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 temperatures 150, 175, 200, 225 and 250 °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 °C) for range 2-6% of weight loss of (HDPE).

The rate of reaction constant (K) for temperatures range (150 – 250 °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 °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:
The previous studies were included the \( \gamma \) 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 modified 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. Bobalek 2003). 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:

   \[ W_0 = W_1 - W_2 \]

   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 °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).
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 various temperature (°C).

<table>
<thead>
<tr>
<th>Time</th>
<th>X% at T=150</th>
<th>X% at T=175</th>
<th>X% at T=200</th>
<th>X% at T=225</th>
<th>X% at T=250</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0.93</td>
<td>1.865</td>
<td>2.8</td>
<td>3.73</td>
</tr>
<tr>
<td>20</td>
<td>1.35</td>
<td>2.795</td>
<td>4.24</td>
<td>5.685</td>
<td>7.13</td>
</tr>
<tr>
<td>30</td>
<td>2.7</td>
<td>4.53</td>
<td>6.35</td>
<td>8.18</td>
<td>10.01</td>
</tr>
<tr>
<td>40</td>
<td>3.5</td>
<td>6.105</td>
<td>8.71</td>
<td>9.815</td>
<td>13.92</td>
</tr>
<tr>
<td>50</td>
<td>4.27</td>
<td>7.54</td>
<td>10.81</td>
<td>14.07</td>
<td>17.34</td>
</tr>
</tbody>
</table>

**Fig. (1):** Isothermal weight loss % of high density polyethylene versus time (Min.) at various 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:

\[
- \frac{d(1-x)}{dt} = K \cdot f(1-x)
\]

\[
- \left[ 0 - \frac{dx}{dt} \right] = K \cdot f(1-x)
\]

\[
\frac{dx}{dt} = K \cdot f(1-x)
\]
Integration of eqn (1), yields:

\[
F(1-x) = Kt \\
F(1-x) = \frac{F(1-x)}{t} = K
\]

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:

\[
X_i = \frac{W_v}{W_0} \times 100
\]

Where, \( W_v \) is the weight of polymer evolved as the volatile fragments, \( W_0 \) 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):

\[
K = A e^{\frac{E}{RT}} \]

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:

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

\[
Ln(t) = \frac{E}{RT} + Ln(\frac{F(1-x)}{t}) = \frac{E}{RT} + Ln(F(1-x)) - Ln(A) ... \ldots \ldots ...
\]

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.

<table>
<thead>
<tr>
<th>( T(\text{°C}) )</th>
<th>( \frac{1}{T} ) (\text{°K})</th>
<th>( X=2% )</th>
<th>( X=2.8% )</th>
<th>( X=4% )</th>
<th>( X=4.8% )</th>
<th>( X=6% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.00236</td>
<td>3.20275</td>
<td>3.43399</td>
<td>3.8373</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>175</td>
<td>0.00223</td>
<td>2.77259</td>
<td>2.99573</td>
<td>3.29584</td>
<td>3.45947</td>
<td>3.66356</td>
</tr>
<tr>
<td>200</td>
<td>0.00211</td>
<td>2.37955</td>
<td>2.63906</td>
<td>2.94444</td>
<td>3.12676</td>
<td>3.3499</td>
</tr>
<tr>
<td>225</td>
<td>0.00201</td>
<td>1.94591</td>
<td>2.30259</td>
<td>2.63906</td>
<td>2.82731</td>
<td>3.04452</td>
</tr>
<tr>
<td>250</td>
<td>0.00191</td>
<td>1.60944</td>
<td>2.0149</td>
<td>2.37955</td>
<td>2.56495</td>
<td>2.80336</td>
</tr>
</tbody>
</table>
The kinetic of thermal degradation for manufactured high density polyethylene (HDPE) was studied by Ismaeel Moslam Alwaan. The equations of activation energy with intercept versus time were found:

\[
\text{LN}(t) = \frac{2709}{T} - 2.381 \quad \text{at} \quad X = 6\%
\]

\[
\text{LN}(t) = \frac{2799}{T} - 2.789 \quad \text{at} \quad X = 4.8\%
\]

\[
\text{LN}(t) = \frac{3185}{T} - 3.750 \quad \text{at} \quad X = 4\%
\]

\[
\text{LN}(t) = \frac{3135}{T} - 3.986 \quad \text{at} \quad X = 2.8\%
\]

\[
\text{LN}(t) = \frac{3552}{T} - 5.168 \quad \text{at} \quad X = 2\%
\]

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 polyethylene 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%.

<table>
<thead>
<tr>
<th>X%</th>
<th>E/R(k)</th>
<th>E</th>
</tr>
</thead>
</table>

Fig.(2): \( \text{LN(Time) in (min.) Versus (1/Temperature) in (°K)} \) for fixed weight loss X% of high density polyethylene.
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 equation (4), the pre-exponential factor in the Arrhenius equation in equation (3). The extrapolation technique yields the estimation of \(A = 502.7032\), as shown in Table (4) and Fig.(3).

\[ \text{INTERCEPT} = \ln\left( F(1 - x) \right) - \ln(A) \] \hspace{1cm} (5)

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

<table>
<thead>
<tr>
<th>X%</th>
<th>([\ln(F(1-X)) - \ln(A)])</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-5.168</td>
</tr>
<tr>
<td>2.8</td>
<td>-3.986</td>
</tr>
<tr>
<td>4</td>
<td>-3.75</td>
</tr>
<tr>
<td>4.8</td>
<td>-2.789</td>
</tr>
<tr>
<td>6</td>
<td>-2.381</td>
</tr>
</tbody>
</table>

**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 equation (6):

\[ F(1 - x) = K \cdot t \] \hspace{1cm} (6)

The first step was done estimated \(\ln(F(1-x))\) at time (10, 20, 30, 40, 50 Min.) for different temperature (150 - 250 °C) as shown in Table (5) below:

From equation (4) find:
\[ \ln(F(1-x)) = \ln(t) + \ln(A) - \frac{E}{RT} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7) \]

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:

\[
\begin{align*}
F(1-x) &= 6E(-6) * t \quad \text{at} \quad T = 250 \degree C \\
F(1-x) &= 4E(-6) * t \quad \text{at} \quad T = 225 \degree C \\
F(1-x) &= 3E(-6) * t \quad \text{at} \quad T = 200 \degree C \\
F(1-x) &= 2E(-6) * t \quad \text{at} \quad T = 175 \degree C \\
F(1-x) &= 1E(-6) * t \quad \text{at} \quad T = 150 \degree C 
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Time(Min.)</th>
<th>( \ln(F(1-X), T=150) )</th>
<th>( \ln(F(1-X), T=175) )</th>
<th>( \ln(F(1-X), T=200) )</th>
<th>( \ln(F(1-X), T=225) )</th>
<th>( \ln(F(1-X), T=250) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.4E-05</td>
<td>2.1E-05</td>
<td>3E-05</td>
<td>4.1E-05</td>
<td>5.6E-05</td>
</tr>
<tr>
<td>20</td>
<td>2.8E-05</td>
<td>4.2E-05</td>
<td>6E-05</td>
<td>8.3E-05</td>
<td>0.00011</td>
</tr>
<tr>
<td>30</td>
<td>4.2E-05</td>
<td>6.2E-05</td>
<td>9E-05</td>
<td>0.00012</td>
<td>0.00017</td>
</tr>
<tr>
<td>40</td>
<td>5.5E-05</td>
<td>8.3E-05</td>
<td>0.00012</td>
<td>0.00017</td>
<td>0.00022</td>
</tr>
<tr>
<td>50</td>
<td>6.9E-05</td>
<td>0.00015</td>
<td>0.00021</td>
<td>0.00028</td>
<td></td>
</tr>
</tbody>
</table>

**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.

<table>
<thead>
<tr>
<th>Rate of reaction constant (K)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L.mol^{-1}.S^{-1}</td>
<td></td>
</tr>
<tr>
<td>1E-06</td>
<td>150</td>
</tr>
<tr>
<td>2E-06</td>
<td>175</td>
</tr>
<tr>
<td>3E-06</td>
<td>200</td>
</tr>
<tr>
<td>4E-06</td>
<td>225</td>
</tr>
<tr>
<td>6E-06</td>
<td>250</td>
</tr>
</tbody>
</table>

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

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