Palestine Polytechnic University

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Optimization Study of the Bio-Plastic Formula at Bio-Zmzm Company: Effect of Oxo-additives Content on Degradation, Thermal and Mechanical Properties

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Abstract

The interest in environmental issues is growing and there are increasing demands to use of polymers that degrade more quickly than conventional plastics. Recent work aims to do a scientific research for a Bio-Zmzm company in Hebron. The study discusses subjects of bioplastic and non-biodegradable plastic. The basic principles of project are an optimization study of the existing formula of bioplastic product at Bio-Zmzm through the use of oxo-additive chemicals to determine the effect of Oxo additive content on degradation, thermal and mechanical properties. Also to improve the ability of plastic to become biodegradable. The experiments were carried out on several samples of plastic bags and packaging films. The samples were produced by changing the mass percent of additives, but percentage of other components (polyethylene (PE), glue, CaCO3, pigment) remain constant. Mechanical tests include each of the free fall test and adhesion test were carried out. The results showed that changing the mass percent of additives (either increase or decrease) did not affect the mechanical properties (durability, Fragility) of product. However, after the tensile and TGA test showed that the highest decomposition rate was for most samples for 2.5974% of oxo- additives. This indicates an increase in the ratio of oxo- additives lead to increases the rate of degradation. Also the marl stone had the highest rates of decomposition. This indicates that it is the best medium and environment for plastic decomposition.

الإهداء

إلى مخرج البشرية جمعاء من الظلمات إلى النور محمد صلى الله عليه وسلم

إلى فلسطين وطني الجريح فخرا لي أن أكون منك واليك انتمي دمت منارة العلم ومنبع العلماء

إلى القدس إليك نجاحي وسجدة شكر أسجدها فيك وأذرف على أعتابك دمعة فرحاَ وشكراَ

إلى أبي سندي في الدنيا ..يا من غرست حُبّ الله في فؤادي .. ورسّخت عقيدة التوحيد في أعماقي يا من كنت لي أُماً في الحنان .. ومعلماً في الأخلاق .. وأختاً في النصح والإرشاد .. نجاحي لا يوفي قطرة من عرق جبينك لكن أعلم أنه يكفيك عندما أرى الفرحة في عيونك

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إلى الشموع التي تحترق لتضيء للآخرين الدروب.. إلى أساتذتنا الذين كان لهم قدم السبق في ركب العلم والتعليم
إلى كل من ساعدنا بجملة أو حتى كلمة

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إلى أولئك الذين جعلوا من عظامهم جسراً ليعبر الآخرون إلى الحرية

نهدي هذا العمل المتواضع راجين من المولى عز وجل القبول والنجاح

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الشكر لوالدينا الأعزاء

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List of Abbreviations

PE: Polyethylene.

PP: Polypropylene.

HDPE: High density polyethylene.

LDPE: Low density polyethylene.

LLDPE: Linear low density polyethylene.

MDPE: Medium density polyethylene.

PVC: Polyvinyl chloride.

PET: Polyethylene terephthalate.

PS: Polystyrene.

PU: Polyurethane.

PLA: Poly-Lactic Acid

TGA: Thermogravimetric Analysis.

Chapter One

Proposal

1.1 Introduction

Plastic is widely used because of its great characteristics and properties such as low cost, light weight, flexibility and durability. Plastics consist of numbers of molecular-monomers joined together by chemical bonds to form macro-molecules. There are many types of plastic used in our daily life including polystyrene, polypropylene, polyethylene and polyurethane [1].

Most of the commercial plastics available in the market such as PE, PS and PP are non biodegradable and they may take hundreds of years to degrade in nature. The use of non-degradable plastic has been increasing exponentially leading to several negative impacts on the environment. The degradation of plastics depends mostly on their chemical structure, thermal and mechanical properties. Degradation takes place through the separation of main or side chains of polymers by biological, chemical, mechanical and thermal degradation mechanisms [2].

Several studies have reported on the biodegradation of plastics. Potential fungi was isolated from a soil of landfill were used for biodegradation of low density polyethylene by Aspergillus clavatus, and monitored for 90 days in aqueous media in the incubation. About 11.11% of low density polyethylene efficiently degraded in one month and 35% of it's weight was lost [3].

Thermal degradation of plastics was studied by various researcher in the literature during pyrolysis technology, the plastic is burned in the absence of oxygen inside a reactor in which the plastic is degraded and converted into engine fuels [4].

Chemical degradation of plastics occurs in the presence of oxidative chemicals. One study reported on the use of acid rain and ultra-violet for degradation of polyethylene. The results show that highly degradation of low density polyethylene during the first weeks [5]. Oxo-degradable additives were also used for speeding up the degradation of plastics. Adding the oxo-additives to polyethylene film promoted the degradation through abiotic factors and raised the activity of microbes from the beginning stages [6].

In Palestine, there are about 165 plastic facilities employing around 1000 workers [7]. Bio-Zmzm is a Palestinian plastic company specialized in producing bio-plastic. The company produces two types of polyethylene including packaging films and plastic bags. It's adding oxo-additives to their manufacturing formula in order to speed up the degradation of plastic. But, the addition of oxo-additive is randomly without taking into account the effects of these random quantities of oxo-additives on product quality, degradation rate, thermal and mechanical properties of the produced plastic.

This study aims at optimizing the manufacturing formula used at Bio-Zmzm. The main focus will be on the oxo-additives, several batches of different oxo-additives content will be prepared, films and bags will be produced accordingly. The effect of additive content on the degradation rate, thermal and mechanical properties will be studied to obtain the optimum formula.

1.2 Problem Statement

1.2.1 Project main question

This project tends to study how does the oxo-additives content affect the degradation, thermal and mechanical properties of Bio-Zmzm plastic bags and films.

1.2.2 Project sub questions

1) What is the effect of the oxo-additives on the degradation rate of polyethylene and thermal properties?
2) What is the amount and rate of change in the mass of samples as a function of temperature or time?
3) What is the effect of the oxo-additives on the degradation rate of polyethylene and mechanical properties such as strength, elastic modulus and elongation at break?

1.3 Goals and Specific Objectives

The main goal of the present study is to investigate optimum bio-plastic formula using oxo-additives with a high degradation efficiency and without affecting the thermal and mechanical properties of polyethylene plastic.

The project targets the following specific objectives:

1) Indentify the effects of oxo-additives on thermal properties of polyethylene.
2) Indentify the effects of oxo-additives on mechanical properties of polyethylene.
3) Determine the degradation rate of the product samples after adding oxo-additives.
4) Evaluate the quality of plastic before and after the additions of the degraded oxo-additives.

1.4 Significance of Study

The importance of this study come from the fact of accumulation of non-degradable plastic material which harms the environment. So that for speeding up the degradation rate of this material, oxo-additives were used. Due to the importance of this subject, a scientific research will done at Bio-Zmzm company in the city of Hebron to improve the ability of plastic to become biodegradable and to improve the conditions of the process.

1.5 Methodology

In this study, we will perform the following work on packages:

1) Preparation plastic samples for producing packaging films and plastic bags using oxo-additives in Bio-Zmzm company (Hebron, Palestine).
2) Mechanical tests will be done for produced samples.
3) Thermogravimetric analysis (TGA).
4) Analyze the data which obtained from the tests to identify the mechanical and thermal properties and also the degradation rate.

1.6 Budget

The total estimated cost for implementing this project is estimated at 2917.58$ as detailed in Table (1.1) below.

Table (1.1): The total estimated cost for implementing the project.

NO	Item	Quantity	Cost	Available	Required
1	Transportation	-	550$	Required, Company	
2	Mechanical Testing Machine	-	2000$	Required, Company	
3	TGA Test	12 samples	342$	Required, Company	
4	LLDPE (FS350A)	1 Kg	1.04$	Available, Company	
5	LLDPE (318B)	1 Kg	1.04$	Available, Company	
6	PIB Master Batch ZN-2	1 Kg	2.30$	Available, Company	
7	White Master Batch	1 Kg	2.20$	Available, Company	
8	Oxo-Degradable Concentrate	1 Kg	4.90$	Available, Company	
9	Stretch Blue	1 Kg	4.10$	Available, Company	
10	Gloves	1 box	10 $	Required, University	

1.7 Action Plan

The action plan of our project is illustrated in Table (1.2) and Table (1.3) below.

Table (1.2): Action plan for the first semester.

Date	September				October				November				December			
Tasks	Wk 1	Wk 2	Wk 3	Wk 4	Wk 1	Wk 2	Wk 3	Wk 4	Wk 1	Wk 2	Wk 3	Wk 4	Wk 1	Wk 2	Wk 3	Wk 4
Identification of Project Idea	🟥	🟥														
Literature Review			🟥	🟥	🟥	🟥	🟥	🟥	🟥							
Preparation of Samples with Oxo-additives								🟥	🟥	🟥						
Experimental Tests									🟥	🟥	🟥					
Documentation						🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	
First Presentation																🟥

Table (1.3): Action plan for the second semester.

Date / **Tasks**	February				March				April				May			
	Wk 1	Wk 2	Wk 3	Wk 4	Wk 1	Wk 2	Wk 3	Wk 4	Wk 1	Wk 2	Wk 3	Wk 4	Wk 1	Wk 2	Wk 3	Wk 4
Preparation of Samples with Oxo-additives	▨	▨	▨	▨												
Mechanical Test				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
TGA Test											▨	▨	▨	▨	▨	
Documentation			▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
Final Presentation																▨

Chapter Two

Literature Review

(Non-Biodegradable Plastic)

2.1 Introduction

The global production of plastic has risen over years because of the wide applications of the plastics in a various sectors such as healthcare, electronic, construction, packaging, automotive, agriculture, toys and others. As a result of the rapid in population growth, the demand for commodity plastics were increased. This demand caused an accumulation of plastic wastes in a large spaces of the landfill and unfortunately led to a big environmental problem, also its getting worse and worse when the plastic waste shipping off from the developed countries to developing countries [8].

At least, Plastic wastes can be categorized into two main types: municipal and industrial plastic waste. In general, industrial plastics are more homogenous and free from contamination, which make them valuable for downcycling into a low-level plastic products. Municipal plastic wastes seems to be heterogeneous and consist of extraneous materials, this waste contain primarily of high density polyethylene, low density polyethylene, polypropylene, polyethylene terephthalate, polyvinyl chloride and polystyrene. Overall, the total plastic waste of packaging materials is about 50-70% gained from several types of plastics, the most commonly used plastics are PE and PP. On average, plastic wastes which from PE are classified as the greatest fraction, especially plastic bags and packaging waste [9].

HDPE can be recycled and found in many uses such as storage boxes, plastic bottles, cable insulations and pipes. LDPE can be used for making toys, computer parts, back sheets for diapers, wrappers, soft bottles and several applications. PP also used in the packaging manufacture and as a rubber and in the computers. Tubings, electrical cable insulation, covers of automobile seat, plumbing pipes, and in some applications of rubber replacement can be made from PVC. PET is also a polymer that has found in beverage bottles, fibers, food containers and films [10].

Everybody using plastic bags, we can obtain them from a vegetable seller to a store designer. Plastic bags are highly common with both consumers and retailers for many reasons such as cheapness, strength, function, lightweight, and a hygienic instrument for carrying food and many other goods. Although they are considered as one of the modernistic conveniences way which we can't be able to work without, they are take the responsibility of causing pollution, death of wildlife, and using up the valuable resources of our earth [11].

2.2 Polymers

Polymers are present everywhere and play an important role in our daily lives. “Polymer” is an ancient Greek word consists of two parts, **poly** which mean “many” and **mer** which mean “parts or units”, it can be defined as a series of repeated molecular or macromolecular units to create chain-like structure as shown in Figure (2.1) below, this chains are built up around a “backbone” that repeats throughout the polymer and held together by the force interactions system between the repeated units of the series. These forces let the material to integrate in order to form a ductile material which can be used in manufacturing products [12].

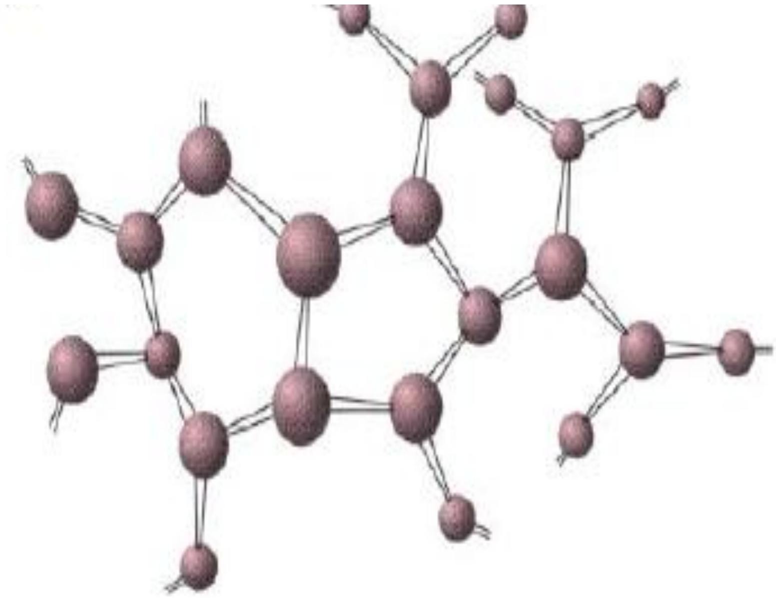
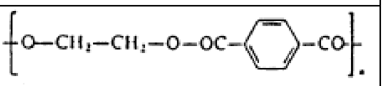
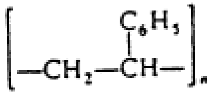
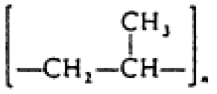
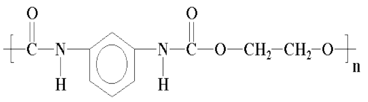


Figure (2.1): Shape of polymer molecules [13].

You may think that the shape of polymers are a straight chain. But in fact, due to the free rotation at around the C-C bonds, a long polymer molecules seems like spaghetti [14]. Table (2.1) shows the structural formula of some plastics.

Table (2.1): Structural formula of some plastics [13].

Polymer	Abbreviation	Molecular category	Formula
Polyethylene	PE	Polyolefin	$[-CH_2-CH_2-]_n$
Polyethylene terephthalate	PET	Polyester	
Polystyrene	PS	Polystyrene	 $[-CH_2-CH(C_6H_5)-]_n$
Polypropylene	PP	---------	 $[-CH_2-CH(CH_3)-]_n$
Polyurethane	PU	---------	

LDPE has a low strength, rigidity and hardness, but has an impact strength, low friction and as well as high ductility. It also offers strong creep under a continues force, which can be minimized by the addition of short fibers. Grades of melting for common commercial LDPE is considered typically from 105 to 115 °C (221 to 239 °F). With respect to biodegradability, it cause a serious problem because of its slowness rate of degradation under natural situations. Also it pose troubles to the animals, freshwater and generally to the environment [15].

Polymers can be categorized according to their physical properties into three groups: elastomers, thermosetting polymers and thermoplastic polymers.

2.2.1 Thermoplastics

Thermoplastics are considered as a linear chain of macromolecules where the molecules and atoms are united end-to-end into a string of lengthy carbon chains. Thermoplastic polymers are tough and cruel at room temperature, and it changes to be soft upon heating and by further heating its being melts. So that, without affecting the physical properties, it can be readily recycled and reshaped into a new article. Examples include nylon, PE, PS, PET and cellulose acetate [16].

2.2.2 Thermosets

Polymers of thermosets plastics are united together with a across-links of chemical bonds. On other word, thermoset plastics can be formed by polymerization as step-growth under appropriate conditions letting the bi-functional molecules of being condense intermolecularly with the reduction of tiny by-products like HCl, H_2O etc. at all reaction step. These polymers are produced and shaped normally within the same step. With heating, thermosetting polymers are becoming soft, but cannot be able to be formed or shaped to any large extent, and definitely will not flow. Examples include Urea formaldehyde, Melamine formaldehyde, Polyimide and Phenol formaldehyde [16].

2.2.3 Elastomers

An elastomer can not be defined by chemical structure, it can be defined by a mechanical response. Elastomers include a various range of chemical structures even though they are recognize as having a slight intermolecular forces. It will undergo a quick, reversible and linear response to the high strain to an applicable force. The response has a mechanical identification with a spring belonging to Hooke's Law. Non-linear, the time dependent mechanical response according to the dashpot model and parallel spring is distinct as viscoelasticity, while time rely on irreversible response belonging to a dashpot form is viscous. Real elastomers will offer a mostly elastic response. An ideal elastomer only can offer an elastic response, however particularly at higher strains, they also offer elastic responses and viscoelastic [17].

2.2.4 Homopolymer and Copolymer

Based on chemical structure, polymers can be classified into two main types: homopolymers and copolymers.

Homopolymers which a polymer like PE, containing identical monomer units polymerized in order to form a macromolecule [18].

Copolymers which a polymer consisting of more than one different type of monomers units polymerized together in a process called copolymerization. It's also known hetropolymer [18].

According to the joining variations, these copolymers can be classified as follow:

1) An alternating copolymer can be formed when two monomers in an alternative way are arranged.
2) Random copolymer also called statistical copolymer is formed when two or more monomers are arranged by any order.
3) Block copolymers are formed when every monomer join with the same sort of monomers, after that, the two homopolymers blocks can joined together.
4) Graft copolymer is a sequences of a repeating unit (one monomer) are "grafted" to be a backbone of another type of monomer [19]. Copolymer types shown in Figure (2.2).

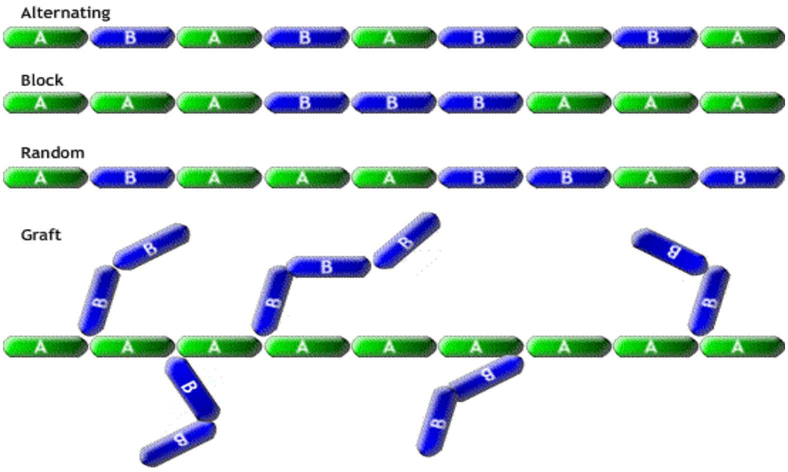


Figure (2.2): Copolymer types [20].

2.3 Polymerization

Polymerization is a chemical reaction for transforming the monomer units into a polymer. To have a polymer with a unique and singular physical properties like the resistance, high tensile strength, and elasticity, one hundred of monomer molecules at least are must be united with each other, this discrimination polymers from the other substances which consist of smaller molecules. There are a numerous shapes of polymerization and several systems presents to classified them, addition (chain-growth) and condensation (step-growth) polymerization [21].

2.3.1 Addition (chain-reaction) Polymerization

Addition polymerization includes the connecting together of molecules integrating double or triple of chemical bonds. These unsaturated monomers have further, internal, bonds which can be able to break and join up with another monomers to get a repeating chain. This type of polymerization is involved in the manufacturing of polymers as PP, PVC and PE. A living polymerization is a special case obtained from addition polymerization [21].

Initiation, propagation and termination are a three steps existed in this mechanism. In the initiation stage an initiator disconnted and an effective centere formed, this effective center could be radical free, anion or cation species, then the initiator hits the monomer and links with it and causes a breaking of the double bond. Propagation stage where the initiated stage continue repeated frequently creating a polymer with long chains. In the end, termination happens by chains combination [22].

2.3.2 Condensation (step-reaction) Polymerization

Condensation polymerization happens when monomers bond jointly through condensation reaction. Usually we can achieve these reactions by reacting of molecules integrating alcohol, amine, or other carboxylic acid groups (–COOH). A peptide bond or an amide is formed when an amine interacts with a carboxylic acid, with the liberation of water and so condensation polymerization. This is the method by which the ameno acids connect to form proteins [21].

2.4 Environmental Impacts of Plastic Pollution

It's clear that the plastics bring lots of societal benefits, progression future technological and medical advances, Plastic can unfavorably affect lands, waterways and oceans. However, Concerns revolved around removal of plastics waste. The most important overriding concern is accumulation of waste in landfills, physical problems for wildlife coming from swallow of plastics, the chemicals leakage from plastic products and the possibility for plastics to transfer chemicals to humans and wildlife [23].

2.4.1 Effects of Plastic on the Environment and Wildlife

Plastics majority are considered non toxic except PVC. For example, PE and PP are inert materials, anyway it should be understand that plastics are not fully stable. In the event of exposure of light, heat or mechanical pressure they can degrade and emit hazardous materials. Both styrene which is utilized to make PS and vinyl chloride utilized to make PVC are consider to be toxic, ethylene and propylene may also make problems. Also the effects of plastics on environment are vary due to the different type and quantity of additives which have been used. For example bromine emissions result from flame retardants which may contaminate the environment, also Pigments may consist of heavy metals that are very toxic to environment like chromium, copper, lead, cadmium and others metals [24].

Plastic bags are obtained from petroleum and PE, due to Petroleum is a non-renewable natural resource the extraction of petroleum may cause decreasing natural resource and damage to the environment. Some plastics can treat with chlorine that release harmful chemicals into the surrounding soil, then seep into groundwater or other surrounding water sources and the ecosystem. This can make ground water pollution, unstable sub-soil conditions and it leads to significant harm to the species that drink the water [25].

Due to the plastic bag is non biodegradable and nearly non-compostable, it remains in the soil for an extremely long period of time, which leads to unbelievable harms to the agricultural sectors. The roots of agricultural crops cannot grow and move because of the presence of plastic bags in soil. The most important negative effects of the plastic bags on agriculture are minimize soil fertility, reduce nitrogen fixation, big loss of nutrients in the soil, reduction in crop harvest, disparity in flora and fauna on soil etc. In fact, these negative effects of plastic bags minimize soil fertility to a great limit and thus reduce agricultural production to a big quantity [26].

Landfill areas consist of several different types of plastics, there are many microorganisms in landfill that increase the biodegradation of plastics. An example of microorganisms bacteria like Pseudomonas, nylon-eating bacteria, and Flavobacteria, which break down nylon during the nylonase enzyme activity. Emissions from methane gas can cause by uncontrolled biodegradation in a landfill, which is a extremely powerful greenhouse gas that participate dramatically increase to global warming [27].

Plastic debris represents an immediate threat to wildlife, which can lead to significant injury in growth of animals, not to mention limitation of motion, banning animals is made up of plastics. There are a wide variety kinds have been negatively impacted by plastic debris such as marine birds, sea turtles, cetaceans and others. Marine birds especially are exposed to ingestion of plastic, which leads to blockage the digestive system, reduced excretion of Stomach enzymes and reduced levels of steroid hormones occurring problems in reproduction, lacerations, ulcers and death [28].

2.4.2 Effects of Plastic on the Humans

The monomers which are made from polymers may be released and may affect human health. The relationship between plastic additives and harmful effects on human submit a number of challenges. Especially, the changing types of production and use of plastics they includes additives, also the confidential nature of industrial specifications makes assessment mostly difficult. In general, Many additives and chemical compounds found in plastics are dangerous and causing biological effects for human health. Two categories of plastic related chemicals like bisphenol A, and phthalates have a critical concern for human health [23].

Bisphenol A is a hard clear plastic used to make polycarbonate plastic, it can be found in water bottles, baby bottles and canned food liners. Human exposure happens by ingestion such as sucking plastics and skin contact. Many studies showed that bisphenol A increases the happening of diabetes, birth defects, heart disease, early puberty, decrease sperm, aggressiveness, hyperactivity and high levels of certain liver enzymes. Women who have contact with this chemical everyday can increase miscarriages, polycystic ovarian syndrome which causes infertility, baldness in women, prostate cancer, breast cancer and ovarian cysts [29].

Phthalates are chemicals that are used to soften plastics such as PVC, humans are exposed to phthalates by various ways. Exposures can be oral like phthalate polluted food, water and other liquids and in children during mouthing of toys and teethers, or dermal like cosmetics and other personal care products. Also, exposure can occurs through Inhalation or fumes from solvents. Human health effects include asthma, genital malformations, hormone disruption, reproductive problems and development of some cancers. Another important chemicals is PVC which lead to decreased lung function, increased resistance to insulin, increased weight gain and DNA damage to sperm [30].

2.5 Management of Plastics in the Environment

2.5.1 Recycling

The process of recovering plastic scraps or waste and re-transforming the material into a valuable products is called plastic recycling, with a completely different in the format from their original state in general. Because plastic is not easily biodegradable, recycling process is consider as a part of global efforts to minimize plastic from the waste stream, particularly when about eight million tons of plastic waste every year enter the oceans [31]. Recycling of plastic waste into useful things is necessary to prevent the depletion of ozone layer. This process convene a great obligation for both the economic and environmental scenarios [4].

Objectives for recycling plastics:

- Through incineration, we can reclaiming the energy saved in the polymers , but this can damage the environment by the liberation of toxic gases to the atmosphere.
- For some polymers, recycling is a practical alternative in restoring some of this energy.
- As a result of increasing prices of petroleum, recycle polymers instead of produce them from raw materials is considering more financially viable [13].

Five steps are carried out in the recycling of plastics process:

1) Plastics collection: plastics are collected through special recycling bins, road side collections, and immediately from industries which use large amount of plastic.
2) Manual sorting: in this stage stones and nails are taken away, and the plastic is sorted into three kinds: high density polyethylene, polyethylene terephthalate and others.
3) Chipping: preparing the sorted plastic for melting down after cutting it into small pieces.
4) Washing stage: contaminants as dirt, paper labels and remnants of the product which originally contained in the plastic are removed.
5) Pelleting: in this stage plastic is melted down and being extruded to a small pellets ready to reuse [32].

2.5.2 Landfilling

Most of waste all around the world is disposed in landfills. The primary effects from landfills are the generation of landfill leachate (which threatens quality of water) and gas generation while escaping of methane (a strong greenhouse gas) which can lead to local explosion risks. In the USEPA (United States Environmental Protection Agency) hierarchy, landfills are rated lowest level because of its ability to environmental effects, especially on surface and groundwater, air, soil, and on human health. Landfill mesocosm and many other laboratory experimental work support the concept that biological processes of degradation are the essential control on quality of leachate. This refers to degradation of organic matter is so important process in landfills [33]. Figure (2.3) shows a Photograph of Al-Minya landfill.

Figure (2.3): Photograph of Al-Minya landfill [34].

The Landfill contains different classifications of waste (hazardous and non-hazardous waste municipal waste, and inert waste) and stratify to all landfills, it can be defined as a sites of waste disposal for depositing waste into or onto land. Landfills are divided to three categories:

1) Landfills for municipal or inert waste.
2) Landfills for hazardous waste.
3) Landfills for non-hazardous waste.

2.5.3 Incineration

Incineration is a treatment technology of waste, by the combustion of waste with the presence of oxygen for recovering energy. Incineration can be recognized as thermal treatments with respect to the high temperature of waste treatments. Through the incineration process, material which treated is transformed into heat, IBM, particles and gases. Later, all of these products are used for electricity generation [35].

A significant trade-off in burning the plastics leads to form a several harmful compounds, mostly of which are emitted to the atmosphere. Polychlorobiphenyls and polycyclic aromatic hydrocarbons, toxic carbon- and oxygen-based free radicals, heavy metals, beside the significant amounts of green house gases, essentially carbon dioxide, are all produced and sent out when plastics are burnt. The significant environmental disadvantages from the disposal of plastic via both incineration and landfill like the expensive management option, includes high capital and operation cost and heavy investments [28].

2.6 Polymer Degradation

The changes in shape, tensile strength, molecular weight and other polymer properties as a result of expose to different agents including chemicals, physical or biological reactions is called polymer degradation. These changes are usually unwanted such as crazing, cracking and erosion. Polymers can exhibit different degradation through a variety of mechanisms. These include thermal, chemical, biological and mechanical degradation [36].

2.6.1 Thermal Degradation

At high temperatures, thermal degradation of polymers occurs, which the molecular is deteriorating due to overheating. The components of chain backbone of polymer start to separate and react with one another. This degradation leads to change the typical properties of the polymer, particularly mechanical property loss including molecular weight and molecular weight distribution. Significant thermal degradation can happen at temperatures very lower than those at which mechanical failure is probable to happen [37].

2.6.2 Chemical Degradation

It's a type of polymer degradation occurs due to a chemical reaction with the polymers surroundings, which leads to change of the polymer properties. This degradation have a several types of probable chemical reactions like photo degradation of polymers by ozone, oxidative degradation in the existence of oxygen and hydrolysis degradation which is a result to exposure to water. However, these reactions leads to the breaking of double bonds within the polymer structure [38].

2.6.3 Biodegradation

A process of polymers degradation involving biological activity, its predicted to be the main mechanism of loss for chemicals emitted into the environment. Biodegradation refers to the degradation by living microorganisms such as fungi, bacteria and algae. This process divided into aerobic and anaerobic degradation. If there is oxygen, aerobic biodegradation happened and produced carbon dioxide. If oxygen is absent, an anaerobic degradation happened and produced methane instead of carbon dioxide [39].

2.7 Literature Review

Degradation of plastics has been studied by several researchers in the literature, in which they have used different techniques for different types of plastics. Table (2.2) lists some of techniques applied in degradation process of polymers.

Table (2.2): Different techniques for different degradation processes of polymers.

Polymer	Degradation mechanism	Degradation agent	Degradation condition/ media	Degradation rate with time	Ref
LDPE LLDPE HDPE	Thermo-oxidative Degradation	-Antioxidant -Irganox® B 561	-Temperatures above 280°C -Exposure time to air and oxygen. -Occurs in the extruder barrel and in the hot molten film.	-Several degradation products were identified, such as aldehydes and organic acids.	[40]
PE PET	Thermal Degradation	Depolymerizing agent and catalyst	-Temperature between (250 - 400 ºC) -Placed into reactor chamber.	-Plastic was converted to fuel. -Product fuel density = 0.76 gm/ml -Fuel production liquid conversion rate = 53.5%	[41]
PE	Biological Degradation	-Pro-oxidant additive -Fungi and protozoa	-Simulated soil in a greenhouse	-Degradation occur after 30 days of exposure.	[42]

PET PU PS LDPE PP	Biological Degradation	-Bacillus bacteria -Chemicals and reagents	-Selective media of Soil	-Biodegradation test are determined after three months. -PP and LDPE were hard for bacteria to attack.	[43]
PE	Biological degradation	-Oxo-additive -UV radiation	-Environmental chamber. -Glass containers of compost stabilized bird guano in static.	-Additive increased the abiotic photodegradation. -At the early stages of the biotic degradation, structural changes of the polymers were occur.	[44]
PE	-Thermal degradation -Bio-degradation	-Pro-oxidant -Fungal strains	-Agar plates -Temperature between (45- 65 ºC)	-After 93 days, a slight increase in both crystallinity and melting temperature for films with additives.	[45]
PE PS PET PVC	Thermal degradation	-UV irradiance	-Water -Salt water	-(89–98%) of the additives leaching from PE. -(74–94%) of additives released from PVC -From the combined annual PVC, PE and PS load, between 35.2 and 917 tons of additives are released into the oceans.	[46]

Chapter Three

Literature Review

(Biodegradable Plastic)

3.1 Introduction

It is very difficult to realize the importance of plastics in our daily lives. Plastic gives us the possibility of manufacturing beautiful products from many different types of plastic materials which became available today dramatically. Currently, about 80% of all polymeric materials is produced from fossil (non-renewable) resources, usually composed of artificial synthetic polymers and are harmful to nature [6]. Their synthesis produces hazardous waste and structure is not naturally occurring. So plastics are not biodegradable [8].

Plastic is a highly useful material because it's a relatively cheap, durable and versatile material. Its applications are expected to increase as more new products which have brought benefits to society [9].

With the increasing consumption of plastic products, the amount of waste is increasing rapidly and disposal of these wastes is an important environmental issue. Because plastic doesn’t degrade naturally under normal conditions; the plastic waste accumulation and the burden on the environment is also increasing. The studies have shown that alone plastic bottle fully biodegrades after 450 years [7].

Environmental issues have led researchers to find alternatives to nonrenewable resources. So the world had decided towards the production of polymers which are bio-degradable or made from renewable resource represents an alternative possibility and environment-friendly [10].

3.2 Overview of Plastic in Palestine in Bio-Zmzm Company

In Palestine, the plastic industry is distributed around different parts of the West Bank to work on several products which include plastic pipes and fittings, sanitation fittings, plastic bags and sacks, different size and multipurpose plastic containers, drinking water containers, polystyrene, rubber and kitchen wear.

Zmzm is the Largest Palestinian company for production of plastic through thousands of products used at all Palestinian house and institutions. it is located in the city of Hebron which is one of the largest companies in the region in this field. The Company launched in 1973 by establishing Khalil Al-Rahman company as the first Plastic Industries Company. by the initiative of the late founder Haj Rafat Hassouna.

With increased awareness of the dangers of plastic waste was established another branch of the company called Bio-Zmzm. It is Producing environmentally friendly biodegradable plastics By mixing additives with PE. that is complying with the International standards of production. The company got several environmental certifications including: EPI certificates and TDPA" to totally degradable plastic additives".

3.2.1 Developments in Biodegradable Plastic Bags and Packaging Films in Bio-Zmzm

In recent years, scientists have devised several approaches to make plastic more biodegradable. Some of the major approaches are: Mixing PE with various fillers (i.e. starch), Combining PE with additives, such as pro-oxidants and Combining PE with various enzymes. Bio-Zmzm followed an approach mixing polyethylene with oxo-additives to get biodegradable plastic bags and packaging films .

Bio-Zmzm produces packaging films and bags. First, packaging films produced by mixing a LLDPE (linear low density polyethylene) with additives and glue. Second, the plastic bags produced by mixing three types of PE (LLDPE, MDPE, HDPE) with $CaCO3$ and additives.

3.3 Plastic Waste

Plastic has a wonderful array of properties that made it ideal for many applications in our daily life. However, the plastic waste generated can be devastating to ecosystems. Furthermore, plastic doesn't biodegrade, but remains in the environment for hundreds of years. Therefore, there is growing concern about the excess use of plastic, particularly in packaging. Concern is the proper disposal of waste plastic [4].

Enormous consumption of plastic products led to the accumulation of huge amounts of plastic waste. Several end-of-life options exist to deal with plastic waste. The reuse and recycling of products are two of the options to reduce the amount of landfilled waste. Polymers which are bio-degradable or made from renewable resources also represent an alternative possibility [11].

Packaging waste constituting 63% of the plastic waste percentage [4]. It has a big chance for recycling, But recycling packaging waste is not common because of concerns about food safety and hygiene standards, though this is beginning to change. Hence the idea of bioplastic production appeared [12].

3.3.1 Environmental Impact of Plastic Waste

1. The Impact on marine Environmental**:** Swallow waste by marine animals that lead to death. Also alteration of habitats and the transport of alien species.
2. Impact of chemicals associated with plastic waste**:** There are many chemicals are added to plastics to give specific properties such as: Bisphenol A, phthalates and flame retardants. These have negative effects on human and animal health, mainly affecting the endocrine system [9].
3. Plastic Waste has ability to attract contaminants, such as persistent organic pollutants (POPs): This is particularly so in the marine environment since many of these contaminants are hydrophobic, which means they do not mix or bind with water [2].
4. Plastic contains several chemicals which are possible under certain conditions, contaminated materials such chemicals may threaten the lives of organisms and environment [9].

3.4 Polymers

Today polymer science is a very important research subject. A large theme of polymer research is modifying the chemical and physical properties and trying to produce environmentally friendly polymers.

3.4.1 Structure of Polymers

Plastic production is one of the biggest industries. All plastics are considered polymers. To understand how plastics are made, and why some types of plastics are suitable for some uses, and others not, it should understand the structure of polymers. Polymers are large molecules made up of many smaller molecules which have high molecular mass ('Poly' means many and 'Mer' means units). These smaller units are called monomers. These monomers connected together through polymerization to form a polymer [8, 13].

Polymerization, is a process by which monomers combine to form polymers, as shown in Figure [3.1].

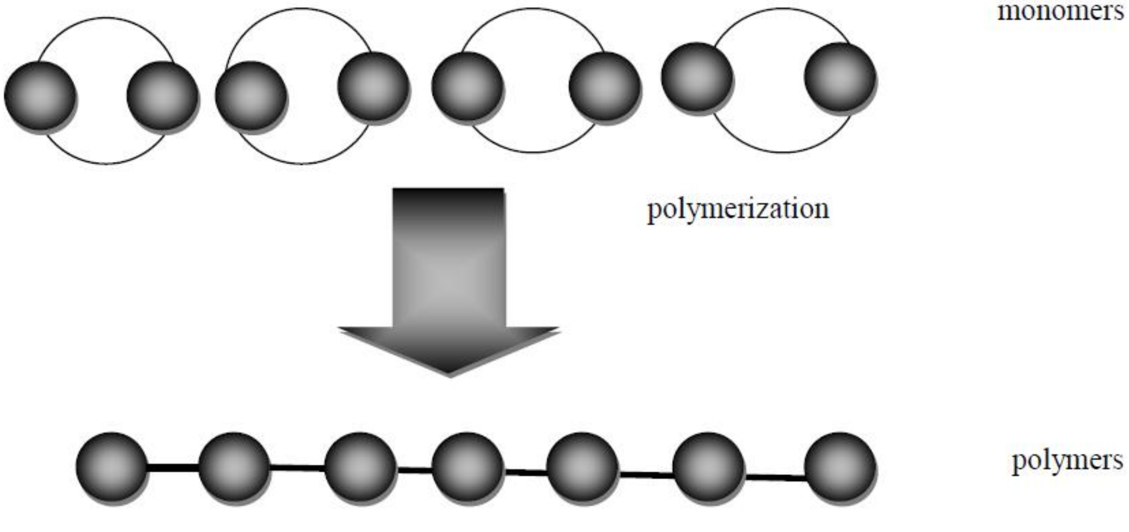


Figure (3.1): Polymerization process.

3.4.2 Type of Polymers

There are several ways of classification of polymers based on some special considerations:

1) **Classification based on source:**

a) Natural polymers: These polymers are found in plants and animals. For example are (starch, proteins, cellulose) [14].

b) Synthetic polymers: is examples on a man-made polymer which are widely used in daily life as well as in industry as plastic (polythene), polyvinyl chloride, and synthetic fibers [8].

2) **Polymers are divided into three types based on their physical properties:**

a) Thermoplastic polymers: are polymers that soften when heated and are molded into different forms and return to their original form, in this type occurs reversible reaction. Examples include PE, PP and PVC [15].

The following describes the types of polymer:

i. PE, LDPE and HDPE: The most common polymer in plastics is polyethylene which is made from ethylene monomers, composed of chains of repeating –CH_2– units. LDPE is produced when ethylene is polymerized at high pressure (1000–2000 atm). This form of PE has molar masses of 20,000 to 40,000 grams and relatively soft, and most of it is used in the production of plastic films, such as those used in sandwich bags. When catalyzed at moderate pressure (15 to 30 atm), the product is HDPE, molar mass in these polymers up to many hundreds of thousands HDPE is hard and tough and It used in plastic bottles and typing and household equipment [8, 16].

ii. PP: made from the combination of propylene monomers It is used in a variety of applications, including packaging [13].

iii. PVC: polymerization of vinyl chloride, (CH_2= CHCl) is a major plastics material used widely in many industries, building, automotive , packaging and healthcare applications PVC is a very durable [8].

b) Thermosetting polymers: are synthetic materials which undergo a chemical change during processing to strengthen and set them into a form. Thermoset plastics have a net-like structure of cross-linked polymers are converted into their final form by heat and once set cannot be softened by further heating can only be heated and shaped once. These cannot be reused. In this type occurs irreversible reaction Some common examples are Bakelite, urea-formaldehyde resins [17].

c) Elastomers: are also cross linked materials but have the capacity for elastic deformation, and return to their original shape after exposure to load. the polymer chains are held together by the weakest intermolecular forces These weak binding forces permit the polymer to be stretched [3].

Plastics are polymers with additives as fillers (inorganic or organic), pigments and lubricants. These materials are able to be shaped or molded by heat, and then formulated and prepared for use [14]. Plastics can be produced by bonding together monomers in a reaction called polymerization. Figure (3.2) describes the process of formation of plastic from monomers.

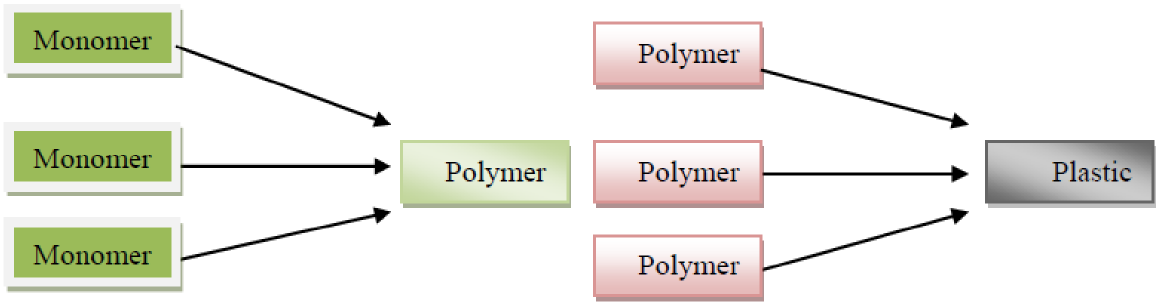


Figure (3.2): Connection of monomer and polymer to form a plastic.

3) **Polymers based on renewable recourses are dived in three categories:**
   a) Polymers directly extracted/removed from biomass: polysaccharides, for example starch and cellulose; proteins, for example casein and gluten.
   b) Polymers made by classical chemical synthesis using monomers from renewable resources. A good example for this category is polylactide, bio-polyester formed by polymerization of monomers, i.e. lactic acid.
   c) Polymers obtained with the help of microorganisms or genetically modified bacteria. The main representatives of this group are polyhydroxyalkanoates (PHA), but research in the field of bacterially synthesized cellulose is also booming.

3.5 Bio-plastic

Bio-plastics are plastics derived from renewable biomass sources, such as vegetable fats and oils, or micro biota. Bio-plastics can be made from many different sources and materials. They include Corn Starch, Potato Starch, Sugarcane, Weeds. These polymers are naturally degraded by the action of microorganisms such as bacteria, fungi and algae. Bio-plastic decomposes through aerobic and anaerobic conditions depending on how they are manufactured [8].

Bio-plastics depending on the type of source are divided into three types:

1. Bio-plastics from renewable resources.
2. Bio-plastics from fossil resources.
3. Bio-plastics from a mixture of renewable and fossil resources.

As shown in the figure (3.3) not all bio-plastic is biodegradable. For example, PE is non biodegradable. Although, it made of renewable resources. On the other hand, bio-plastic made from lactic acid is biodegradable. Plastic produced from non-renewable sources, some of biodegradable and some other non-biodegradable. For example, conventional plastic (PE, PET, PS) is non biodegradable, but plastic produces from biopolymer is degradable [8].

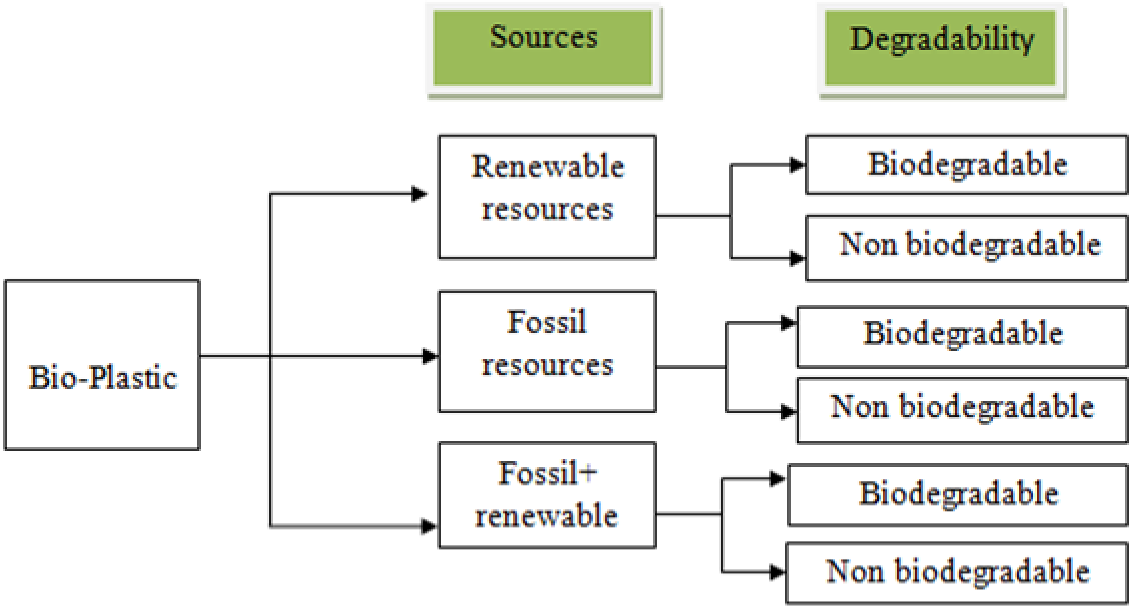


Figure (3.3): Distribution of bio-plastics according to the source and the susceptibility to biodegradation**.**

3.5.1 Degradation

Degradable is a general term used to denote a product will break down into smaller parts or become transformed into another form. Widely used plastics do not naturally degrade to a large degree when released into the environment. Any physical or chemical change in polymer as a result of environmental factors, such as light, heat, moisture, chemical conditions or biological activity. Processes inducing changes in polymer properties (deterioration of functionality) [7]. There are four mechanisms by which plastics degrade in the environment: photodegradation, thermo oxidative degradation, hydrolytic degradation and biodegradation by microorganisms. These causes the plastic break into smaller and smaller pieces, until the polymer chains reach a sufficiently low molecular weight to be metabolised by microorganisms. These microbes either convert the carbon in the polymer chains to carbon dioxide or incorporate it into biomolecules. However, this entire process is very slow, and it can take 50 or more years for plastic to fully degrade [18].

3.5.2 Biodegradable

Biodegradable is a more specific term that explains the process of how a product degrades. When a product biodegrades it is digested by bacteria, fungi or algae and it is broken down into a biogas, (CO_2 for aerobic degradation and $CH_4$for anaerobic degradation) and a soggy biomass or humus which makes plant fertilizer. The biodegradable by-products are then naturally recycled back into the cycle of earth [8].

3.5.3 Degradation Mechanisms of Conventional Plastic

Traditional plastic needs hundreds of years to decompose. To accelerate the decomposition process should be added degradable additives. These additives are based on chemical catalysts containing transition metals such as cobalt, manganese , iron or organic materials, which may cause fragmentation as a result of a chemical oxidation of the plastics‟ polymer chains triggered by ultraviolet irradiation or heat exposure, or outright biodegradation of the organic additive. However, the main effect of oxidation is fragmentation, not biodegradation, into small particles, which remain in the environment for an indeterminate amount of time, becoming uncontrollable in terms of their final disposition [6, 8].

3.5.4 Degradation Mechanisms of Bio-Plastic

Biodegradable polymers (BDPs) or biodegradable plastics: refer to polymeric materials that are capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, as shown in figure (3.5) [8].

As shown in figure (3.4) the first stage in degradation is Fragmentation. This process occurs in macroscopic level by a self-decomposition. The main change in polymer properties is the losses of mechanical properties such as e.g. tensile strength, tenacity and flexural strength. The final stage is mineralization. The process may occur under aerobic or anaerobic conditions [18].

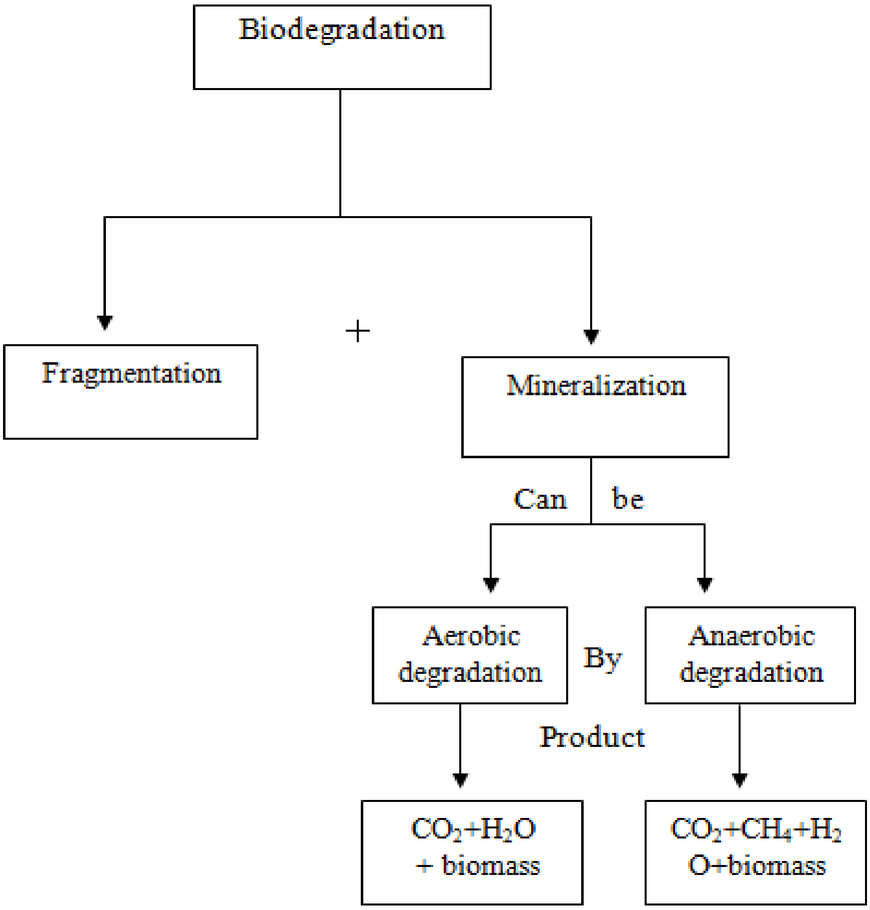


Figure (3.4): Description degradation of bio-plastics**.**

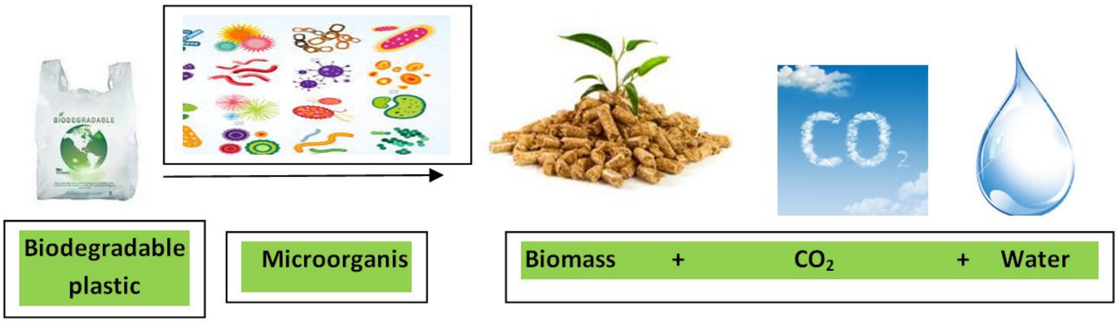


Figure (3.5): Biodegradable bag.

1. Aerobic biodegradation: biopolymer turns into carbon dioxide and water, and there remains some residual biomass as shown in equation (2.1) [19]:

$$C_{\text{polymer}} + O_2 \longrightarrow CO_2 + H_2O + C_{\text{residue}} + C_{\text{biomass}} \ldots\ldots\ldots\ldots\ldots (2.1)$$

2. Anaerobic biodegradation: In the absence of oxygen biopolymer turns into carbon dioxide and water, and there remains some residual biomass and methane. As shown in equation (2.2) [19]:

$$C_{\text{polymer}} \longrightarrow CO_2 + H_2O + CH_4 + C_{\text{residue}} + C_{\text{biomass}} \ldots\ldots\ldots\ldots\ldots (2.2)$$

When mineralization process is completed the polymer returned to their original material. The conditions affecting on polymer degradation:

1. Temperature.
2. PH.
3. Moisture.

3.6 Bio-Plastic Production of Natural Polymers

Natural polymers are made from renewable resources. These are formed in the natural environment by living organisms; they are extracted from plants or animals. starch, cellulose, protein are the examples of natural polymers that are widely used in modern life. Currently, there is a great interest in biopolymers as an alternative to petroleum -based plastics in some applications. Natural polymers can be degraded biologically in the environment much more easily than oil-based polymers [20].

Bio-plastics from renewable resources represent a new generation of plastics that reduces the impact on the environment, both in terms of energy consumption and the amount of greenhouse gas emissions. Also, they are reducing the amount of waste that must be disposed of in landfills or burned in incinerators. The use of polymers from renewable resources can reduce dependence on fossil fuels [8, 19].

Based on previous studies, some types of natural polymers that produced bio-plastic will be presented. The best examples of plastics from renewable resources are plastics from plant such as cellulose, polylactides, plastics based on starch and plastics from soya. The problems with these polymers have been poor commercial availability, poor process ability, low toughness, high price and low moisture stabile.

3.6.1 Starch Based Bio-plastics

Starch is a carbohydrate, a plant reserve polysaccharide. Most of the plants produce starch. It is use for energy storage inside the cells in the form of spherical granules. The monomer of starch is – D – glucose. When a polymer of starch is formed hundreds of – D – glucose molecules are joined through a linkage known as glycoside linkage. Most commercially available starch is derived from corn (79 %), potato (9 %), wheat (7 %), rice, and barley. These plants contain large amounts of starch, usually between 60 and 90 % of the dry weight [3, 21].

Starch is economically competitive with petroleum and has been used in several methods for preparing compostable plastics. The starch has been processed in various ways to produce starch plastics. Scientists reached to invent a new type of plastic made from starch. It found in corn, wheat and sugar beet [20]. Corn is the primary source of starch for bio-plastics. Some studies have shown that after starch was filled with synthesized polymer, the synthetic fraction of the oil source has not better susceptible to biodegradation. So the most recent research has focused on pure starch-based materials [22].

According to studies carried out at Leicester University in 2016 has shown that, starch-based plastics can be formed by the same processes as current commercial plastics. The study also showed that plastics made from the starch are flexible and have good mechanical properties [23].

The following is one of the ways that describes how to produce plastics from the starch:

a. The molecular structure of starch must be undergo to process of breaking down by exposure to high temperature and to isolate the sugar from starch [23].
b. The sugar is ferment by adding bacteria to turn into a condensed lactic acid which changes physically to become a monomolecular. then assembled to form a multi-yeasts acid (polymers).
c. After that polymer is ready for the manufacturing plastic from starch [23].

Product based on starch:

1. Shopping bags.
2. Bags for the bio-waste storage.
3. Food packaging and packaging (e.g. bags for fruit, vegetables, bread - their important advantage over other materials is ventilation, which improves the storage conditions of these foods).
4. Hygiene products and cosmetics products.

3.6.2 Poly-Lactic Acid (PLA)

Polylactic acid polymers are polyesters of lactic acid. It is different than most thermoplastic polymers in that it is derived from renewable resources such as corn starch. Recently, these polymers have been introduced commercially for products where biodegradability is wanted [8].

The monomer of lactic acid is found in blood and muscle tissue as a metabolic product of the metabolism of glucose. Polylactic acid is made from renewable agricultural raw materials which are fermented to lactic acid through the fermentation of glucose [19].

The study was conducted at Norwegian University of science and technology in 2003 showed polylactates have good mechanical properties, similar to PET and PP. According to that polylactic acid can be processed similarly as polyolefines and other thermoplastics although the thermal stability could be better. Also Polylactide polymers are stiff and brittle materials. Therefore it is necessary to use plasticizers to improve the elongation and impact properties [24].

The polylactide is fully biodegradable. The degradation occurs by hydrolysis to lactic acid, which is metabolised by micro-organisms to water and carbon monoxide. Industrial production of polylactic acid started in 2002 [24]. After that Polylactide became the first polymer from renewable resources to be produced on an industrial scale.

PLA is naturally degrades when exposed to the environment. For example, a PLA bottle would typically degrade in six to 24 months. Compared to conventional plastics can take several hundred to a thousand years to degrade in the same environment [25].

Product based on Polylactic acid:

1. PLA is currently used for packaging(cups, bowls, foils and food storage container).
2. plastic bags.
3. hygiene products.
4. plastic water bottle.
5. plastic electronics part.

3.6.3 Plastics Based on Cellulose

Cellulose, as starch, is a carbohydrate. It is a structural polysaccharide, while starch is one of the storage polysaccharides. In terms of quantity, cellulose is the most represented polymers on Earth and is the main support for trees and other plants (cotton, sugarcane) [20]. An experiment was conducted at Hail University in Saudi Arabia in 2015. To produce bioplastic from nano-cellulose found in bananas as follows in procedure [26].

3.6.4 Bio-Polyethylene

Biopolyethylene is also obtained from renewable resources (sugar cane), it is not biodegradable and its characteristics are the same as those of polyethylene obtained from oil. Polyethylene from renewable resources is obtained by polymerization of ethylene, obtained from renewable resources [3, 16].

The production of biopolyethylene is based on the use of sugar cane as the source of ethanol. The sugar cane is cleaned and crushed in a sugar grinder. After that the sugar cane fermented to ethanol in anaerobic conditions. The obtained ethanol is distilled in order to create 98.5 % ethanol that is then dehydrated at temperatures between 300 and 600°C [3]. The following equation describes the process of bio-polyethylene production:

Chapter Four

Experimental Work

4.1 Introduction

In this project, packaging films and plastic bags made of the polyethylene polymer with different quantities of oxo-additive are investigated. PE films and bags are prepared in the company through the extruder machine, then, samples are cultivated in a three different media (soil, marlstone and air). The resulting films were evaluated on their mechanical properties (maximum strength, elongation at break, and modulus of elasticity), and thermal properties (melting point temperature). Besides, the degradability of the films was measured by TGA analysis related to the mass losses observed from the test .

We will then discuss the main target of this project, which is to prepare PE plastic bags and films with the best quantities of oxo-additive with a specific properties.

4.2 Materials

For preparation of packaging films, LLDPE (318B) (Sabic Company, Saudi Arabia), LLDPE (FS350A) (Petro Rabigh & Petrochemical Company, Saudi Arabia) and Pib Masterbatch Zn-2 (Shenzhen Beihua Plastic Co.ltd, China) were used. As degradation agent, oxo-additives (OX5854PE) (Tosaf, Industrial zone, Afula-Occupied Palestine) were applied.

For preparation of Plastic bags, LLDPE (HP2023) (Sabic Company, Saudi Arabia), LLDPE (218) (Sabic Company, Saudi Arabia), HDPE (FI0750) (Sabic Company, Saudi Arabia), Medium density polyethylene (TR-131) (Qatar chemical company, Qatar), Calcium carbonate ($CaCo_3$) (Dai A Industry Joint Stock Company, Vietnam) and oxo-additives were added . For free fall test, tap water and wood shavings were used.

4.3 Methods

4.3.1 Samples Preparation of Packaging Films

To prepare packaging films, 25 kg of 318B LLDPE and 5 kg of Pib Masterbatch Zn-2 were mixed with different amount of oxo-additives as shown in Table (4.1).

Table (4.1): Quantities of material used in packaging films.

Sample Number	LLDPE (kg)	Pib Masterbatch Zn-2 (kg)	Oxo-additives (kg)
Sample 1	25	5	0.0
Sample 2	25	5	0.025
Sample 3	25	5	0.050
Sample 4	25	5	0.100
Sample 5	25	5	0.200
Sample 6	25	5	0.400
Sample 7	25	5	0.800

Then, the mixture was fed into the extruder machine (fully automatic stretch film machine) (Dongguan Xinhuida Machinery Company, China) for 15 min. Packaging film products are shown in Figure (4.1).

(a) (b)

Figure (4.1): Preparing samples for packaging films. (a) Fully automatic stretch film machine and (b) Produced samples of packaging films.

4.3.2 Samples Preparation of Plastic Bags

To prepare plastic bags, 12.5 kg of FI0750 HDPE , 6.25 kg of Marlex HHM TR-131 MDPE, 6.25 kg of 218 LLDPE, 4.15 kg of HP2023 LLDPE and 1.25 kg $CaCO_3$ were mixed with different amount of oxo-additives as shown in Table (4.2).

Table (4.2): Quantities of material used in plastic bags.

Sample Number	FI0750 HDPE (kg)	Marlex HHM TR-131 MDPE (kg)	218 LLDPE (kg)	HP2023 LLDPE (kg)	$CaCO_3$ (kg)	Oxo-additives (kg)
Sample 1	12.5	6.25	6.25	4.15	1.25	0.00
Sample 2	12.5	6.25	6.25	4.15	1.25	0.0375
Sample 3	12.5	6.25	6.25	4.15	1.25	0.075
Sample 4	12.5	6.25	6.25	4.15	1.25	0.150
Sample 5	12.5	6.25	6.25	4.15	1.25	0.300
Sample 6	12.5	6.25	6.25	4.15	1.25	0.600
Sample 7	12.5	6.25	6.25	4.15	1.25	1.200

After that, the mixture was fed into the extruder machine (blowing film machine) (Shanghai Lansheng Light Industrial Products IMP, China) for 20 min. Plastic bags products shown in Figure (4.2).

(a) (b)

Figure (4.2): Preparing samples for plastic bags. (a) Blowing film machine and (b) Produced samples of plastic bags.

4.4 Characterization of Plastic Bags

4.4.1 Free Fall Test

The free fall test was carried out to examine the rapture resistance of plastic bags upon sudden loading. The test was prepared by filling the bags with 2 kg of tap water and 2 kg of wood shavings then deflated from the air with vacuum. After that, the plastic bags were allowed to freely fall from a height of 1 m as shown in figure (4.3). Rupturing of the bags upon falling indicates bad quality. Else, the bags meet the standard quality.

Figure (4.3): Free fall device.

4.4.2 Adhesion Test

The adhesion between plastic bags were conducted by using oven test to check the adhesion strength of bags. The test was prepared by placing two pieces of same sample of plastic bags with (10*10) cm dimension between two flat plate glass and 2 kg weight was put above it in the oven at 45°C as shown in figure (4.4). After 48 hours, Sticking of the bags together indicates bad quality. Else, the bags meet the standard quality.

Figure (4.4): Oven device.

4.5 Characterization of Plastic Packaging Films

4.5.1 Mechanical Test

For tensile test, plastic samples were cut in a rectangular shape (70*30) mm, then the films were cultivated in a three different media (soil, marlstone and air) and buried during three months at room temperature in desiccator jars in presence of silica gel to absorb the moisture as shown in figure (4.5).

Figure (4.5): Packaging Films in different media in desiccator jars.

After three months, the sample was installed on the tensile testing machine (Dongguan Sinowon Precision Instrument CO., Ltd., China) from both ends with a dimension of (40*30) mm and then turn on the machine from connected computer. The machine pulls the sample from both ends and measures the force required to pull the specimen apart and how much the sample stretches before breaking as shown in figure (4.6). The tensile tests were performed with three samples of each film at constant crosshead speed of 15 mm/min until break. After that, the data are collected and calculations for strength ,elongation at break, modulus of elasticity are done.

Figure (4.6): Tensile test device.

where stress (σ [Pa]) is defined as force (F [N]) per cross sectional area (A [m^2]), elongation at break (ε) is defined as the elongation (ΔL [m]) per length (L [m]) and E [Pa] is modulus of elasticity (Young's Modulus) defined as a slope of stress-strain diagram [Pa].

4.5.2 Thermogravimetric Analysis (TGA) Test

The polymer samples were tested using thermogravimetric analysis (TGA) to determine the weight loss. TGA analysis gives the measures the amount of weight change in the mass of a sample as a function of temperature or time in a controlled atmosphere. After three months from sampling in the different environments, samples sent to Jordan University of Science and Technology for the test. For TGA tests, the crucible was cleaned using acetone or alcohol prior, then the crucible filled with the sample then Placed it on the machine and turn on from connected computer. All samples heated from room temperature to 900 ºC at same rate of 0.001 k/min to 100 k/min, the PE film heated 10º C in 1 minute that means the each sample take about one to one and half hours. After that, the sample cooled from 900 ºC to room temperature which take about 40 minutes then the data are collected from computer. See figure (4.7).

Figure (4.7): Thermogravimetric analysis (TGA) test device.

Chapter Five

Results and Conclusion

5.1 Free Fall and Adhesion Test Results

The effect of oxo-additives content on rapture and adhesion strength of the plastic bags were investigated. The results showed that the oxo-additives content which applied (0.0, 0.0375, 0.075, 0.150, 0.300, 0.600 and 1.200 kg) did not affect on rapture strength and all samples successfully passed the test. The results also showed that the different content of oxo-additive had no effect on adhesion strength.

5.2 Mechanical Test Results

5.2.1 Effect of Oxo-Additives Content on Packaging Films

Figure (5.1) shows typical stress-strain dependency curves of PE plastic films after three months in marlstone media. The maximum strength, elongation values at break and elastic modulus, are shown in figures (5.2), (5.3) and (5.4), respectively. High maximum strength were found in neat PE film of approximately 18.4 MPa, elastic modulus of around 146.3 MPa, and an elongation at break of 406%. The lowest maximum strength and elongation at break were found in 2.5974% of oxo-additive content at about 16.2 MPa and 369% respectively.

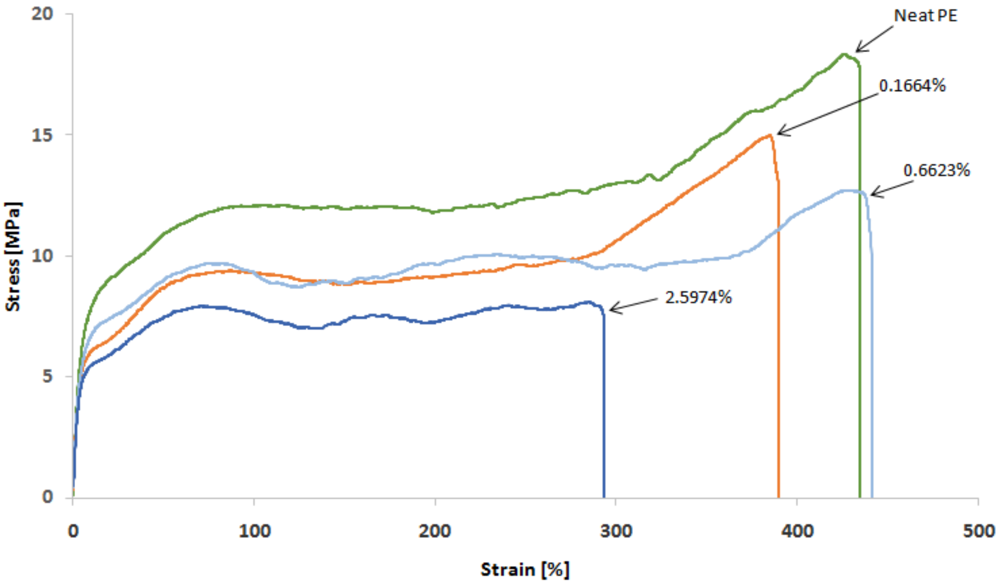


Figure (5.1): Stress-strain diagrams of PE films after three months in the marlstone media prepared with different amount of oxo-additives.

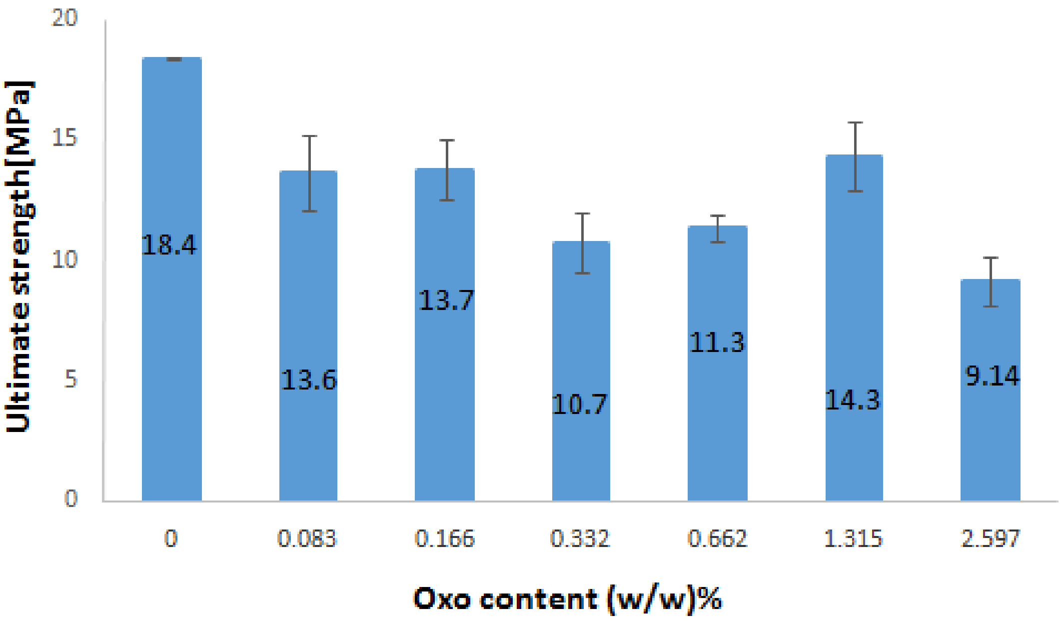


Figure (5.2): Ultimate strength of PE films after three months in marlstone media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

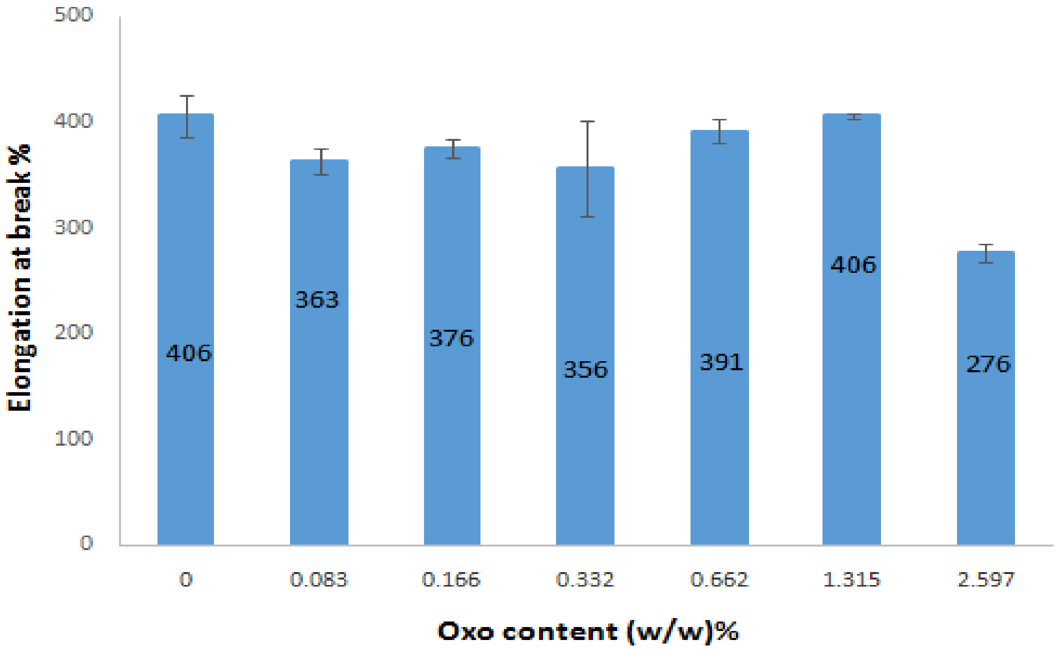


Figure (5.3): Elongation at break of PE films after three months in marlstone media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

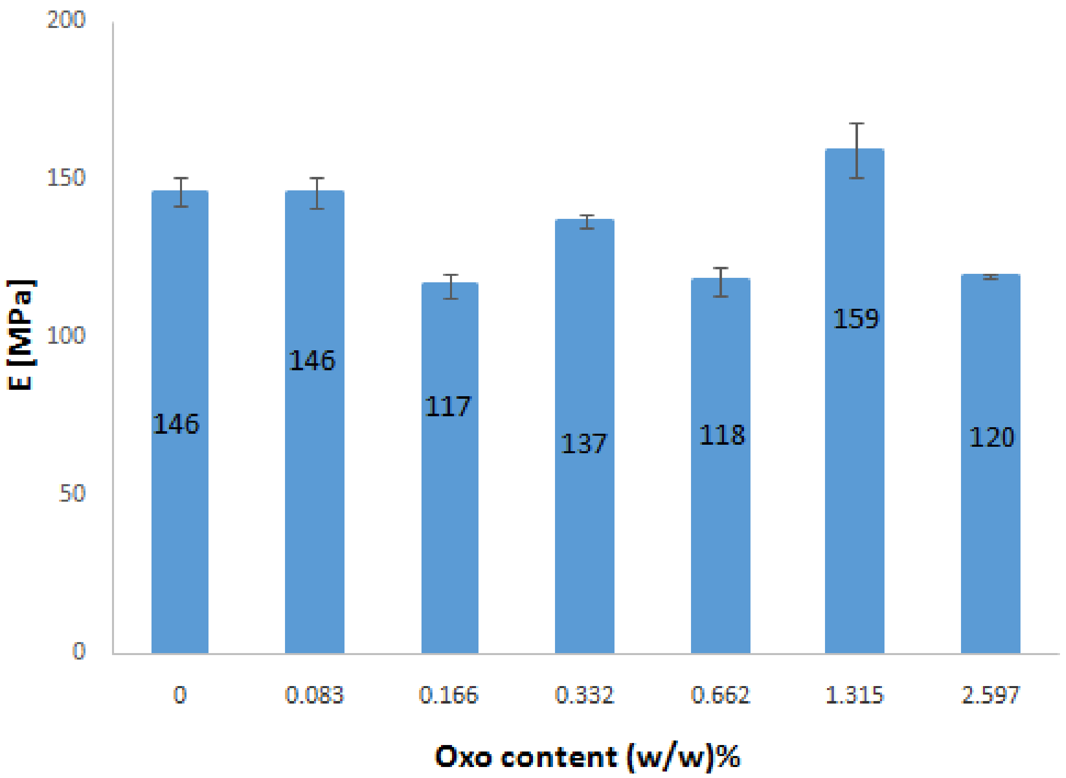


Figure (5.4): Elasticity modulus of PE films after three months in the marlstone media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

Figure (5.5) shows typical stress-strain dependency curves of PE plastic films after three months in the soil media. The maximum strength, elongation values at break and elastic modulus, are shown in figures (5.6), (5.7) and (5.8), respectively. High maximum strength were found in 0.0826% of oxo-additive content in the PE film of approximately 17 MPa, elastic modulus of around 206 MPa, and a high elongation at break of 409%. The lowest maximum strength and elongation at break were found in 1.1357% of oxo-additive content at about 10.6 MPa and 371% respectively.

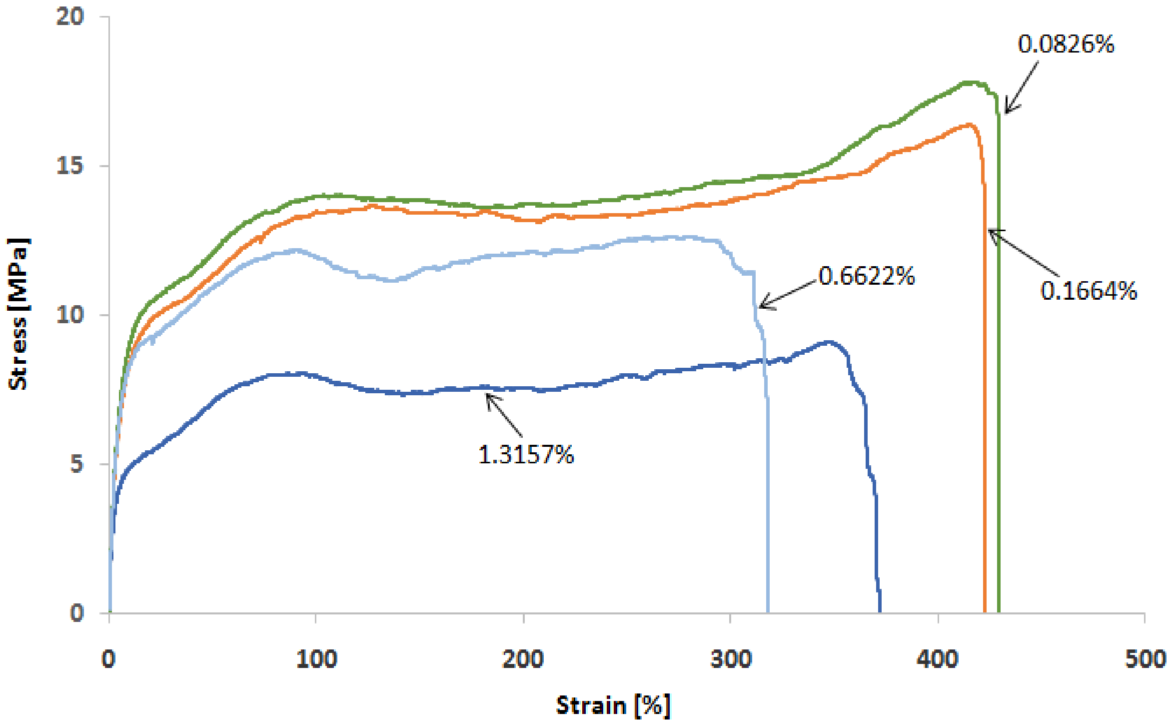


Figure (5.5): Stress-strain diagrams of PE films after three months in the soil media prepared with different amount of oxo-additives.

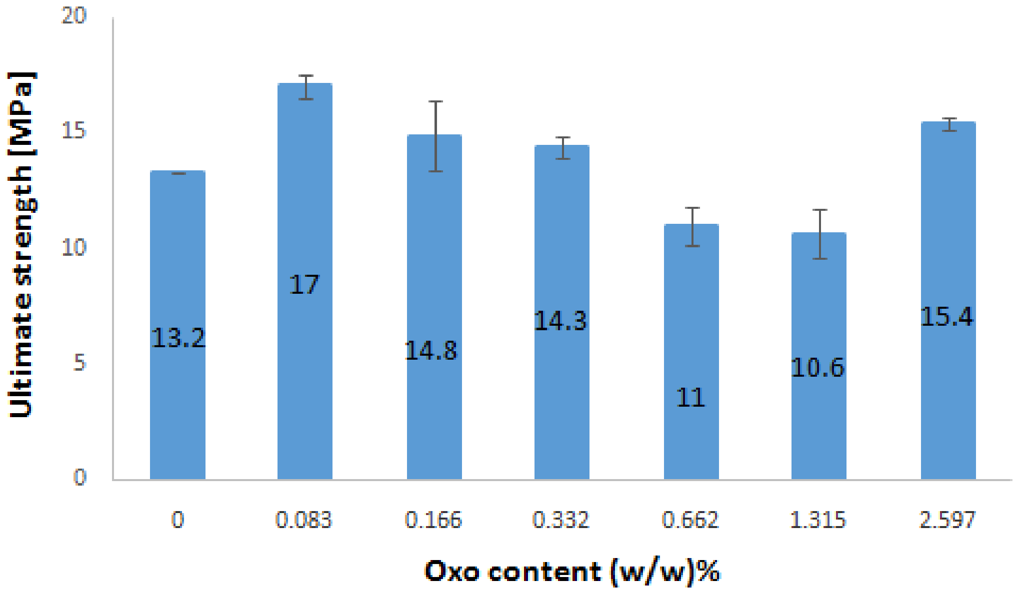


Figure (5.6): Ultimate Ultimate strength of PE films after three months in the soil media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

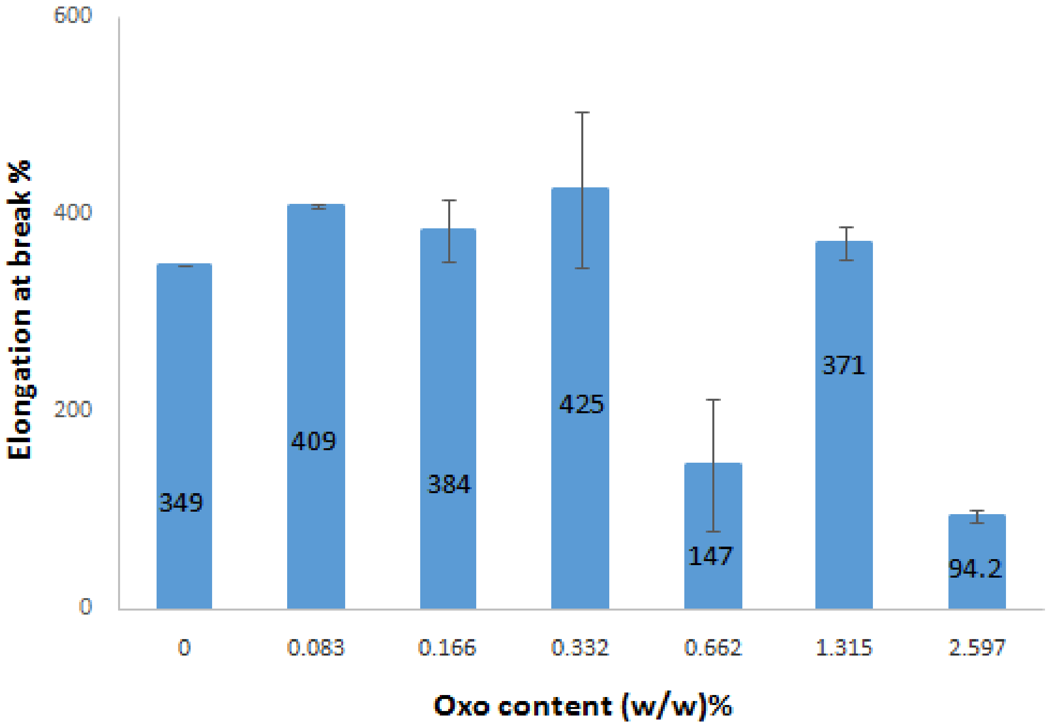


Figure (5.7): Elongation at break of PE films in after three months the soil media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

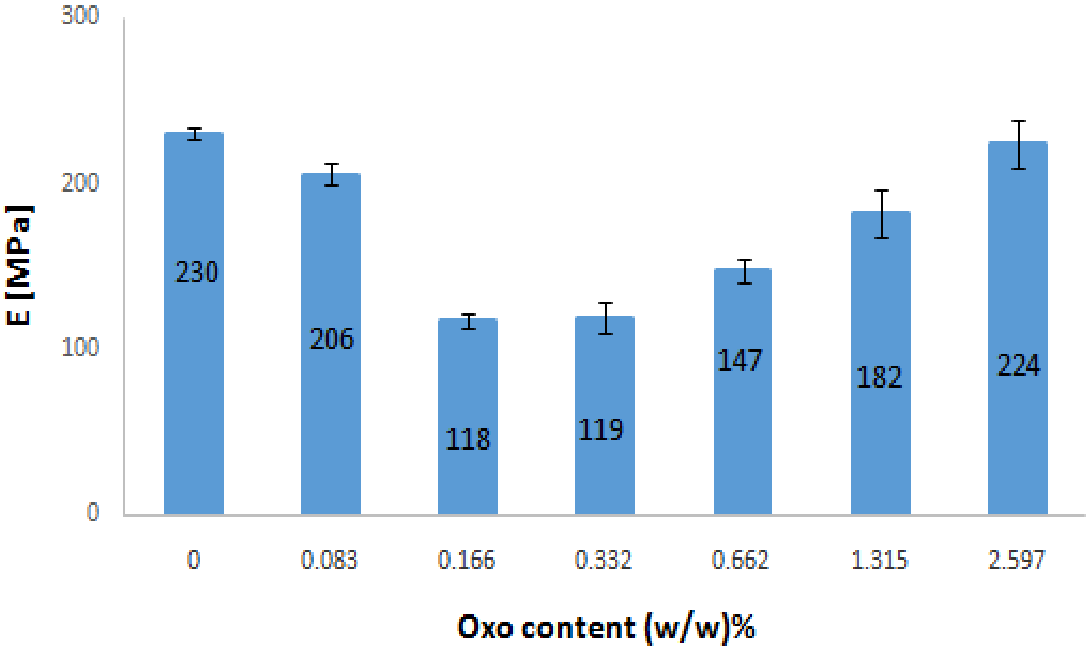


Figure (5.8): Elasticity modulus of PE films after three months in the soil media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

Figure (5.9) shows typical stress-strain dependency curves of PE plastic films after three months in the air media. The maximum strength, elongation values at break and elastic modulus, are shown in figures (5.10), (5.11) and (5.12), respectively. High maximum strength were found in 0.1664% of oxo-additive content in the PE film of approximately 33.5 MPa, elastic modulus of around 221 MPa, and a high elongation at break of 516%. The lowest maximum strength and elongation at break were found in 2.5974% of oxo-additive content at about 16.2 MPa and 369% respectively.

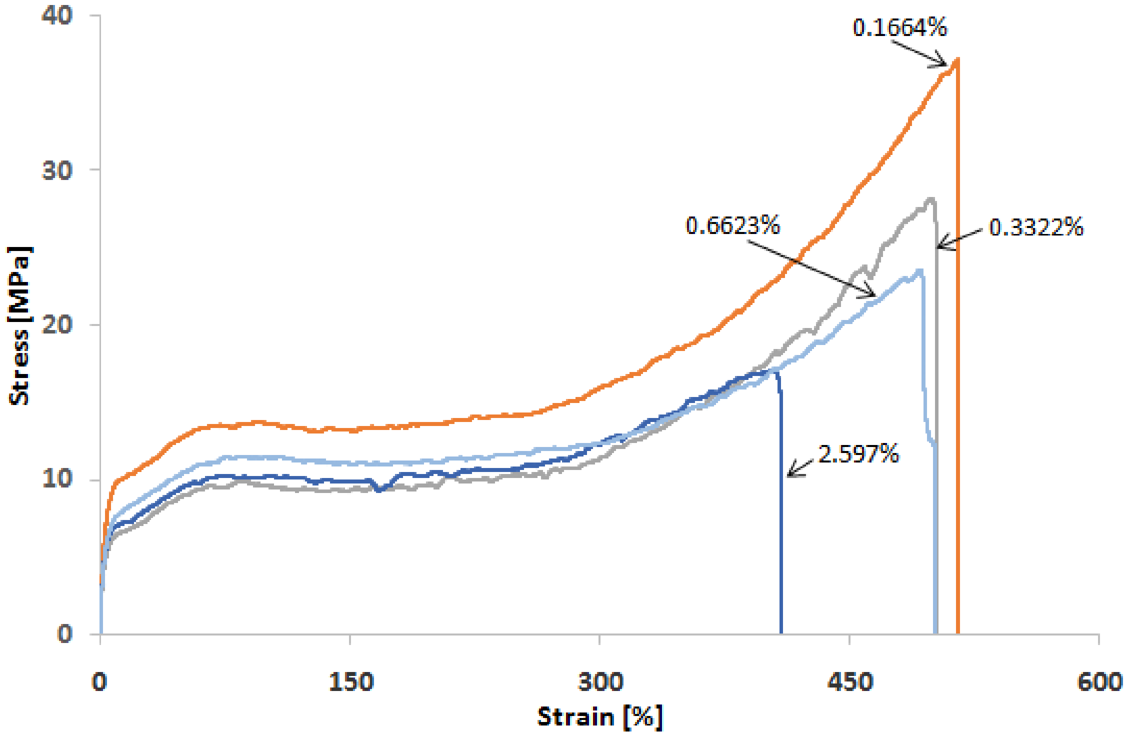


Figure (5.9): Stress-strain diagrams of PE films after three months in the air media prepared with different amount of oxo-additives.

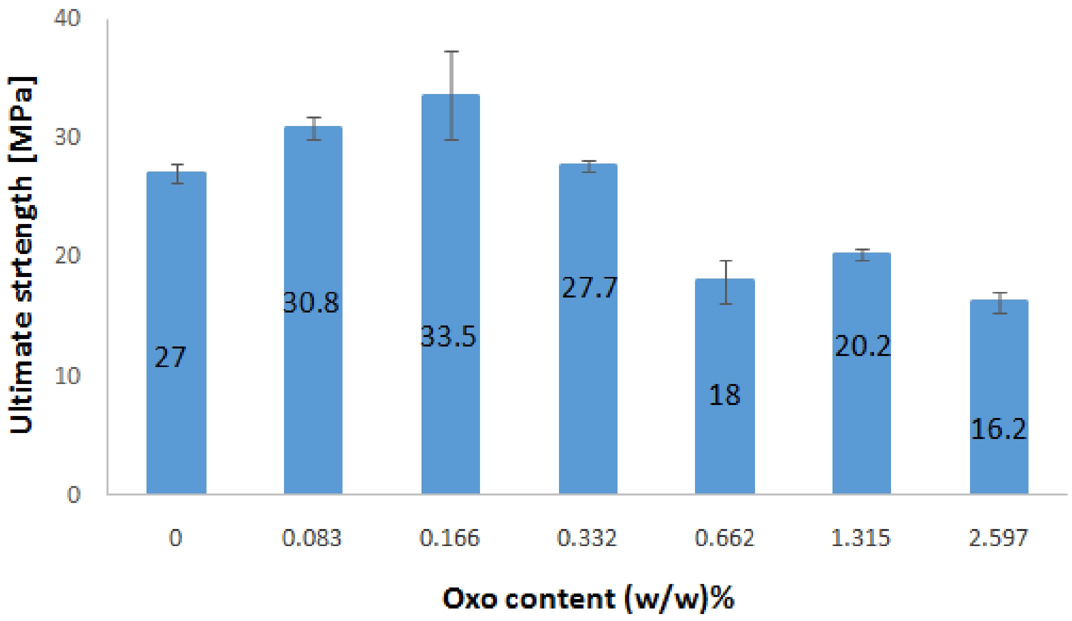


Figure (5.10): Ultimate Ultimate strength of PE films after three months in the air media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

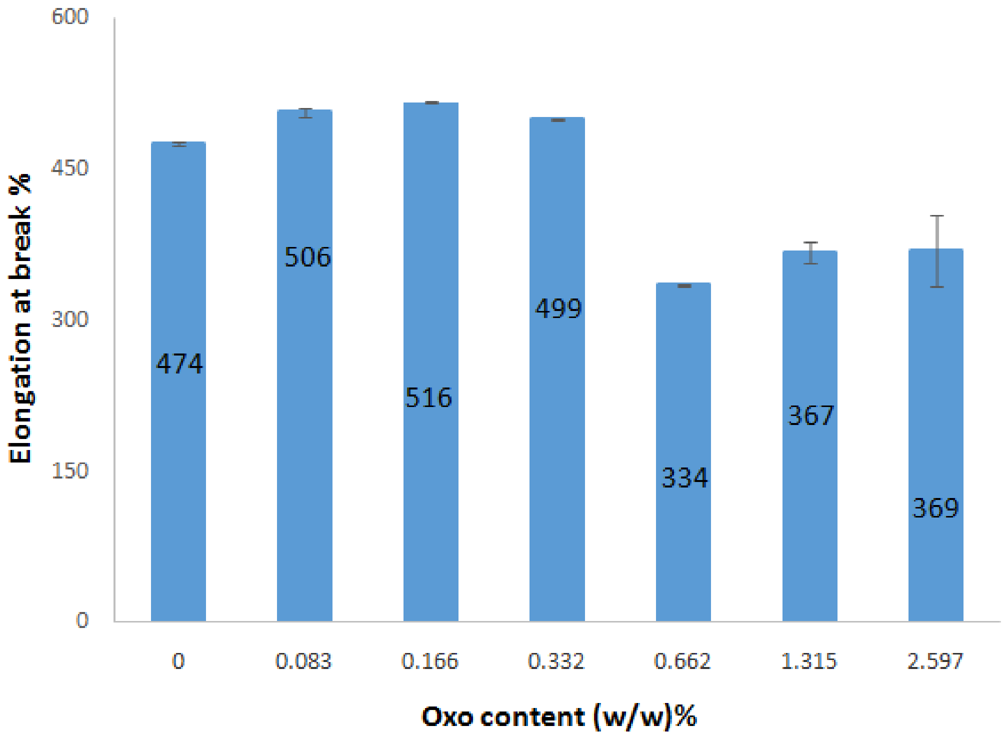


Figure (5.11): Elongation at break of PE films after three months in the air media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

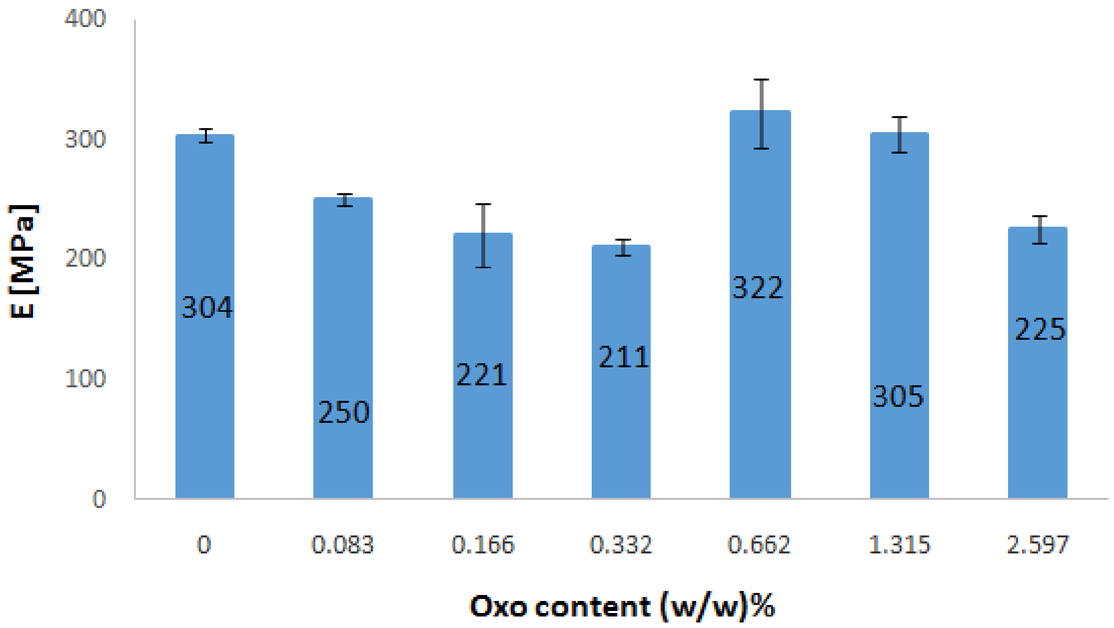


Figure (5.12): Elasticity modulus of PE films in after three months the air media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

Figure (5.13) shows typical stress-strain dependency curves of PE plastic films after five months in the air media. The maximum strength, elongation values at break and elastic modulus, are shown in figures (5.14), (5.15) and (5.16), respectively. High maximum strength were found in 0.0826% of oxo-additive content in the PE film of approximately 19.2 MPa, elastic modulus of around 399 MPa, and a high elongation at break of 276%. The lowest maximum strength and elongation at break were found in 2.5974% of oxo-additive content at about 12.6 MPa and 371% respectively.

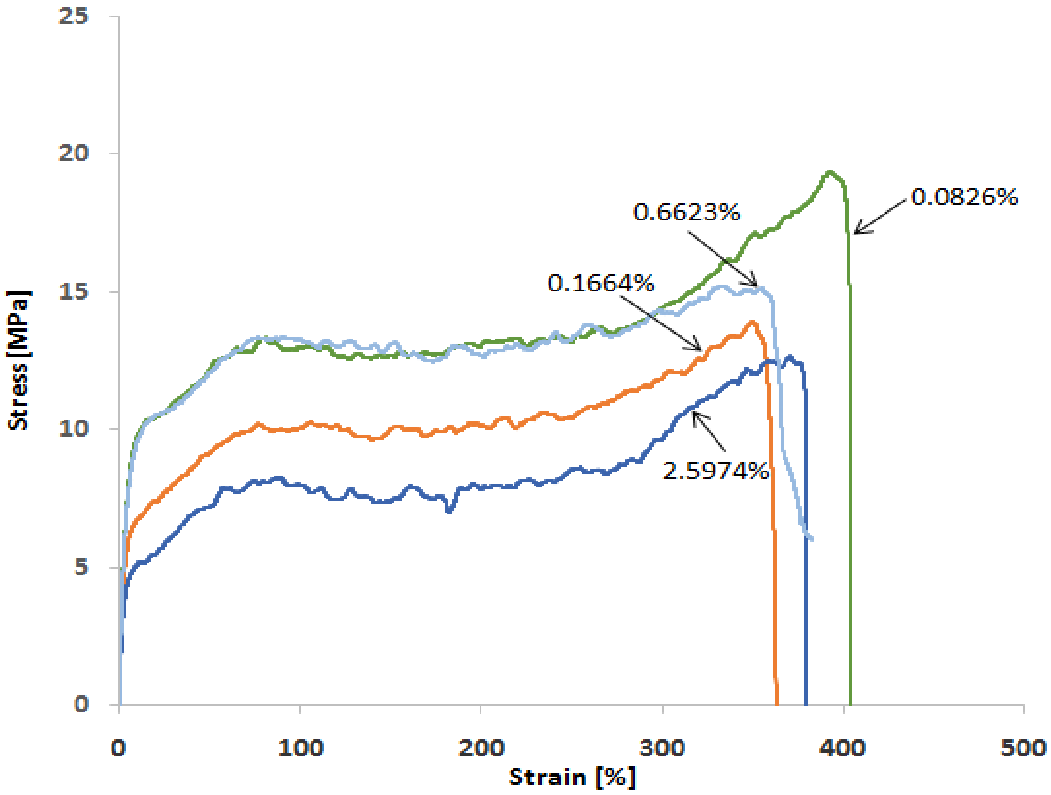


Figure (5.9): Stress-strain diagrams of PE films after five months in the air media prepared with different amount of oxo-additives.

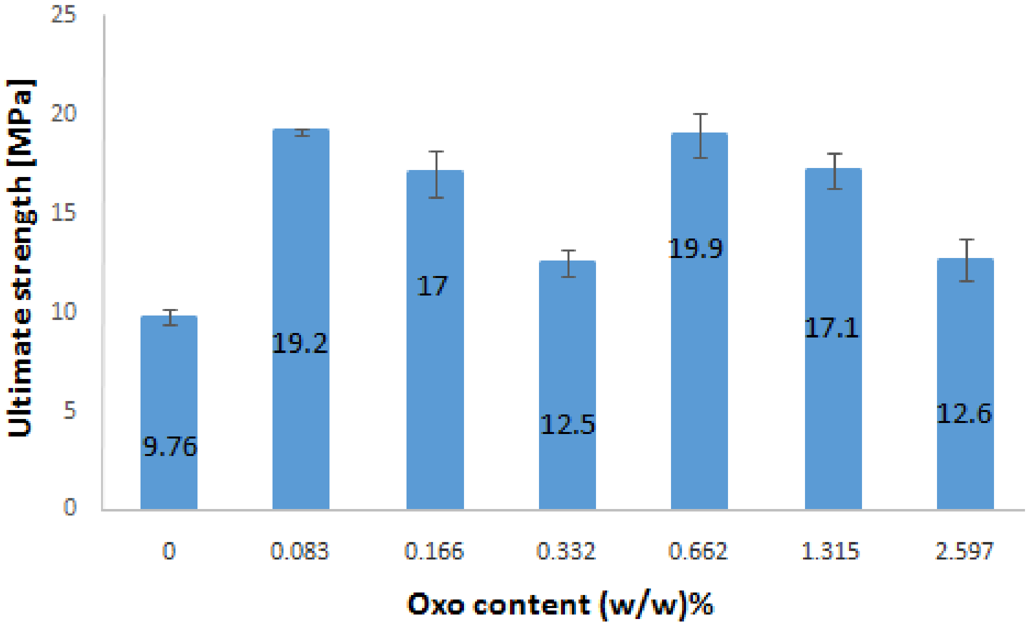


Figure (5.14): Ultimate Ultimate strength of PE films after five months in the air media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

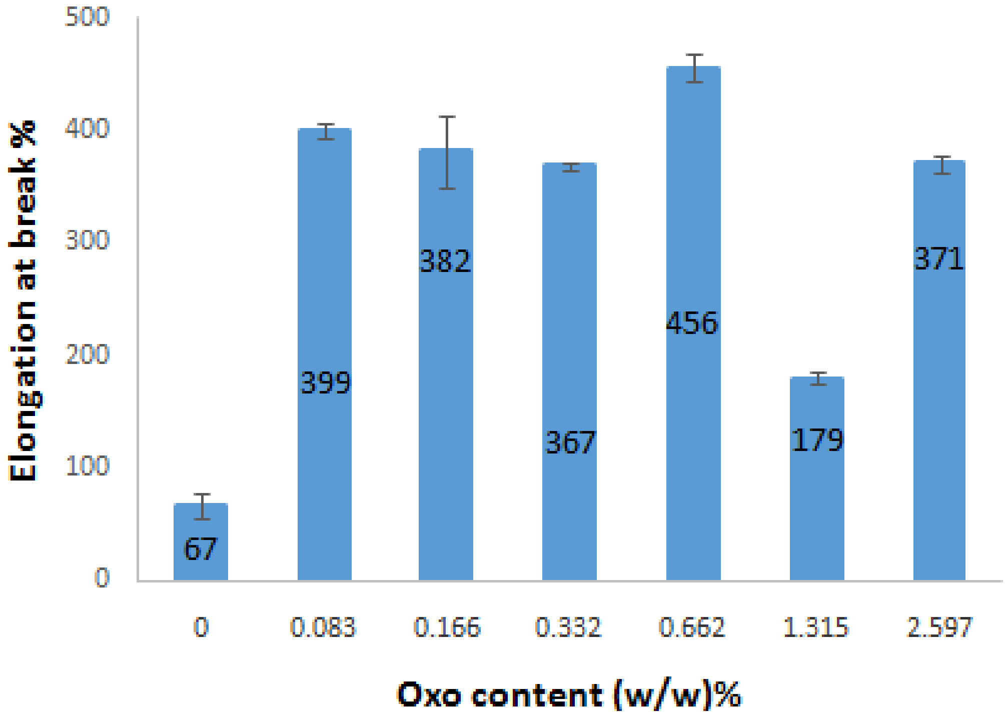


Figure (5.15): Elongation at break of PE films after five months in the air media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

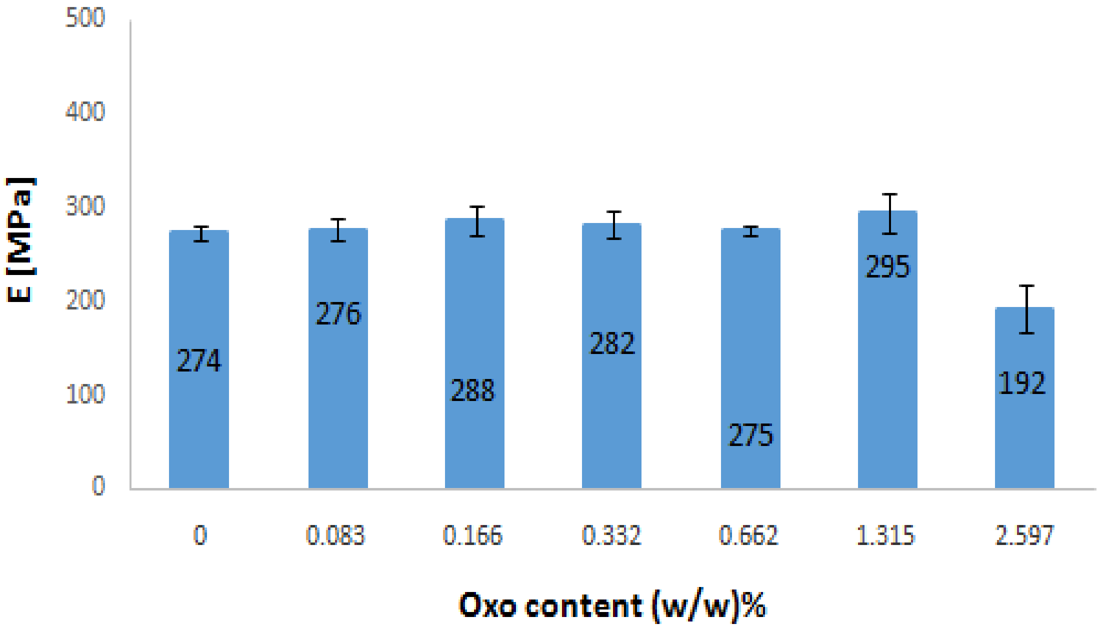


Figure (5.16): Elasticity modulus of PE films in after five months the air media prepared with different amounts of oxo-additives. The initial oxo-additive content was 0.0833% w/w in packaging films.

The results show that the oxo-additive content plays an important role in plastic degradation process, it fits a directly proportional relation with the degradation, and also it affects the mechanical properties of plastic packaging films, such as tensile strength, elongation at break and modulus of elasticity, the increased addition of the oxo-additive decreased the values of the tensile strength and elastic modulus, and a slightly decreasing in the values of elongation at break. The films also became weaker than before, this indicates a possible degradation of PE will occur. The low density polyethylene films which prepared with air have the highest maximum tensile strength of 33.5 MPa, elastic modulus of around 221 MPa, and a high elongation at break of 516%. films which prepared with soil have the medium tensile stress of 17 MPa, the lowest elongation at break of about 147% and a medium elasticity around 182 MPa between the three media. The lowest tensile strength, elastic modulus are found for the films which prepared in the marlstone media of about 10 MPa, 117 MPa respectively. And a medium elongation at break could be up to 391%.

5.2.2 Effect of Media on Packaging Films

Figure (5.17), (5.18), (5.19) and (5.20) shows typical stress-strain dependency curves of PE plastic films with different amount of oxo-additives content after three months in different media respectively. For 2.5974% of oxo-additive content, the high maximum strength were found in air media of approximately 16.2 MPa and an elongation at break of 369%. The lowest maximum strength and elongation at break were found in marlstone media at about 9.14 MPa and 276% as shown in figure (5.17).

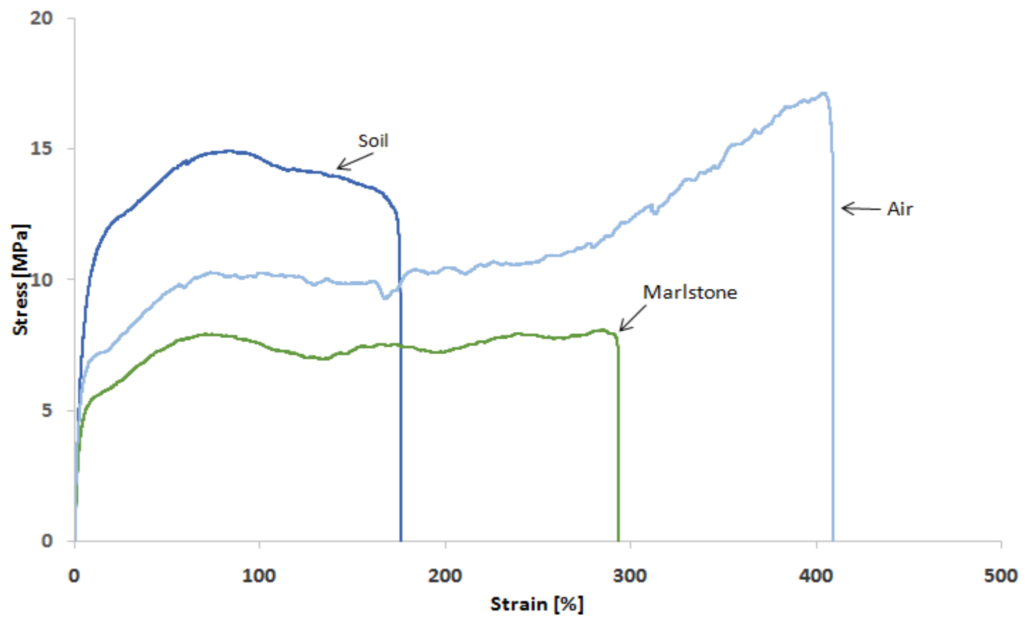


Figure (5.17): Stress-strain diagrams of PE films with 2.5974% of oxo-additive content after three months in the different media.

For 0.6623% of oxo-additive content, the high maximum strength were found in air media of approximately 18 MPa and an elongation at break of 334%. The lowest maximum strength and elongation at break were found in marlstone media at about 11.3 MPa and 391% as shown in figure (5.18).

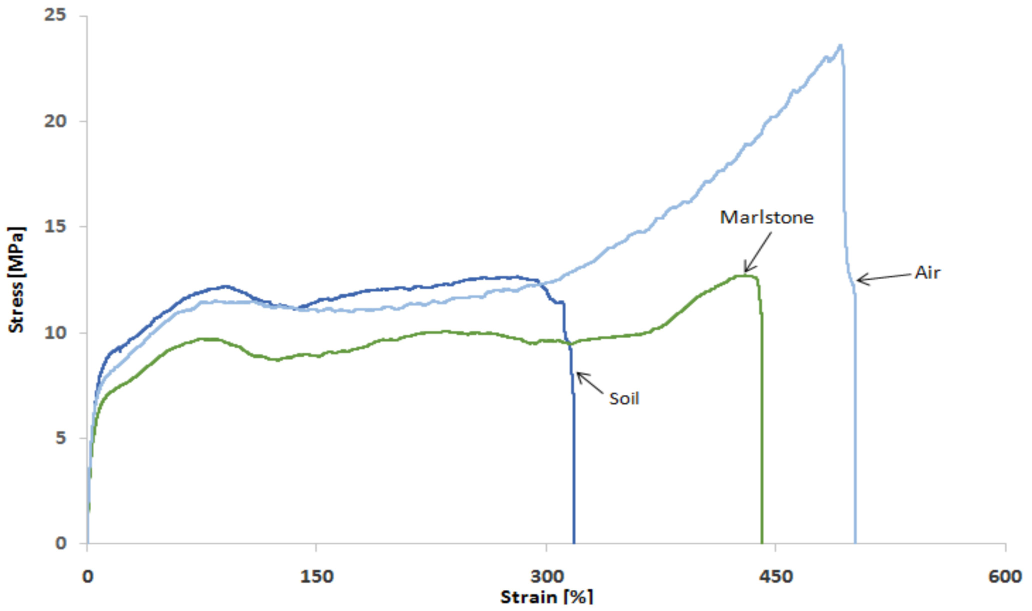


Figure (5.18): Stress-strain diagrams of PE films with 0.6623% of oxo-additive content after three months in the different media.

For 0.1164% of oxo-additive content, the high maximum strength were found in air media of approximately 18 MPa and an elongation at break of 334%. The lowest maximum strength and elongation at break were found in marlstone media at about 11.3 MPa and 391% as shown in figure (5.19).

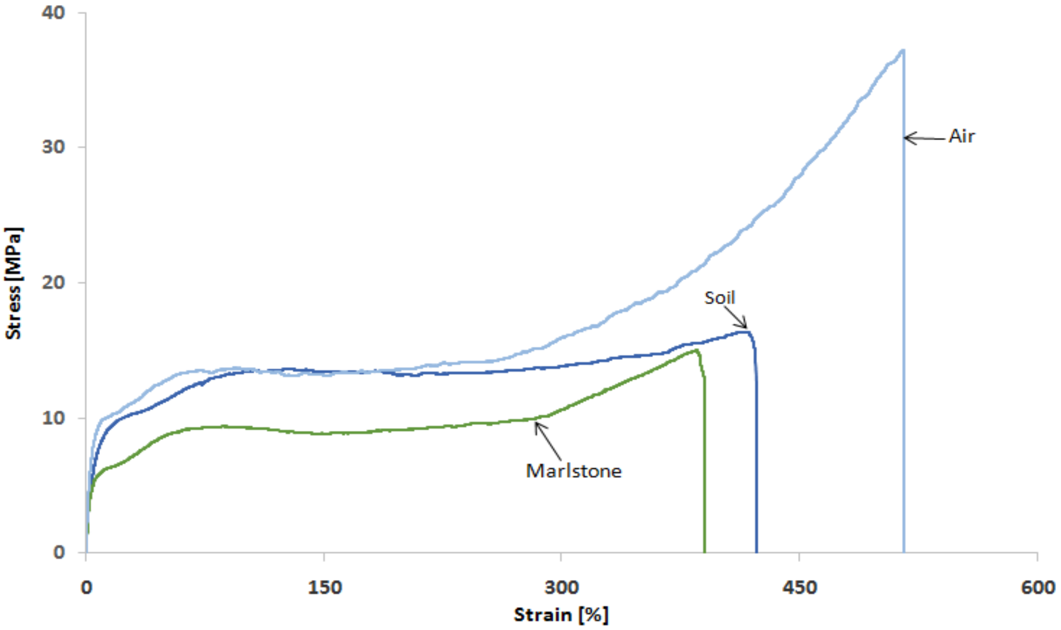


Figure (5.19): Stress-strain diagrams of PE films with 0.1664% of oxo-additive content after three months in the different media.

For Neat PE, the high maximum strength were found in air media of approximately 27 MPa and an elongation at break of 474%. The lowest maximum strength and elongation at break were found in soil media at about 13.2 MPa and 349% as shown in figure (5.20).

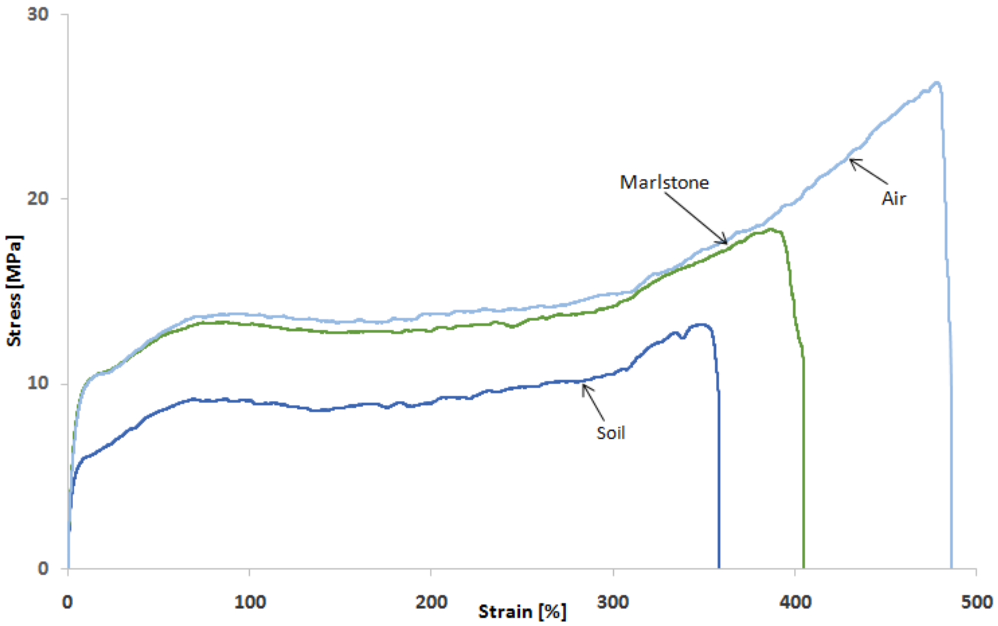


Figure (5.20): Stress-strain diagrams of neat PE films after three months in the different media.

When comparing the mechanical behavior of LDPE films with different oxo-additive for the three different media, one can see clearly that most of changes in mechanical properties occur in the marlstone media with a very low stress, strain and elasticity. Similar trends were given for the samples in the air media, such as a convergence in the elongation at break and elastic modulus, but with a high tensile strength value. Besides this, mechanical properties of samples which cultivated in soil media are not affected significantly. Changes in mechanical properties of plastic films in marlstone indicates a low interaction between the polymers and so a potential degradation of LDPE occur, followed by air and soil media respectively. The reason behind this may because of the marl content and structure. Although it should be noted that the preparation method of packaging films is depend on the different in w/w percentage of oxo-additive content. Oxo-additives are rather important for the degradation of the polymer. The results obtained so far clearly demonstrate that the oxo-additive can be effectively used to influence the mechanical properties of the PE packaging films.

5.3 Thermogravimetric Analysis (TGA) Test Results

5.3.1 Effect of Oxo-Additives Content on Packaging Films

Figure (5.21), (5.22), (5.23), (5.24), (5.25), (5.26), (5.27), (5.28), (5.29), (5.30), (5.31) and (5.32) shows the amount of weight change in the mass of a sample as a function of temperature for PE plastic films with different amount of oxo-additives content after three months in different media.

For neat PE plastic films in marlstone media, the sample start to decompose rapidly at about 420 ºC and finished at 500 ºC. The majority of the mass was lost at (420-480) ºC, where the sample lost 92.38% of its original mass as shown in figure (5.21). In soil media, it's clear that the neat PE plastic film start to decompose at 450 ºC to 500 ºC and the mass was lost at (450-490) ºC, where the sample lost 95.36% of its original mass as shown in figure (5.22). In air media, the decomposition start at 420 ºC and finished at 500 ºC and the mass was lost at (420-480) ºC, where the sample lost 98.51% of its original mass as shown in figure (5.23).

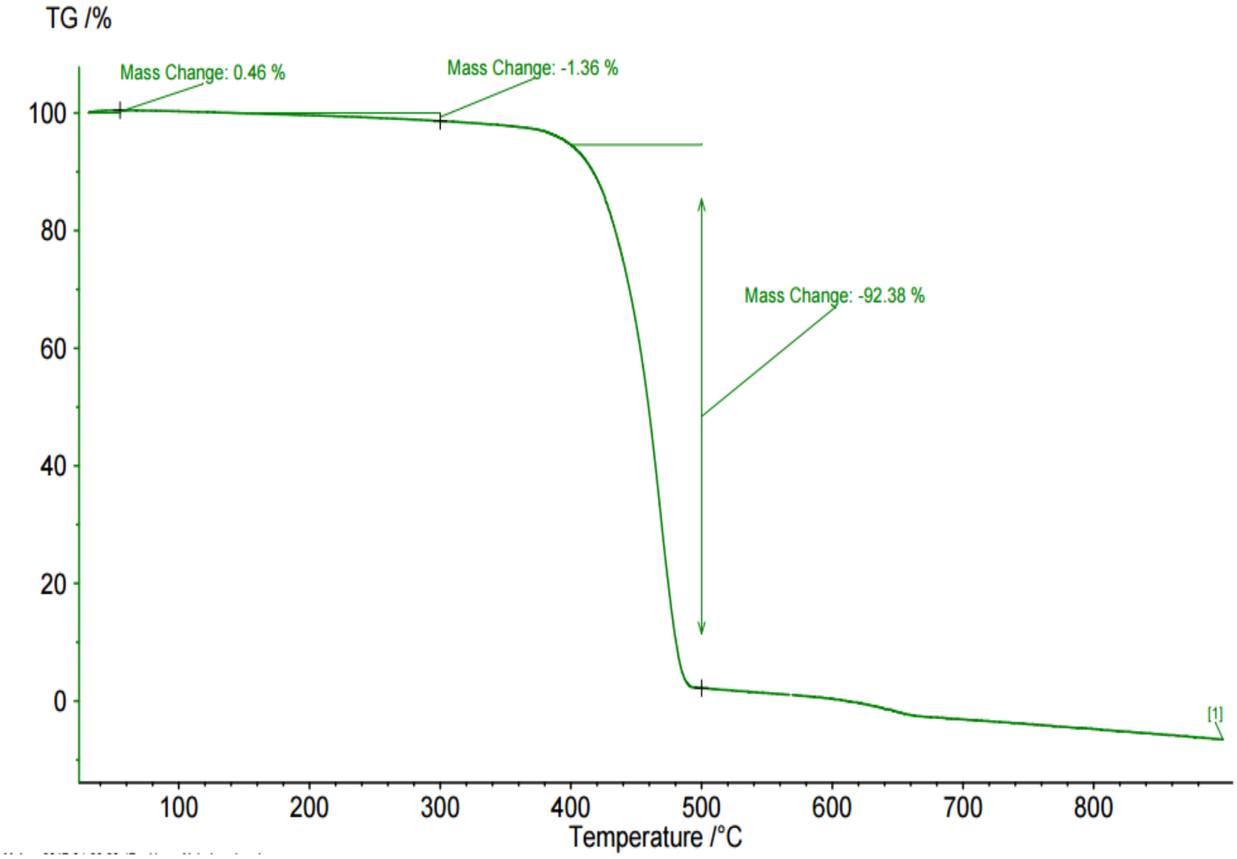


Figure (5.21): TGA curve for decomposition of neat PE films after three months in marlstone media.

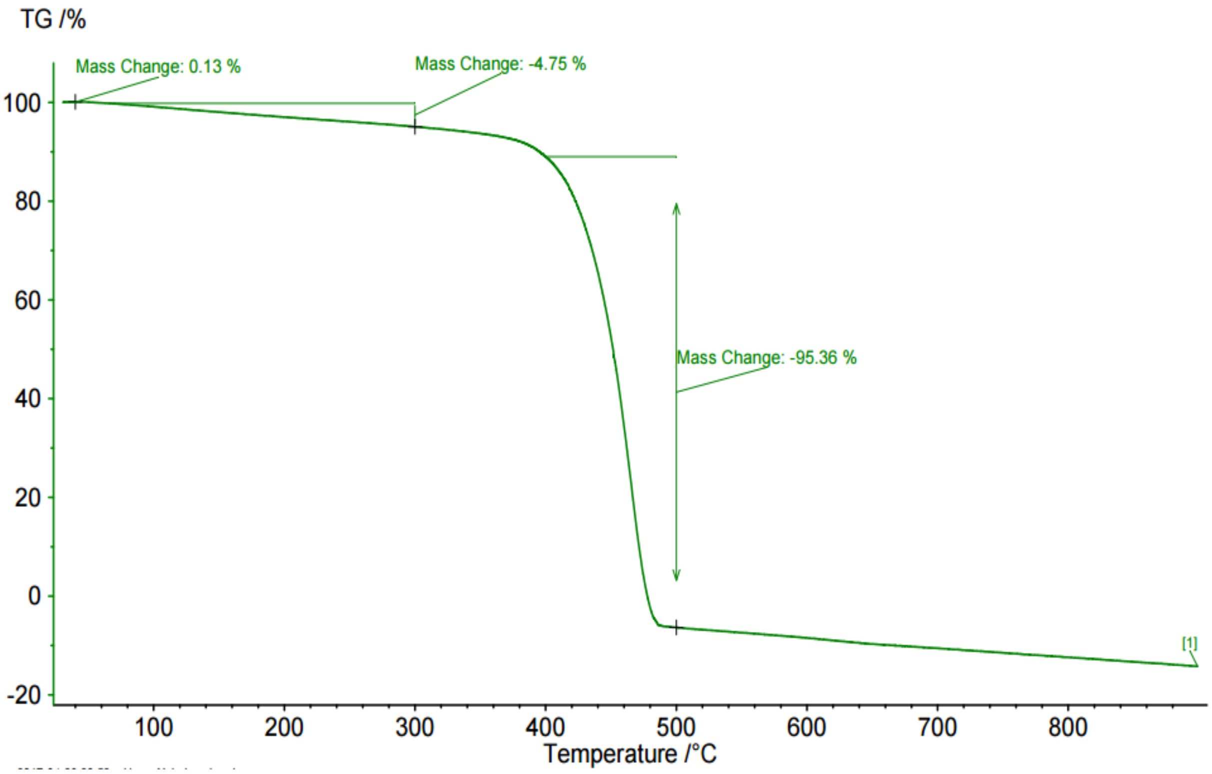


Figure (5.22): TGA curve for decomposition of neat PE films after three months in soil media.

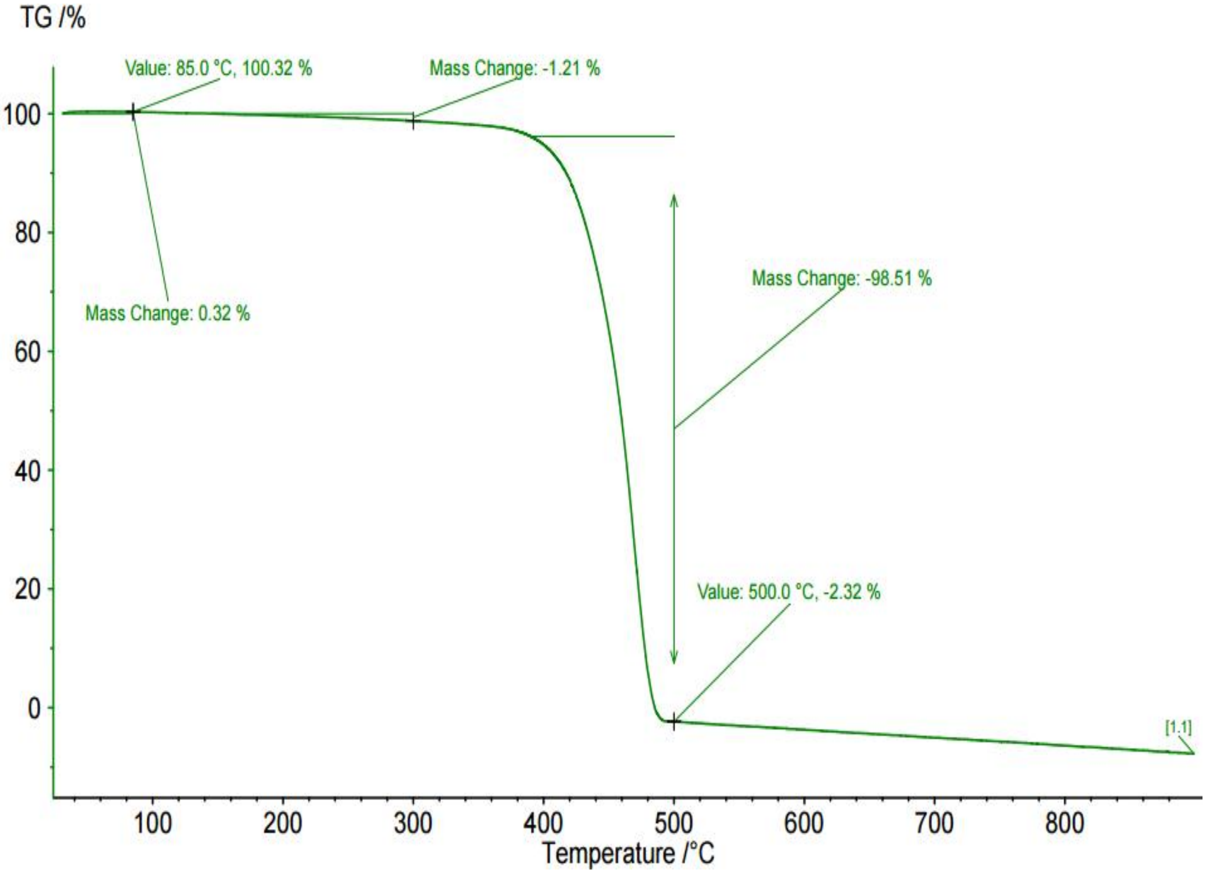


Figure (5.23): TGA curve for decomposition of neat PE films after five months in air media.

For PE packaging films with 0.1664% of oxo-additive content in marlstone media, the sample start to decompose rapidly at about 420 °C and finished at 500 °C. The majority of the mass was lost at (420-480) °C, where the sample lost 94.29% of its original mass as shown in figure (5.24). In soil media, it's clear that the PE plastic film start to decompose at 400 °C to 500 °C and the mass was lost at (420-486) °C, where the sample lost 93.95% of its original mass as shown in figure (5.25). In air media, the decomposition start at 420 °C and finished at 500 °C and the mass was lost at (420-500) °C, where the sample lost 93.44% of its original mass as shown in figure (5.26).

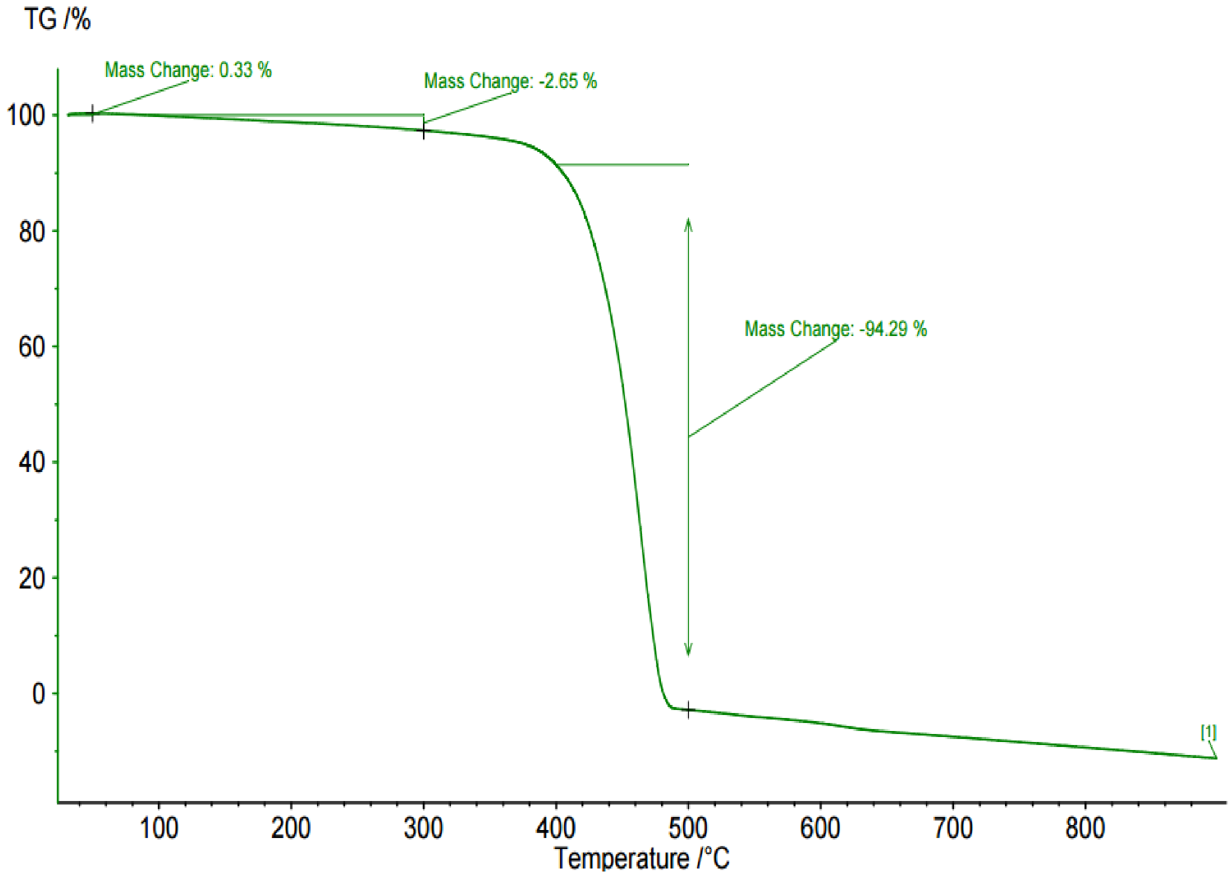


Figure (5.24): TGA curve for decomposition of PE films with 0.1664% of oxo-additive content after three months in marlstone media.

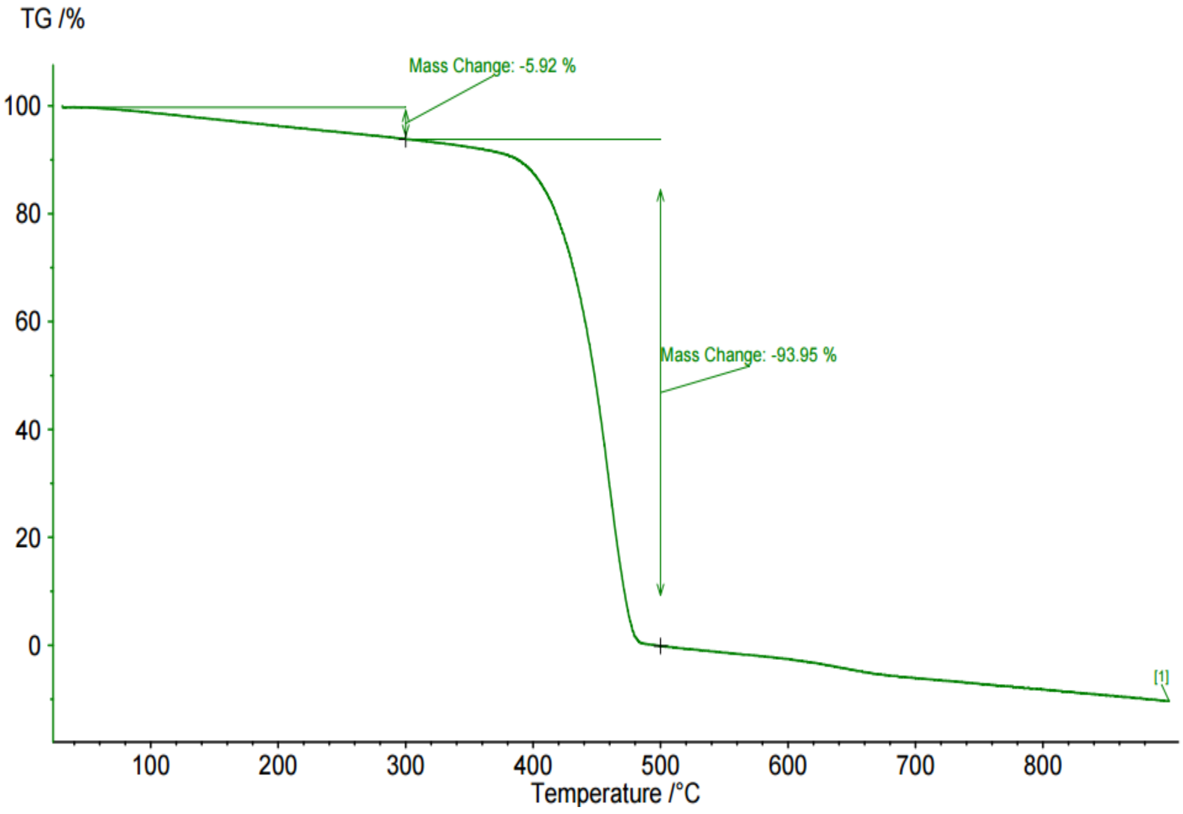


Figure (5.25): TGA curve for decomposition of PE films with 0.1664% of oxo-additive content after three months in soil media.

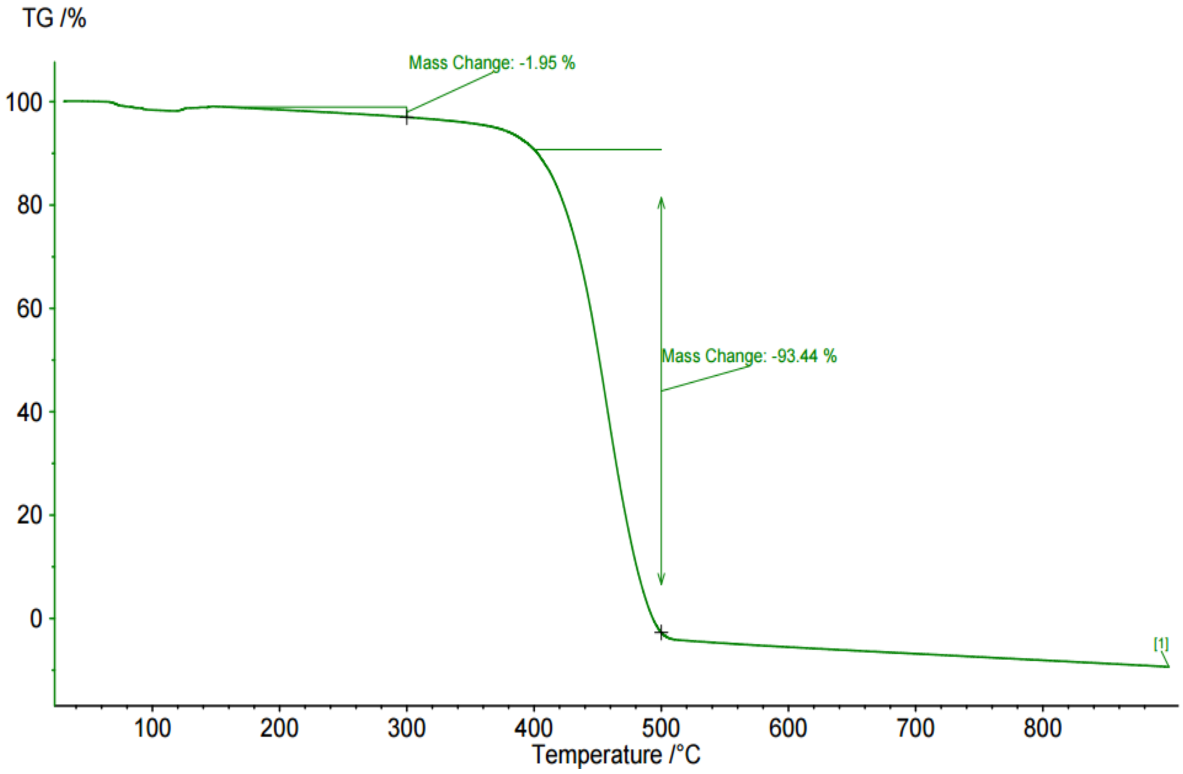


Figure (5.26): TGA curve for decomposition of PE films with 0.1664% of oxo-additive content after five months in air media.

For PE packaging films with 0.6623% of oxo-additive content in marlstone media, the sample start to decompose rapidly at about 430 °C and finished at 500 °C. The majority of the mass was lost at (430-480) °C, where the sample lost 92.60% of its original mass as shown in figure (5.27). In soil media, it's clear that the PE plastic film start to decompose at 410 °C to 500 °C and the mass was lost at (410-480) °C, where the sample lost 92.77% of its original mass as shown in figure (5.28). In air media, the decomposition start at 420 °C and finished at 500 °C and the mass was lost at (420-480) °C, where the sample lost 96.81% of its original mass as shown in figure (5.29).

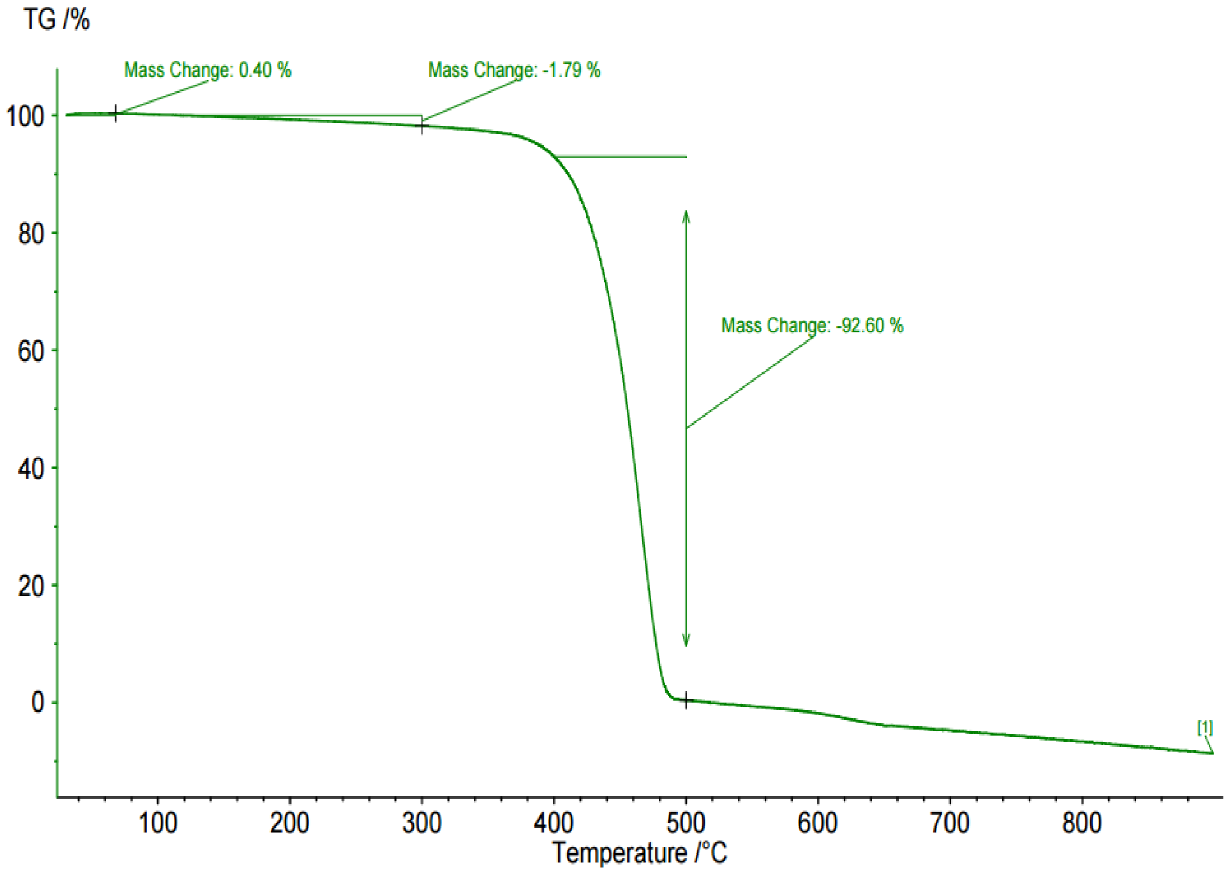


Figure (5.27): TGA curve for decomposition of PE films with 0.6623% of oxo-additive content after three months in marlstone media.

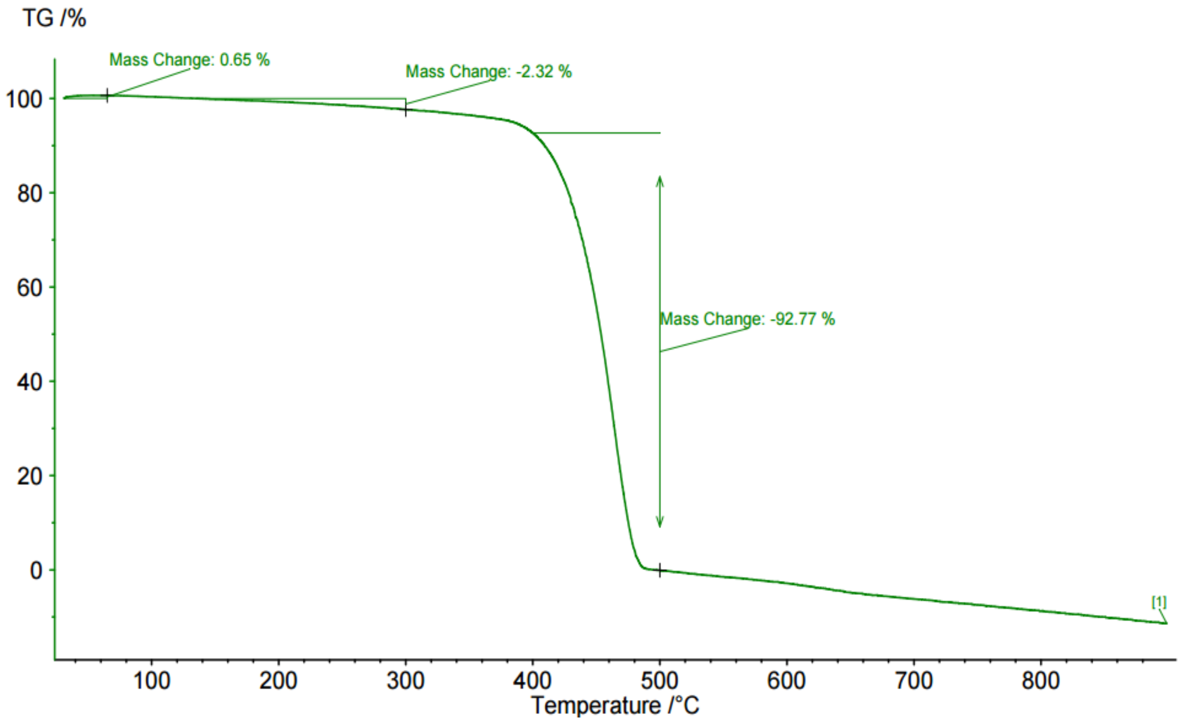


Figure (5.28): TGA curve for decomposition of PE films with 0.6623% of oxo-additive content after three months in soil media.

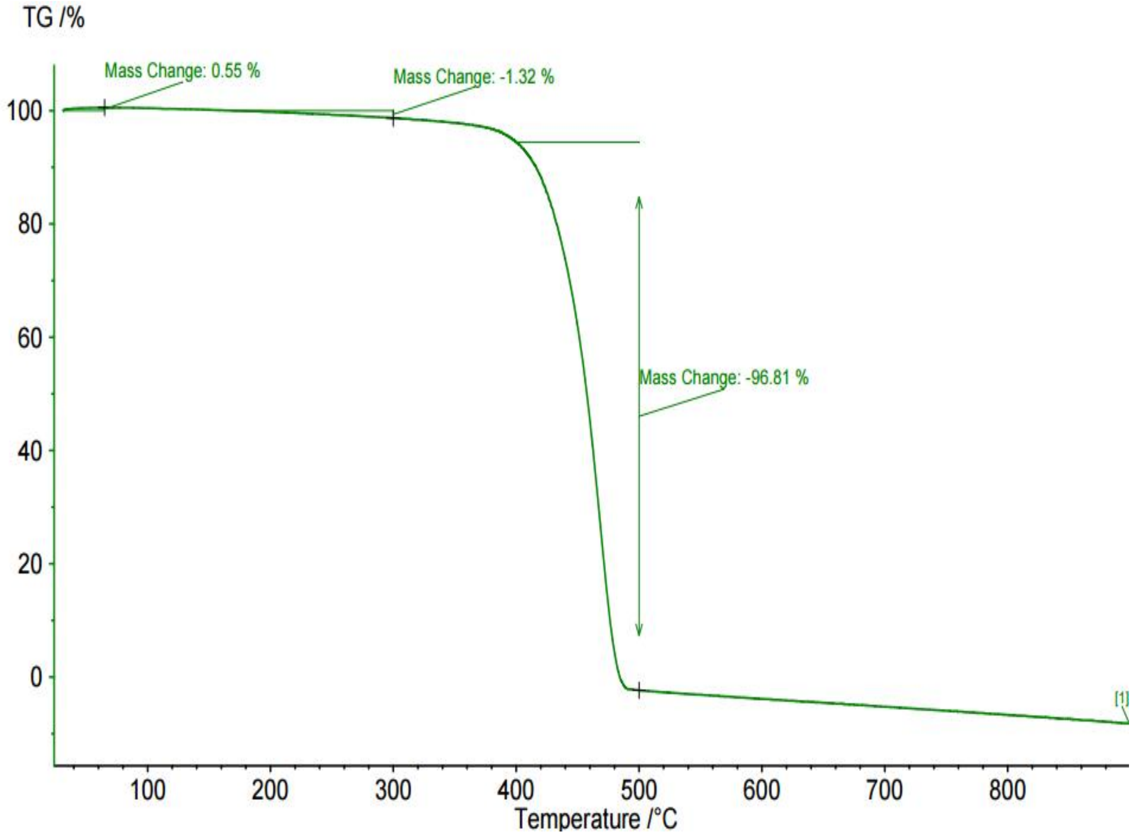


Figure (5.29): TGA curve for decomposition of PE films with 0.6623% of oxo-additive content after five months in air media.

For PE packaging films with 2.5974% of oxo-additive content in marlstone media, the sample start to decompose rapidly at about 420 ºC and finished at 500 ºC. The majority of the mass was lost at (420-487) ºC, where the sample lost 98.38% of its original mass as shown in figure (5.30). In soil media, it's clear that the PE plastic film start to decompose at 410 ºC to 500 ºC and the mass was lost at (410-480) ºC, where the sample lost 95.43% of its original mass as shown in figure (5.31). In air media, the decomposition start at 420 ºC and finished at 500 ºC and the mass was lost at (420-480) ºC, where the sample lost 97.80% of its original mass as shown in figure (5.32).

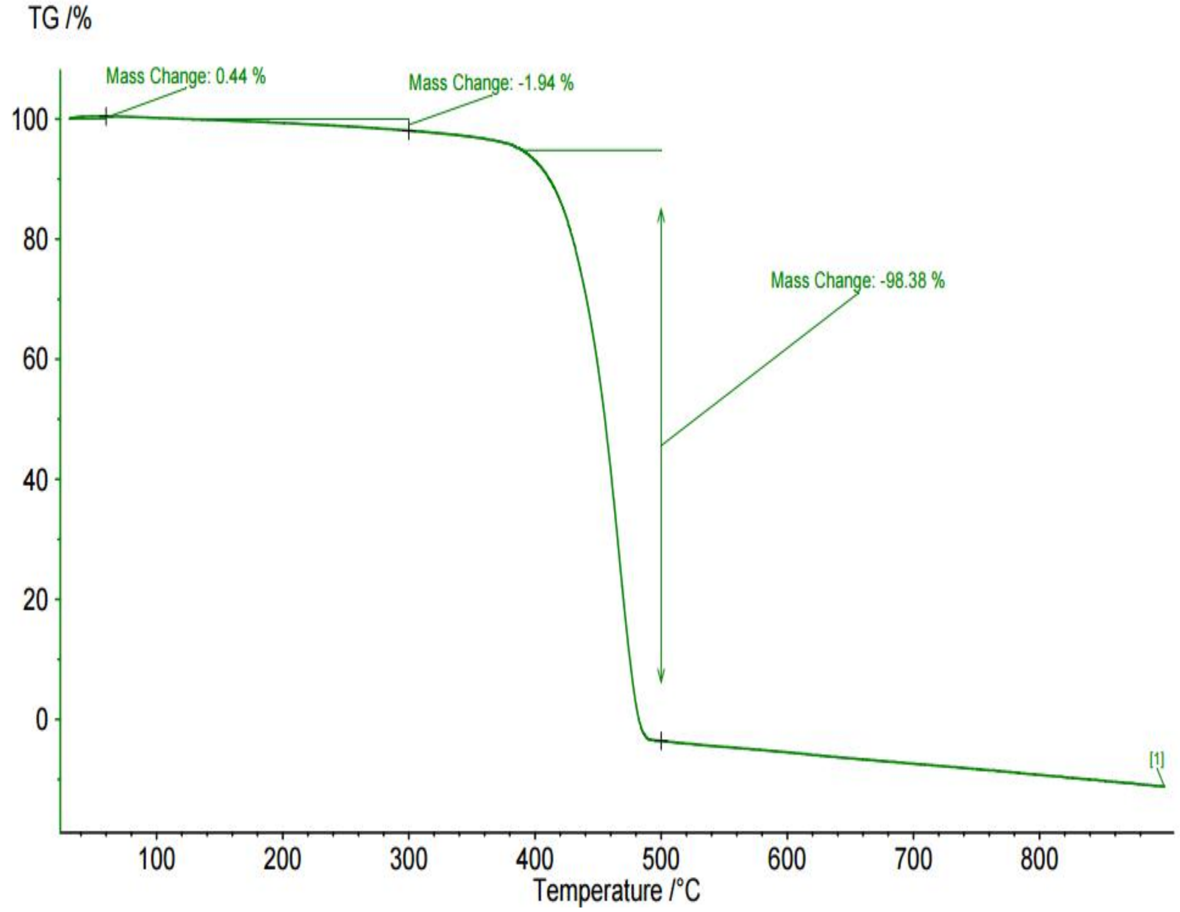


Figure (5.30): TGA curve for decomposition of PE films with 2.5974% of oxo-additive content after three months in marlstone media.

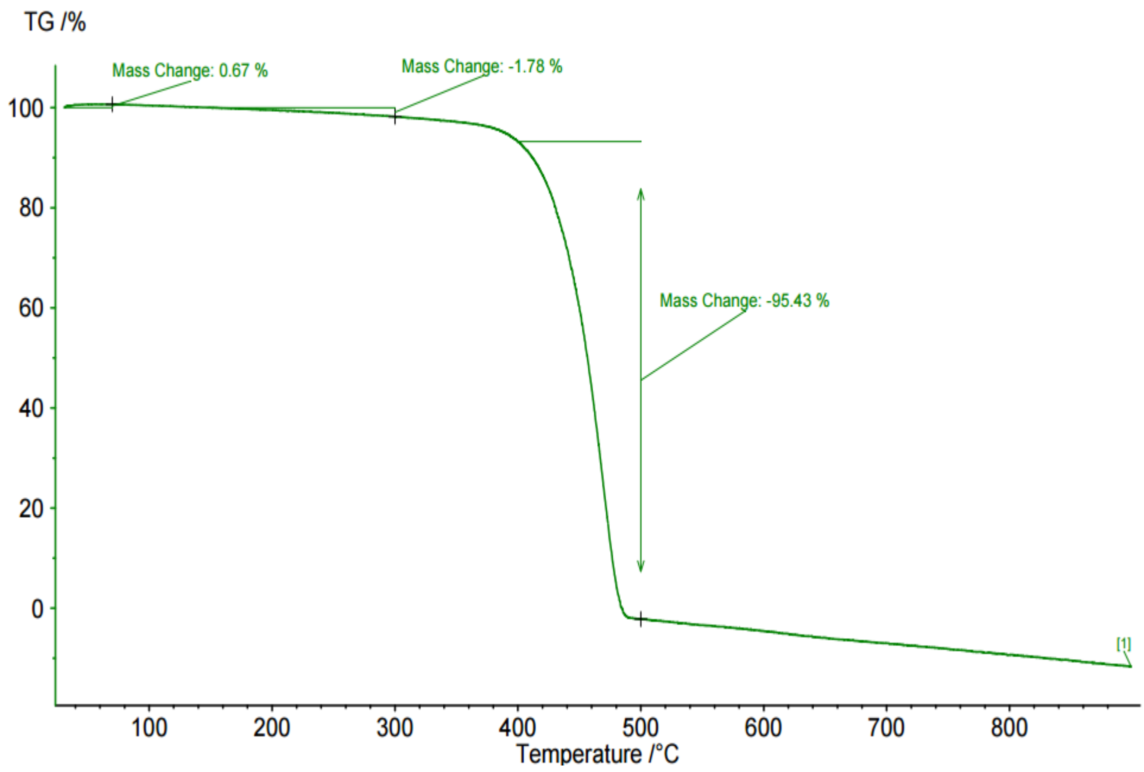


Figure (5.31): TGA curve for decomposition of PE films with 2.5974% of oxo-additive content after three months in soil media.

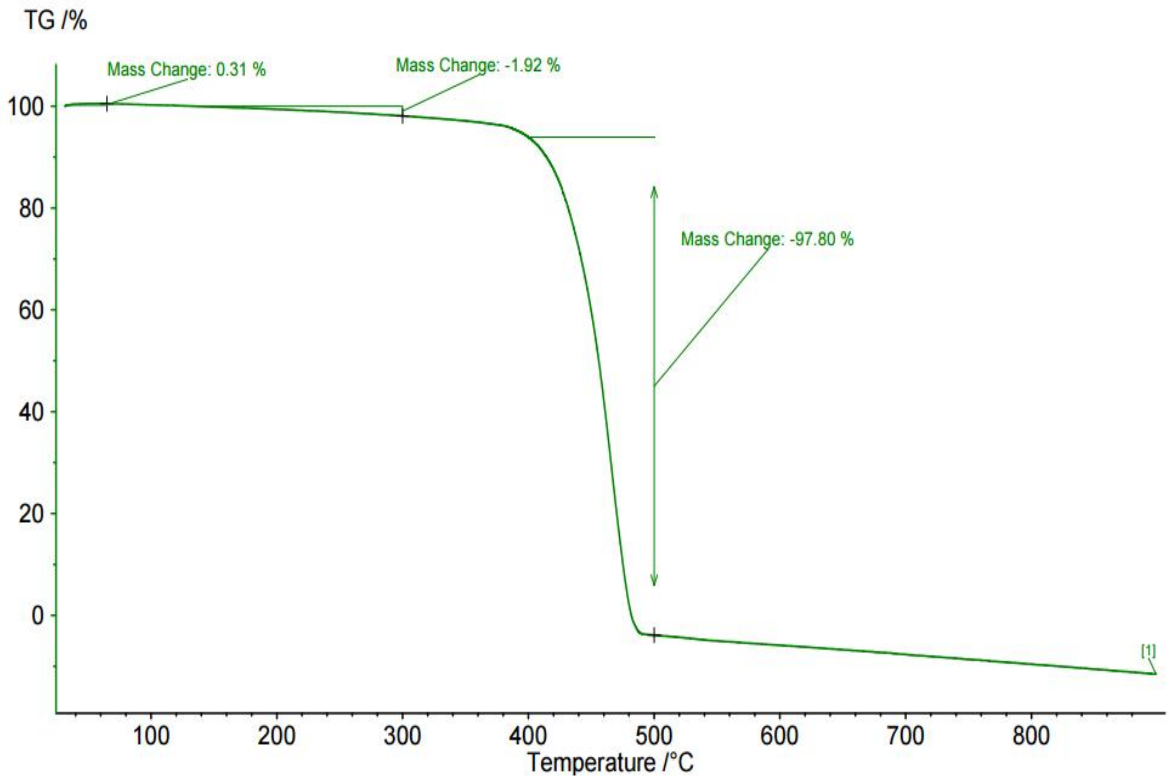


Figure (5.32): TGA curve for decomposition of PE films with 2.5974% of oxo-additive content after five months in air media.

The results show that the all samples have the same decomposition temperature about (420-480) ºC and the same finishing temperature at 500 ºC because they have the same components. The highest decomposition rate was found in the neat PE sample in air which lost 98.5% from original mass and then the sample with 2.5974% of oxo-additive content in marlstone which lost from original mass 98.3% as shown in table (5.1) and figure (5.33), (5.34) and (5.35).

Table (5.1): The decomposition rate based on oxo-additive content and media.

Oxo-Additive Content / **Media**	**Neat PE**	**0.1664% Oxo-Additive Content**	**0.6623% Oxo-Additive Content**	**2.5974% Oxo-Additive Content**
Soil Media	95.36%	93.95%	92.77%	95.43%
Marlstone Media	92.38%	94.92%	92.6%	98.38%
Air Media	98.51%	93.44%	96.81%	97.8%

The difference of the highest decomposition rate between neat PE and 2.5974% of oxo-additive content in air media was very small as shown in figure (5.33).

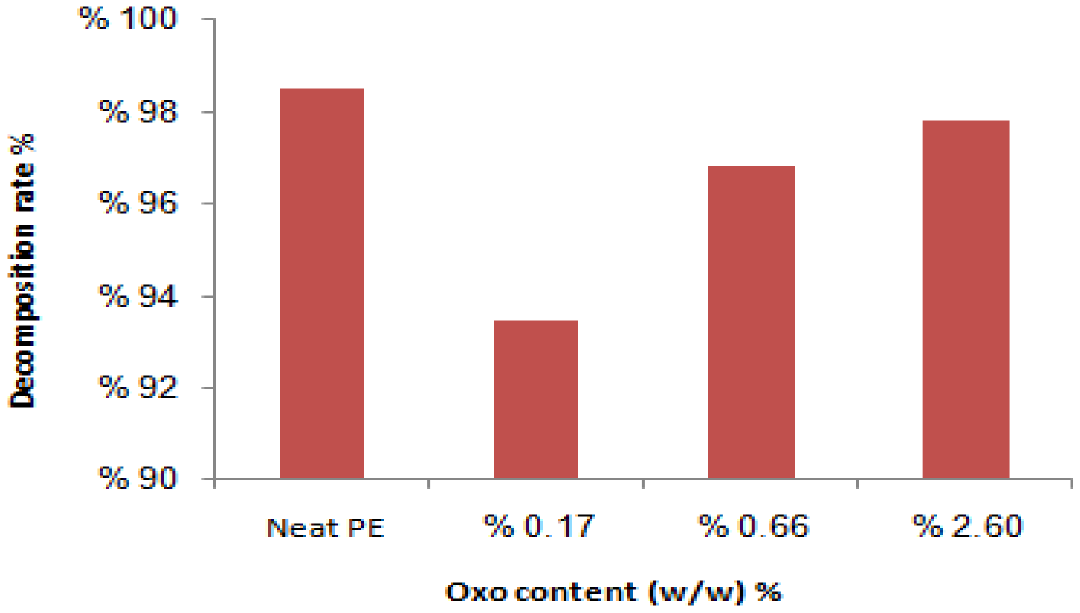


Figure (5.33): Effect of oxo-additives content on decomposition rate in air media.

The sample with 2.5974% of oxo-additive content have the highest decomposition rate in marlstone and soil media. See figure (5.34) and (5.35).

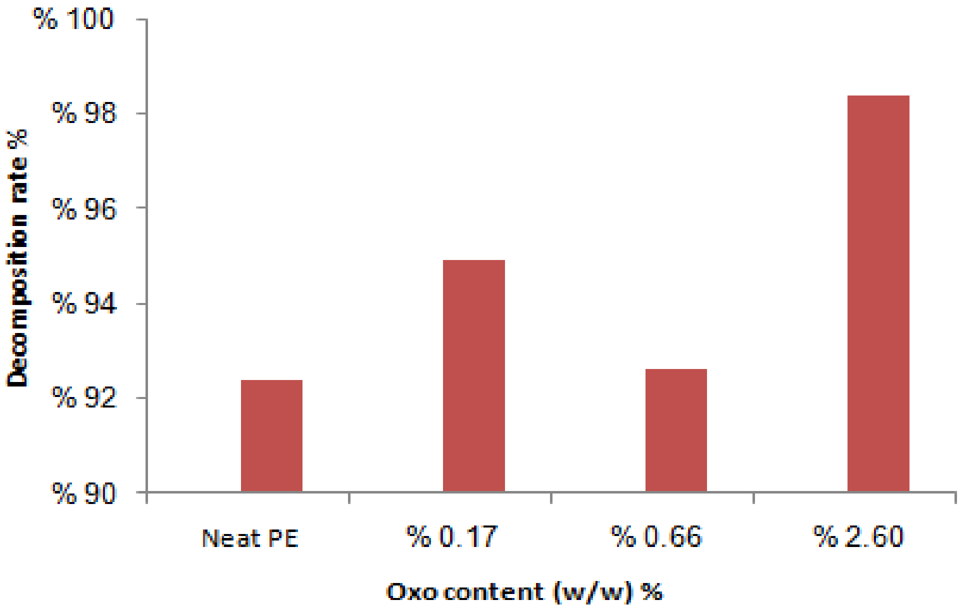


Figure (5.34): Effect of oxo-additives content on decomposition rate in marlstone media.

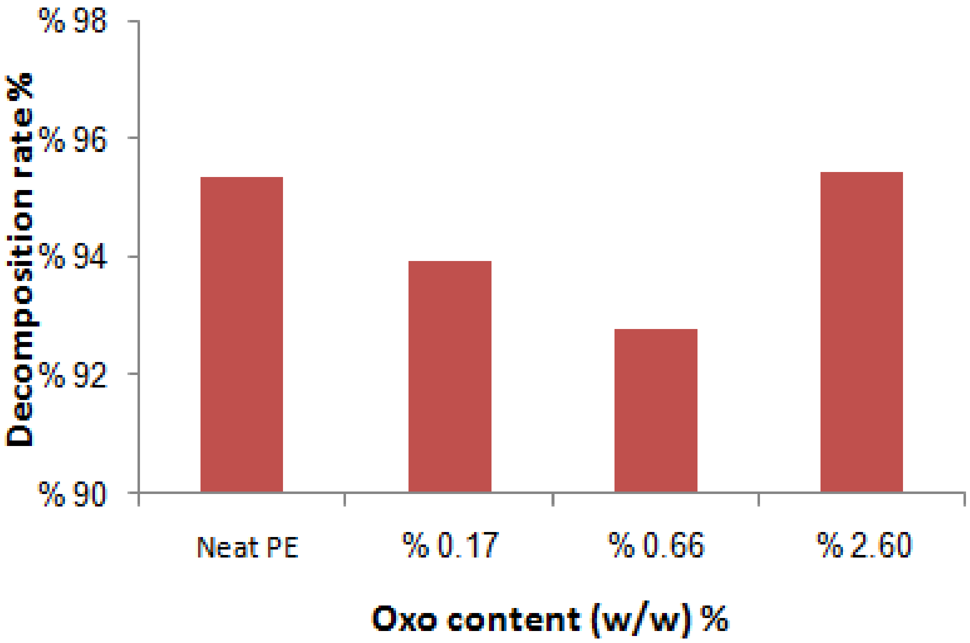


Figure (5.35): Effect of oxo-additives content on decomposition rate in soil media.

5.3.2 Effect of Media on Packaging Films

Figure (5.36), (5.37), (4.38) and (5.39) shows the effect of media on packaging films with different amount of oxo-additives content. For neat PE, the highest decomposition rate was found in air media of approximately 98.51% as shown in figure (5.36).

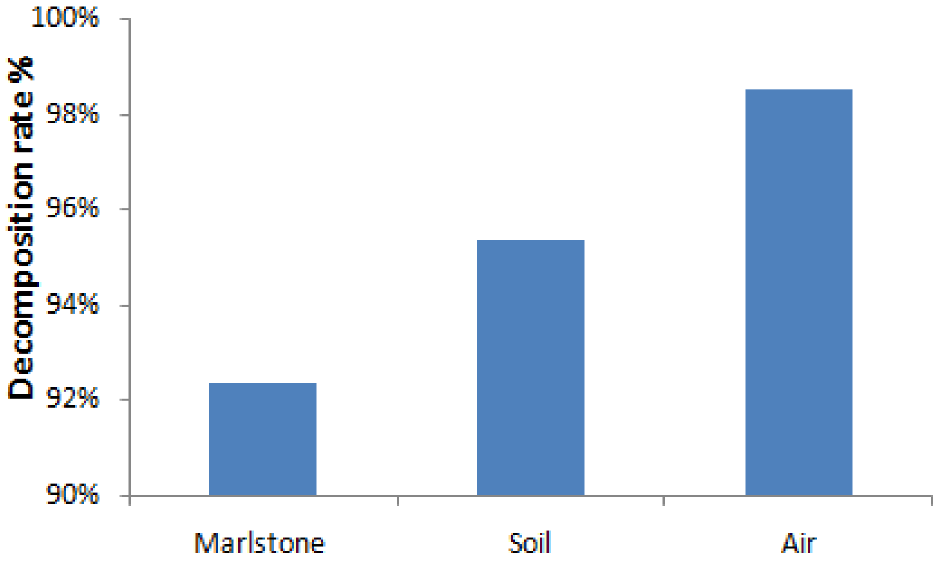


Figure (5.36): The decomposition rate of neat PE films in different media.

For 0.1664% of oxo-additive content, the highest decomposition rate was found in marlstone media of approximately 94.92% as shown in figure (5.37).

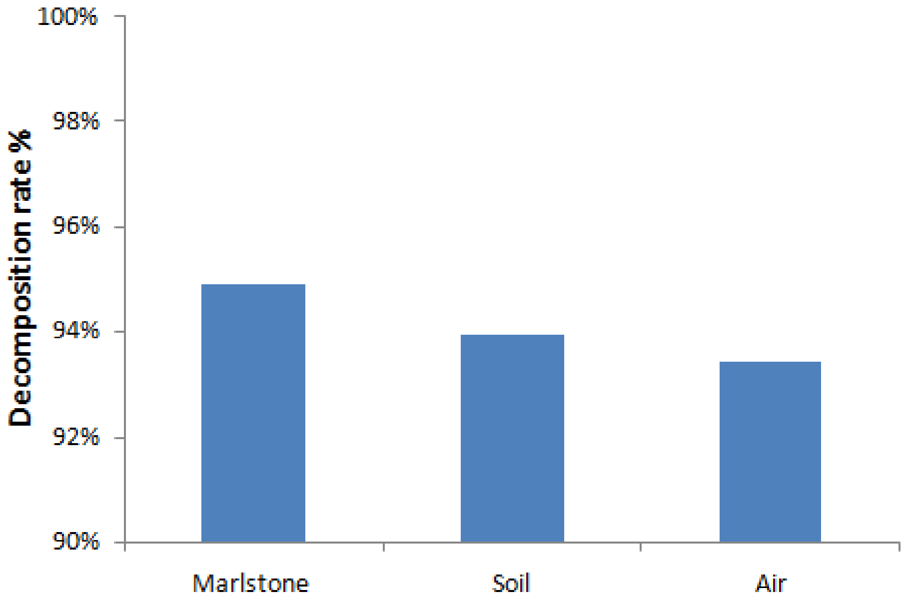


Figure (5.37): The decomposition rate of 0.1664% oxo-additive content in different media.

For 0.6623% of oxo-additive content, the highest decomposition rate was found in air media of approximately 96.81% as shown in figure (5.38).

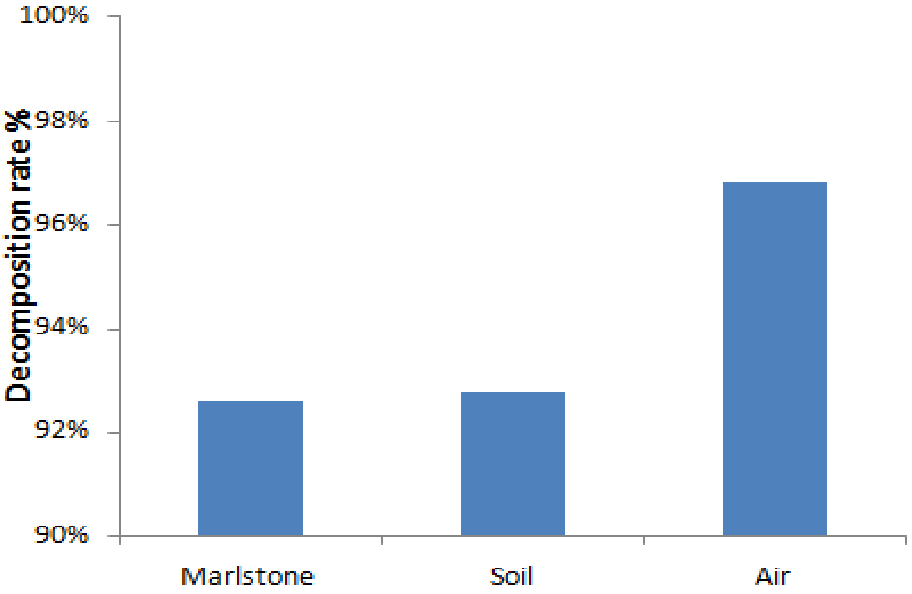


Figure (5.38): The decomposition rate of 0.6623% oxo-additive content in different media.

For 2.5974% of oxo-additive content, the highest decomposition rate was found in marlstone media of approximately 98.38% as shown in figure (5.39).

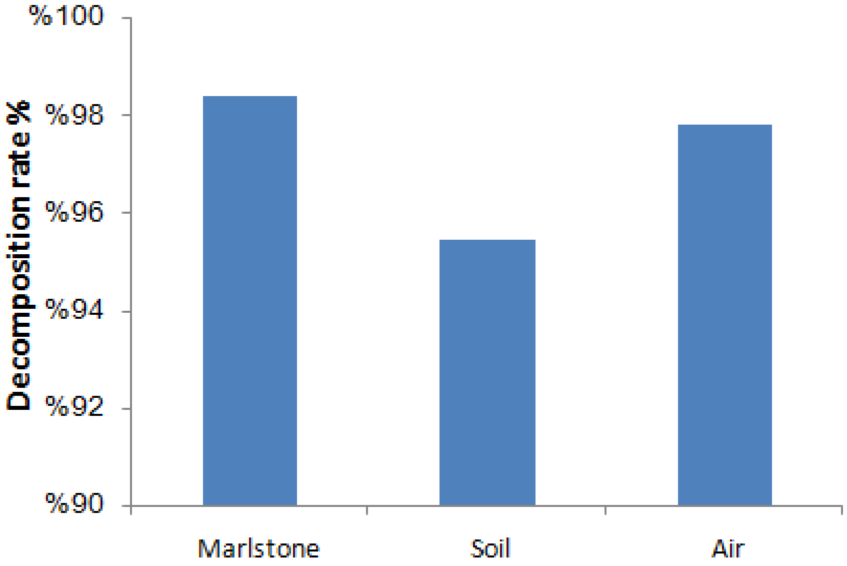


Figure (5.38): The decomposition rate of 2.5974% oxo-additive content in different media.

The results show that when comparing the decomposition rate of LDPE films with different oxo-additive content for the three different media, one can see clearly that most of changes in weight of a sample occur in the marlstone media with a high decomposition rate. Similar trends were given for the samples in the air media. Besides this, the weight change of samples which cultivated in soil media are not affected significantly.

Conclusion

The project is study the degradation of LDPE plastic films and bags, by the addition of oxo-additive content. Oxo-additives material forms a good structure of polymer such that did not affect the rapture and adhesion strength within applied different amount of oxo-additives. The mechanical and thermal properties of LDPE films were determined by use tensile test and TGA tests, which can be influenced through oxo addition. In general, addition of oxo-additives leads the films to be more ductile, lowers the tensile strength, elongation at break and modulus of elasticity, Also a significantly increasing in the mass loss were measured. This is depend on the amount of oxo-additive added and the media of cultivation.

The best and the optimum bio-plastic formula using oxo-additives with a high degradation efficiency and without affecting the thermal and mechanical properties of polyethylene plastic negatively between the seven percentages which used are found in oxo-additive content of 2.5974% which cultivated in marlstone media.

Recommendations

- We recommended to continue the analysis by using other methods like differential scanning calorimetry (DSC) device
- Analyze the other properties of polyethylene such as crystallization temperature, melting temperature and study the biodegradation process.
- Design of bioreactor for plastic degradation.
- Studying and analyzing the characteristics of oxo-additives itself.

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