# CHAPTER ONE INTRODUCTION

#### 1.1 Background:

Although one of the major features which might prompt a designer to consider using plastics is corrosion resistance, nevertheless plastics are susceptible to chemical attack and degradation. As with metals, it is often difficult to predict the performance of a plastic in an unusual environment so it is essential to check material specifications and where possible carry out proving trials. Clearly, in the space available here it is not possible to give precise details on the suitability of every plastic in every possible environment.

Therefore the following sections give an indication of the general causes of polymer degradation to alert the designer to a possible problem. The degradation of a plastic occurs due to a breakdown of its chemical structure. It should be recognised that this breakdown is not necessarily caused by concentrated acids or solvents. It can occur due to apparently innocuous mediums such as water (hydrolysis), or oxygen (oxidation). Degradation of plastics is also caused by heat, stress and radiation. During moulding the material is subjected to the first two of these and so it is necessary to incorporate stabilisers and antioxidants into the plastic to maintain the properties of the material. These additives also help to delay subsequent degradation for an acceptably long time. As regards the general behaviour of polymers, it is widely recognised that crystalline plastics offer better

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environmental resistance than amorphous plastics. This is as a direct result of the different structural morphology of these two classes of material. Therefore engineering plastics which are also crystalline e.g. Nylon 66 are at an immediate advantage because they can offer an attractive combination of load-bearing capability and an inherent chemical resistance. In this respect the anival of crystalline plastics such as PEEK and polyphenylene sulfide (PPS) has set new standards in environmental resistance, albeit at a price. At room temperature there is no known solvent for PPS, and PEEK is only attacked by 98% sulphuric acid.

#### 1.1.1 Weathering:

This generally occurs as a result of the combined effect of water absorption and exposure to ultra-violet radiation (u-v). Absorption of water can have a plasticizing action on plastics which increases flexibility but ultimately (on elimination of the water) results in embrittlement, while u-v causes breakdown of the bonds in the polymer chain. The result is general deterioration of physical properties. A loss of colour or clarity (or both) may also occur. Absorption of water reduces dimensional stability of moulded articles. Most thermoplastics, in particular cellulose derivatives, are affected, and also polyethylene, PVC, and nylons.

#### **1.1.2 Oxidation:**

This is caused by contact with oxidising acids, exposure to u-v, prolonged application of excessive heat, or exposure to weathering. It results in a deterioration of mechanical properties (embrittlement and possibly stress cracking), increase in power factor, and loss of clarity. It affects most thermoplastics to varying degrees, in particular polyolefins, PVC, nylons, and cellulose derivatives.

#### 1.1.3 Environmental Stress Cracking (ESC):

In some plastics, brittle cracking occurs when the material is in contact with certain substances whilst under stress. The stress may be externally applied in which case one would be prompted to take precautions. However, internal or residual stresses introduced during processing are probably the more common cause of ESC. Most organic liquids promote ESC in plastics but in some cases the problem can be caused by a liquid which one would not regard as an aggressive chemical. The classic example of ESC is the brittle cracking of polyethylene washing-up bowls due to the residual stresses at the moulding gate coupled with contact with the aqueous solution of washing-up liquid. Although direct attack on the chemical structure of the plastic is not involved in ESC the problem can be alleviated by controlling structural factors. For example, the resistance of polyethylene is very dependent on density, crystallinity, melt flow index (MFI) and molecular weight. As well as polyethylene, other plastics which are prone to ESC are ABS and polystyrene. The mechanism of ESC is considered to be related to penetration of the promoting substance at surface defects which modifies the surface energy and promotes fracture.

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#### **1.2 Objectives of present study:**

The objective of this research is summarized in the following points:

- $\checkmark$  To study the effect of degradation of thermoplastics properties .
- $\checkmark$  To determine the best testing methods to detect plastics degradation .
- $\checkmark$  To detect the quality of the recycled plastics .
- $\checkmark$  To study the effect of stabilizers on the degradation process .

#### **1.3 Boundaries:**

#### Temporal boundaries: 2013-2014

**Spatial boundaries :** Republic of Sudan- Khartoum- Sudan University of Sciences & Technology- collegeof Engineering.- plastic engineering department.

#### 1.4 Thesis out lines:

This thesis is divided into five chapters :

- Chapter one gives relevant information on Degradation of polymers.
- Chapter two presents introduction of polymers, the thermal stability of polymeric materials and degradation Processes.
- Chapter three explains the experimental procedures to determine the resulting MFI test and DSC graphs to analyst information calculate the OIT and thermal properties (percentage of crystallinity and melting temperature Tm).

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- Chapter four present all the resultant graphs ,tables and discussions this results .
- Chapter five the conclusion and recommendations based on this study are summarized in this chapter.

# CHAPTER TWO LITERTURE REVIEW

#### 2.1 Introduction:

The past decade has seen a tremendous increase in the use of industrially synthesized polymers as materials of construction. Plastics, elastomers, adhesives, coatings, and lubricants are all polymeric types of material. It would be difficult indeed to find a retailed end item today that did not contain at least one form of polymeric material. The reasons for the development and use of such polymers is readily explained. They can easily be molded, extruded, and applied. Their weight is much less than such conventional materials of construction as wood, metal, or masonry. Most polymers can be colored or dyed prior to their fabrication or application. Finally, cost of many polymeric materials is quite low. Thus, literally thousands of different polymers are currently in use, with new types being continually brought into research and development.

The thermal stability of polymeric materials was not rigorously questioned until the advent of the manned space flight program conducted by the National Aeronautics and Space Administration (NASA) in 1959. As materials of construction, polymers seemed to be ideal from the point of being light in weight. However, their stability over long periods of time in an enclosed high oxygen content atmosphere was questioned. During extended flights in space, man would have to breathe the same atmosphere over and over again. Any toxic contaminants envolved into this atmosphere from man himself, his food, clothing, and the items of equipment he carried with him would have to be removed from the atmosphere. Thus, NASA initiated a standard program to test the stability of proposed construction materials under thermo oxidative conditions. Pure oxygen was chosen as the test atmosphere. Pressure of the test system was set at five pounds per square inch absolute and temperature at 200°F. Any proposed materials, polymeric or otherwise, evolving toxic or noxious gases in significant amounts at these conditions were then rejected.

The number of thermo oxidative degradation analyses of polymers has increased tremendously since the advent of the NASA manned space flight program. However, the bulk of these analyses have been limited to systems at or near conditions of pyrolysis. Rate and activation energy data for such techniques obtained mainly with the have been of systems thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Pyrolysis, followed by chromatography, mass spectroscopy, or infrared spectroscopy has provided some data on the products of polymer degradation. Kinetic and thermodynamic data for polymer degradations between ambient temperature conditions and conditions of pyrolysis are somewhat limited. Also, little work has been done to relate the effects of oxygen concentration on thermo oxidative degradation and the types of degradation products.

#### 2.2 Degradation Processes:

The degradation of polymers has been under studied for many decades due to its commercial production. Most plastics are affected by exposure to sunlight in conjunction with other natural weathering forces such as oxygen, humidity and heat. Synthetic polymers are now often used in applications where the service life is short and the use of long-lived plastics has resulted in criticism because of their non-degradability after they are discarded.

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Due to superior properties of plastics they have been used in many outdoor applications such as packaging. These products result in garbage collection problem and become litter. The waste products arising from plastics packaging, which accounts for about 30% of the total plastics consumption, has contributed to the perception of the plastics as a major environmental problem and to the introduction of legislation prescribing targets for recycling. The recycled high-density polyethylene (HDPE) can be utilized in too many consumer plastics products, which needs shorter photostability in their service lifetime. These recycled plastics can be made more useful for the commodity products by adding small percentage of virgin resins, processing agents and thermal stabilizers and can save lots of environmental problems arising due to plastics waste material.

The degradation of polymer is chemical reaxion resulting from sunlight. The most effective waves in the sunlight in the UV which has enough energy to break C - C bond. The influence of processing (extrusion, molding, etc) in terms of exposure to shear forces, temperature, oxygen can also add in the degradation process of the polymers. During the end use application polymers are exposed to different environments, which eventually affect polymer lifetime.

The consequences of degradation depend on the nature of the polymer and can cause polymer chain scission and cross-linking leading to changes at the molecular level. These irreversible processes eventually change the physical or visual properties of polymer to such extent that the end product cannot serve its purpose.

The purpose of this work was to evaluate the outdoor stability of pure, recycled and reprocessed HDPE material with the addition of small

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percentage of thermal stabilizers in the base formulations. Various reactions undergone by polymers:

- Random chain scission.
- Depolymerization.
- Cross-linking.
- Side group elimination.
- Substitution.
- Reactions of side groups among themselves.

# 2.3 Types of polymer degradation:

- Thermal.
- Thermooxidative.
- Photo.
- Photooxidative.
- Mechanical.
- Hydrolytic.
- Chemical.
- Biological.
- Degradation by irradiation.
- Pyrolysis.
- Oxidative pyrolysis.

# 2.3.1 Photolysis:

gives unsaturated product at broken chain ends.

#### 2.3.2 Photo oxidation:

gives aldehydes, ketones and acids either along or at the end of the polymer chain.

## 2.3.3 Bio degradation

Microorganisms generally cause degradation. However, they do not have polymer – specific enzymes. Polymers are to be initially broken down to smaller fractions

#### 2.3.3.1 Biodegradability requires

- Low molecular weight.
- Presence of certain end groups
- Polarity
- Hydrophilicity

## 2.3.4 Photodegradation

It is the photo –initiated oxidation. Primary effect of light is the generation of free radicals. It has relatively little effect on the propagating steps of the radical chain reactions.

# 2.4 Effect of polymer properties on oxidation:

## 2.4.1 Crystallinity :

Rate of oxidation is inversely proportional to degree of crystallinity. Crystallinity increases with degree of oxidation ( due to chain breaking and chain orientation)

## 2.4.2 Tacticity:

Stereoregular polymers are more crystalline and are more resistant to Oxidation.

## 2.4.3 Molecular weight:

In solid polymers there no significant effect as both the rate of initiation and rate of termination are reduced. In solution, rate decreases with molecular weight.

# 2.4.4 Chemical structure:

Higher branching leads to higher rate of oxidation due to the presence of more number of tertiary H atoms and slow termination of tertiary peroxy radicals. Presence of double bonds results in more allylic positions which are inherently more reactive and hence increases oxidation rate.

# 2.4.5 Film Thickness:

Generally rate of oxidation decreases with increase in thickness as the reaction becomes diffusion controlled.

## 2.4.6 Additives:

Many ingredients eg. catalyst residues, processing aids, metallic impurities etc increase oxidation rate.

# 2.5 Review of literature:

Throughout the years, research has been intensively going on which various publications on the degradation of polymer such as Maryudi, Anwaruddin Hisyam (etal), March -April 2013, "Thermo-oxidative Degradation of High Density Polyethylene Containing Manganese Laurate ..., International

Journal of Engineering Research and Applications (IJERA) ISSN: 2248-9622 www.ijera.com Vol. 3, Issue 2, pp.1156-1165, studied of utilization of manganese laurate for accelerating the degradation process of high density polyethylene (HDPE). Specimens were prepared by loading manganese laurate from 0 to 1 %(w/w) in HDPE resins using twin screw extruder followed by injection molding. Thermal treatment was performed at 70°C, for maximum duration of 1000 hours to examine the thermo-oxidative degradation of HDPE blends. Tensile testing, FTIR analysis, molecular weight analysis, melt flow index (MFI) analysis, differential scanning calorimetry (DSC) test, thermogravimetric analyzer (TGA) test, were carried out to assess the changes during treatment. The results reveal that sample containing manganese laurate are readily to undergo thermo-oxidative degradation under temperature condition of 70 °C. Tensile strength and elongation at break decreased during treatment. Pure and HDPE containing 1 % of manganese laurate (ML10) samples have lost about 11.74 and 43.33% of tensile strength, and about 16.21 and 55.85 % of elongation at break respectively. FTIR traces exhibited that carbonyl group's peak in the region 1700-1800 cm-1 arise during thermal treatment as the result of oxidation. Average molecular weights were found to decrease about 16.12 and 67.51% from their initial value for pure and ML10 samples respectively, and consequently MFI increased significantly. Thermal stability and melting temperature were found to shift to lower temperature, while crystallinity generally increased. The degradation rate of HDPE increased by increasing the amount of manganese laurate incorporated.

Finally, The mechanical properties were found to be decreased with increasing amount of manganese laurate loading.

Another study, "Jovan Radulović,2006 " studied the resistance of biaxial oriented polyethylene terephtalate foil to outdoor natural weathering factors was investigated in two different climatic areas. Physical, mechanical and optical properties of polyethylene terephtalate before, during and after two years of exposure were determined. Factors affecting natural weathering of this material were described. It was concluded that this material could be used for up to 18 months in outdoor static conditions.

Finally, obtained for polyethylene Constant reduction of longitudinal and perpendicular tensile strength, tensile strain and tear resistance actually starts from the moment of exposure to the outdoor conditions at continental (Nikinci) and marine (Kumbor) environments. There are no changes, regarding the initial quality in colour, thickness and integral light transparency, after 24 months of exposure. The trend of decreasing i.e. retaining the mentioned properties is observed during the whole period of weathering, in all but flexibility; after 24 months of exposure, specimens break, for the first time, when testing flexibility at low temperatures (-30oC). The drop of tensile strength of about 80 %, of tensile strain and tear resistance of about 95 %, compared to the initial quality, and breaking of specimens for the first time during low temperature flexibility testing, proved that there is no rational point in exploring natural weathering process in the open after 24 months of exposure. A severe drop of tensile strain after only 6 months of exposure indicates that this material can not be used outdoor in dynamic conditions. The obtained results of testing confirmed that biaxial oriented polyethylene terephtalate foil can be used outdoors in static conditions up to 18 months.

# CHAPTER THREE MATERIAL AND METHOD

#### 3.1 Material:

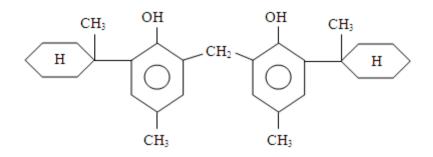
In this study used Thermoplastic materials SABIC HDPE (High density polyethylene) grade M200053 was used as virgin HDPE material for mixing with the recycled HDPE.

## 3.2 Preparation of Samples:

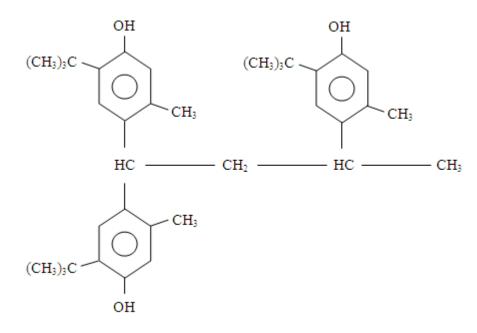
Different mixtures were used for preparing the HDPE samples for this study. A total of four types of samples were prepared in Adeb Factory for Plastic in Omdurman Industry in the injection-molding machine. Certain percentage of processing agents in the form of antioxidants and lubricants agents were added to protect the polymer material from thermal degradation during molding. The following four combinations of HDPE virgin and HDPE/recycled were extruded with the addition of thermal stabilizers, 0.2% Irgafos 168, 0.2% Irganox 1010 and lubricants agent 0.1% Ca stearate.

- Sample 1 Virgin HDPE (M-200053)
- Sample 2 50/50 (virgin HDPE/Recycled HDPE + 0.2% Irgafos 168 + 0.2% Irganox 1010 + 0.1% Ca stearate)
- Sample 3 Virgin HDPE + (0.2% Irgafos 168 + 0.2% Irganox 1010 + 0.1% Ca stearate)
- Sample 4 Recycled HDPE + (0.2% Irgafos 168 + 0.2% Irganox 1010 + 0.1% Ca stearate)

Irgafos is Bis – [ 2- hydroxy – 5 – methyl -3 – ( 1 – methyl cyclohexyl) phenyl methane ] .



Irganox is 1, 1, 3 – Tris – (4 - hydroxyl - 2 - methyl - 5 - t - buty lphenyl) butane .



The weathering trials for the HDPE samples were done in the hot and climate of Khartoum. This region has high level of temperature and solar radiation and proved to be more aggressive to the plastics material. The sample was exposed for the period of three months and were withdrawn with the predetermined interval.

## 3.3 Method:

In this study used Melt flow index test (MFI) and Differential scanning calorimeter (DSC) to found the OIT (oxidation induction time) and thermal properties (crystallinity % and melting temperature Tm).



# 3.3.1 Melt Flow Index (MFI):

Figure 3.1:Melt flow index

Melt Flow rate Index Testing instrument was used. It consists of a heated barrel and piston assembly to contain a sample of resin. A specified load (weight) is applied to the piston, and the melted polymer is extruded through a capillary die of specific dimensions. The mass of resin, in grams, that is extruded in 10 minutes equals the MFR; expressed in units of g/10 min.

#### **3.3.1.1 Testing Procedure:**

A small amount of the polymer sample 4 grams for (HDPE) is taken in the specially designed MFI apparatus. The apparatus consists of a small die inserted into the apparatus, with the outside diameter is 9.475mm, inner diameter is 2.095 mm and the length of die is 8.000mm. The material is packed properly inside the barrel to avoid formation of air pockets. A piston is introduced which acts as the medium that causes extrusion of the molten polymer.

The sample is preheated for a specified amount of time: 5 min at 190°C for polyethylene. After the preheating a specified weight is introduced into the piston. Examples of standard weights are 2.16 kg. The weight exerts a force on the molten polymer and it immediately starts flowing through the die.

A sample of the melt is taken after desired period of time and is weighed accurately.

MFI is expressed as grams of polymer/10 minutes of total time of the test.

#### **3.3.2 Differential scanning calorimeter (DSC):**



Figure 3.2 : ZF-DSC-D1 Differential scanning calorimeter

A calorimeter measures the heat into or out of a sample, a differential calorimeter measures the heat of a sample relative to a reference, a differential scanning calorimeter (DSC) does all of the above and heats the sample with a linear temperature ramp. Differential Scanning Calorimetry is a technique used to measure thermal properties of polymers based on the rate at which they absorb heat energy compared to a reference material. The technique takes advantage of the energy changes involved in the various phase transitions of certain polymer molecules. This allows several properties of the material to be ascertained; melting points, enthalpies of

melting, crystallisation temperatures, glass transition temperatures and degradation temperatures.

A heat flux differential scanning calorimeter will be used in the experiment. This is one in which a sample is heated along with a reference material with a known specific heat. One of the criteria of this technique is that the sample and reference material remain at the same temperature during heating. This can be achieved by Setting the machine to heat both the sample and reference material at a specific rate (In this experiment, the rate is set to 10°C per minute). This allows the heat flux or difference in energy input between the sample and reference to be measured. Maintaining a constant supply of heat to both materials would not (unless the materials have the same heat capacity at all points, which are unlikely) maintain a minimal temperature difference between them. Instead, a computer is connected to the machine, and using the software and various signals from the calorimeter, "decides" when to supply heat to either material. This information is then dealt with by the computer software and presents it as a graph of the energy changes versus the temperature. A standard DSC curve for a particular polymer is shown in figure 3.3

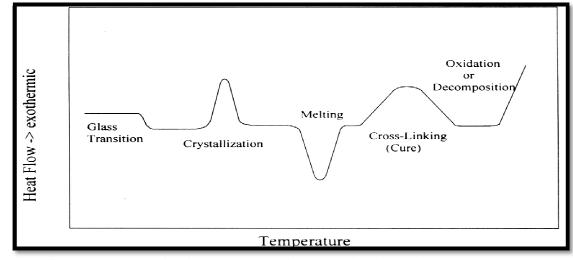


figure 3.3 :standard DSC curve for a particular polymer

#### **3.3.2.1** The OIT test:

Polymer is oxidized in the atmosphere including Oxygen which deteriorates mechanical strength and electrical property. This decomposition by the oxidation starts from the low temperature than thermal decomposition in the inert gas.

The sample  $(5 \sim 15 \text{ mg})$  to be tested and the reference material are heated at a constant rate in an inert gaseous environment (nitrogen 50 ml/min). When the specified temperature has been reached  $(200^{\circ}C \text{ for PE})$ , the atmosphere is changed to oxygen (50 ml/min) maintained at the same flow rate. The specimen is then held at constant temperature until the oxidative reaction is displayed on the thermal curve. The time interval from when the oxygen flow is first initiated to the oxidative reaction is referred to as the induction period. The end of the induction period is signaled by an abrupt increase in the specimen's evolved heat or temperature and may be observed by a differential scanning calorimeter (DSC). The OIT is determined from the data recorded during the isothermal test.

# **3.3.2.2 Thermal properties (crystillinity % and melting temperature Tm):**

Firstly, samples were prepared for analysis. In order to avoid confusion, this was performed as the samples were required as opposed to preparing all samples at once. Extreme care was taken not to contaminate samples or sample pans with either other chemicals or matter from human skin. This meant that all equipment had to be handled with tweezers. Samples were prepared as follows:

The tare weight of the sample pan and lid were obtained. Sample pans with flat undersides were selected so as to make the maximum contact possible with the bottom of the calorimeter. Following this, between 5 and 10 milligrams of polymer were placed in the sample pan and the mass of the filled sample pan and lid were found. This was the mass of polymer to be used. Again using tweezers, the sample pan and lid were moved to the crimping press whereupon crimping the lid sealed the pan. Another sample pan was weighed along with its lid. This, however, was left empty and sealed using the crimping device, forming the reference pan to be heated along with the sample.

The first sample to be observed was the Indium reference material. This was placed in the left hand side of the furnace in the calorimeter while the empty reference pan was placed in the right hand position, where it was to remain for the duration of the experiment.

Heating cycle for Indium: Nitrogen atmosphere, with a gas flow rate of  $10 \text{ cm}^3/\text{min}$ , heating rate of  $10^\circ\text{C}/\text{min}$  from  $120^\circ\text{C}$  to  $180^\circ\text{C}$ .

For the polymer samples, the heating cycle proceeded as follows:

The same gas flow rate was maintained, along with the heating rate of  $10^{\circ}$ C/min. The only change was that the range of temperature was modified so that it ranged from  $30^{\circ}$ C to  $250^{\circ}$ C. Following this, the furnace was allowed cool to room temperature before the next sample could be introduced.

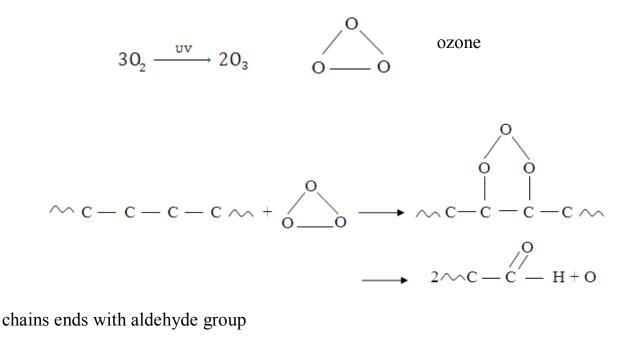
The resulting graphs are then analysed and information about onset, peak and endpoint temperatures for the various processes can be obtained using the computer software.

# CHAPTER FOUR RESULT AND DISCUSSION

#### 4.1 Introduction:

In this chapter we present our experimental data in many different charts. The degradation mechanism can be written in the following reactions sequence:

(i) Scission reactions:



(ii) Cross-linking reaction:



#### 4.2 Melt Flow Index :

The MFI result for the types of HDPE are table:

<b>Table 4.1:</b>	result of MF	l test

	Number of reprocessing				
Samples	1	2	3	4	
Sample 1	6.4	5.4	4.8	4.0	
Sample 2	6.3	6.5	6.6	6.7	
Sample 3	6.8	7.0	7.1	7.2	
Sample 4	6.4	6.4	6.4	6.5	

These results show that the :

- 1. Virgin HDPE the MFI decreases as the number of reprocessing times increases this. Indicates that the dominant reaction is cross-linking occurred and the material is brittle.
- 2. HDPE type that contains recycle, the MFI is slightly increases with number of reprocessing this indicates that the types of reaction chain scission and cross-linking are competing where chain scission increases MFI and cross-linking decrease it.
- 3. The other two types of HDPE formulations that contain stabilizer the MFI increases with number of reprocessing. This indicts that the cross-linking is limited and chain scission is the dominating. That is the effective role of the stabilizer is to capture the oxygen ion's that leads to cross-linking.

## 4.3 Oxidation Induction time (OIT) :

The result obtained from the OIT test show in figure 4.1,4.2,4.3.4.4.

OIT results for the four types of HDPE are almost similar. Oxidation Induction time cannot detect the degree of degradation. It may reasonable that the OIT can evaluate the degree of pretection of the antioxidants.

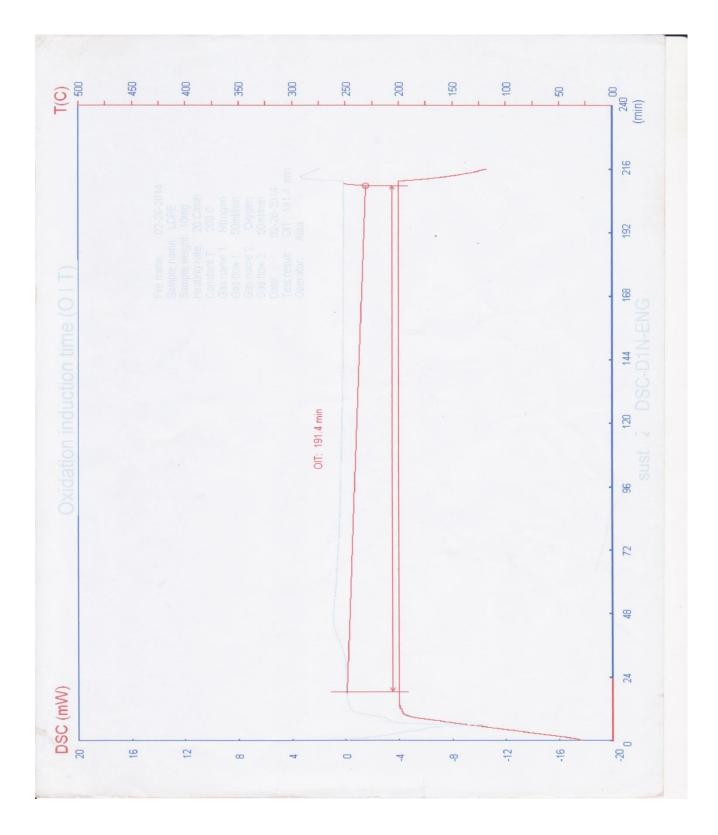


figure (4.1) result of OIT test

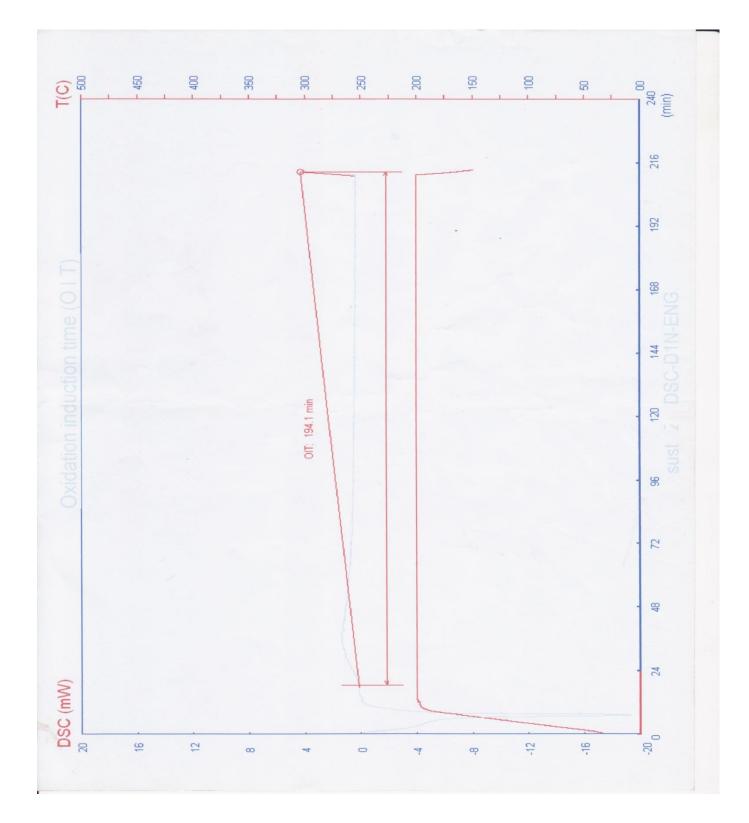


figure (4.2) result of OIT test

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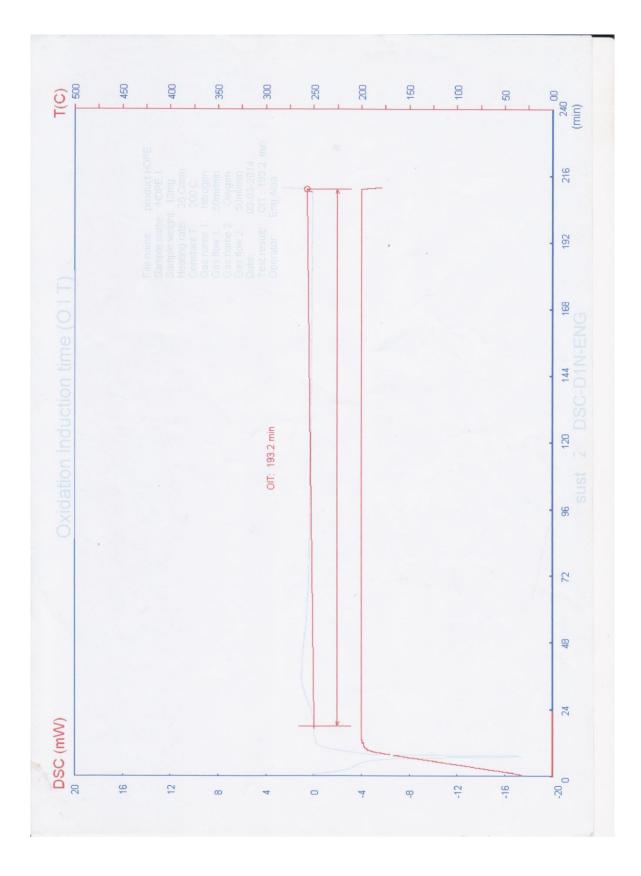


figure (4.3) result of OIT test

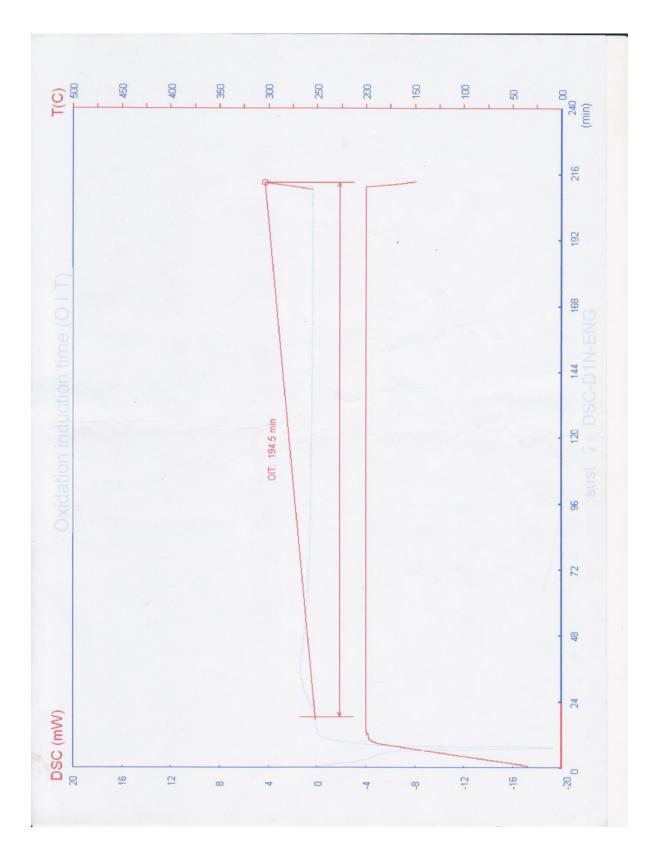


figure (4.4) result of OIT test

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# 4.4 Thermal properties (crystallinity and melting temperature $(T_m)$ ):

The thermal properties in terms of melt temperature Tm, and percent of crystallinity were monitored by using DSC. Table 4.2 present the change in melt temperature Tm and percent of crystallinity for the four HDPE samples exposed three months in the outdoor.

	Time	Crystallinity (%)			Melt temperature ( <i>T</i> m)		
Samples	(months)	1 <sup>st</sup> mold	3 <sup>rd</sup> mold	5 <sup>th</sup> mold	1 <sup>st</sup> mold	3 <sup>rd</sup> mold	5 <sup>th</sup> mold
	0	59.88	60.05	61.22	132.04	133.39	132.34
Sample	2	62.99	63.56	65.1	131.42	132.45	132.8
1	3	68.49	69.06	74.25	132.97	131.84	131.1
	0	61.55	61.9	62.4	133.97	132.93	132.15
Sample	2	62.44	63.21	63.91	131.36	132.09	132.10
2	3	64.22	66.33	68.5	133.62	132.22	131.85
	0	60.11	61.43	62.31	131.83	132.82	131.69
Sample	2	63.21	64.3	65.19	131.56	132.20	131.83
3	3	65.55	63.51	69.22	131.86	131.97	131.31
	0	61.79	62.11	62.5	133.43	132.12	131.74
Sample	2	63.00	64.18	63.44	131.64	133.77	132.08
4	3	64.11	65.9	64.12	132.07	132.28	131.57

#### Table 4.2 :change in thermal properties with time

The gradual increment in the percent crystallinity was observed for all the four samples from its initial value. The percent of crystallinity of five times reprocessed and weathered samples clearly indicates the lowest increase of 2.59 percent in crystallinity from its initial value for sample4 as compared to other samples. The other samples 1, 2 and 3 have shown increase of 21.28%, 9.77% and 11.08% from its initial value in the percent of crystallinity.

The gradual addition in percent of crystallinity is due to oxidative crystallization and scission allowing the freed segments to crystallize in the polymer matrix.

The results also present the melt temperature (Tm) for all the samples. A downward trend was observed for the Tm from its initial value for all the weathered samples. The possible reason for this drop in Tm could be the secondary crystallization, resulting in the creation of new intermolecular polar bonds due to formation of oxygen containing carbonyl groups [11].

# CHAPTER FIVE CONCLUSIONS AND RECOMMENDATIONS

# 5.1 The Conclusions of this study are summarized as follows:

Articles made from HDPE are of two types, One type the article should be durable for many years and degradation should be completely prevented these articles such as pipes conveying portable water and other fluids and their storage tanks. The other type the articles that should degrade within few months such as polyethylene films which may cause environmental problem if it does not degrade. It is clear from this study that the protective system that consist of stabilizers and antioxidants can provide durable articles that persist degradation to fifty years or more required in water pipes. For the other type of articles fact degradation is a must. In this direction many researches has been conducted during the last 40 years. Which resulted in the process of oxy-degradation that uses compounds containing heavy metals such as cobalt. The heavy metals are a health hazard to human being. More researches must be carried to formulate new materials that accelerate the degradation of PE film.

#### 5.2 Recommendation :

In addition to prohibit the use of stabilizers in PE that intended for film production.

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