Characterization the Thermal Degradation E Kinetic of Unsaturated Polyester and Polyester/Silica Nanoparticles Composites by TGA and DSC Analysis

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ARTICLE INFO	ABSTRACT
	The development of polymer nanocomposites is rapidly emerging as a multidisciplinary research field with results that could broaden the applications of polymers to many different industries. The nanocomposites were prepared from unsaturated polyester (UPE) mixed with a different percentage (10, 20, and 30%) of silica nanoparticles. TGA and DSC curves were obtained from the thermal degradation computed by using Coast-Redfern technique. Kinetic and thermodynamic parameters were studied for all specimens were presented a good linear correlation coefficient close to unity using Minitab 16. Experimental work was showed that the degradation of composites that obtained from thermal gravimetric analysis was slower than the resin. Also, the decomposition under the oxidative environment was much faster than the inert environment. The enhancement of stability was attributed to silica content.

1. Introduction

Poly condensation polymers considered very practical in several usages due to its price and easily fabricated, good mechanical property, and higher corrosion property [1]. It is widely employed especially in the area of coating, electrical application, fabrication parts of automotive, and construction fields [2-4].

Kinetic parameter and thermodynamic prosperities and thermal stability determined by utilizing TGA and DSC which gives a very clear idea about the structure of the polymers and the behaviour of various composites under severe heat [5-8]. Oxidative and thermal decomposition of polymers and composite occurs usually at higher temperature by the elimination of molecules along the polymer chain followed by random scission of the backbone chain, however these changes produce more

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volatiles, gases and eventually all the polymer convert to high molecules of poly nuclear ring so called chars [9-12]. However, polyester decomposition occurs in two stages, in the first stage the degradation of the backbone of the main chain occurs by ester change and hydrogen elimination and finally coverts to volatiles, gases, and char because of its strong hydrogen bond prevent it from melting in the second stage [13-15].

Recently the kinetic of decomposition have been studied by many researchers, however they concentrated on constant decomposition rate, activation energy and thermodynamic properties of different polymers and its different composite and they showed the enhancement in thermal stability of composites by using different inclusions [16-18].

2. Kinetic Theory

The Coats-Redfern method is a multi-heating rate application of the Coats-Redfern equation [19] has been applied to study the kinetics of the decomposition of the polymer and its composite.

$$\ln \left[\{-\ln (1-\alpha) / T^2\} \right] = \ln (A_o R / \beta E_a) \{1-(2R T / E_a)\} - (E_a / R T) \tag{1}$$

where
α = The extent of the reaction
β = The constant heating rate
A_o = The frequency factor
R = The universal gas constant
T = The decomposition temperature
E_a = The activation energy

By plotting $\ln[\{-\ln(1-\alpha)/T^2\}]$ 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:

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

3. Results and Discussion
3.1 Composite Fabrication

The materials employed to fabricate the nano composites are unsaturated polyester resin (UPE) as a matrex. It is a liquid with moderate viscosity which can be cured to the solid state by adding (Methyle Ethyle Keton Peroxide, MEKP) as a hardener, while cobalt octoate acts as a catalyst to accelerate the solidification process. The percentage of the hardener to the resin is (2%) while it is (0.5%) for the accelerator. Desirable physical properties, easily handled, quickly cured and stable dimensions after solidification. The properties of unsaturated polyester resin are given in Table 1. Hardener: is a chemical material, which is added to thermosetting resin for the purpose to cause curing or hardening. The terms hardener and curing agent are used interchangeably. Note that these can differ from catalysts, promoters, and accelerators. Curing: To change the physical properties of the material (usually from a liquid to a solid) by chemical reaction, by the action of heat and catalysts, alone or in combination, with or without pressure. accelerator: A chemical used to speed up a reaction or cure. The term accelerator is often used interchangeably with the term promoter [20]. Silica nano particles with a particle size of 100 nm were used as commercial filler. The chemical

composition of nano silica is given in Table 2. Atomic force microscopy (AFM) was used (CSPM scanning probe microscope) to measure the average particles size of nano silica, the particles size distribution is shown in Figure 1.

Samples of the polymer and nano composites at different Silica content (10, 20, and 30 %) are fabricated by cast moulding. All content mixed thoroughly before casting, then the samples left at ambient temperature for 24 hr, and then cured, the specimens were left for 2 hr in an oven at temperature 60 °C.

Table 1
Typical properties of unsaturated polyester resin [21]

Property	Unsaturated Polyester (UPE)
Density (gm/cm3)	1.05-1.4
Tensile strength (MPa)	45-103
Tensile modulus (GPa)	1.3-4.5
Cure shrinkage %	5–12
Tg(k)	340

Table 2
Chemical composition for the silica nanoparticles

Material	Components %									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	Pb_2O_3	Cu_2O
Silica	0.96	0.14	2.16	53.67	0.84	0.006	0.006	0.019	0.013	0.005
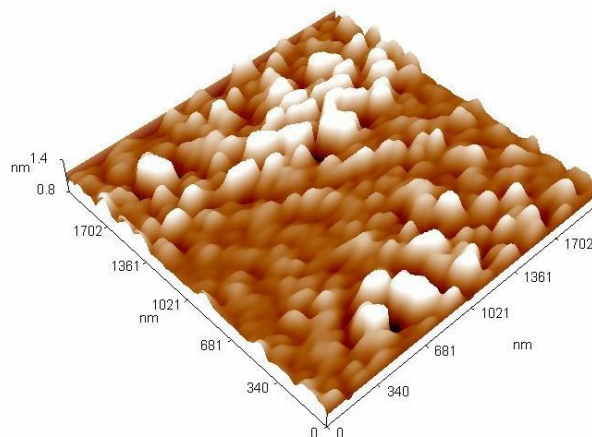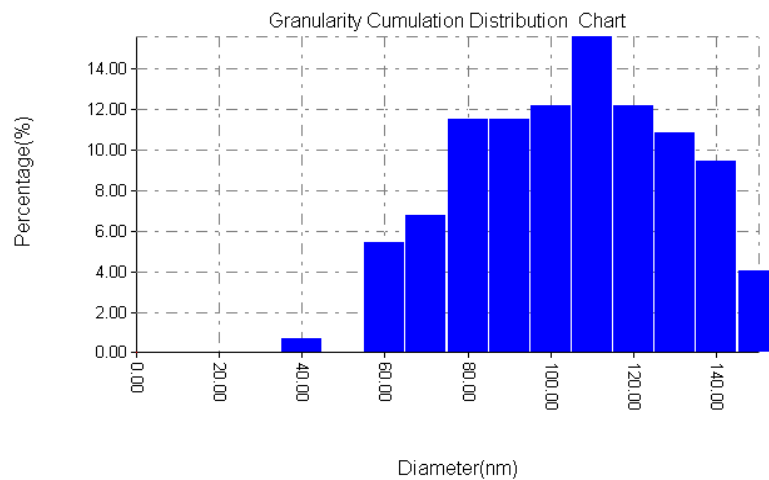
Fig. 1. AFM of silica nanoparticles

3.2 Thermogravimetric Analysis

TGA and DSC is an important tool to study the kinetic of thermal decomposition, and to describe the way were the polymer degrade and to determine the melting point and glass transition temperature and to study the thermodynamics of thermal and to demonstrate the stability. Thermal decomposition carried out at constant heating rate of 10 ℃/min in inert atmosphere between 35-650 ℃ .

Figure 2 shows TGA and DSC profiles for pure polyester resin under oxidative agent, it can be seen the polymer start in losing its weight initially about 6 wt% at temperature between 190 ℃ and 300 ℃ then start losing major weight 60.9 wt% between 300 ℃ and 430 ℃, however this represents the first stage degradation, while the second stage starts 405 ℃ till 462 ℃ with weight lose 9.97 wt% then the char start to gasify. From DSC profile observed two peaks which represent exothermic decomposition, first small peak at 407.3 C° which represent the backbone scission followed with a big peak at 478.9 ℃ which represent the gasification of char.
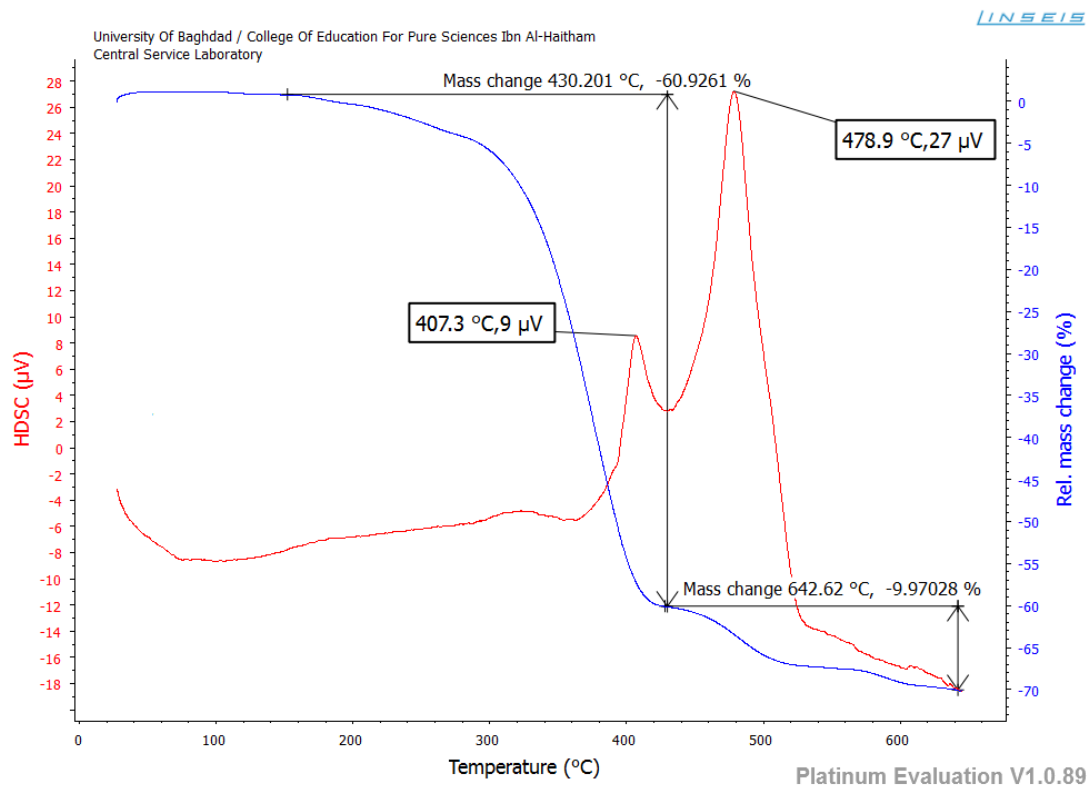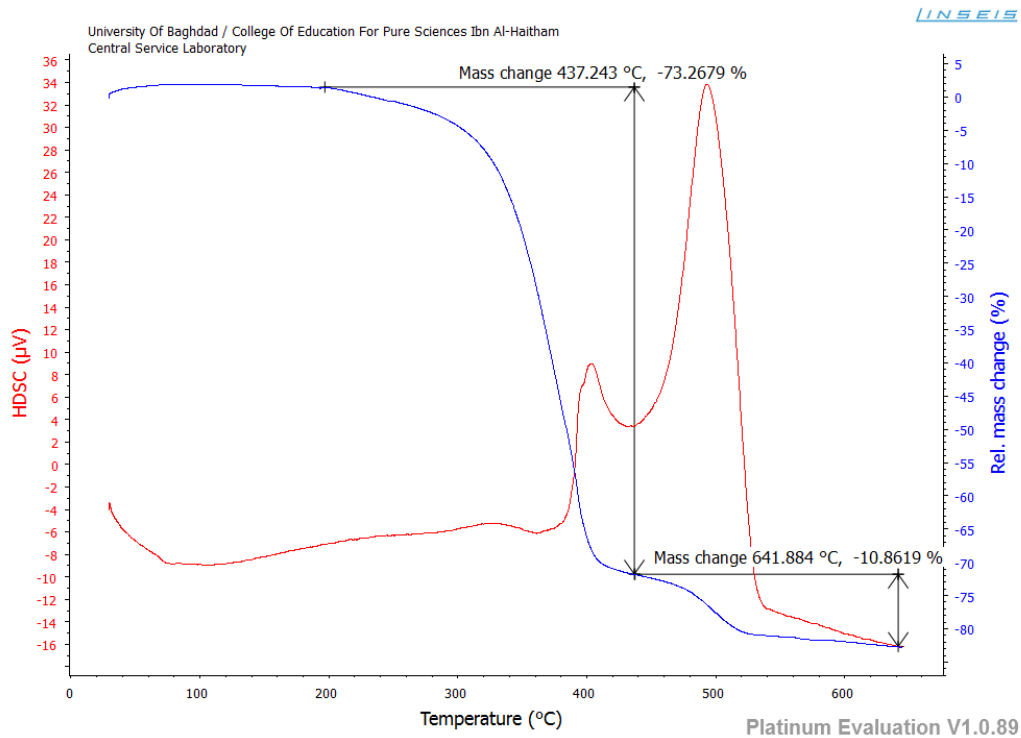

Fig. 2. TGA and DSC curve for pure polymer under oxidative environment

Figure 3 shows the profiles of pure polyester under inert conditions were initial lose weight starts 237 ℃ till 310 ℃ with weight lose 5.5 wt% followed by the first stage with weight lost 73.2 wt% between temperature range 310 ℃ to 437 ℃ and the second stage lose 18.8 wt% which ends at 641.8 ℃, the DSC profile also showed two peaks first at 415 ℃ and the second one at 435 ℃ . Table 3 shows the mass loss of polyester pure and with various weight percent of Silica content. However, there is a difference in activation energy of oxidative and non-oxidative agent. In oxidative the activation energy is much lower than non-oxidative as shown in Table 4. This is because oxygen enhance the decomposition, consequently reducing activation energies of decomposition.

Fig. 3. TGA and DSC curve for pure polymer under inert environment

Table 3
Mass lost during decomposition for unsaturated poly ester and its composite

| The samples	environment	loss first stage	loss second stage	Total mass loss
UPE pure	oxidative	430.2℃, 60.92%	642.6℃, 9.97%	70.89%
UPE pure	inert	437.2℃, 73.26%	641.8℃, 10.86%	84.12%
UPE +10% Silica	inert	438.2℃, 80.73%	643.9℃, 11.34%	92.07%
UPE +20% Silica	inert	435.9℃, 82.74%	643.7℃, 15.05%	97.79%
UPE +30% Silica	inert	443.8℃, 72.51%	643.2℃, 12.49%	85.00%

Table 4
Kinetics data of non-isothermal degradation of UPE and its composites according to Coats-Redfern method

| The samples	environment	Peak Temperature, T_p (K)	Activation Energy, E_a(kj/mol)	Reaction rate constant, A_o(S^{-1})	R^2
UPE pure	Oxidative	652	78.0680	0.3164 x10^4	99.1%
UPE pure	Inert	660	99.0030	22.260 x10^4	99.7%
UPE +10% Silica	Inert	665	100.358	31.708 x10^4	99.6%
UPE +20% Silica	Inert	656	111.382	308.222 x10^4	98.7%
UPE +30% Silica	Inert	661	117.934	835.108 x10^4	99.6%

The effect of addition Silica filler at different percentages are shown in Figure 4, Figure 5 and Figure 6. However it can be seen the thermal stability increases with increasing Silica content Figure 6 is differ completely than Figure 2 and Figure 3 especially at the initial stage which start 327 C with initial mass loss of composite 5.5 wt% followed with first stage decomposition which ends at 443 ℃ with mass loss 72.5 wt%, while the stage mass loss is 12.49 wt% which is considered much lower comparing with pure polyester Figure 3. DSC profile showed two peaks, the first appeared at 399 ℃, while the second at 508.2 ℃ which is considered much higher comparing with Figure 3, this is because of increasing thermal stability.
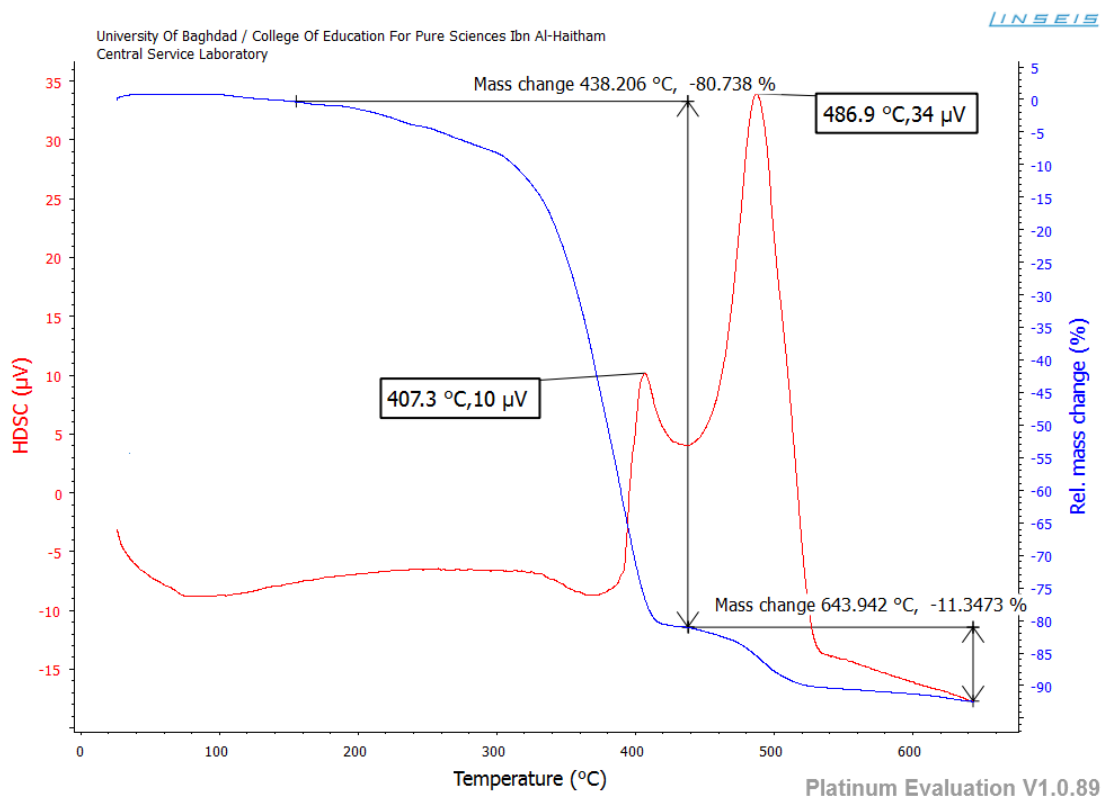
Fig. 4. TGA and DSC curve for unsaturated polyester/Silica 10 wt%
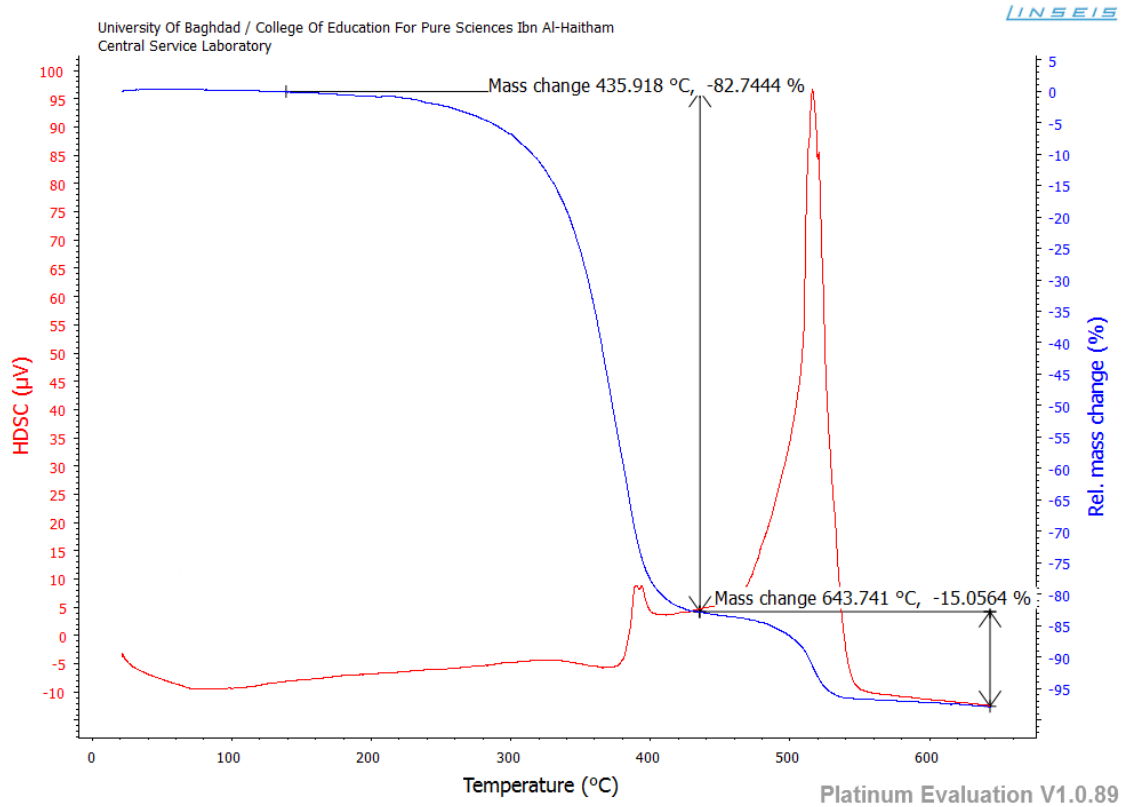
Fig. 5. TGA and DSC curve for unsaturated polyester/Silica 20 wt%
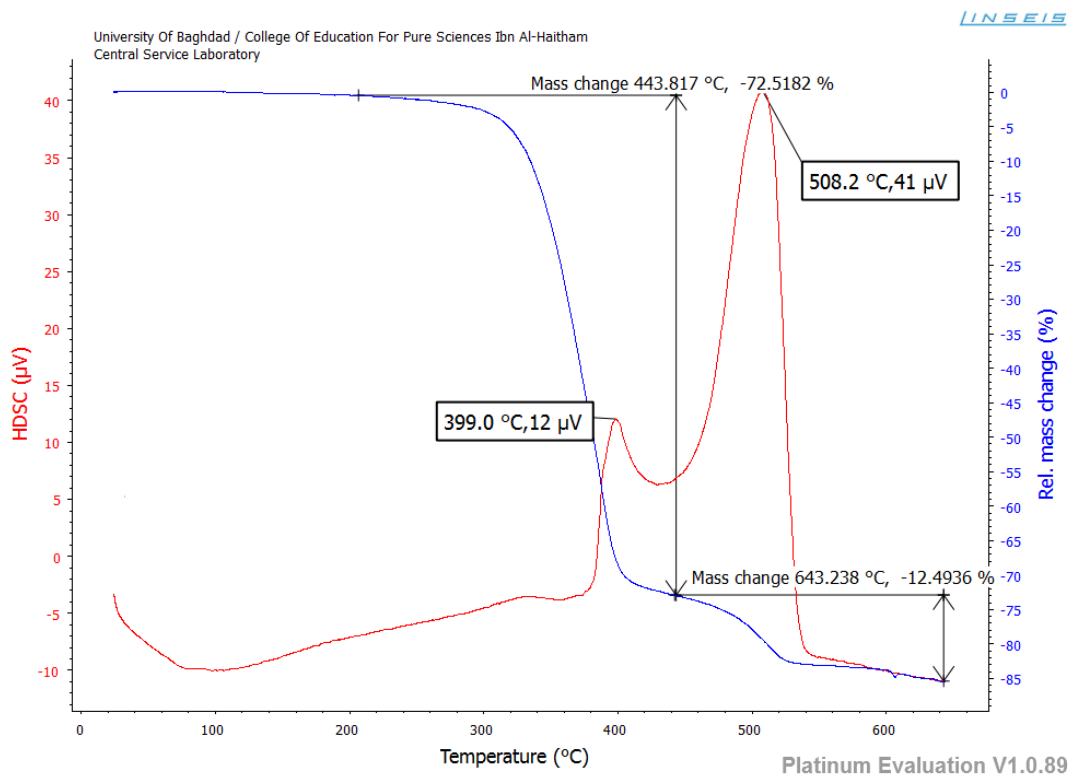
Fig. 6. TGA and DSC curve for unsaturated polyester/Silica 30 wt%.

Applying the Coast-Redfern method as shown in Figure 7 a typical plot of ln (-ln(1-α)/T^2) against (1/T) for oxidative thermal decomposition pure unsaturated polyester, for first order reaction.
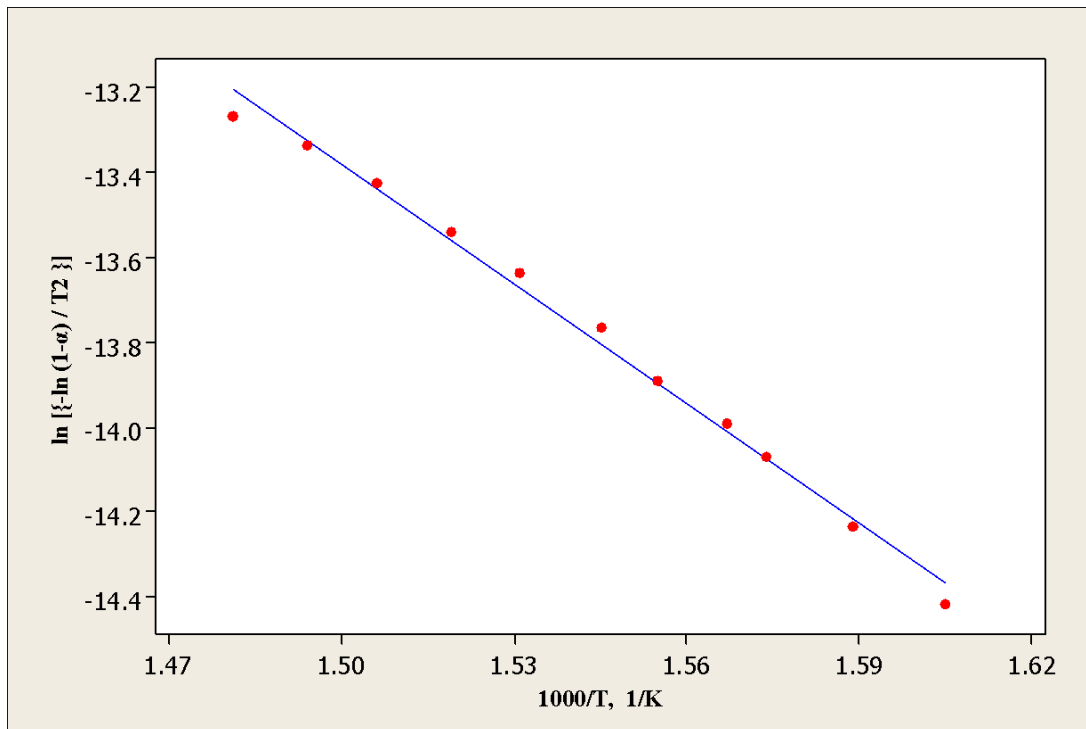

Fig. 7. A plot of oxidative thermal decomposition utilizing Coast-Redfern method

The method applied for pure unsaturated polyester and its composites at different Silica content is shown in Figure 8.
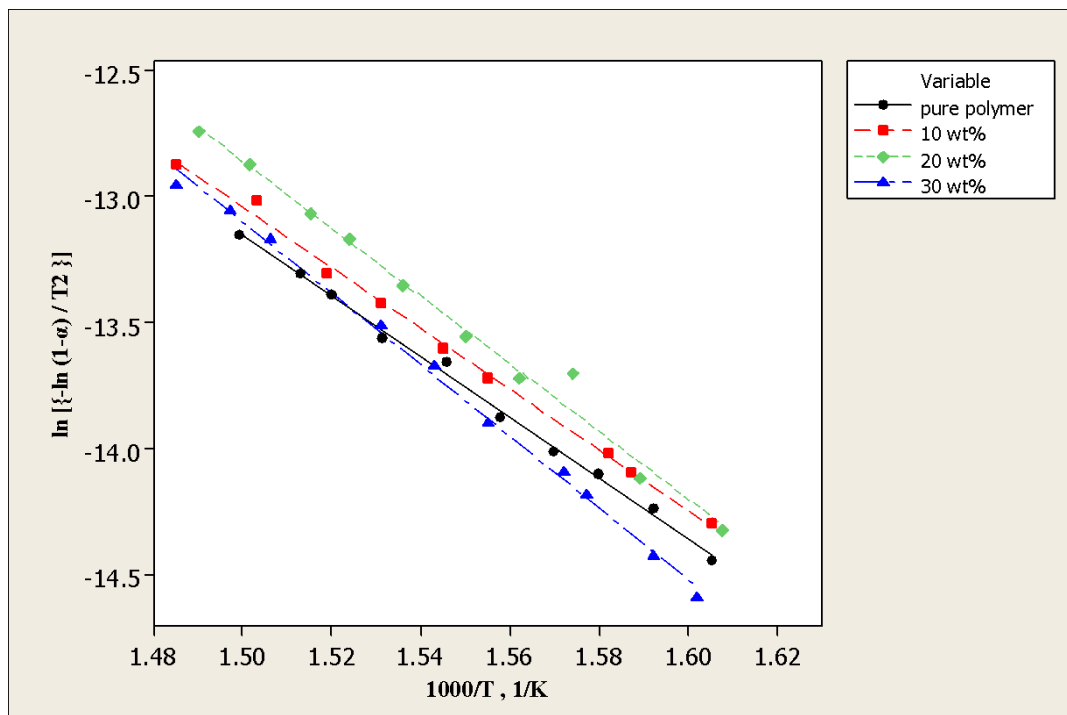

Fig. 8. A plot of non-oxidative thermal decomposition utilizing Coast-Redfern method

The thermodynamic properties were estimated by the following equations [22-23]:

$$\Delta H = E - R\, T_{peak} \qquad\qquad (3)$$

$$\Delta S = R\,[\,\ln(h\, A_o/k_b T_{peak}) - 1\,] \qquad\qquad (4)$$

$$\Delta G = \Delta H - T_{peak}\, \Delta S \qquad\qquad (5)$$

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. Table 5 shows the thermodynamics property of pure unsaturated polyester and its composites according to Coast-Redfern method used in determining kinetic data.

Table 5
Thermodynamics property of UPE/Silica composites

The samples	Environment	T_{peak} ,(K)	ΔH, KJ/mol	$-\Delta S$, J/mol	ΔG, kJ/mol
USP Pure	Oxidative	652	72.647	192.721	198.301
USP Pure	Inert	660	93.515	157.459	197.438
USP+10% Silica	Inert	665	94.829	154.758	197.743
USP+20% Silica	Inert	656	105.928	135.559	194.854
USP+30% Silica	Inert	661	112.438	127.334	113.496

Figure 9 shows there is a linear relationship between activation energy, E_a and Entropy, ΔS with accuracy R^2=99.3% [24-25]. Table 5 shows that the activation energy increases with increasing entropy and the positive values of internal energy means the degradation process is not spontaneous [26].
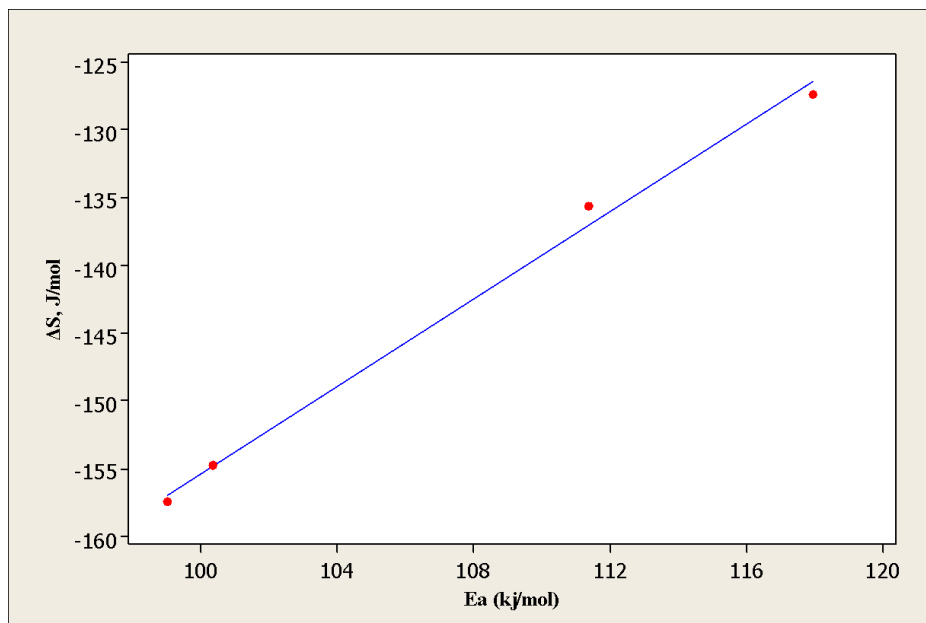
Fig. 9. Plot of Entropy against Activation energy for thermal decomposition of UPE and its composite

4. Conclusions

Thermal decomposition of unsaturated polyester and silica nanocomposite has been studied by TGA and DSC technique. UPE and UPE/Silica were degraded in two stages and almost 94% of original mass was decomposed into volatiles and char. The activation energy and the entropy of the composite materials were higher than the pure UPE in oxidation and inert environment, the reason being that the presence of silica powder increased the thermal stability. DSC profile was showed there were a shift of decomposition peaks towards right side because of enhancement of thermal stability for composite as compared with pure UPE.

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