})	R^2
5.0	80.669	4.90440×10^3	0.961
10	97.312	16.6755×10^4	0.989
15	112.261	417.542×10^4	0.987
20	116.178	951.005×10^4	0.975

Fig (6) shows Coast-Redfern plot for different percentages of TCNP at constant heating rate 5 K/min again the data fits linearly, the kinetics parameter are extracted from Fig (6) are shown in Table (6) shows the activation energy increased as comparing with pure EP this indicates that TCNP increases thermal stability but at the same time fostering the reaction to produce the layer of char eventually protect EP from fire or heat, therefore the stability increases (17)
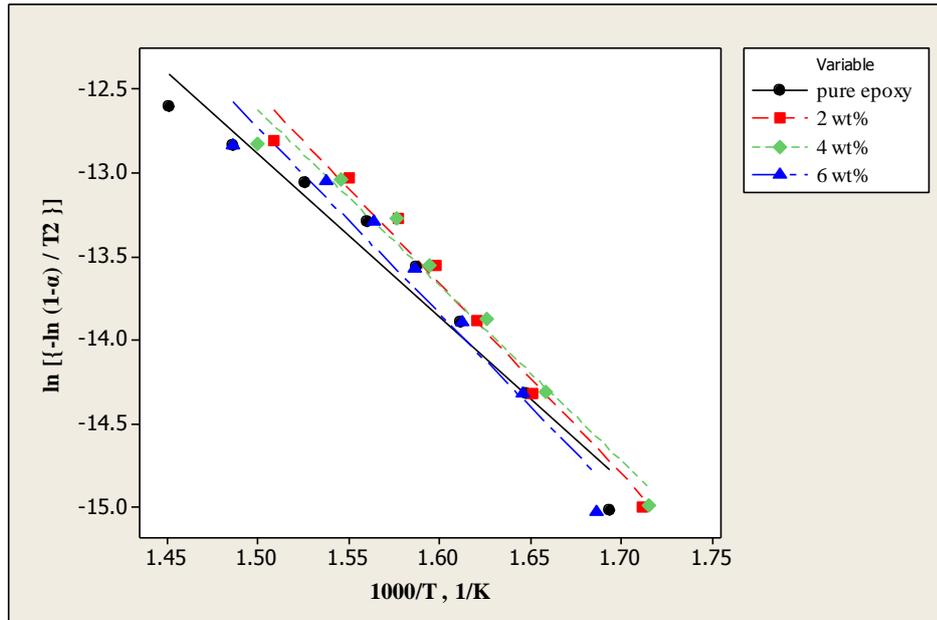
Fig (6) Coast-Radfern plot for thermal degradation of EP/TCNP composite, $\beta=5C^o$/min

Table (6) kinetic parameters obtained by Coast-Radfern of EP/TCNP composite

Wt% TCNP	Activation energy	Frequency factor, A_o, (S^{-1})	R^2
0.0	80.6690	4.9044×10^3	0.961
2.0	93.9679	8.8209×10^4	0.979
4.0	86.8219	1.9314×10^4	0.974
6.0	92.1636	5.1392×10^4	0.950

By using isoconversional methods of Kissinger-Akahira-Sunose (KAS), which represent one of simplest approximation, by using equation (1) for constant conversion , the plot $\ln(\beta/T^2)$ versus $1/T$ should be straight line as shown in Fig.(7) . However, the slops of the lines can be correlated to $-E/R$. The values of activation energy related to conversion rates with correlation factor are listed in Table (7).
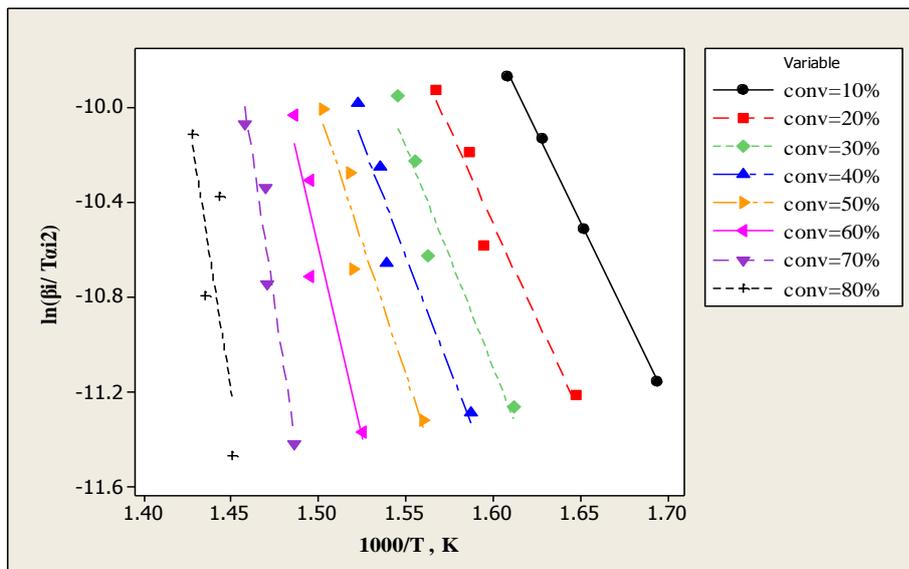
Fig (7) Plot $\ln(\beta_i/T^2)$ vs. $1/T$ according to Kissinger-Akahira-Sunose methode

Table (7) Activation energy obtained by Kissinger-Akahira-Sunose methode

Conversion	0.1	0.2	0.3	0.4	0.5	0.6	0.7
E, KJ/mol	123.588	132.6647	153.6308	157.8019	185.5640	261.4471	406.2210
R^2	0.998	0.958	0.924	0.913	0.927	0.890	0.927

4. CONCULUSIONS

Thermal degradation kinetics of EP and EP/TCNP composite has been investigated by thermogravemetry non isothermal method. To obtain a data to design optimum pyrolysis regimes, the kinetics parameter, should be estimated, Coats-Redfern method have been used. Heating rate play an important factor on degradation reaction, the activation energy and pre exponential factor k and degradation temperature increases with increasing heating rate, temperature of thermal degradation found much faster in EP/TCNP samples decomposition comparing with EP, however the reason is the presence of iron nano size in TCNP powder which enhances the pyrolysis reaction, the activation energy of samples EP/TCNP higher than EP gaining thermal stability. The activation energy obtained by Kissinger-Akahira-Sunose method as function of conversion was higher at final stages because of formation of char layer.

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