

Thermal Oxidative of UP/MgO Nanocomposites Using TGA and DSC Analysis

Malik J. Zayza, Najwa J. Jubier, Subhi A. Al -Bayaty

Abstract— The work focuses on the preparation of polymer matrix nanocomposite materials by hand lay-up, it was prepared from the unsaturated polyester resin as a matrix reinforced with a different weight percent of Magnesium oxide nanoparticles (MgO NPs).

This research includes studying the thermal analysis, (TGA, DTG, and DSC) for this nanocomposite material. Study of non-isothermal kinetics decomposition of (UP) and (UP/MgO NPs) nanocomposites were carried out by utilizing (TGA). The samples were heated from room temperature to (600°C) at a constant heating rate of (10°C/min) under an oxidative atmosphere using air. TGA and DTG curves obtained from the decomposition were analyzed using the Coast- Redfern method. Kinetic parameters were determined for all specimens that show a good correlation with the linear correlation coefficient. It was found that the Coast –Redfern procedure the best to obtain results in good estimate of the kinetic parameters.

Index Terms— polymer nanocomposites, unsaturated polyester resin, Magnesium oxide nanoparticles (MgO), thermal decomposition, TGA, DTGA, DSC.

I. INTRODUCTION

Polymer nanocomposite may be defined as a composite system containing a polymer matrix and homogeneously dispersed filler particles having at least one dimension below (100 nm). Polymer nanocomposites have received enormous attention both in academia and industry over the past decades. The excellent properties of nanocomposites are attributed to the large surface to volume ratio of the nanofillers [1].

Degradation of polymers includes all the changes in the chemical structure and physical properties of the polymers due to external chemical or physical stresses caused by chemical reactions, involving bond scissions in the backbone of the macromolecules that lead to materials with characteristics different from (usually worse than) those of the starting material [2,3].

The thermal degradation of polymers refers to the case where polymers at elevated temperatures start to undergo chemical changes without the simultaneous involvement of another compound [3]. Thermal degradation of polymers is of paramount importance in developing a rational technology for polymer processing, in using polymers at higher temperatures, and in understanding thermal decomposition mechanisms for the synthesis of fire-safe polymeric materials [4,5.]

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In this study, influences of different weight fractions of magnesium oxide nanoparticles on the decomposition process of unsaturated polyester resin were investigated by Thermogravimetric Analysis (TGA), Derivative Thermo-Gravimetric (DTG), and Differential Scanning Calorimetry (DSC). Several reports have been carried out about the investigated such properties as by Evans et al. (1997) investigated the effects of different fillers such as silica, calcium carbonate or glass fibers and different curing regimes on the degradation of polyester resins. The products were analyzed by TGA, DTA, DSC, and Pyrolysis-GC. As a result of their study, different curing regimes didn't affect the stability of polyesters significantly. The addition of fillers reduced the stability of polyesters but these changes were relatively low [6], Fernandes Jr. et al. (2002) produced composite materials by commercial polyester resins containing decabromodiphenyl oxide and antimony trioxide. Thermal degradation of these products was studied by the UL-94 flammability test, TGA and DSC. Char formation of the flame retardant system used in this work did not increase. DSC curves indicated that additives were effective for limiting combustion. TGA results showed that activation energy for degradation of polyester containing additives was much larger than that of untreated resin [7], Seki et al. (2012) used huntite mineral as reinforcement for unsaturated polyester. Huntite mineral was turned into powder form and added into the resin. The highest values of tensile and flexural strength were found for the composite with 3% huntite which may be attributed to the more uniform distribution of the fillers. TGA results showed that the degradation temperature of a polyester matrix was improved by adding huntite. DSC curves showed that the curing behavior of polyester resin was not influenced by huntite filling [8].

II. MATERIALS AND METHOD

Experimental: Use unsaturated polyester resin (UP) made by (Polres) company from Turkey. This resin in the form of a viscous liquid, transparent purple color at room temperature and converts from a liquid to the solid state by adding Hardener Methyl Ethyl Keton Peroxide by rate of 2 % which manufactured by the same company.

The Magnesium Oxide (MgO) nanoparticles (NPs) utilized in the present study have been produce from (Skyspring Nanomaterials, Inc. USA) (99%) purity as per suppliers' data), Atomic Force Microscopy (AFM) was used (SCPMS canning Probe Microscope) to measure the average particles size, surface roughness and Root Mean Square (RMS) of MgO nanoparticles as shown in Table 1, Fig.1 shows image (3D -AFM) of nanoparticles MgO and particles size distribution.

Samples of the unsaturated polyester resin (UP) and unsaturated polyester resin nanocomposites at a different weight percentage of MgO nanoparticles (0, 1, 3, 5, 7,10 and 15%) are prepared by hand lay-up technique and use

ultrasonic for mixing process. All content mixed thoroughly before casting, then the samples left at room temperature for (24) hours and then for post curing the samples were left for (1) hour in an oven at temperature 50 °C.

Table 1: Average diameter, surface roughness and root mean square values of nanoparticles MgO.

Materia l	Average diameter (nm)	Surface roughness (nm)	RMS	Peak to peak (nm)
MgO	54.19	2.9	3.36	12.3

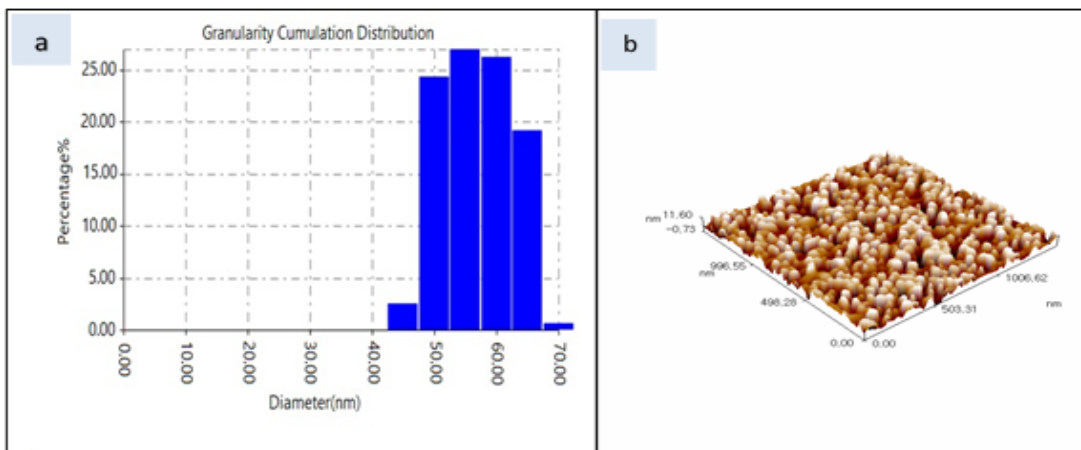


Fig. (1): AFM of nanoparticles MgO; (a) Granularity distribution of nanoparticles; (b) 3D image AFM.

III. RESULT AND DISCUSSION

It is obvious from a thermal graph of (DSC and TGA) as shown in figures (2,3,4,5,6,7,8) thermal decomposition occurs at early stages in pure polymer, and by increasing the weight percentages of (MgO) nano sizes, polymer decomposition become very slow and it occurs higher temperature comparing with pure one. Table (1) represents the extent of polymer and composite thermal decomposition. It is clear that for pure polymer at (10%) decomposition rate occurs at (308.4°C), While with increasing weight percentage

of (MgO) up to (15%) the decomposition rate of (10%) occurs at (360.3°C), however the same attitude occurs at decomposition rates of (20%,40%,60%,80%), this is because of the increase of thermal stability of composites as well as (MgO) have high thermal resistance properties. DSC profile showed the thermal decomposition occurs at two stages, the first represents random suction of polymer chain followed by CO₂ and H₂O vapors .

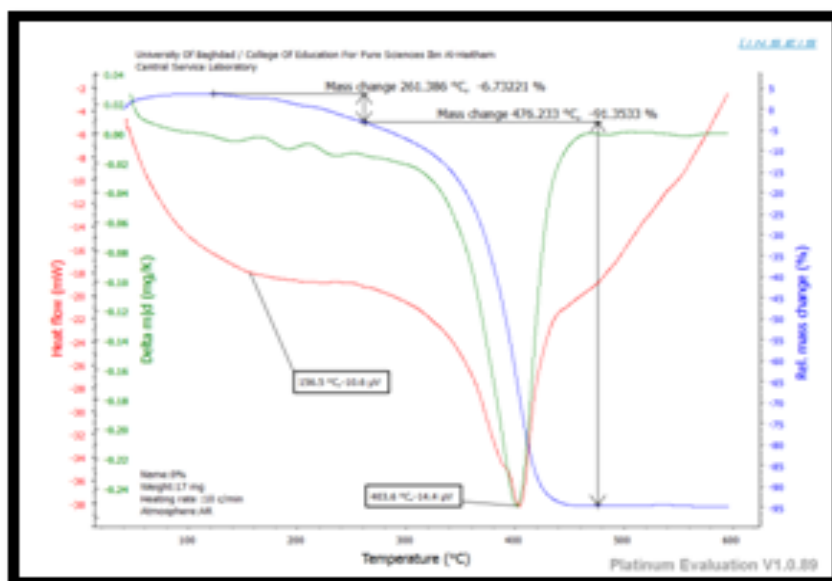


Fig. (2): TGA, DSC, DTG curves of pure unsaturated polyester resin.

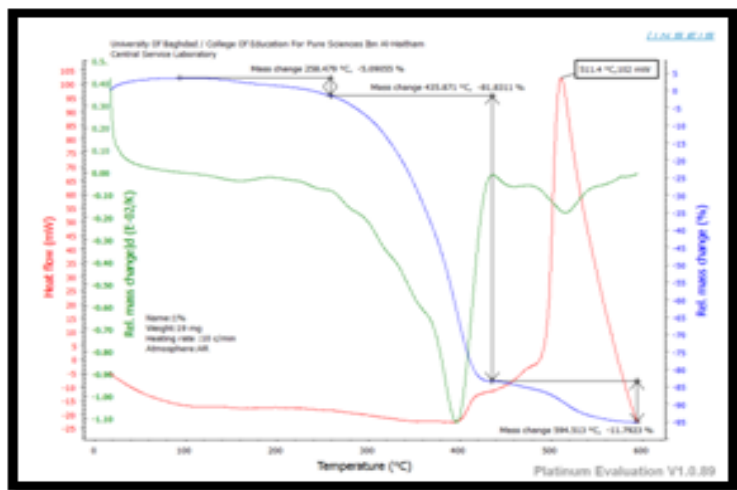


Fig. (3) (DSC, TGA, DTG) curves for (UP/1% MgO NPs) nanocomposite.

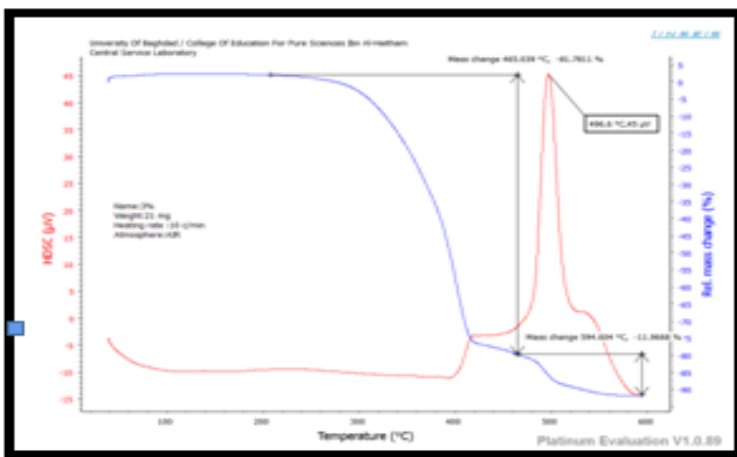


Fig. (4) (DSC, TGA) curves for (UP/3%MgO NPs) nanocomposite.

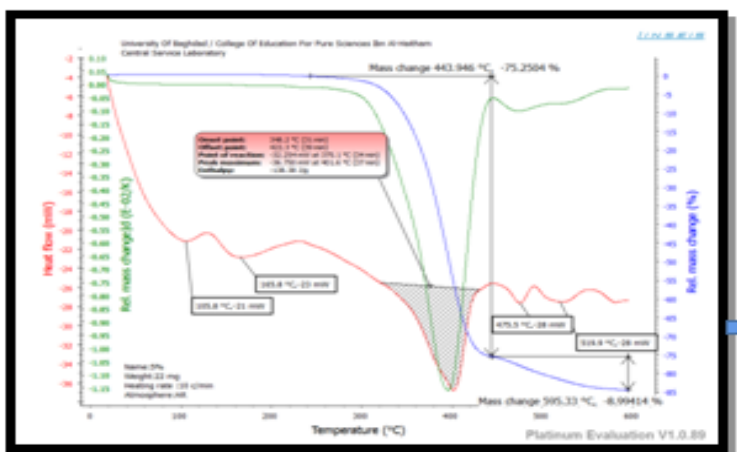
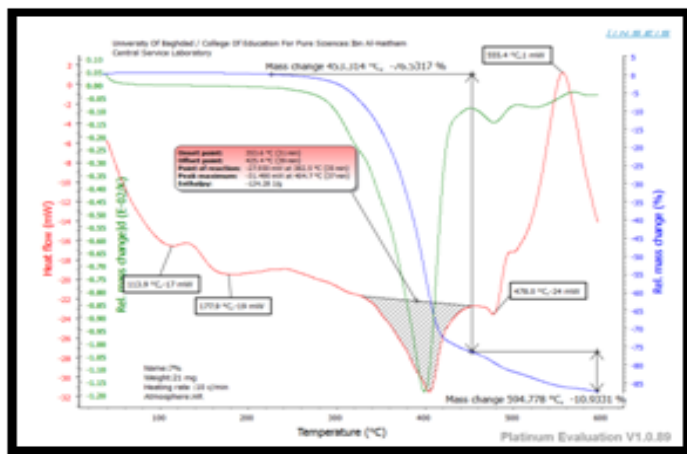


Fig. (5) (DSC, TGA, DTG) curves for (UP/5%MgO NPs) nanocomposite.



(6) (DSC, TGA, DTG) curves for (UP/7%MgO NPs) nanocomposite.

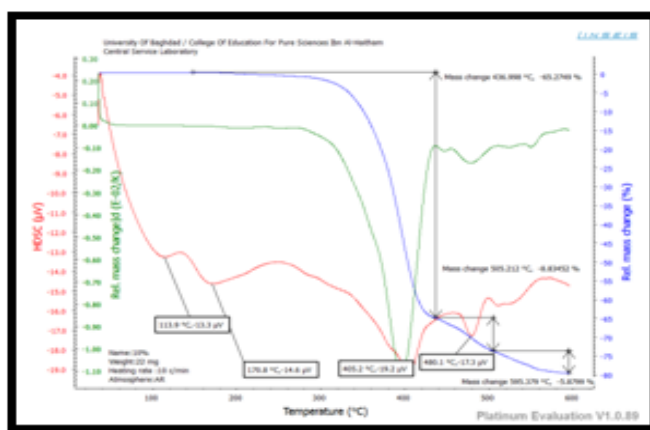


Fig. (7) (DSC, TGA, DTG) curves for (UP/10%MgO NPs) nanocomposite.

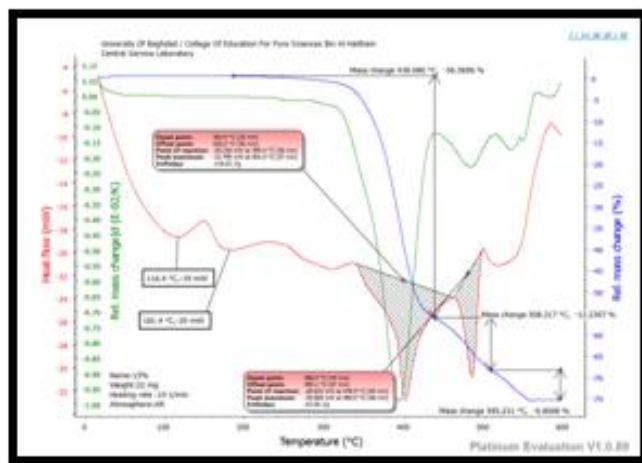


Fig. (8) (DSC, TGA, DTG) curves for (UP/15%MgO NPs) nanocomposite.

Table (1): The extent of thermal decomposition of unsaturated polyester resin and its nanocomposites.

Wt% MgO	Weight percent loss of thermal decomposition				
	10%	20%	40%	60%	80%
	Temperature profiles, C°				
0.0	308.4	335.8	372.4	393.0	413.0
1.0	310.0	345.2	378.9	394.7	408.2
3.0	315.5	349.5	376.1	390.1	401.0
5.0	333.9	357.7	385.3	400.2	481.4
7.0	348.1	365.9	389.3	406.5	497.5
10.0	348.8	369.5	392.1	413.9	580.5
15.0	360.3	378.6	399.2	460.3	596.9

Fig. (9) represent the relationship between the activation energy of thermal decomposition of the polymer and its nanocomposite. It was noticed the activation energy increases by

increasing the weight percentage of (MgO), however, this means the thermal stability of nanocomposite increased, in another word, nanocomposite needed more heat to start decomposition [10,11].

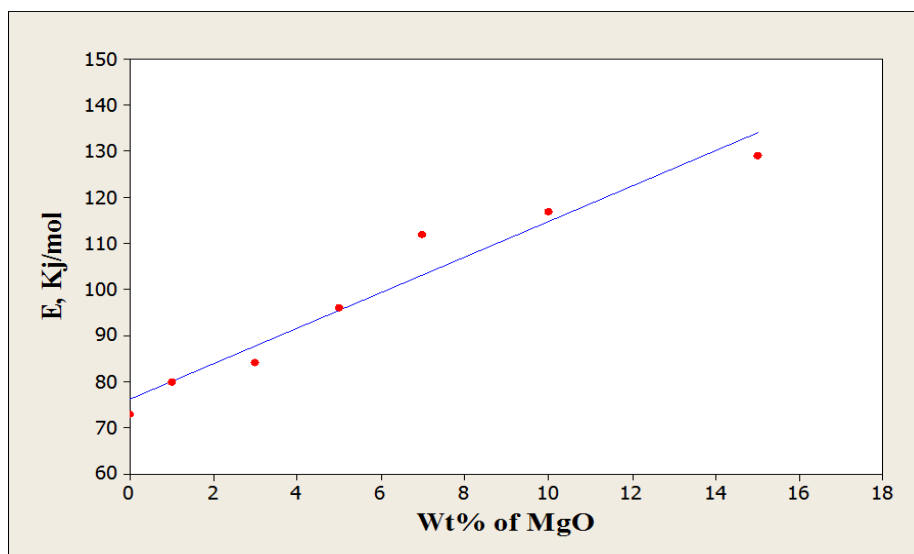


Fig. (9): The effects of (MgO) content on Activation Energy.

Fig. (10) Shows the relationship between entropy and the activation energy, however, it can be seen when activation energy increases the entropy increases also in other word the

random of system increases negatively. It is important that the relation is linear with (R2 = 96%) this means Coats- Redfern method is suitable and fits all experimental data, therefore, all kinetics parameter is correct [10,11].

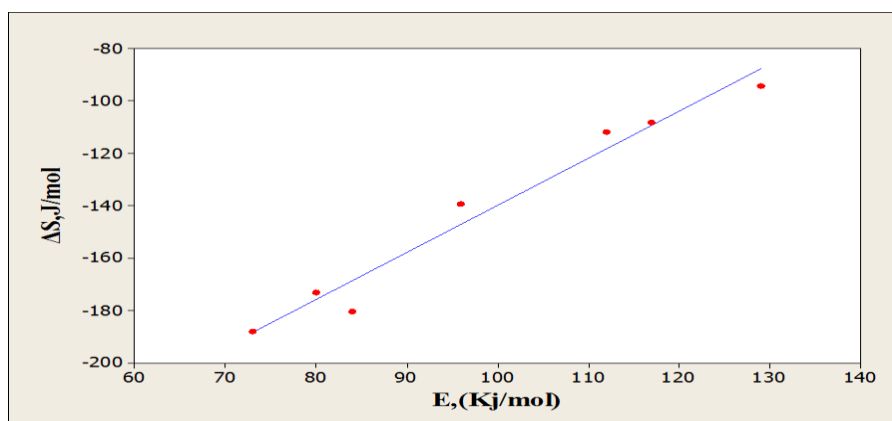


Fig. (10): Plot of Entropy against Activation Energy for thermal decomposition of unsaturated polyester and its nanocomposite.

Fig. (11) Shows a series of parallel lines between $\ln[-\ln(1-\alpha)/T^2]$ versus $(1/T)$ plotted according to Coats-Redfern. It can be seen all points fitted in linearly with (R^2) around (99%), however, this graph used to determine all experiment kinetic data for oxidation decomposition of

polymer and its composites. Table (2) shows kinetic data of thermal decomposition non- isothermal of unsaturated polyester and its nanocomposites according to Coats-Redfern method.

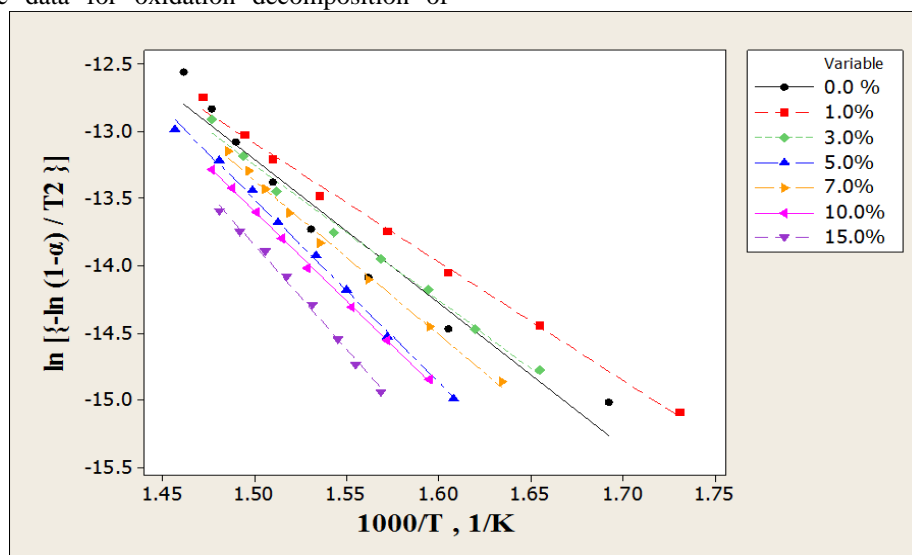


Fig. (11): A plot of oxidative thermal decomposition utilizing Coats-Redfern method.

Table (2) shows kinetic data of thermal decomposition non- isothermal of unsaturated polyester and its composites according to Coats-Redfern method.

Wt% MgO	Peak Temperature, T_p (K)	Activation Energy, E_a (KJ/mol)	Reaction rate constant, A_0 (S^{-1})	R^2
0.0	652	73.00	0.1747×10^4	99.1%
1.0	669	80.00	2.9139×10^4	99.7%
3.0	672	84.32	1.397×10^4	99.0%
5.0	670	96.43	1.242×10^5	99.6%
7.0	673	112.31	1.970×10^6	99.8%
10.0	668	117.53	5.552×10^7	99.6%
15.0	666	129.81	4.413×10^8	98.0%

Glass- transition point (T_g)

It is obvious that coherent between polymer chains determined Vander- Wall forces, as well as cross-linkage therefore when weight percent of (MgO) increases, glass transition temperature increases as shown in Fig. (12), this means the nanocomposite becomes more rigid [10, 11].

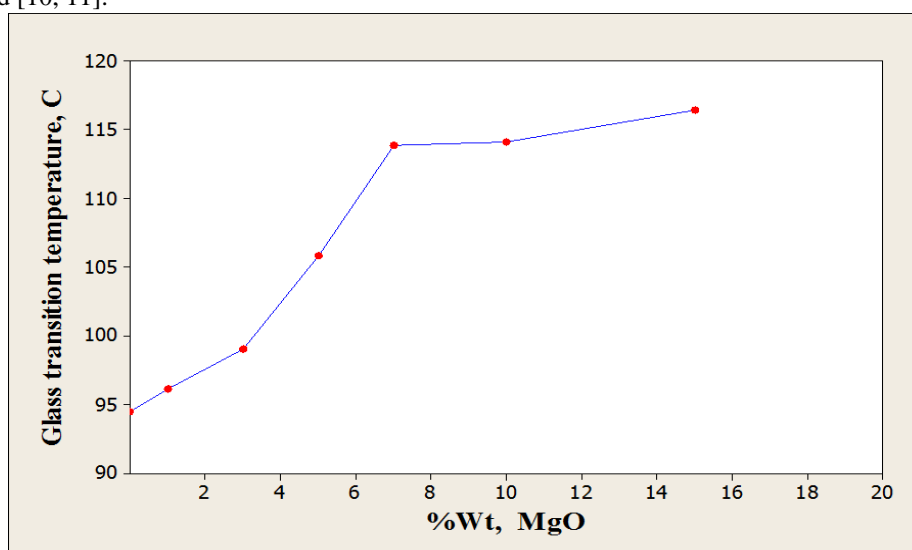


Fig. (12): Effect of wt. %MgO content on Glass transition temperature.

Table (3) shows all thermodynamic properties for oxidative decomposition of polymer and its nanocomposite, however, it can be seen when the weight percent of (MgO) increases more heat stored inside of nanocomposite and there is no enough time to heat transfer from nanocomposite, therefore the values of enthalpy increases according to it as well as entropy, the parameters of thermodynamics were

calculated according to the following equations:

$$\Delta H = E_a - RT_{p_{\text{peak}}} \dots (1)$$

$$\Delta S = R \left[\ln \left(\frac{HA_0}{KbT_{p_{\text{peak}}}} \right) - 1 \right] \dots (2)$$

$$\Delta G = \Delta H - T_{p_{\text{peak}}} \Delta S \dots (3)$$

Table (3): Thermodynamics property of unsaturated polyester and its nanocomposites.

Wt.% MgO	Tg , C°	ΔH,KJ/mol	-ΔS, J/mol	ΔG, KJ/mol
0.0	94.5	67.437	188.183	193.413
1.0	96.1	74.404	173.271	191.016
3.0	99.0	78.724	180.607	200.273
5.0	105.8	106.767	139.415	199.756
7.0	113.9	111.972	111.684	186.689
10.0	114.1	90.863	108.333	163.446
15.0	116.4	124.276	94.4120	187.154

IV. CONCLUSION

TGA, DTG and DSC analysis of nanocomposites shows enhancement in the thermal stability of nanocomposites, the TG will increase when increased the weight fraction of (MgO NPs), the activation energy, activation entropy shows the linear relationship between them that's mean the Coast-Redfern method is suitable and fits all experimental data for nanocomposites. Enthalpy and entropy also increases with increasing of wt. % of MgO since it retarded heat loss which accumulates inside the specimens during oxidative decomposition.

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