

Thermal Decomposition Kinetics Unsaturated Polyester and Unsaturated Polyester Reinforcement by Toner Carbon Nano Powder (TCNP) Composites

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ABSTRACT

In this study unsaturated polyester resin (UPE) mixed with different weight percent 2, 4, and 6% of toner carbon nano powder (TCNP) were used to prepare polyester composite. The molding method was used to prepare UPE and UPE/TCNP composites specimens. Study of non isothermal decomposition kinetics of UPE and UPE/TCNP composites were carried out by utilizing thermo gravimetric analysis (TGA). The samples were heated from ambient temperature to 800 °C at different heating rates 5, 10, 15, and 20 °C/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 Flynn and Ozawa, Coast-Redfern, and Horowitz-Metzger's 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 UPE/TCNP composites obtained from thermal gravimetric analysis is faster comparing with those UPE 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, and thermodynamics property.

Keywords:-Thermal decomposition, Thermo gravimetric analysis, Unsaturated polyester composites, Toner carbon nano powder

1. INTRODUCTION

Unsaturated polyester resins one of the most widely used for fabrication of polymer composite because of their competitive price and easy processing [1], and used in different area including automotive filed, construction, and electrical application and coating [2,3], because it have good mechanical property, good corrosion resistance, and low weight [4].

Thermal degradation is very important process which helps to know the polymer structure on the thermal stability, the optimum temperature of use, kinetic parameters, and thermodynamic properties. [5-8].

Oxidative thermal degradation of vinyl ester/glass composite occurs over lower temperature range, in pyrolysis commones, elimination of small molecules from polymer chain ends take place followed by cleavage reaction involving the side chains and random chain scission of main polymer chain. These reactions produces higher amount of volatiles, gases, and 5-10% of the original mass converted to char [9]. Other workers [10,11,12] reported that the decomposition of all types of unsaturated polyester in the initial stages probably governed by scission of highly strain portion of polystyrene cross-links, with formation of free radicals that promotes further decomposition. Polyester decomposition is arguably a two stage process, single stage Arrhenius kinetics is sufficiently accurate to model the process [13]. A number of workers including Tagle et al, [14], and Pielichowski et al,[15] have reported on decomposition of polyester which occurs by intermolecular ester exchange and β -CH hydrogen transfer are mainly responsible for primary steps of thermal decomposition. However, for polyester derived from aliphatic dicarboxylic acids and diphenol, and totally aromatic polyester, the ester exchange process prevails in the primary thermal cleavage.

2. KINETICS THEORY

According to the Flynn-Wall-Ozawa method [16, 17] which involves measuring the temperature corresponding to fixed value of α from experiments at different heating rates β , the activation energy, E at any particular value of α is determined by the following equation

$$\log \beta = \log \{A_0 \cdot E_a / R g(\alpha)\} - 2.315 - 0.4567(E_a / R \cdot T) \quad (1)$$

Where $g(\alpha)$ is the integral form of $f(\alpha)$, A_0 is pre-exponential factor and R is gas constant. Thus at a constant conversion the plot of $\log \beta$ vs. $1/T$, obtained from a series of experiments performed at several heating rates, should be a straight line whose slope allows evaluation of the activation energy.

$$\text{Slope} = d(\log \beta) / d(1/T) = -0.4567(E_a / R)$$

The Coats-Redfern method is a multi-heating rate application of the Coats-Redfern equation [19].

$$\text{Ln} \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln(A_0 R / \beta E_a) \{1 - (2R.T / E_a)\} - (E_a / R.T) \quad (2)$$

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

$$\text{Intercept} = \ln(A_0 R / \beta E_a) \{1 - (2R.T / E_a)\}$$

For first order reaction Horowitz-Metzger equation [19], is

$$\ln \ln \{1 / (1-\alpha)\} = E_a \theta / R T_s^2 \quad (3)$$

Where T_s is the temperature at which $(1-\alpha) = 0.368$ and $(\theta = T - T_s)$. Thus a plot of $\ln \ln \{1 / (1-\alpha)\}$ against θ allows to determine the activation energy. The frequency factor determined by substituting values of activation energies in the equation:

$$-1 = - (A / \beta) \{ (R T_s^2 / E_a) \}. \text{Exp} (- E_a / R T_s)$$

3. EXPERIMENTAL AND DISCUSSION

3.1 RAW MATERIAL AND COMPOSITES PREPARATION

The materials used to prepare the nano composites are unsaturated polyester resin type (A-50) with hardener MEKP and with accelerator cobalt naphthenate (having a symbol SIR SIROPOL) which was supplied by Saudia industrial resin. 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 before casting, then 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° .

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°/min in Helium atmosphere with a flow rate of 20 ml/min between 30-800 C° . The sample mass was heated in a standard ceramic pan.

In order to determine the kinetic, and thermodynamic parameters to thermal degradation of unsaturated polyester 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 a heat transfer lag. It can be seen that about 95– 97% of original mass is decomposed into volatiles rather than char. This the main reason for the relatively high flammability and heat release of polyester composite [13]. Fig. (2) shows the effect of TCNP content on decomposition process; however the curves are shifted to the left as comparing with pure UPE as shown in Fig. (1). This high decomposition attributed to the enhancement effect of iron, consequently reducing activation energies of decomposition .

However it is obvious from Fig. (3) the degradation process occurs in two steps [18], it evident there are more than one peak occurring in DTG curve the first at temperature 370.7 C° occurring at $(1-\alpha = 0.948\%)$, while the second the at temperature 500.5 C° at $(1-\alpha = 0.0948)$. Fig. (4) shows TG/DTG curve for 2 wt% of TCNP , the first at 359.9 C° at $(1-\alpha = 0.849)$, while the second at temperature 491.8 C° at $(1-\alpha = 0.108)$, however this obviously emphasizes the catalyzing effect of iron which enhances the two stages of decomposition .

There are several methods to determine the kinetic and thermodynamics parameters of degradation process. However three type of model have been employed Ozawa, Coast-Radfern, and Horowitz-Metzger. The estimated kinetic parameters by these models does not differ significantly, therefore the three models have employed at the present study.

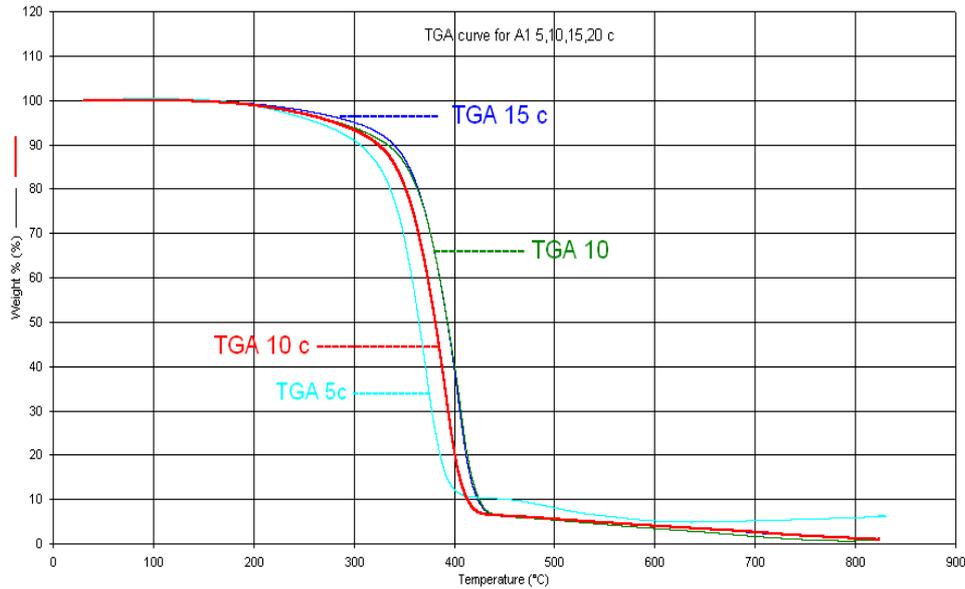


Figure (1): TGA curves recorded at different heating values

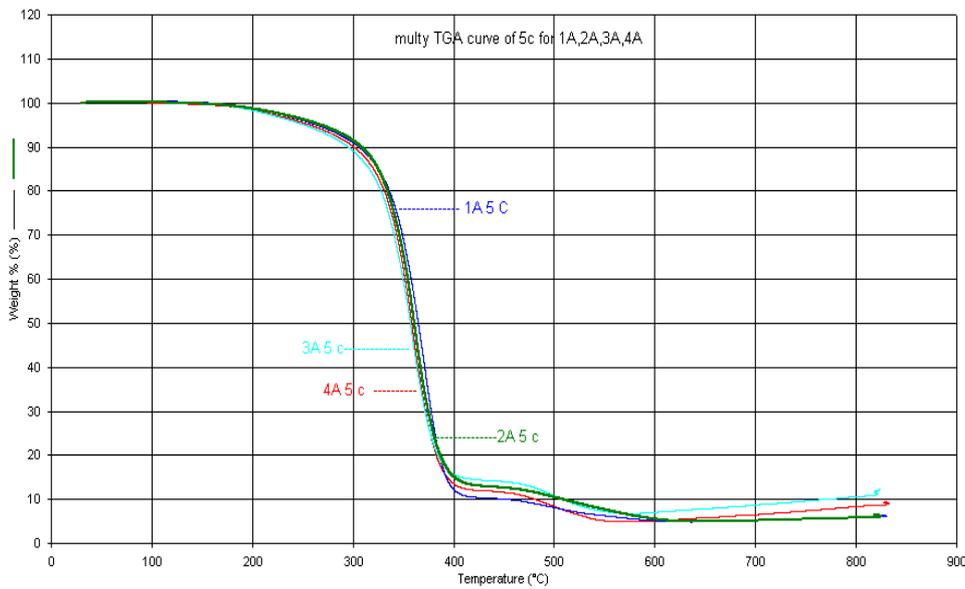


Figure (2): Effect of TCNP content of decomposition

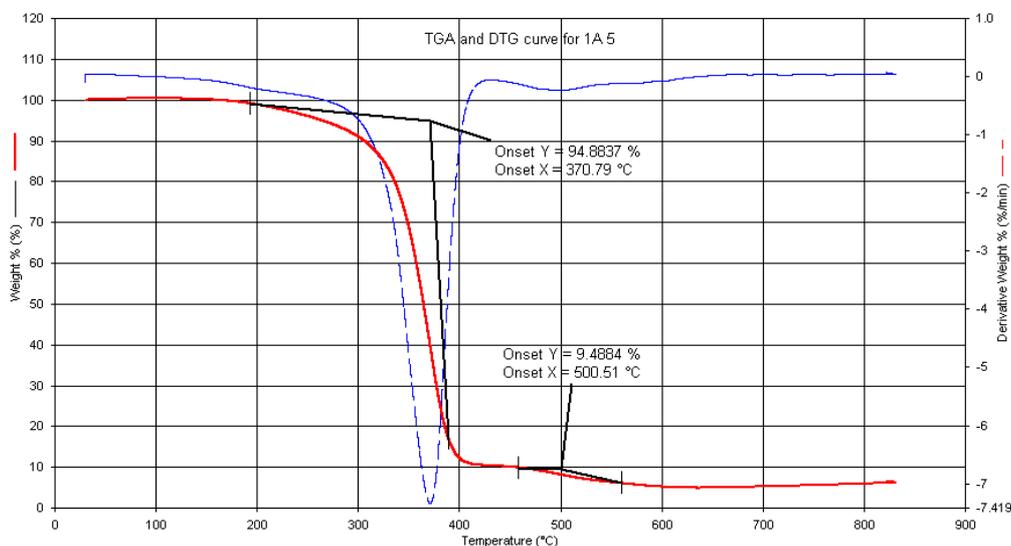


Figure (3): TG and DTG curves for PUE

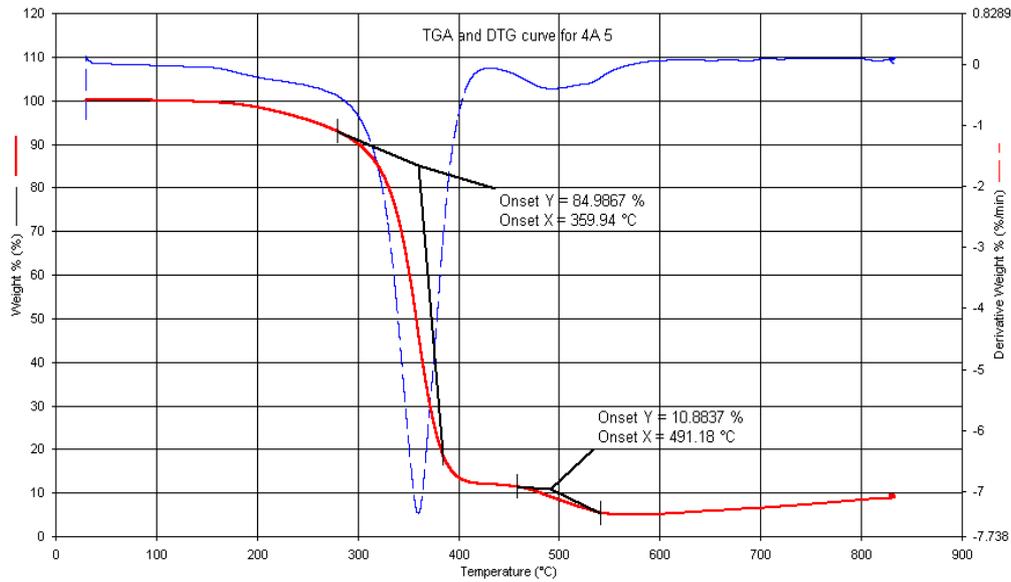


Figure (4): TG and DTG curves for PUE/2%TCNP composite

By using isoconversional methods of Flynn and Ozawa which represent one of simplest approximation, by using equation (1) for constant conversion, the plot $\log \beta$ versus $1/T$ should be straight line as shown in Fig.(5). However, the slopes of the lines can be correlated to $0.457Ea/R$. The values of activation energy related to conversion rates with correlation factor are listed in Table (2). The deviation in activation energy relative to conversion is due to different reaction take place in the course of degradation. Initially chain scission of highly strained portions, with formation of free radicals which promote further decomposition, following with intermediate radical that are more stable. However this results low molecular weight volatiles including CO, CO₂, methane, ethylene, propylene, butadiene, naphthalene, benzene, and toluene. Finally the decomposition occurs with slower volatilization of the residue which again requires less activation energy [13].

Table (2): Kinetic parameter of UPE decomposition obtained by Flynn and Ozawa method

conversion	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E, KJ/mol	197.95	148.49	135.61	134.09	136.21	136.03	135.16	131.58	84.56
	9	7	4	9	2	8	4	3	3
R ²	0.992	0.959	0.955	0.942	0.964	0.960	0.968	0.960	0.994

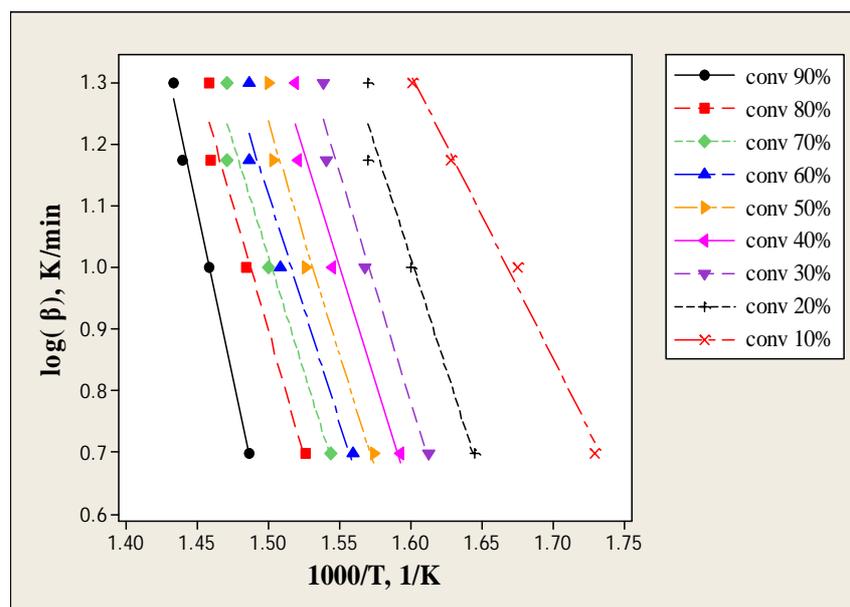


Figure (5): plot $\log \beta$ vs. $1/T$ of constant conversion and Ozawa method

It can be observed that the activation energy in the range about 197.959 to 84.563 KJ/mol, the obtained data shows that activation energy significantly reduced because of the catalyzing effect of iron which promotes decomposition. According to Coast-Redfern method Fig. (6) shows typical plot of $\ln\{-\ln(1-\alpha)/T^2\}$ against $(1/T)$ for different heating rates, and assumed that this decomposition is a first order reaction. Strong linear relationship which describe thermal degradation very strongly for pure unsaturated polyester.

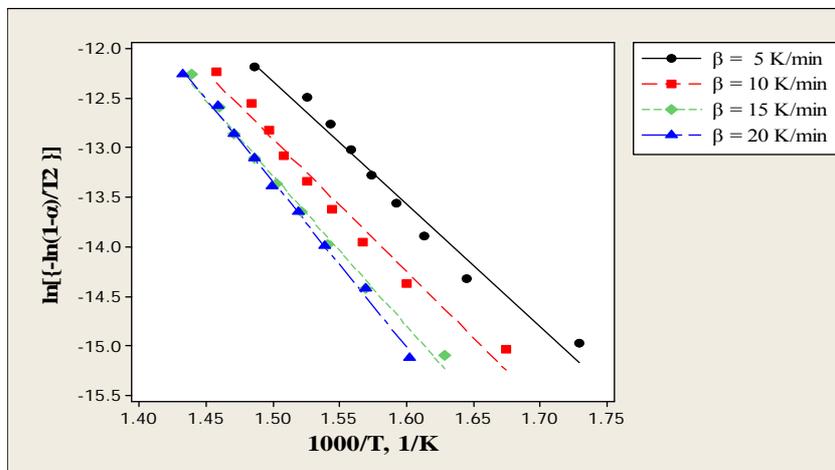


Figure (6): Coast-Redfern plot for thermal degradation UPE at different β

Table (3) shows kinetic parameters that determined at different heating rates. It can be seen activation energy and reaction rate constant dependent on heating rates and tends to increase with increasing heating rate.

Table (3): Kinetic parameters for UPE determined by Coast-Redfern method

Heating rate, β (K/min)	Peak temperature, K		Activation Energy, E (Kj/mol)	Reaction rate constant, A_0 (S^{-1})	R^2
	1st	2nd			
5.0	643.7	773.5	102.385	1.0881434×10^5	0.988
10	663.6	791.5	110.971	3.023890×10^6	0.978
15	675.0	955.0	125.947	7.714147×10^7	0.968
20	678.0	805.2	139.019	7.589030×10^8	0.996

Fig (7) shows Coast-Redfern plot for different wt% of TCNP for constant heating rate, 5 K/min again it shows linear dependency. The results obtained with this method are cited in Table (4), activation energies were reduced upto 4.0 wt% TCNP content, then starts to increase because it gained some stability at 6% TCNP content with increasing of carbon which acts as a barrier for volatiles evolution.

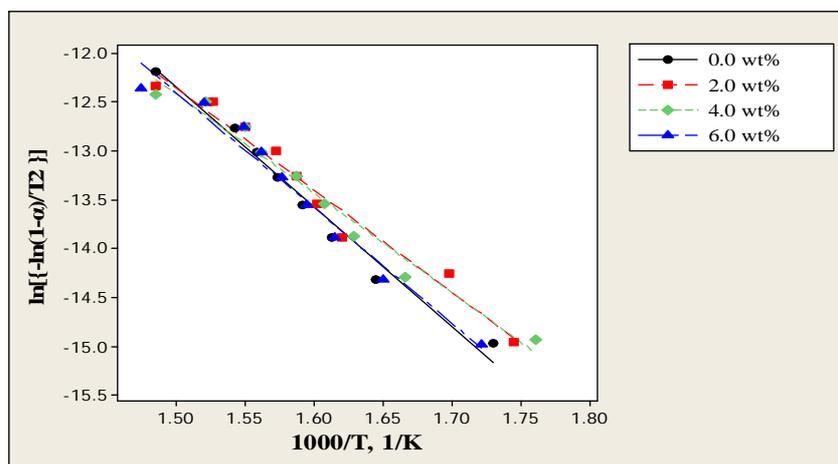


Figure (7): Coast-Redfern plot for thermal degradation UPE/TCNP at $\beta = 5$ K/min

Table (4): Kinetic parameters for UPE/TCNP determined by Coast-Redfern method

TCNP wt%	Peak temperature, K		Activation Energy, E (Kj/mol)	Reaction rate constant, A _o (S ⁻¹)	R ²
	1 st	2 nd			
0.0	643.7	773.5	102.385	5.909585 x 10 ⁵	0.988
2.0	632.9	764.8	87.5440	3.274755 x 10 ⁴	0.972
4.0	632.6	770.4	84.6560	1.696899 x 10 ⁴	0.974
6.0	634.6	781.5	98.4010	2.345326 x 10 ⁵	0.968

The same trend was observed in Horowitz-Metzger's method, according to this method a plot of double logarithm of reciprocal of (1-α) against (θ) gives the activation energy of first order pyrolysis as shown in Fig.(8) which describe also more effectively the degradation reaction for pure unsaturated polyester .

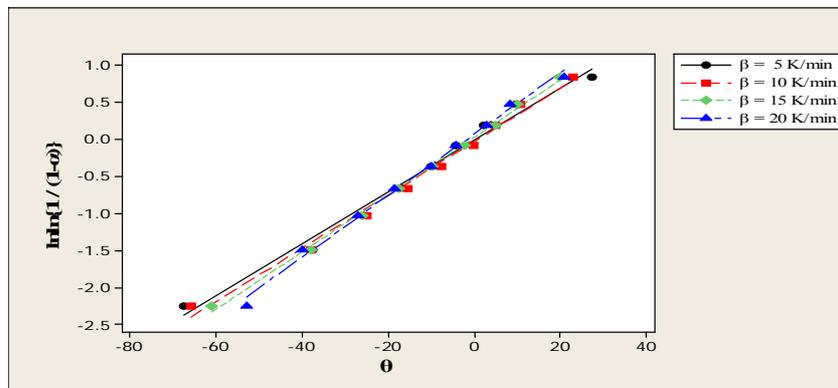


Figure (8): Horowitz-Metzger's plot for thermal degradation UPE at different β

Table (5): Kinetics parameter UPE estimated by Horowitz-Metzger's method

Heating rate, β (K/min)	Activation Energy, E (KJ/mol)	Reaction rate constant, A _o (S ⁻¹)	R ²
5.0	121.246	1.8898940 x 10 ⁹	0.985
10	131.564	1.392604 x 10 ¹⁰	0.991
15	147.734	2.640948 x 10 ¹¹	0.997
20	156.232	1.549872 x 10 ¹²	0.995

Fig. (9) shows the effect of different heating rate on activation energy for Coast-Redfern, and Horowitz-Metzger models. However it concluded that, the use of multiple heating rate method represented more realistically the verity of heating rate used for thermal degradation of polymers because of the wide variation obtained when using various heating rates.

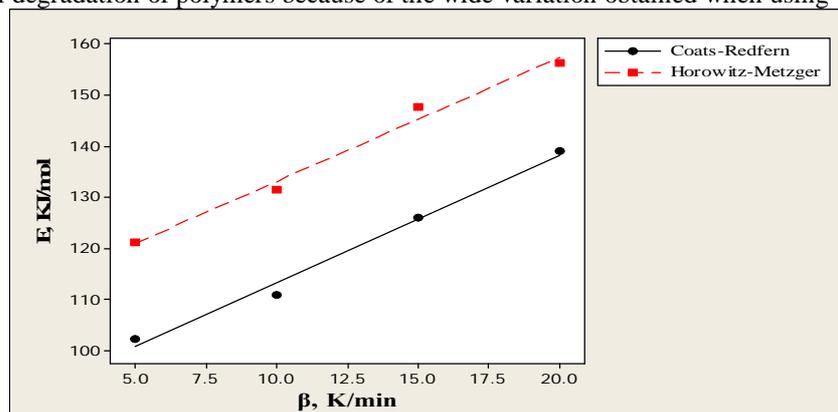


Figure (9): Comparison of activation energy obtained by different method

The thermodynamic properties were determined by the following equations [20, 21]:

Where ΔH is activation enthalpy, ΔS is activation entropy, ΔG is activation free energy of decomposition, T_{peak} is maximum peak temperature, h is Plank constant and k_b is Boltzmann constant.

$$\Delta H = E - R T_{peak} \tag{4}$$

$$\Delta S = R [\ln(h A_0/k_b T_{peak}) - 1] \tag{5}$$

$$\Delta G = \Delta H - T_{peak} \Delta S \tag{6}$$

Table (6) and Table (7), shows the thermodynamics property of pure unsaturated polyester and pure and its composites where Coast-Redfern method employed in estimation kinetic parameter.

Table (6): Thermodynamics property of UPE

TCNP, Wt%	T_{peak} ,(K)	$\Delta H, KJ/mol$	$-\Delta S, J/mol$	$\Delta G, KJ/mol$
0.0	643.7	97.032520	163.19840	202.08381
2.0	632.9	82.394060	173.04133	109.60025
4.0	632.6	79.396563	178.50335	192.31778
6.0	632.9	93.124935	156.69531	192.56378

Table (7): Thermodynamics property of UPE/TCNP composites

Heat rate β (C°/min)	T_{peak} ,(K)	$\Delta H, KJ/mol$	$-\Delta S, J/mol$	$\Delta G, KJ/mol$	R^2
5.0	643.7	97.03327	163.19840	202.08381	0.999
10	663.6	105.45382	135.81062	195.57776	0.999
15	675.0	120.33505	109.02214	193.92499	0.999
20	678.0	133.38210	90.051270	194.43686	1.000

Fig. (12) Shows the relationship between values of activation energy, E (estimated by Coast-Redfern method) and Entropy, ΔS clearly shows a good linear relationship between them with accuracy $R^2=0.962$ as it has been investigated by several workers [22, 23] The existence of the same linear dependence between activation energy and entropy, however that is a compensation effect and can be interpreted as a proof that the mechanistic kinetic equations employed adequately reflect the specific kinetic parameters characterizing these process were correctly calculated. On the other hand the existence of linear relationship between activation energy and entropy provide a solid basis for seeking directly relationship between them, that is the value of activation energy of similar decomposition process exert a certain effect of value of the change in entropy. The negative value of entropy show that the degradation activated complex is a more organized structure than the initial polymer, while the positive values of free energy and enthalpy indicate that the UPE and UPE/TCNP composites are non spontaneous reaction [24].

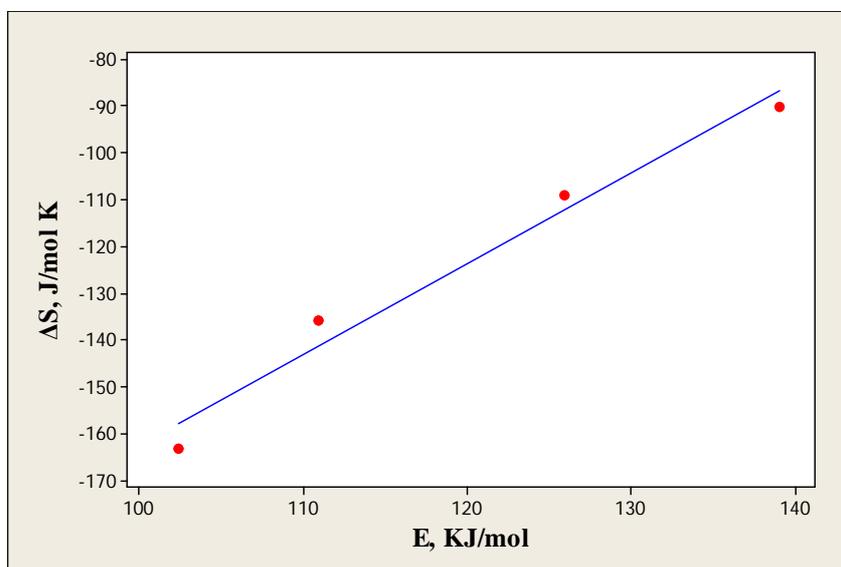


Figure (12): Plot of ΔS against E for thermal decomposition of UPE

4. CONCLUSIONS

Thermal decomposition of unsaturated polyester and TCNP composite has been investigated by thermogravimetry method UPE And UPE/TCNP degraded in two stages and 95– 97% of original mass is decomposed into volatiles rather than char volatiles with. The kinetics parameter, activation energy, and reaction rate constant as well as thermodynamics property was found to be higher than composites, however the reason is the presence on iron nano size in TCNP powder which enhances the pyrolysis reaction.

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