

# Study of Thermal Decomposition Behavior and Kinetics of Epoxy/Polystyrene Composites by using TGA and DSC

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## ABSTRACT

The present study demonstrates the behavior of thermal oxidative and non oxidative decomposition of polystyrene and study the kinetics of degradation of epoxy mixed with different weight percentages of 10, 15, 20 polystyrene powder were used to form epoxy composites. TGA, DTGA, and DSC were employed to reveal the behavior of thermal degradation as well as to study the thermal stability by utilizing Coats-Redfern methods. Activation energy and thermodynamic properties were determined according to this model. The experimental work performed by using heating rate of 10 C°/min. Oxidative atmosphere of air used in all experiments except for a comparison purpose one run employed Nitrogen to study the effect of non oxidative process. All statistical analysis performed by using MINITAB 16 to determine the kinetics result. TGA profiles showed that decomposition occurred by three steps. While DSC profile reveals two peaks. Effect of polystyrene powder content on decomposition of epoxy were studied and all results showed there is an increase in stability of composites.

**Keywords:** Epoxy, polystyrene, TGA, DTGA, DSC, thermal decomposition, composites.

## 1. INTRODUCTION

Epoxy resin considered as important material and have its way in the industry for various purposes since it poses many different properties such as an electrical insulation in electricity sector since it have excellent resistance towards electrical leakage [1]. Due to cross-linking structure of epoxy, therefore it neither melts at high temperature nor dissolves in many different chemical solvent [2]. Varun Dixit et al. [3] studied the effect of addition of phenoxy to two different kind of epoxy of DGEBA and TGDDM however the results showed an increase in thermal stability and the composite of DGEBA is miscible with Phenoxy while the other was partially miscible. The addition effect of propylene fiber to epoxy showed an increase in thermal stability of the composite since it affects the behavior of the decomposition at earlier stages [3]. While other worker reported an enhancement in thermal stability of epoxy/phosphorus composite at elevated temperature at middle stages of decomposition [4]. Phosphorus has been employed to enhance the thermal stability of epoxy by utilizing TGA analysis in air atmosphere [5]. Thermal degradation process investigated by many workers to reveal the behavior of thermal decomposition and study the kinetics at elevated temperature [5-12]. Other worker modified epoxy with different filler in order to enhance its thermal conductivity, which in turn increases its thermal stability [13, 14]. The present works combined polystyrene powder as filler thermoplastics and epoxy as a matrix thermosets, however there is a big shortage in researches, which takes into account of incorporating thermoplastics and thermosets to develop a unique composites. The main objective of the present work is to study the miscibility of epoxy and polystyrene powder, and its effect on glass transition temperature by employing DSC analysis technique and to study the decomposition kinetics and thermodynamic properties by applying TGA analysis.

## 2. EXPERIMENTAL

The raw material employed in this work to form the composites were epoxy, di-glycidyl ether of bisphenol-A with Metaphenylene Diamine, MPDA as a hardener with polystyrene powder 125 produced at Sabic enterprise. All composites were formed by mold casting using laboratory high-speed blender, then left for one day at room temperature, and cured in an oven at 60 C° for two hours. The thermo gravimetric analysis performed by a Linseis STA. All runs achieved at central service laboratory at Bin Al-haitham College. Different percentages of polystyrene (10, 15, 20) were used in blending with epoxy in order to get a different epoxy/polystyrene composites. Decomposition process carried out with heating rate of 10 C°/min under oxidative atmosphere of air with a flow rate of 20 ml/min between 30-600 C°. However, the work included a study of effect non-oxidative atmosphere of Nitrogen on mechanism of decomposition of epoxy.

## 3. RESULTS AND DISCUSSION

The thermal decomposition rate of epoxy and epoxy/Polystyrene determined by utilizing of TGA and DSC in order to obtain the kinetic parameters. The profile of TGA and DSC for thermal degradation of epoxy under inert and oxidative environment is showed in Fig (1) and Fig (2) respectively. Effect of different environments on decomposition process is shown in Fig (3). However it can be seen from Fig (1) epoxy is more stable toward decomposition especially at the initial stage were 3.5 %wt of mass lost, it can be concluded that all weak linkage in polymer does got affected. While the mass loss in the end of middle stage was 31.2 %wt and in the last stage mass loss was 76.0 %wt , these results showed a stability toward heat as compared with Fig (2) the same conditions were employed except using air instead of nitrogen, degradation takes place in three steps, at the first step epoxy loses about 17.71 %wt at temperature 300 C°, this is because of attacking the oxygen of air the weak linkages more effectively as comparing with inert atmosphere, and causes to break the weaker linkages on the backbone of polymer chain like dehydration of the epoxy, hydrogen bond in the backbone and among backbones of polymer chain and epoxy/polystyrene interaction. However at the second main stage the polymer degraded very effectively through destroying the three dimensional skeleton of cross linking and breaking the backbone carbon chains at different position along the chain in polymer, the mass loss in this stage 54 %wt finally converting to char in last stage with mass loss 21.8 %wt, However there is evidence of existence of phenol and bisphenol-A in the gaseous products in this stage [10]. Fig (3) shows the difference in decomposition profiles between oxidative and non-oxidative environments.

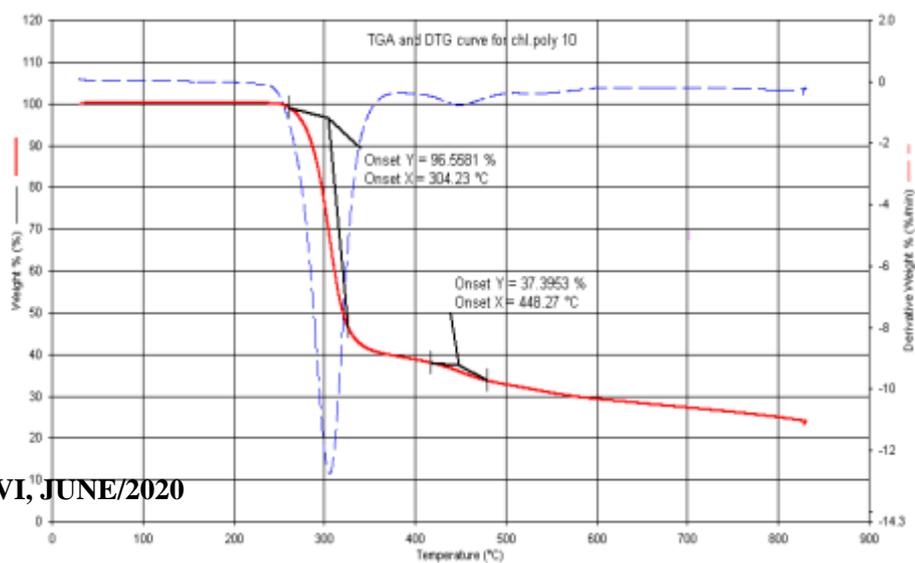


Figure 1. TGA and DTGA curves of epoxy under nitrogen environment.

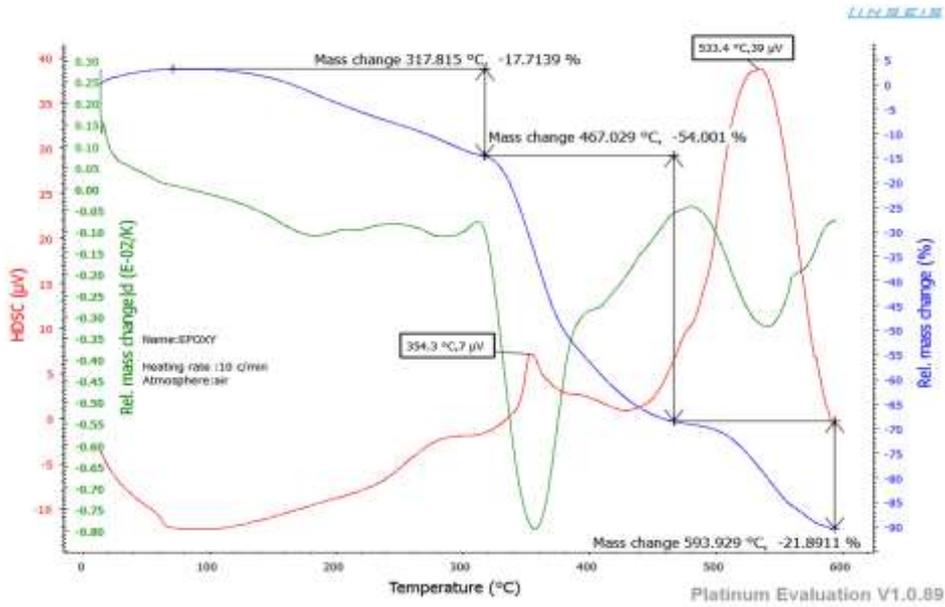


Figure 2. TGA, DTGA, DSC curves of epoxy under air environment.

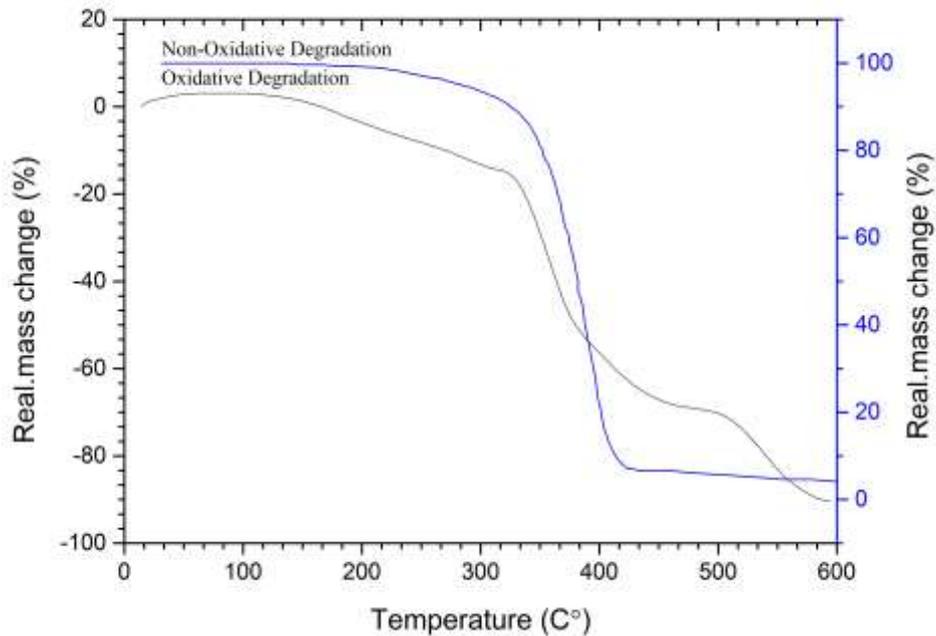


Figure 3. Effect of oxidative and non-oxidative environment on epoxy thermal decomposition

In all experimental runs three steps of degradation observed as mentioned, however the profiles apparently are not linear during the decomposition reaction course as shown in Fig (2), Fig (4), Fig (5) and Fig (6). The first stage ends at temperature 317.8 C° with mass loss 17.71%wt and the second stage ends at 467 C° with mass loss 54 %wt finally the third stage ends at 593.9 C° with mass loss 21.8 %wt as in Fig (2) for epoxy under inert environment, while for epoxy/20% polystyrene in Fig (6), first step ends at 308.7 C° with mass loss 14.9 %wt, the second step ends at 470.1 C° with mass loss 60.43 %wt and the third step ends at 593.7 C° with mass loss 16.18 %wt . These results indicates an increase in thermal stability of composite in the first stage and certain extent from second stage. Concluded from these observed phenomena some sort of a key facts that in the initial stages rate decomposition of epoxy cross linking network of resin chain is much higher than carbon-carbon bond breaking, while in the second stage degradation rate will be much higher therefore it can be observed an increase in activation energies and entropies of decomposition, a similar trend of first stage observed in the last stage with only difference is gasification takes place to char.

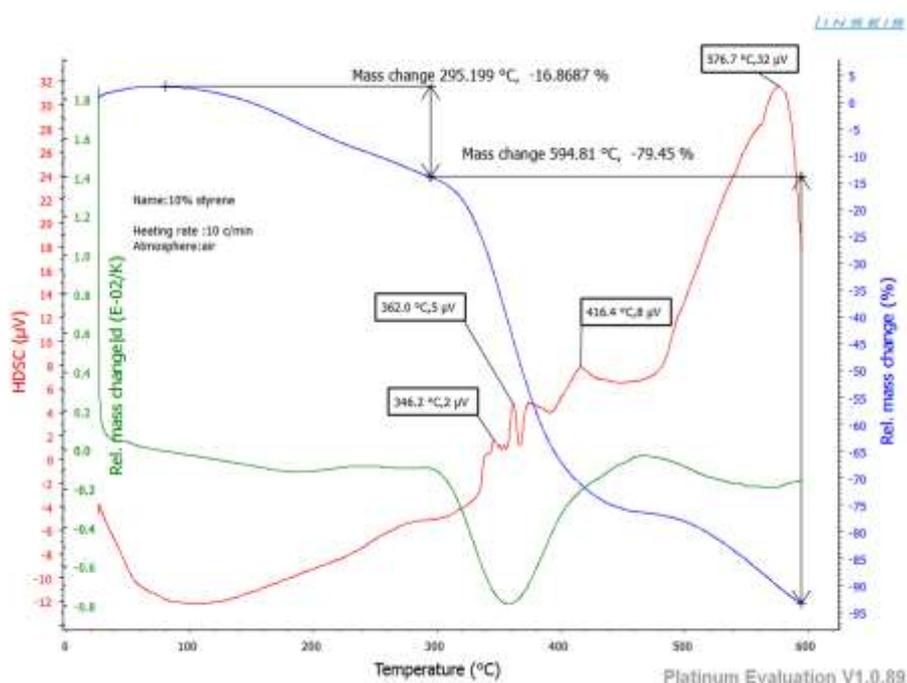


Figure 4. TGA, DTGA and DSC curves of epoxy/10% polystyrene under nitrogen environment.

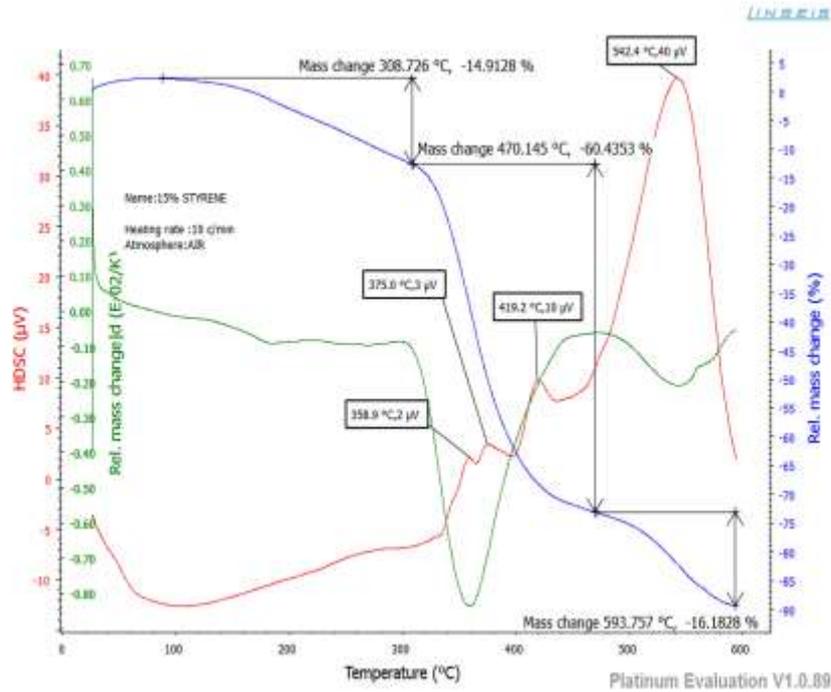
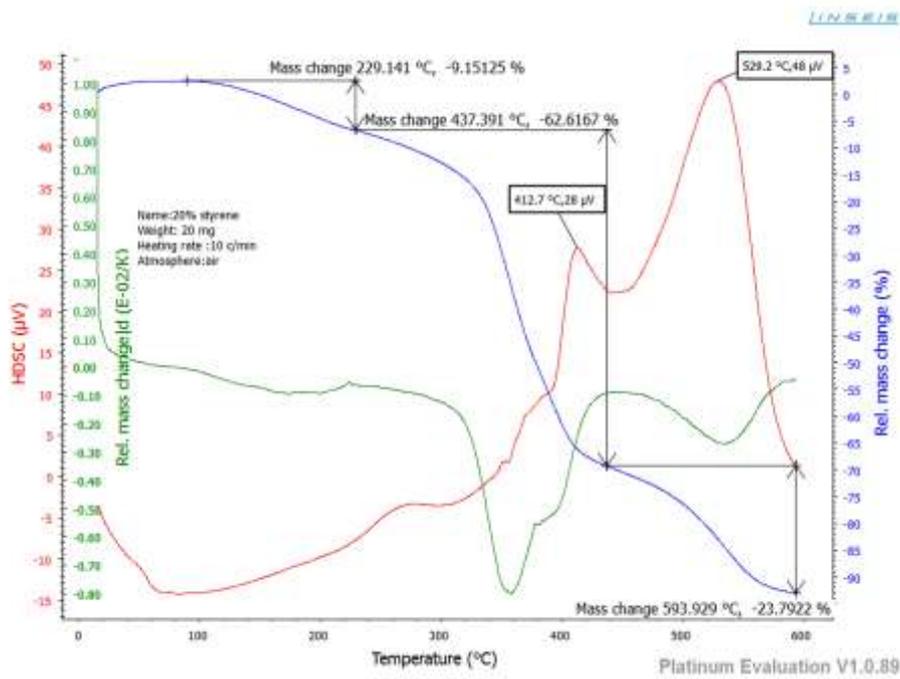
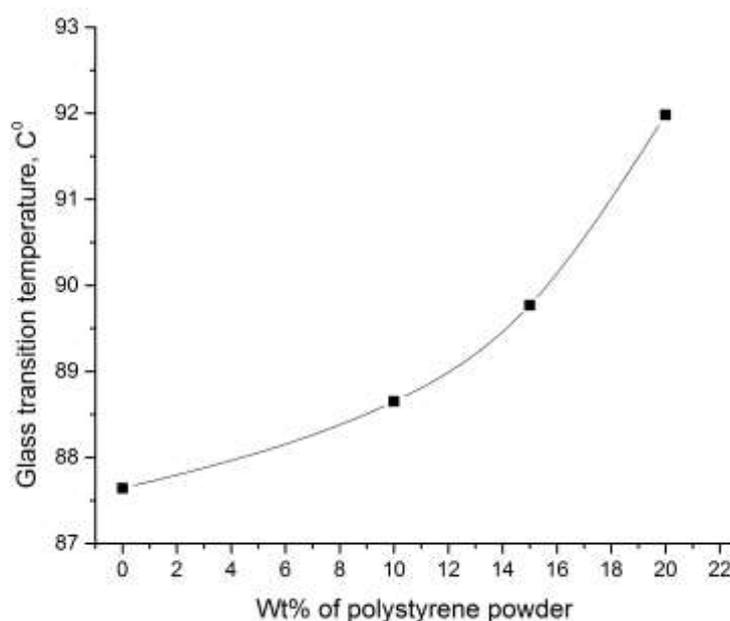


Figure 5. TGA, DTGA and DSC curves of epoxy/15% polystyrene under nitrogen environment.



**Figure 6. TGA, DTGA and DSC curves of epoxy/20% polystyrene under nitrogen environment.**

In order to obtain a very clear picture for the bath of decomposition reaction of epoxy and epoxy/polystyrene composites DSC have been employed simultaneously along with TGA as shown in Fig (2), Fig (4), Fig (5) and Fig (6), It can be seen all results showed two exothermic peaks, the first peak which represents the reaction of breaking of cross linkage network and carbon-carbon bond scission randomly, while the second major peak is oxidative gasification of formed char through the end of second stage. Another benefit of DSC analysis is to determine the glass transition temperature. However epoxy considered a thermo set polymer and cross linked by a chemical agent; therefore epoxy does not melt during heating up due to dipole and hydrogen bond forces but is slightly soften due to changing in its phase in other word so-called glass transition temperature. Fig (7) shows the effect of polystyrene powder content on glass transition temperature of epoxy. However adding polystyrene powder enhance the rigidity of epoxy by dispersion among the polymer chains, therefore glass transition temperature increases with further add.

**Figure 7. Effect of polystyrene % wt content on Glass transition temperature.**

### DSC and TGA analysis

Differential scanning calorimetry and thermo gravimetric analysis has been employed under nitrogen gas and under oxidative air with heating rate of 10 C°/min to study the behavior of thermal decomposition process and its kinetics as well as thermodynamic properties and glass transition

temperature. The TGA profiles analysed by using the Coats-Redfern method is a multi-heating rate application [14].

$$\ln\{-\ln(1-\alpha)/T^2\} = \ln(A_0R/\beta E)\{1-(2RT/E)\}-(E/RT) \quad \dots\dots\dots (1)$$

By plotting  $\ln\{-\ln(1-\alpha)/T^2\}$  against  $1/T$  for each heating rate gives a family of straight lines of slope  $-E/R$ , as shown in Fig (8) and Fig (9). Table (1) and Table (2) shows the kinetic data for non-oxidative by using nitrogen gas for epoxy, and oxidative air decomposition for epoxy and epoxy/polystyrene composite s.

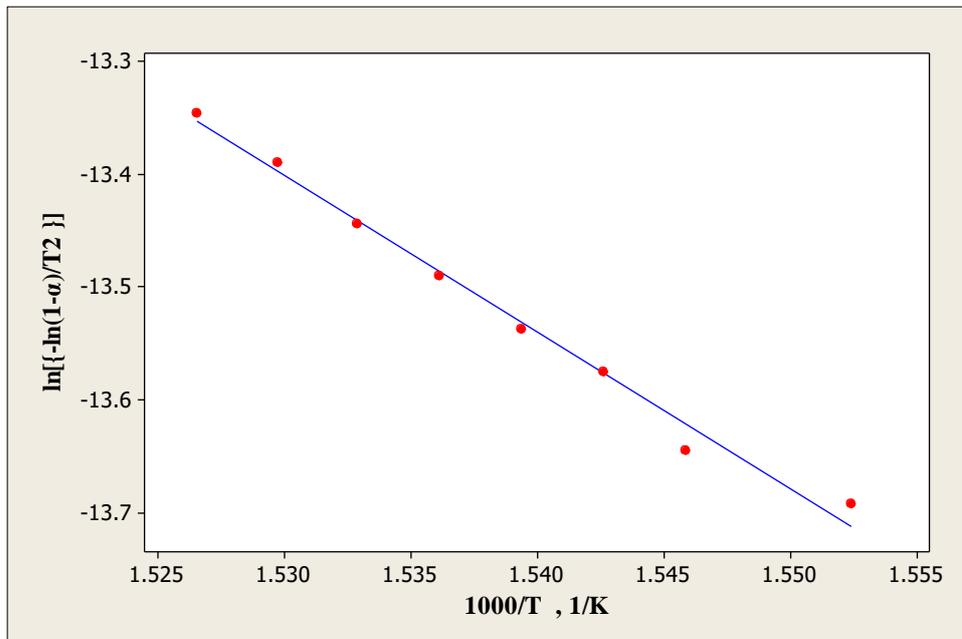


Figure 8. Plot of Coats-Redfern plot for epoxy thermal decomposition under nitrogen.

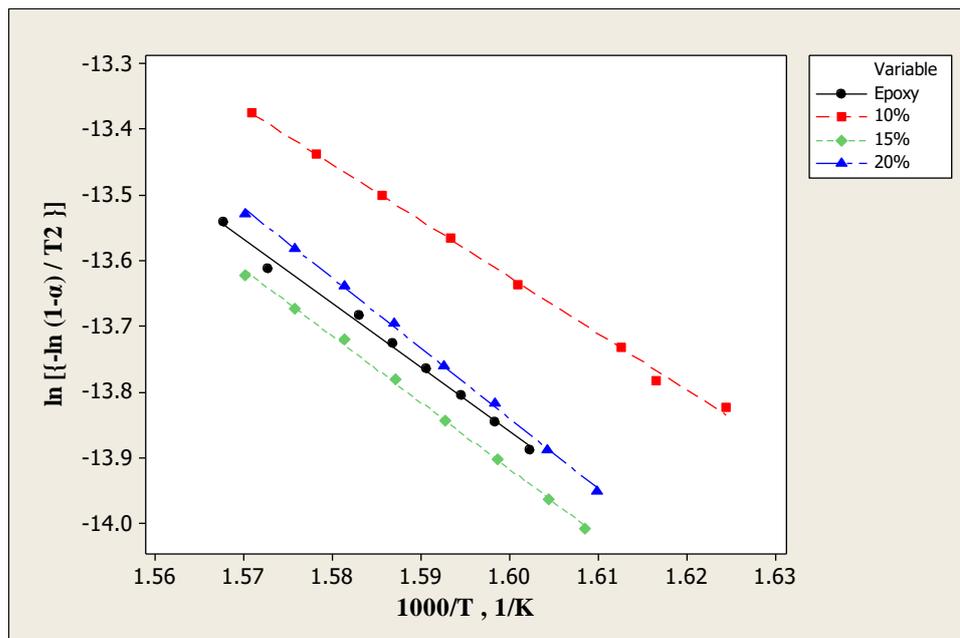


Figure 9. Plot of Coast-Radfern plot for epoxy and epoxy/polystyrene thermal decomposition under air.

Table (1): Kinetics data for epoxy decomposition under non oxidative nitrogen environment.

Specimen	Peak temperature, C°	Activation energy, E (Kj/mol)	Reaction rate constant, A <sub>o</sub> (S <sup>-1</sup> )	R <sup>2</sup>
Epoxy	359.25	129.42	3.39279x10 <sup>11</sup>	0.993

Table (2): Kinetics data for epoxy and epoxy/polystyrene decomposition under oxidative air environment.

Polystyrene %	Peak temperature, C°	Glass transition temperature, C°	Activation energy, E (Kj/mol)	Reaction rate constant, A <sub>o</sub> (S <sup>-1</sup> )	R <sup>2</sup>
0.0	357.25	87.64	74.490	1.0356x10 <sup>7</sup>	0.999
10	357.60	88.65	74.920	1.3845x10 <sup>7</sup>	0.998
15	356.34	89.77	88.499	1.6283x10 <sup>8</sup>	0.998
20	357.90	91.98	96.800	9.4299x10 <sup>8</sup>	0.998

Thermodynamics property was estimated by using the following equations [13, 14]:

Where  $\Delta H$  represents the enthalpy of decomposition,  $\Delta S$  is the entropy,  $\Delta G$  is the free energy,  $T_{\text{peak}}$  is the peak temperature of DTGA profile,  $h$  is Plank constant and  $k_b$  is Boltzmann constant.

$$\Delta H = E - R T_{\text{peak}} \quad \dots (2)$$

$$\Delta S = R [ \ln(h A_o / k_b T_{\text{peak}}) - 1 ] \quad \dots (3)$$

$$\Delta G = \Delta H - T_{\text{peak}} \Delta S \quad \dots (4)$$

Table (3) and Table (4), shows the thermodynamics property of the thermal decomposition of epoxy under non-oxidative nitrogen atmosphere, and thermal decomposition of epoxy and epoxy/polystyrene composites under oxidative atmosphere of air.

**Table (3): Thermodynamics data for epoxy decomposition under non-oxidative nitrogen environment.**

Specimen	$\Delta H$ , KJ/mol	$-\Delta S$ , J/mol	$\Delta G$ , KJ/mol
Epoxy	126.164	38.738	141.332

**Table (4): Thermodynamics data for epoxy and epoxy/polystyrene decomposition under non-oxidative nitrogen environment.**

Polystyrene %	$\Delta H$ , KJ/mol	$-\Delta S$ , J/mol	$\Delta G$ , KJ/mol
0.0	69.249	125.186	148.148
10	69.676	122.734	147.073
15	83.266	102.276	147.633
20	91.554	87.499	146.757

#### 4. CONCLUSION

Non-oxidative and oxidative thermal decomposition have been utilized the TGA and DSC to study the miscibility of epoxy and polystyrene with different percentages and the kinetics. The results indicated that the reaction is first order and the thermal stability increased with increasing of polystyrene content, activation energy increased from 74.490 to 96.80 KJ/mol.K and rate constant increased from  $1.0356 \times 10^7$  to  $9.4299 \times 10^8$  S<sup>-1</sup>. In addition, entropy showed an increase -125.186 to -87.499 J/mol. DSC curves showed for all specimens under thermal decomposition a single glass transition temperature emphasizing epoxy and polystyrene is completely miscible system. In oxidative decomposition, oxygen accelerates the reaction of all three stages, therefore activation energy dropped to 74.490 KJ/mol.K.

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