THE KINETIC OF THERMAL DEGRADATION FOR MANUFACTURED HIGH DENSITY POLYETHYLENE (HDPE).

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Summary:

The goal of this study is to know how effected the manufactured high density polyethylene (HDPE) bag during reprocessing with various temperatures and various times. The isothermal weight loss (X%) of manufactured high density polyethylene was investigated at temperature 150, 175, 200, 225 and 250 ^{o}C at period of times (10 – 50 min.). The result was the amount of weight loss (X%) of manufactured (HDPE) increases with increasing temperature and time.

Calculation of the activation energy of the thermal weight loss process from these experiments was calculated and it was changed between (22-29 kJ/mol) at changing temperatures between (150 – 250 ^{o}C) for range 2-6% of weight loss of (HDPE).

The rate of reaction constant (K) for temperatures range (150 – 250 ^{o}C) was changed from (1E-06 - 6E-06 L.mol^{-1}.S^{-1}). The degree of reaction was found 2nd order reaction in all range of temperature (150 – 250 ^{o}C).

الخلاصة:

الهدف من هذا البحث هو لمعرفة مدى تأثير البولي اثلين العالي الكثافة المصنع على شكل اكياس النايلون عند اعادة تصنيعة عند درجات حرارة مختلفة ولازمنة مختلفة.وقد درس في هذا البحث النسبة المؤوية لفقدان الوزن (X%) بثبوت درجة الحرارة ،ودرست النسبة المؤوية لفقدان الوزن في كل من درجات حرارة الاتية: (C^{o} 250 ,225 ,200 ,175 ,150) ولفترات زمنية مختلفة هي (. 50 Min – 10) لكل من درجات الحرارة السابقة.النتيجة كانت هي الزيادة بفقدان الوزن (X%) مع زيادة درجة الحرارة والزمن للبولي اثلين العالي الكثافة المصنع.

طاقة التنشيط لعملية فقدان الوزن بثبوت درجة الحرارة تم حسابها من التجارب العملية وكانت قيمها بين(29-22 KJ/mol) لمدى من درجات حرارة هو (C^{o} 250 – 150) وضمن نسبة فقدان الوزن هي (6% – 2) لبولي الاثلين العالي الكثافة.

و وجد ان معدل ثابت سرعة التفاعل (K) لمدى من درجات الحرارة (C^{o} 250 – 150) هو (-6E – 1E-06 L.mol^{-1}.S^{-1} 06).و وجد كذلك ان درجة التفاعل هي من الدرجة الثانية ضمن مدى درجات حرارة هي (150 – 250 ^{o}C).

Keyword: **HDPE** , **Degradation** , **Kinetic** ,**Weight Loss**, **Rate Of Reaction**, **Degree Of Reaction**.

INTRODUCTION

The goal of this study is to know how effected the manufactured high density polyethylene (HDPE) bag during reprocessing with various temperatures and various times. As known the (HDPE) has a low degree of branching and thus stronger intermolecular forces and tensile strength. The structure of (HDPE) is:

$$\left(\begin{array}{cc} \overset{H}{\underset{H}{|}} & \overset{H}{\underset{H}{|}} \\ C & C \\ \end{array} \right)_n$$
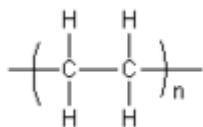
The previous studies were included the ƴ radiation sterilization of ultrahigh molecular weight polyethylene (UHMWPE) components in air generates long-lived free radicals that oxidize slowly over time during shelf storage and after implantation (Steven 1998).   Ultra high molecular weight polyethylene (UHMWPE), used in total joint replacement implants, undergoes oxidative degradation due to gamma radiation sterilization and to exposure to oxidizing agents in the body environment (Clare 2004). The degradation of different polyethylenes - low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE) - with and without antioxidants and at different oxygen concentrations in the polymer granulates, have been studied in extrusion coating processing (Thorbjörn 2003). The effect of a simulated marine environment on unstabilized polyethylene-polyethylene oxide blends, having varying polyethylene oxide content (up to 40% by weight), with or without a metal catalyst (e.g., cobalt (III) acetylacetonate) and a metal containing plasticizer (e.g., aluminum stearate), has been studied for 10 weeks exposure time (K. E. Gonsalves 2003).   The kinetics of degradation of fenprostalene (I) in polyethylene glycol 400 solution was examined. The autoxidation of the polyethylene glycol 400 was concurrent with degradation of (I) in the apparent pH. Antioxidants were very effective in retarding the rate of degradation in the presence of oxygen(.David M.2006). The study of high density polyethylene (HDPE)/ethylene-vinyl acetate (EVA)/and organically-modified nanocomposites prepared by melt followed by exposure to gamma-rays have been carried out. The purpose of the study focuses on the influence of gamma irradiation on the morphology, thermal stability and flammability properties of the nanocomposites (Hongdian 2004). The potential of catalytic processing as an effective method for polymer recycling was studied using various modfled zeolites catalysts in the degradation of low-density polyethylene (LDPE). Particular attention was paid to catalytic activity, and selectivity and yield of liquid products (P. Tu 2008). The thermal and thermo-oxidative degradation of reprecipitated and "as received" samples of different types of high-density polyethylene (HDPE) have been studied. Two of the samples were of conventional Phillips type, being essentially linear and having one vinyl group per molecule. The other two HDPE's were also produced by chromium catalysts, but according to Union Carbide's fluidized bed process(Arne 2007) .Polyethylene films and sheets were oxidized in oxygen, air, or aqueous nitric acid at temperatures up to 100°C., and the decay of physical properties was measured by mechanical testing (E. G. Bobalek2003). Through the use and re-extrusion of virgin high-density polyethylene (HDPE), the effects of the degradation level of HDPE as a matrix phase on its mechanical properties and the mechanical performance of composites produced with the degraded polyethylene have been examined (A. Shojaei 2006) . A study of the effect of extrusion conditions on the degradation of high density polyethylene was carried out. The extent of degradation was quantified by dynamic viscometry. The effect of barrel temperature profile, screw speed, and feed rate on the degradation of high density polyethylene was determined. The viscosity response of high density polyethylene is complex with respect to extrusion conditions (N. Dontula 2004). The comparative of two different types of 'degradable' polymer was studied, polyethylene (PE) sacks are not degrading as anticipated within open windrow conditions, whilst the degradable starch based sacks appear to actively degrade within open windrow compost conditions (Georgina Davis 2003). The fourth type of

polyethylene - very low density polyethylene (VLDPE) - has been developed very recently. VLDPE is a copolymer of ethylene and 1-butene. The radiation and photo degradation of VLDPE was studied using gel, FT-IR, and UV spectral measurements (R. Geetha 2003). The kinetic specificity of polyethylene terephthalate (PET) degradation in a living body was investigated. The polyethylene terephthalate net implanted subcutaneously in the backs of rabbits and dogs usually degrades from the surface very slowly. The time of complete degradation of PET fibers in both dogs and humans amounts to 30 ± 7 yr (T. E. Rudakova 2003) . The properties of two polyethylenes [a high-density polyethylene (HDPE) and a low-density polyethylene (LDPE)] were studied after several extrusion cycles. To reduce the degradation effects during the reprocessing, a mixture of two stabilizers was added to the formulations (M. J. Abad 2004).

Experimental:

The following is the procedure to curing the manufactured high density polyethylene with temperatures and times:

(1)It was weighted the crucible when it was empty.

(2)It was weighted the crucible with sample of manufactured HDPE.

(3)It was determined the initial weight by the law:

$$W_o = W_1 - W_2$$

Where: W_1=weight of crucible with sample of HDPE.

W_2= weight empty crucible.

(4) It was putted the crucible with HDPE sample in the furnace to require heating time and temperature.

(5) When curing was completed, the HDPE sample get out from furnace.

(6) When the sample of HDPE was cooled, it was weighted to estimate the weight loss of HDPE.

(7) The procedure above was repeated for every curing samples of HDPE in each temperature and time.

Results And Discussion

The isothermal weight loss (X%) of manufactured high density polyethylene was investigated at temperature 150, 175, 200, 225 and 250 ^{o}C and for period of time (10 - 50 min.). It can be seen that the amount of weight loss (X%) of manufactured high density polyethylene increases with increases temperature and time that because the kinetic energy of molecular increase with increase temperature (Ana1984). The

behavior of weight loss (X%) versus heating time in isothermal heating experiments are shown in figure (1)and Table (1) below.

Table(1): Isothermal weight loss (X%) of High density polyethylene versus time (Min.) at verious temperature (^{o}C).

Time	X% at T=150	X% at T=175	X% at T=200	X% at T=225	X% at T=250
0	0	0	0	0	0
10	0	0.93	1.865	2.8	3.73
20	1.35	2.795	4.24	5.685	7.13
30	2.7	4.53	6.35	8.18	10.01
40	3.5	6.105	8.71	9.815	13.92
50	4.27	7.54	10.81	14.07	17.34
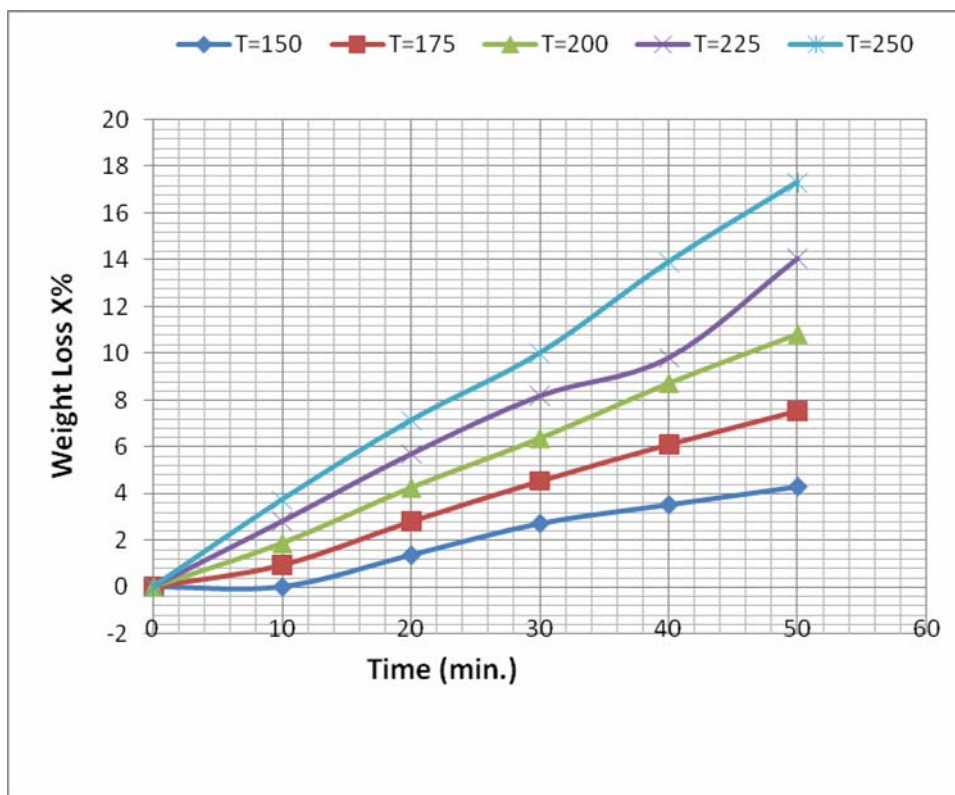
Fig.(1): Isothermal weight loss % of high density polyethylene versus time (Min.) at verious temperature (C).

In order to calculate the activation energy of the thermal weight loss process from these experiments, the method recommended by MacCallum (Atkinson 1972) was used. A rate of reaction expression for the global degradation reaction is obtained [David 1988, Thomas 2006], and it is being:

$$- \frac{d(1-x)}{dt} = K.f(1-x)$$

$$- \left[0 - \frac{dx}{dt} \right] = K.f(1-X)$$

$$\frac{dx}{dt} = K.f(1-x)$$

$$\frac{dx}{f(1-x)} = Kdt \ldots\ldots\ldots\ldots\ldots (1)$$

Integration of eqn (1), yields:

$$F(1-x) = \int_{x=0}^{x=x} \frac{dx}{f(1-x)} = K. \int_{t=0}^{t=t} dt$$

$$F(1-x) = K.t \quad \rightarrow \quad K = \frac{F(1-x)}{t} \ldots\ldots\ldots\ldots (2)$$

In this expression, t is time, K is the rate constant of the global degradation process, f(1-X) is a function of the degree of degradation and x is the percent extent of weight loss given by:

$$X\% = \frac{Wv}{W^o} = \frac{W^o - W}{W^o} * 100$$

Where, Wv is the weight of polymer evolved as the volatile fragments, Wo is the initial weight of the polymer, and W is the weight of the polymer at anytime during the thermal degradation process.
It is also assumed that the variation of K with temperature is of Arrhenius type (J.M.Smith 1981):

$$K = Ae^{-\frac{E}{RT}} \ldots\ldots\ldots\ldots\ldots (3)$$

Where, E is the activation energy, R is the universal gas constant, T is the absolute temperature and A is the pre-exponential factor. From equation 2 substitute K in equation 3 resulting:

$$\frac{F(1-x)}{t} = Ae^{-E/RT}$$

$$LN(\frac{F(1-x)}{t.A}) = -\frac{E}{RT}$$

$$Ln(t) = \frac{E}{RT} + Ln(F(1-x)) - Ln(A) \ldots\ldots\ldots\ldots (4)$$

From the equation 4 when plotted Ln(t) against (1/T) ,the slope is (E/R) and the intercept is [Ln(F(1 – x)) – Ln(A)].As it known the value of F(1-x) have same value at same value of X% conversion even at different temperature, therefore for a range of experiments at different temperatures, the logarithm of the time Ln(t) taken to reach a fixed conversion X% plotted versus the reciprocal of the experiment's temperature, in Kelvin, thus will yield the activation energy, E from the slope as shown in Table (2) and Fig.(2).

Table(2): Time (min.) required to fixed weight loss X% of high density polyethylene at different temperature.

T(^{o}C)	1/T (^{o}K)	X=2%	X=2.8%	X=4%	X= 4.8%	X= 6%
150	0.00236	3.20275	3.43399	3.8373	-	-
175	0.00223	2.77259	2.99573	3.29584	3.45947	3.66356
200	0.00211	2.37955	2.63906	2.94444	3.12676	3.3499
225	0.00201	1.94591	2.30259	2.63906	2.82731	3.04452
250	0.00191	1.60944	2.0149	2.37955	2.56495	2.80336
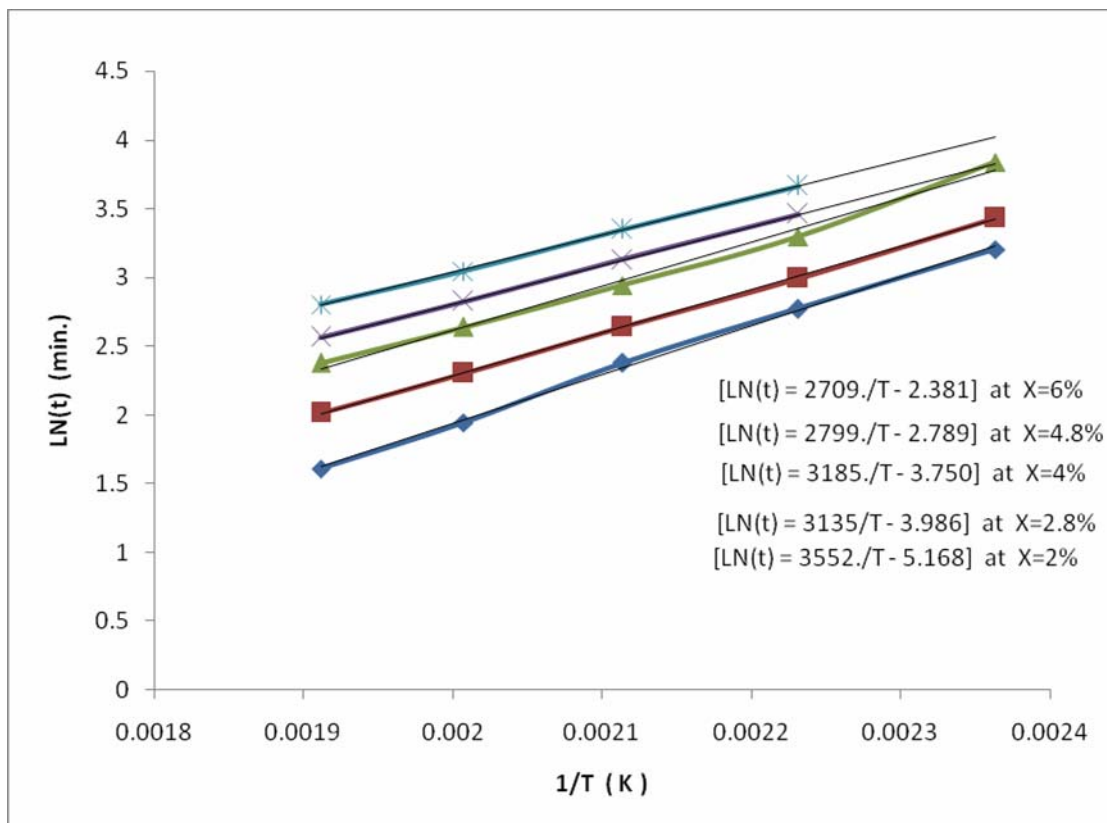
Fig.(2): LN(Time) in (min.) Versus (1/Temperature) in (^{o} K) for fixed weight loss X% of high density polyethelyene.

The equations of activation energy with intercept versus time were found:

$$Ln(t) = \frac{2709}{T} - 2.381 \qquad at \quad X = 6\%$$

$$Ln(t) = \frac{2799}{T} - 2.789 \qquad at \quad X = 4.8\%$$

$$Ln(t) = \frac{3185}{T} - 3.750 \qquad at \quad X = 4\%$$

$$Ln(t) = \frac{3135}{T} - 3.986 \qquad at \quad X = 2.8\%$$

$$Ln(t) = \frac{3552}{T} - 5.168 \qquad at \quad X = 2\%$$

The global activation energy, E, for the degradation was estimated from the slopes as shown in Table(3). It can be seen that E nearly remains almost constant with increased in extent of weight loss. This suggestion lead to have the same pathway of degradation reaction may be involved within the range 2-6% of weight loss. Thus, the activation energy for thermal degradation of used high density poly ethylene under the atmosphere air was found to be 22-29 kJ/mol. Therefore if we would like to prevent the degradation of polymer, we must do not supply this energy to the polymer (J.M.Smith 1981).

Table (3): the activation energy with conversion X%.

X%	E/R(^{o}k)	E

		(KJ/mol)
6	2709	22.52263
4.8	2799	23.27089
4	3185	26.48009
2.8	3135	26.06439
2	3552	29.53133
	Average	25.57386

A plot of the intercepts [LN(F(1-X)) - LN(A)], against weight loss X% will allow extrapolation to X=0, which yields an estimation of A, , based on eq^n (4), the pre-exponential factor in the Arrhenius equation in eq^n(3). The extrapolation technique yields the estimation of A= 502.7032, as shown in table(4) and Fig.(3).

$$INTERCEPT = Ln\big(F(1-x)\big) - Ln(A) \dots\dots\dots\dots\dots\dots\dots (5)$$

Table(4): The intercepts [LN(F(1-X)) - LN(A)] versus weight loss (X%) of high density polyethylene.

X%	[LN(F(1-X)) – LN(A)]
2	-5.168
2.8	-3.986
4	-3.75
4.8	-2.789
6	-2.381
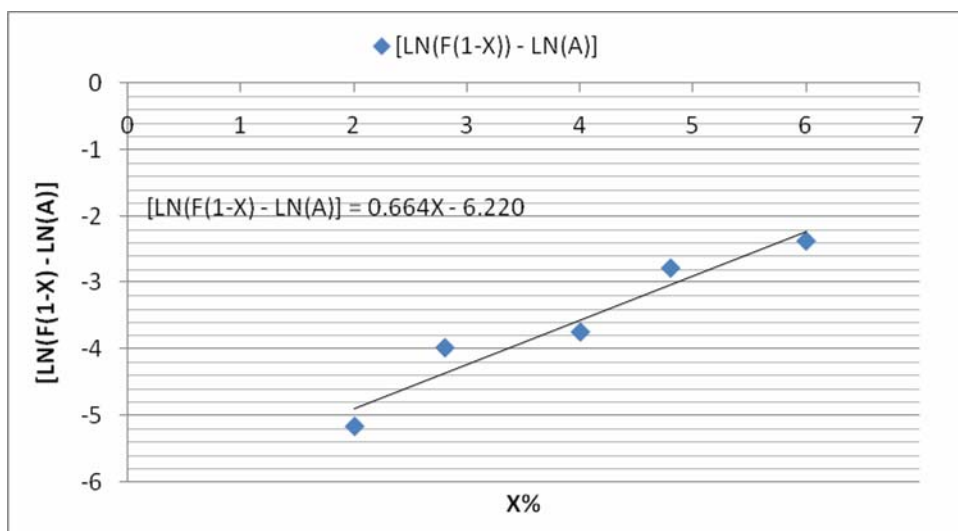
Fig.(3): The intercepts [LN(F(1-X)) - LN(A)] versus weight loss (X%) of high density polyethylene.

To find the rate of reaction constant (K) for each temperature, we will plot F(1-x) versus time (t) according to eqution (6):

$$F(1-x) = K.t \quad \dots\dots\dots\dots\dots\dots\dots (6)$$

The first step was done estimated Ln(F(1-x)) by equation (7) at time (10,20,30,40, 50 Min.) for different temperature (150 - 250 ^{o}C) as shown in Table (5) below:

From equation (4) find:

$$Ln\big(F(1-x)\big) = Ln(t) + Ln(A) - \frac{E}{RT} \ \text{............... (7)}$$

The second step was plotted F(1-x) versus time to find rate of reaction constant (K) and the results as shown in Fig.(4) are:

$$F(1-x) = 6E(-6) * t \quad at \quad T = 250\ °C$$
$$F(1-x) = 4E(-6) * t \quad at \quad T = 225\ °C$$
$$F(1-x) = 3E(-6) * t \quad at \quad T = 200\ °C$$
$$F(1-x) = 2E(-6) * t \quad at \quad T = 175\ °C$$
$$F(1-x) = 1E(-6) * t \quad at \quad T = 150\ °C$$

Table (5): The amount of integration as LN{ $\int_{x=0}^{x=x} \frac{dx}{f(1-x)}$ }=LN{F(1-x)} versus time at different temperature.

Time(Min.)	LN(F(1-X),T=150	LN(F(1-X),T=175	LN(F(1-X),T=200	LN(F(1-X),T=225	LN(F(1-X),T=250
10	1.4E-05	2.1E-05	3E-05	4.1E-05	5.6E-05
20	2.8E-05	4.2E-05	6E-05	8.3E-05	0.00011
30	4.2E-05	6.2E-05	9E-05	0.00012	0.00017
40	5.5E-05	8.3E-05	0.00012	0.00017	0.00022
50	6.9E-05	0.0001	0.00015	0.00021	0.00028
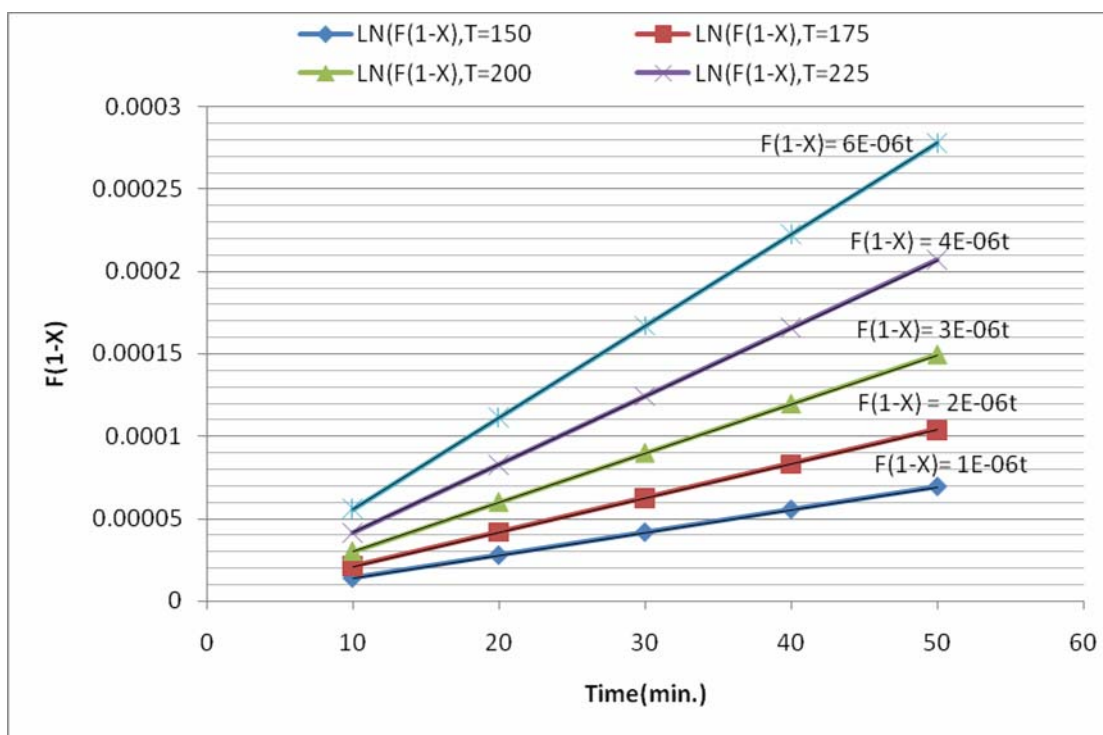
Fig.(4): The amount of integration as LN{F(1-x)} versus time at different temperature.

The rate of reaction constant as related with temperature shown in table (6):

Table(6): The rate of reaction constant versus temperature.

Rate of reaction constant (K) $L.mol^{-1}.S^{-1}$	Temperature (^{o}C)
1E-06	150
2E-06	175
3E-06	200
4E-06	225
6E-06	250

The rate of reaction constant was very low (1E-06 - 6E-06 $L.mol^{-1}.S^{-1}$), therefore the reaction of degradation is very low too. As shown in the table (6) the rate of reaction constant increase with increase the temperature because the kinetic energy of molecular increase with increase temperature (Ana1984). As shown in the figure (4) the relation between integration { $\int_{x=0}^{x=x} \frac{dx}{f(1-x)}$ } and (t) is linear and started from origin point, therefore the degree of reaction is 2nd order reaction in all range of temperature (150 – 250 ^{o}C) (J.M.Smith 1981, Thomas M.2006).

Conclusion:

The isothermal weight loss (X%) of manufactured high density polyethylene was investigated at temperature 150, 175, 200, 225 and 250 ^{o}C and at period of times (10 – 50Min.) The result was found the amount of weight loss (X%) of manufactured (HDPE) increases with temperature and time. The activation energy was changed from (22-29 kJ/mol) at changed temperature (150 – 250 ^{o}C) for range 2-6% of weight loss of (HDPE)**.** The rate of reaction constant (K) for temperatures range (150 – 250 ^{o}C) was changed from (1E-06 - 6E-06 $L.mol^{-1}.S^{-1}$). The degree of reaction was found 2nd order reaction in all range of temperature (150 – 250 ^{o}C).

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