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Chemical Degradation of Polymer

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صدق الله العلي العظيم

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Dedication

To the one who is familiar with the secrets of what our hearts contain, and the witness to the heart and its intention .To those who wait for knowledge from us that we will help him with when we stand with him under the shade of his banner.

To the dream of the prophets and messengers and the family of the descendants .

To the imam of time The rest of God on earth, the owner of the age and time, the awaited Imam Mahdi (may God hasten his honorable reappearance) ...

To the inhabitant of Najaf, to whom his mark shook the pillars of the elites, to his eminence, the reference Sayyid Ali al-Sistani, his shadow lasted...

To (the Popular Mobilization Mujahideen), those who were martyred among them and those who are waiting, and to the leaders of the battles of victory If it wasn't for them, we wouldn't have reached the outskirts of our dreams... I dedicate this my graduation thesis, asking them to be accepted....

Acknowledgement

I wish to first thank God for the strength and sustenance He gave me to labour on until this study was completed, it wasn't easy but it was worth it.

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List of Abbreviations

No.	Abbreviations	Description
1	PS	Polystyrene
2	HDPE	High Density Polyethelne
3	PDMS	Polydi methylsiloxane
4	PLA	Poly (lactic acid)

5	PGA	Poly (glycolic acid)
6	PPDS	Para-Phenylene Diamines
7	HCL	Hydrochloric acid
8	NACL	Sodium Chloride

Abstract

In the current work, two types of chemical degradation (hydrolysis and solvolysis) were studied for HDPE sheets (40 x 20 x 2 mm). These sheets were immersed in three different solutions for two interval times; 28 and 56 days. In hydrolysis degradation, High density Polyethelne immersed in tap water, while in solvolysis degradation, PE immersed in 36% HCl acidic solution and in 3.5 wt% saline solution separately. The immersed samples were dried in 90°C for 45 min, then tested.

To evaluate the effects of immersion durations upon these sheets, many tests were carried out, such as morphological tests. swelling, hardness and contact angle. Morphological tests were carried out by two devices, which are optical and digital microscopes.

Results of the hydrolysis degradation, showed that the HDPE sheets experiences slight weight loss, slight hardness reduction, announced wettability and its surface become smoother and their roughness reduced clearly.

In the acidic solvolysis degradation type, results showed that a weight gain happened, moderate hardness reduction, announced reduction in the wettability. Its surface morphology showed two different actions, where at the first immersion period (28 days), there is a swelling in the amorphous regions so that the grooves filled with the swollen parts, which resulted in the smooth surface. At the second period, these swollen amorphous parts continue in swelling so that the surface retain to be rough again.

Results of the saline solvolysis degradation showed that, the hardness increased clearly, the wettability increased slightly, moderate weight gain and its surface morphology altered in two stages likes what happened with acidic solvolysis degradation.

الخلاصة

في العمل الحالي تمت دراسة نوعين من التحلل الكيميائي (التحلل المائي والتحلل المذاب) لألواح البولي ايثيلين عالي الكثافة (٤٠ × ٢٠ × ٢ مم). تم غمر هذه الألواح في ثلاثة حلول مختلفة لفترتين ، ٢٨ و ٥٦ يومًا. في حالة التحلل المائي ، يتم غمر البولي ايثيلين عالي الكثافة في ماء الصنبور ، بينما في حالة التحلل المذاب ، يتم غمر البولي ايثيلين عالي الكثافة في محلول حامض الهيدروكلوريك بنسبة ٣٦٪ وفي محلول ملحي بنسبة ٣.٥٪ بالوزن بشكل منفصل .

تم تجفيف العينات المغمورة في ٩٠ درجة مئوية لمدة ٤٥ دقيقة ، ثم اختبارها لتقييم آثار فترات الغمر على هذه الألواح ، تم إجراء العديد من الاختبارات ، مثل الاختبارات المورفولوجية. انتفاخ وصلابة وزاوية التلامس. تم إجراء الاختبارات المورفولوجية بجهازين هما مجهر ضوئي ورقمي. أظهرت نتائج التحلل المائي أن صفائح البولي ايثيلين عالي الكثافة تعاني من نقص طفيف في الوزن ، وانخفاض طفيف في الصلابة ، وقابلية البلل المعلنة ، وأصبح سطحها أكثر نعومة وتقليل خشونتتها بشكل واضح. في نوع التحلل المذاب الحمضي ، أوضحت النتائج حدوث زيادة في الوزن ، انخفاض معتدل في الصلابة ، انخفاض معن في قابلية البلل. أظهر شكل سطحه عمليين مختلفين ، حيث في فترة الغمر الأولى (٢٨ يومًا) ، هناك انتفاخ في المناطق غير المتبلورة بحيث. في العمل الحالي تمت دراسة نوعين من التحلل الكيميائي (التحلل المائي والتحلل المذاب) لألواح البولي ايثيلين عالي الكثافة (٤٠ × ٢٠ × ٢ mm). تم غمر هذه الأوراق في ثلاثة حلول مختلفة لفترتين ، ٢٨ و ٥٦ يومًا. في حالة التحلل المائي ، يتم غمر البولي ايثيلين عالي الكثافة في ماء الصنبور ، بينما في حالة التحلل المذاب ، يتم غمر البولي ايثيلين عالي الكثافة في محلول حامض الهيدروكلوريك بنسبة ٣٦٪ وفي محلول ملحي بنسبة ٣.٥٪ بالوزن بشكل منفصل. تم تجفيف العينات المغمورة في ٩٠ درجة مئوية لمدة ٤٥ دقيقة ، ثم اختبارها.

لتقييم آثار فترات الغمر على هذه الألواح ، تم إجراء العديد من الاختبارات ، مثل الاختبارات المورفولوجية انتفاخ وصلابة وزاوية تلامس. تم إجراء الاختبارات المورفولوجية بجهازين هما مجهر ضوئي ورقمي.

أظهرت نتائج التحلل المائي أن صفائح البولي ايثيلين عالي الكثافة تعاني من نقص طفيف في الوزن ، وانخفاض طفيف في الصلابة ، وقابلية البلل المعلنة ، وأصبح سطحها أكثر نعومة وتقليل خشونتتها بشكل واضح.

في نوع التحلل المذاب الحمضي ، أوضحت النتائج حدوث زيادة في الوزن ، انخفاض معتدل في الصلابة ، انخفاض معن في قابلية البلل. أظهر شكل سطحه عمليتين مختلفتين ، حيث في فترة الغمر الأولى (٢٨ يومًا) ، يوجد انتفاخ في المناطق غير المتبلورة بحيث تمتلئ الأخاديد بالأجزاء المنتفخة ، مما أدى إلى سطح أملس. في الفترة الثانية ، تستمر هذه الأجزاء غير المتبلورة المنتفخة في الانتفاخ حتى يظل السطح خشبًا مرة أخرى.

أظهرت نتائج التحلل المذاب بالمحلول الملحي زيادة الصلابة بشكل واضح وزيادة قابلية البلل بشكل طفيف وزيادة معتدلة في الوزن وتغير شكل سطحه على مرحلتين مثل ما حدث مع التحلل الحمضي.

CHAPTER ONE

INTRODUCTION & LITERATURE REVIEW

1.1 Introduction

Polymer degradation is a change in the properties—tensile strength, color, shape, etc. of a polymer or polymer-based product under the influence of one or more environmental factors such as heat, light or chemicals such as acids, alkalis, and some salts. Degradation is often due to a change in the chemical and/or physical structure of the polymer chain, which in turn leads to a decrease in the molecular weight of the polymer. These changes are usually undesirable, such as cracking and chemical disintegration of products or, more rarely, desirable, as in biodegradation, or deliberately lowering the molecular weight of a polymer for recycling. Such changes occur primarily because of the effect of these factors on the chemical composition of the polymer. The changes in properties are often termed “aging”.

Polymer degradation includes all changes in both the chemical structure and physical properties of polymers or polymer-based products that lead to the loss of properties such as tensile strength, color, shape, etc., under the influence of processing conditions, or one or more environmental factors. In a finished product, such a change is to be prevented or delayed. The degradation of polymers to form smaller molecules may proceed by random scission or specific scission. Degradation can be useful for recycling/reusing polymer waste to prevent or reduce environmental pollution. The degradation of high density Polyethelne occurs by random scission – a random breakage of the bonds within the polymer. Degradation can also be

induced deliberately to assist in structure determination. As the recognition of polymer degradation improves, conservation guidelines are beginning to emerge [1].

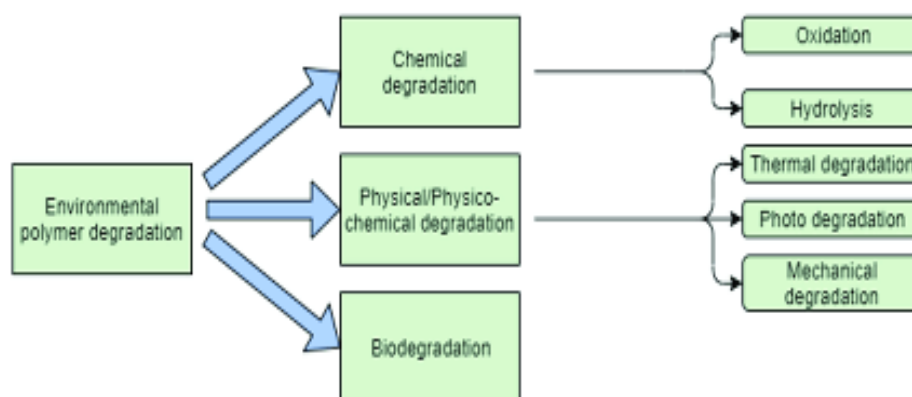


Fig.1.1 : Schematic presentation of polymer degradation [2]

1.2 Literature Review

research Studying degradation in polymers by heat and high radiation. samples were tested (weight, hardness, optical microscope, surface roughness) before and after exposure to ultraviolet rays; sunlight and heat The results show that weight and hardness is reduced by a large margin when samples exposed to heat and reduced by less when exposed to ultraviolet rays and less when exposed to sunlight The Surface roughness and cracking increasing when heating samples increasing by less when exposed to ultraviolet rays and less when exposed to sunlight.

1.3 Aims of Research

Study the chemical degradation (hydrolysis and solvolysis) of high density Polyethelne.

1.4 Chemical Degradation of Polymer

It is a type of polymer action however most of these reactions result in the breaking of double bonds within the polymer structuredegradation that involves a change of the polymer properties due to a chemical reaction with the polymer's surroundings. There are many different types of possible chemical reactions causing degradation however most of these reactions result in the breaking of double bonds within the polymer structure.

The chemical degradation of polymers is really an encompassing topic that can refer to thermal degradation or oxidative degradation as well.

The main three aspects of chemical degradation are:

- Solvolysis: occurs under solvents action
- Oxidation: occurs under oxygen action
- Ozonolysis: occurs under ozone action

1.4.1 Solvolysis :The basic issue in reference to chemical degradation is solvolysis. It concerned with the breaking of C-X bonds where X is a non-carbon atom, mostly O, N, P, S, Si, or a halogen. Solvolysis agents, such as water, alcohols, ammonia, lubricants, acids, alkalies, halogens etc., rupture the main chain of the polymer and break it down. A common solvolysis reaction is hydrolysis, in which one of the degradation products is water. Water soluble polymers succumb easily to hydrolysis, while water insoluble polymers are degraded only on the surface of the specimen [3].

- Step-growth polymers like polyesters, polyamides and polycarbonates can be degraded by solvolysis and mainly hydrolysis to give lower molecular weight molecules.
- The hydrolysis takes place in the presence of water containing an acid or a base as catalyst. Polyamide is sensitive to degradation by acids and polyamide mouldings will crack when attacked by strong acids.
- For example, the fracture surface of a fuel connector showed the progressive growth of the crack from acid attack (Ch) to the final cusp (C) of polymer. The problem is known as stress corrosion cracking, and in this case was caused by hydrolysis of the polymer. It was the reverse reaction of the synthesis of the polymer [4]:



1.4.2 Oxidative Degradation

Involves the disintegration of macromolecules by the action of oxygen on the substrate (oxidation). Free radicals are formed which react with oxygen-producing oxy- and peroxy-radicals. These, on the other hand, can participate in many reactions: they may react with each other or remove hydrogen from polymer chains. Oxidative degradation can be initiated by three factors such as UV light, heat, or mechanical stress in the presence of oxygen atmosphere [5].

Oxidative degradation can proceed according to two mechanisms : photooxidation and thermal oxidation. Photooxidation is caused by the action of UV light in the presence of oxygen, and due to its limited penetration capability, it takes place only on the surface and subsurface layers of polymer. Thermal oxidation, on the other hand, can extend throughout the material. It takes place as a result of the simultaneous interaction of oxygen with the polymer and high temperature. Oxidation leads to formation of, inter alia, hydroxyl, carbonyl, aldehyde groups, or peroxides, along the polymer chain or at its ends.

As a result of oxidation, the mechanical properties and utility of the polymer are significantly reduced. This is due to secondary cross-linking and disruption of molecular chains, which may lead to softening of the surface of the polymer. Cross-linking may cause excessive embrittlement of the material. The result is thermal oxidation or breaking bonds in the main chain of the macromolecule, which occurs when the thermal energy is higher than the energy required to break the bond. As a result of the photooxidation occurs the recombination or disproportionation of radicals and microradicals. The occurrence of structural defects in the material benefits the process, leading to the breakdown of the chains to free radicals that participate in chain propagation reactions. The prerequisite to the start of the process is that the energy of absorbed quantum of radiation is higher than the chemical bond dissociation energy [6].

Oxidative degradation not only leads to chemical structure changes in polymers, but also to scratches and fine cracks on the material surface. This leads to a reduction in polymer molecular weight due to the breakage of molecular chain or its increase by cross-linking or chain branching. Physical and mechanical properties of polymeric materials change, which is visible in the reduced flexibility, impact resistance, and breaking strain, as well as discoloration and transparency change or reduced gloss.

The course of the oxidative degradation depends on the chemical structure of the polymer, the degree of crystallinity, and its morphology. The rate of oxidation depends on the number of double bonds present in the macromolecule. Thus, most polymers slowly react with oxygen, and even a slight increase in the number of double bonds increases the stability of polyolefins. For polyolefins or polystyrene (PS), oxidation always occurs before the process of biodegradation. Oxidation occurs at every stage of life of the polymer during the manufacturing processes, usage, and storage [7].

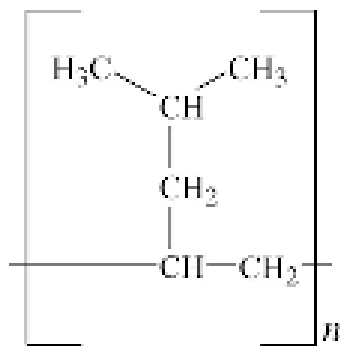


Fig.1.2 : chemical structure polyolefin [8]

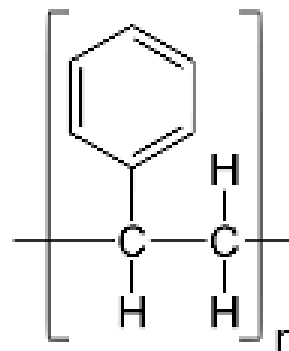


Fig.1.3 : chemical structure polystyrene [9]

1.4.3 Degradation of Polymers by Ozone

- The reaction of a polymer with ozone causes chain scission and oxidation and a steady decline in the (mechanical) properties.
- The degradation by ozone attack is greatly accelerated by stress but does not depend on temperature.
- The minute amounts of ozone in the atmosphere will cause cracking over time if an elastomer is stretched above a critical value.
- The resistance of a polymer to ozone degradation will depend on the chemical composition. Unsaturated elastomers (i.e. rubbers), are particularly susceptible to ozone attack, especially those with electron donating side groups.
- Ozone is generated in the atmosphere by photolysis of oxygen, and thus, the concentration depends primarily on the amount of sunlight available [10].

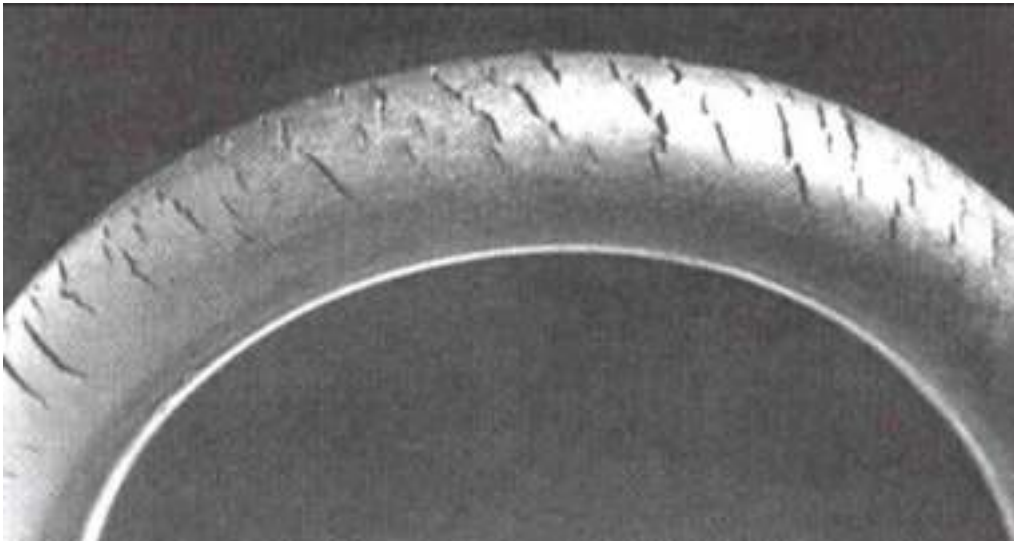


Fig.1.4 : Ozone cracking [11]

1.5 Degradation During Processing

Thermoplastic polymers (be they virgin or recycled) must be heated until molten to be formed into their final shapes, with processing temperatures anywhere between 150-320°C (300–600°F) depending on the polymer.[12] Polymers will oxidise under these conditions, but even in the absence of air, these temperatures are sufficient to cause thermal degradation in some materials. The molten polymer also experiences significant shear stress during extrusion and moulding, which is sufficient to snap the polymer chains. Unlike many other forms of degradation, the effects of melt-processing degrade the entire bulk of the polymer, rather than just the surface layers. This degradation introduces chemical weak points into the polymer, particularly in the form of hydroperoxides, which become initiation sites for further degradation during the object's lifetime.

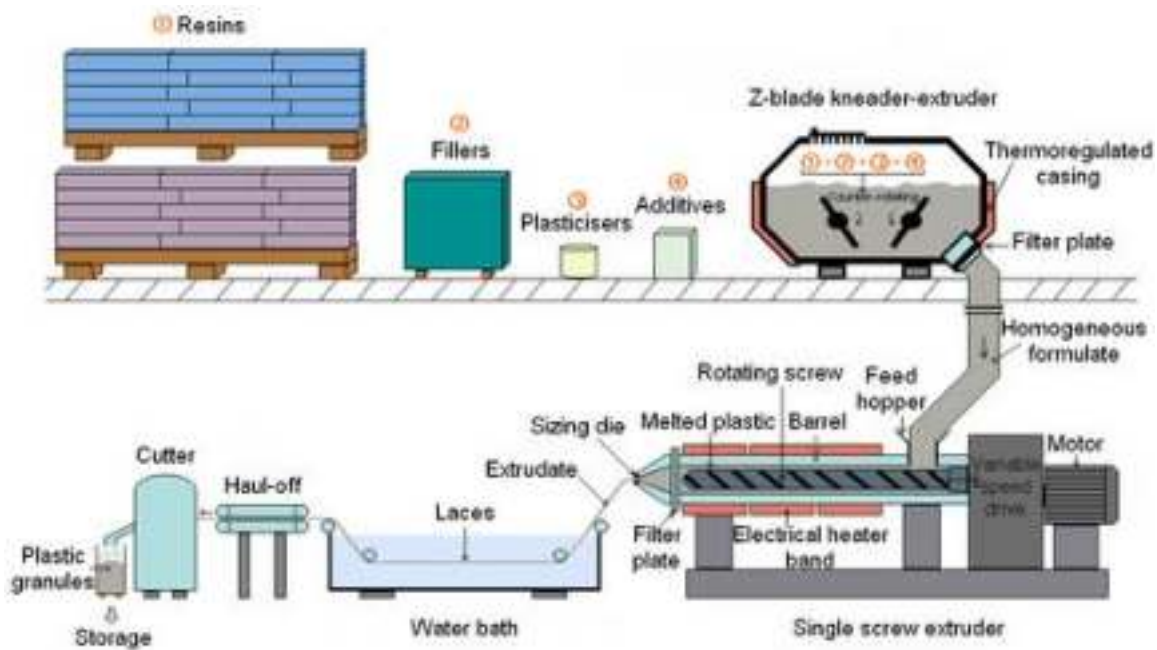


Fig.1.5 : Plastic compounding scheme [13].

Polymers are often subject to more than one round of melt-processing, which can cumulatively advance degradation.

Virgin plastic typically undergoes compounding (masterbatching) to introduce additives such as dyes, pigments and stabilisers. Pelletised material prepared in this may also be pre-dried in an oven to remove trace moisture prior to its final melting and moulding into plastic items. Plastic which is recycled by simple re-melting (mechanical recycling) will usually display more degradation than fresh material and may have poorer properties as a result [14].

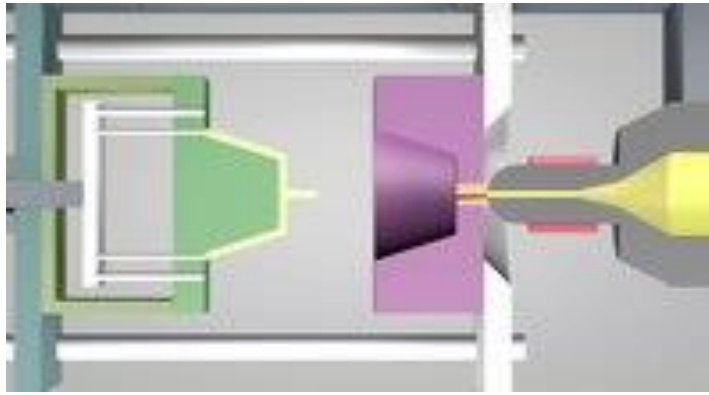
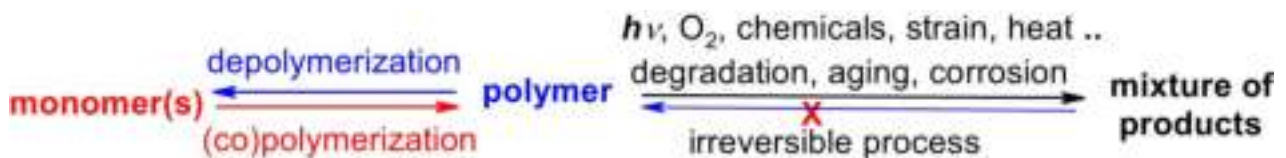


Fig.1.6 : Injection molding [15]

1.6 Mechanism of Polymer Degradation

The major factors causing degradation are heat, mechanical energy, radiation and ozone leading to various types such as thermal, thermo oxidative, photo degradation, chemical, biological, hydrolytic and degradation by irradiation. In a depolymerisation reaction, a reversal of polymerization occurs which includes Initiation at chain ends, Depropagation, Termination.

- Depolymerization In depolymerisation process low activity free radical takes place at the end of polymer chain. The change in molecular chain takes lot of time as the monomers are lost by polymeric chain one by one as per the mechanism of chain reaction :



- Random scission Decrease in the molecular weight occurs rapidly as the backbone breaks down randomly which occurs at any site of backbone. Here two reactions namely dispropo

rtion termination and intermolecular chain transfer occurs resulting into formation of new free radicals having high reactivity example:

- Side –group elimination Bonds connecting the backbone are much stronger than the bonds which connect the side groups to the backbone chain. When depolymerisation occurs side groups are removed from the backbone before any further breakage.

For depolymerisation of PVC: $\text{CH}_2(\text{Cl})\text{CHCH}_2\text{CH}(\text{Cl}) \rightarrow \text{CH}=\text{CH}-\text{CH}=\text{CH}+2\text{HCl}$
 Depolymerisation of polymers is favoured when initiation by main chain depletion is

possible or intermediates formed during the degradation reaction are stable or the activation energy required for the degradation reaction is very less. Therefore, Activation energy of depropagation = (activation energy of polymerization propagation) + (heat of polymerization ΔH_p) [16].

1.7 Chemistry of Hydrolytic Decomposition of Polymers

In hydrolytic degradation, polymer bonds react with water molecules, break up, and produce new chain ends. The original chains break up into smaller segments, resulting in polymer degradation. Most chemical groups that react with water contain O, N, S, P, and other non-carbon atoms. These atoms cause the adjacent carbon atoms to be positively charged. Electron-withdrawing oxygen atoms of water molecules attack these positively charged carbon atoms through a 2nd order nucleophilic substitution reaction resulting in the formation of two new chemical species. A general reaction mechanism is illustrated in Scheme 1

The reactant molecules, X, Y, Z, and R, can be C, O, N, and other atoms. The charge value of the reacting C atoms is a primary factor affecting the hydrolysis reactivity. Charge values of a few common groups have been calculated using Accelrys Material Studio® and are listed in Tabl 1. The chemical groups such as esters, anhydrides, orthoesters, etc. are usually more susceptible to hydrolysis than C-C, C-O-C moieties, etc. The charge values of these two types of chemical groups seem to be distinguished by a value of 0.3 electron charges. The chemical groups having charge higher than 0.3 electron charges seem to be hydrolytically more active than those with charge lower than 0.3. However, hydrolytic activities of chemical groups also depend on many other factors such as conjugate structures that stabilize chemical groups

For example, urethane, carbonate, and aromatic ester groups have large conjugate structures; so they are generally more stable than aliphatic esters against hydrolysis, even when their charge values are high. The side groups also reduce hydrolytic activity of carbons via steric effects. For example, the silicon atoms in polydimethyldioxane (PDMS) have 0.62 electric charges, but the two methyl groups closely protect the silicon atoms and PDMS is rather stable towards hydrolysis. For the same reason, poly(lactic acid) (PLA) is less reactive than poly(glycolic acid) (PGA). On the other hand, polyorthoester, even with a relatively low charge at its central carbon atoms, reacts with water rather fast. This is due to the high bond tension caused by the three RO- groups around the carbon atoms. Besides these, the dielectric constant, degradable bond concentration, and water solubility also affect the hydrolytic activities of polymers. Overall, all chemical groups, except pure C-C bond, can undergo hydrolysis reaction. The only difference is that they react at different rates[17].

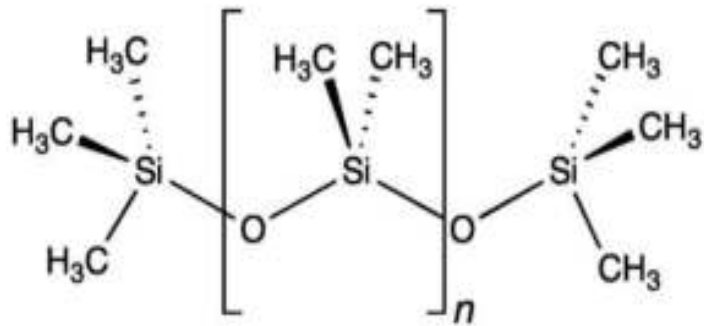


Fig.1.7 : chemical structure PLA [18]

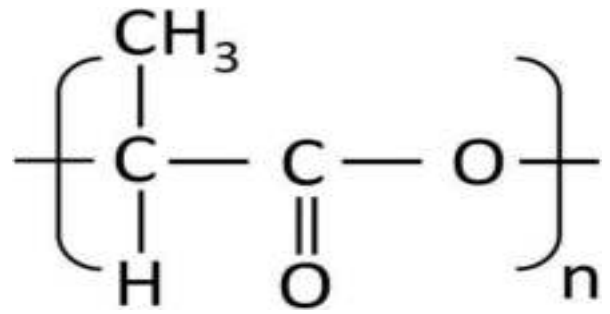


Fig.1.8 : chemical structure PDMS [19]

Table 1.Charge of atoms in different chemical groups calculated with Material Studio[®].

Very low hydrolytic activity (with low charge and protecting groups)		
Polyolefin	$-\overset{*}{\text{C}}\text{H}_2-\text{CH}_2-$	-0.11
Polyether	$-\overset{*}{\text{C}}\text{H}_2-\text{O}-\text{CH}_2-$	0.054
Polysulfone (aromatic)	$-\overset{*}{\text{C}}-\text{SO}_2-\text{C}-$	0.073
PDMS	$-\overset{*}{\text{Si}}-\text{O}-$	0.62
Low hydrolytic activity (due to conjugate structures)		
Polycarbonate	$-\text{O}-\overset{*}{\text{C}}\text{O}-\text{O}-$	0.72
Polyimide	$-(\text{CH}_2-\overset{*}{\text{C}}\text{O})_2-\text{N}-$	0.45
Polyurethane	$-\text{O}-\overset{*}{\text{C}}\text{O}-\text{NH}-\text{C}-$	0.63
Polyester (aromatic)	$-\overset{*}{\text{C}}\text{O}-\text{O}-\text{C}-$	0.60
Polyamide	$-\overset{*}{\text{C}}\text{O}-\text{NH}-\text{C}-$	0.45
High hydrolytic activity (due to high charge and steric effects)		
Polyanhydride	$-(\text{CH}_2-\overset{*}{\text{C}}\text{O})_2-\text{O}-$	0.56
Polyorthoester	$-\text{R}-\overset{*}{\text{C}}-(\text{O}-\text{R})_3$	0.49
Polyketal	$-\text{R}_2-\overset{*}{\text{C}}-(\text{O}-\text{R})_2$	0.32
Polyester (aliphatic)	$-\overset{*}{\text{C}}\text{O}-\text{O}-\text{C}-$	0.56

1.8 Effect of Polymer Properties on Oxidation

- Crystallinity - Rate of oxidation is inversely proportional to degree of crystallinity. Crystallinity increases with degree of oxidation (due to chain breaking and chain orientation) Tacticity Stereoregular polymers are more crystalline and are more resistant to oxidation (PP is an exception) Molecular weight IN SOLID POLYMERS THERE NO significant effect as both the rate of initiation and rate of termination are reduced. In solution, rate decreases with molecular weight Chemical structure. Higher branching leads to higher rate of oxidation due to the presence of more number of tertiary H atoms and slow termination of tertiary peroxy radicals.

- Presence of double bonds results in more allylic positions which are inherently more reactive and hence increases oxidation rate. Film Thickness Generally rate of oxidation decreases with increase in thickness as the reaction becomes diffusion controlled Additives Many ingredients eg. catalyst residues , processing aids, metallic impurities etc increase oxidation rate. Oxidation products First oxidation products are more easily oxidised than the parent polymer. Eg. Hydroperoxides are potentially powerful initiators of further degradation. They decompose thermally , photochemically or catalytically to form free radicals[20].

1.9 Ozonation Reactions and Ozone Cracking in Elastomers

Both ozone and sunlight rapidly attack unprotected polymers which can significantly reduce the service life of a plastic. Particularly polymers with high unsaturation (i.e. rubbers) will suffer from ozone degradation, because the double bonds in unsaturated polymers readily react with ozone. However, ozone also reacts with saturated polymers but at a comparatively slower rate. The reaction of ozone with double bonds causes chain scission. The general mechanism of ozone degradation is shown below.

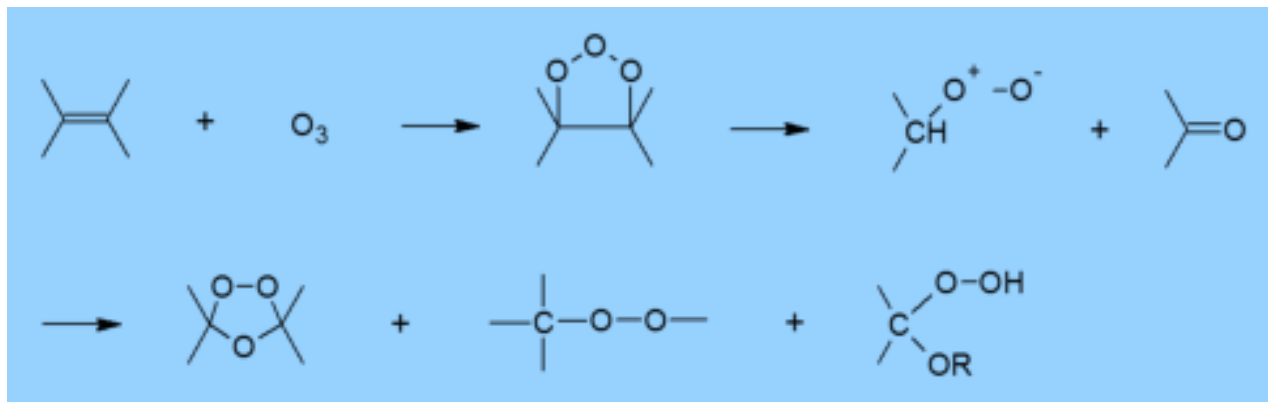


Fig.1.9 : Mechanism of ozone degradation.

Chain scission and oxidation causes a decrease in cross-link density (elastomer), or molecular weight and molecular weight distribution (thermoplast), and a change in composition (oxidation). The result is a more or less steady decline in the (mechanical) properties.

The aging is greatly accelerated by stress; one usually observes surface cracks in the direction perpendicular to the applied strain when a critical stress value is exceeded. At rather low stress values just above the critical value, long and deep cracks are observed, whereas at high stress values, the ozone cracks become more numerous and are finer in size. The microscopic disintegration of the surface causes dulling and a bluish sheen of the surface of rubber goods. This phenomenon is known as "frosting" because it often resembles actual frost.¹ It is greatly accelerated by humidity and heat and is most noticeable on the bright finish of air-cured rubber goods.² Frosting can be avoided or reduced by certain types of high melting point waxes or by antiozonants such as para phenylenediamines (PPDs) and derivatives thereof (Dialkyl PPD).

In general, the resistance to ozone cracking and frosting will depend on the chemical composition of the polymer. Elastomers are particularly susceptible to ozone attack, particularly those with electron donating side groups (e.g. methyl groups in isoprene), whereas rubbers with electron-withdrawing side groups (e.g. chlorine in neoprene) are noticeably less susceptible to ozone attack due to the deactivating effect of the halogen on the double bond.

The degree of ozone degradation will depend on the composition of the atmosphere and temperature. Usually, the ozone concentration is rather low.³ Nevertheless, even if frosting should not be confused with blooming which is caused by migration to the surface of certain constituents of the rubber composition which can often be removed by heating to the vulcanization temperature

² W.F. Tuley, *Ind. Eng. Chem.*, 31 (6), pp 714–716 (1939)

³ The average ozone concentration is about 5 to 10 pphm. However, the actual value can fluctuate and depends on weather conditions, geographic location, and is strongly affected by pollution; in unpolluted areas the ozone concentration is about 1 to 50 pphm, whereas in polluted areas it can reach much higher values of more than 100 pphm[21].

1.10 Effect of Polymer Structure on Solubility-Based Fractionation

➤ Effect of chemical type

The solubility of polymers is primarily determined by their chemical compositions. So that fractionation is likely to occur as a result of these compositions.

➤ Effect of chain branching

Branching increases the solubility of high polymers. Branched polymers being separated will consist of a mixture of species, some with low branching and low molecular weight, others with more branched but with higher molecular weight.

➤ Effect of crystallinity

Fractionation by molecular weight can be done for precipitation of polymer to a crystalline phase, especially if crystalline melting point is a strong function of molecular weight [22].

CHAPTER TWO

THEORETICAL PART

2.1 Introduction

Polymer degradation is a complex process by which the polymer loses its original functional properties owing to irreversible changes in its structure. All types of polymer reactions take part in corrosion: (i) chemical transformation of functional groups, (ii) cleavage of polymer molecules by oxidation, hydrolysis, photochemical and other chemical reactions, mechano-chemical processes and by depolymerization, and (iii) crosslinking of polymer molecules as well as their fragments. Crosslinking makes the aged polymer brittle while cleavage processes makes it waxy or sticky and, in addition, yellowish or brownish owing to unsaturated chromophores formed.

Undesirable degradation processes are significantly reduced by stabilizers admixed into the polymeric material. A single stabilizer is usually not enough; a mixture of a few stabilizers mostly has to be used. According to the function, stabilizers are roughly divided to photostabilizers, antioxidants, antiozonants, radical scavengers, peroxide scavengers, acid scavengers, fire retardants and biocides. Because the stabilizer is in general only admixed into a polymer, not bound to it, its second key property is a good compatibility with the polymer. When the compatibility mediated by the intermolecular interactions is poor, the stabilizer is spontaneously displaced to the polymer surface by the ever-present thermal motion, from where it is removed by external influences. As a result, the polymer becomes unprotected. If a good compatible stabilizer is not accessible, a new one can be obtained by connecting one or more oligomeric chains good compatible with the polymer to an available stabilizer with the given basic function [23].

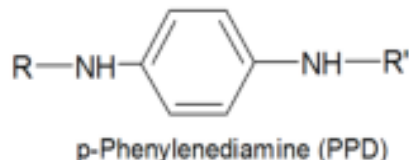
2.2 Reducing Solvent Degradation

The extent to which a solvent degrades a polymer can be reduced by:

- Limiting the time that the solvent is in contact with the polymer
- Limiting the temperature at which the solvent and the polymer are in contact.
- The concentration of the solvent [24].

2.3 Antiozonants : Para-phenylenediamines

Ozone and sunlight rapidly attack unprotected polymers which can significantly reduce their service life. Particularly polymers with high unsaturation, i.e. rubbers, are prone to suffer from ozone degradation because the double bonds in unsaturated polymers readily react with ozone. To prevent or to slow down ozone initiated oxidative degradation, antiozonants are frequently added. The most powerful and most common class of antiozonants are para-phenylene diamines (PPDs) which have the general structure



Type I : N,N'-dialkyl-p-phenylenediamine
Type II : N-alkyl-N'-aryl-p-phenylenediamine
Type III : N,N'-diaryl-p-phenylenediamine

Paraphenylenediamines are not only efficient antiozonants but are also very effective primary antioxidants. Their reactivity and efficiency depends on the substituents on the nitrogen. In general, dialkyl substituted amines are the most reactive PPDs followed by arylalkyl-substituted and bisaryl-substituted amines; probably because the N-H bond of alkyl substituted PPDs has a lower bond dissociation enthalpy than those of aryl substituted amines. However, the activity of the different types of PPDs also depends on their solubility in the rubber, the temperature, and aging conditions. For this reason, blends of PPDs are often used. In some cases, the efficiency of antiozonants can be further increased by incorporation of waxes and certain synergistic antioxidants.¹⁻³ All three types of PPDs are effective antiozonant in natural rubber and polyisoprene because they are only moderately soluble in these rubbers and, thus, can

migrate to the rubber surface to provide good ozone protection. Diaryl PPDs, on the other hand, are usually more effective in polychloroprene than the others .

There are at least three competing mechanism of ozone protection:

- The antiozonants react faster with ozone than the rubber and, therefore, acts as ozone scavengers.
- The ozone-antiozonant reaction products form a protective film on the rubber surface preventing ozone from reacting with the rubber.
- The antiozonants react with the radical sites of the rubber fragments, forming new cross-links and, thus, restore the rubber network.

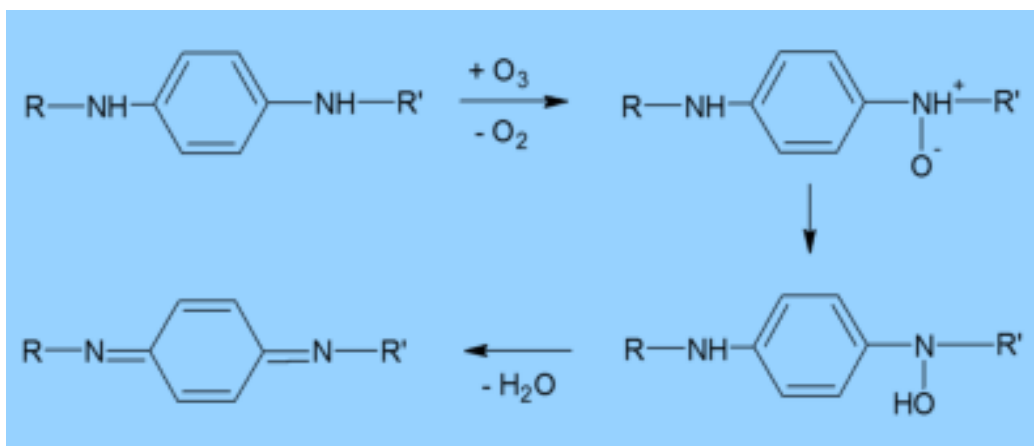


Fig.2.1 : reaction between N-alky-substituted para-phenylenediamines and ozone.

Ozone oxidizes the amino group of the phenylenediamine yielding a hydroxylamine. Subsequent elimination of water yields quinonediimine which can be further oxidizes by peroxy radicals to produce nitrones and dinitrones (not shown) [25].

2.3 Antioxidants

Polymers will change over time when exposed to radiation, excessive heat and/or corrosive environments. These changes are the result of oxidative degradation caused by free radicals which form through hydrogen abstraction or homolytic scission of carbon-carbon bonds when polymers are exposed to heat, oxygen, ozone, or light. These changes can have a dramatic effect on the service life and properties of the polymer.

To prevent or slow down degradation, antioxidants and UV stabilizers are often added. The two main classes of antioxidants are free-radical scavengers and peroxide scavengers. The free-radical scavengers are sometimes called primary antioxidants or radical chain terminators whereas peroxide scavengers are often called secondary antioxidants or hydroperoxide decomposers.

➤ **Primary Antioxidants (free –radical scavengers)**

As the name suggests, free-radical scavengers react with chain-propagating radicals such as peroxy, alkoxy, and hydroxy radicals in a chain terminating reaction. To be more specific, these antioxidants donate hydrogen to the alkoxy and hydroxy radicals which converts them into inert alcohols and water respectively.

Typical commercial primary antioxidants are hindered phenols and secondary aromatic amines. These compounds come in a wide range of molecular weights, structures, and functionalities

The most widely used primary antioxidants are sterically hindered phenols. They are very effective radical scavengers during both processing and long-term thermal aging, and are generally non-discoloring. Many also have received FDA approval. The mechanism of scavenging oxy radicals is shown below :

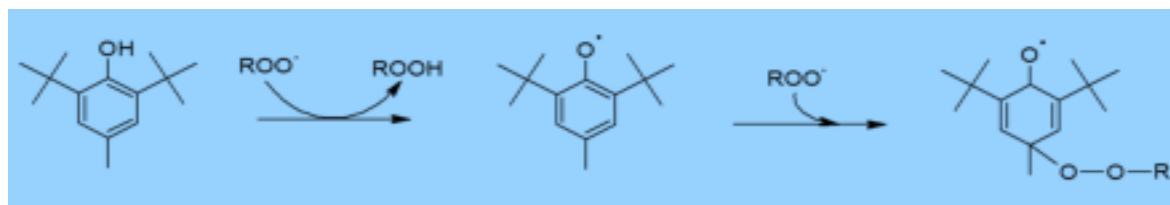


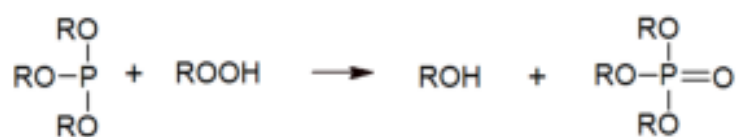
Fig.2.2 : The mechanism of scavenging oxy radicals.

The most effective primary antioxidants are secondary aromatic amines. However, they cause noticeable discoloration and can only be used if discoloration is not a problem, like carbon filled rubber products. They also function as antiozonants and metal ion deactivators.

➤ Secondary antioxidants (peroxide scavengers)

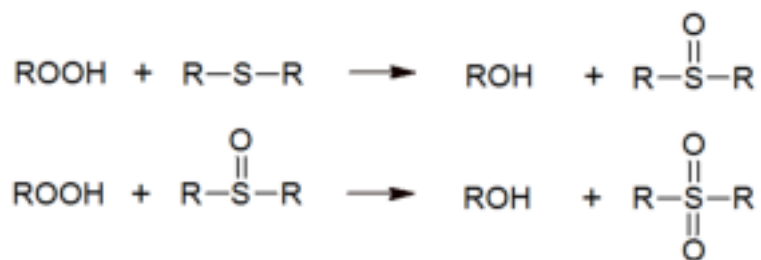
As the name suggests, peroxide scavengers (secondary antioxidants) decompose hydroperoxides (ROOH) into nonreactive products before they decompose into alkoxy and hydroxy radicals. They are often used in combination with free radical scavengers (primary antioxidants) to achieve a synergistic inhibition effect.

The most common secondary antioxidants are trivalent phosphorus compounds (phosphites). They reduce hydroperoxides to the corresponding alcohols and are themselves transformed into phosphates.



➤ The general mechanism of peroxide decomposition.

Another class of secondary antioxidants are thioethers or organic sulfides. They decompose two molecules of hydroperoxide into the corresponding alcohols and are transformed to sulfoxides and sulfones:



Organic sulfides are very effective hydrogen peroxide decomposers during long-term thermal aging and are often used in combination with other antioxidants that provide good protection during processing, like hindered phenols.

In order to choose the most effective stabilizer package, it is important to know what temperature range the polymer will be exposed to. A good stabilizer package should protect the plastic during both processing, where high temperatures are encountered to melt and form the resin, and during lifetime when exposed to its upper service temperature [26] .

CHAPTER THREE

EXPERIMENTAL PART

3.1 Introduction

This chapter includes the following sections:

- 1- Listing the used materials and mention their properties.
- 2- Describe the procedures those used to prepare high density polyethylene (HDPE) samples
- 3- Procedures used to achieve the chemical degradation types (hydrolysis and solvolysis) which include immersed in water, 3.5 wt% saline solution (NaCl solution) and acidic solution (36% HCl).
- 4- Listing the required tests and the devices used.

3.2 Materials

3.2.1 High Density Polyethylene (HDPE)

Polyethylene was first synthesized by the German chemist Hans von Pechmann who prepared it by accident in 1898 while heating diazomethane. His colleagues Eugen Bamberger and Friedrich Tschirner characterized the white, waxy, substance and recognized that it contained long $-CH_2-$ chains and termed it polymethylene. The first industrially practical polyethylene synthesis was discovered (again by accident) in 1933 by Eric Fawcett and Reginald Gibson at the Imperial Chemical Industries (ICI) works in Northwich, England.

High-Density Poly Ethylene (HDPE) is a petroleum-based thermoplastic polymer considered one of the most versatile plastic materials available today. It is used to manufacture numerous items, including food and beverage containers, cleaning product bottles, pipes, cutting boards, and some shoe parts.

The used HDPE is with the properties maintain in Table (3.1) [27].

Table 3.1: Properties of the used HDPE

Propriety	Data
Chemical formula	$(C_2H_4)_n$
Color	White
Melting point	115–135 °C (239–275 °F; 388–408 K)

3.2.2 Hydrochloric Acid (HCL)

Hydrochloric acid was historically called acidum salis, muriatic acid, and spirits of salt because it was produced from rock salt and green vitriol (by Basilius Valentinus in the 15th century) and later from the chemically similar common salt and sulfuric acid (by Johann Rudolph Glauber in the 17th century). The used HCl is with the properties maintain in Table (3.2) [28].

Table 3.2: Properties of the used Hydrochloric Acid

Propriety	Data
Chemical formula	HCL
Appears	Transparent liquid
Molecular weight	36.458 g/mol
Boiling Point	Depends on the concentration

3.2.3 Sodium Chloride (NaCl)

Sodium chloride (NaCl), also known as salt, is an essential compound our body uses to: absorb and transport nutrients. maintain blood pressure. maintain the right balance of fluid. transmit nerve signals.

Sir Humphry Davy was able to discover sodium (Na) in the laboratory. In 1807, he used electrolysis to remove this element from melted caustic soda. The used salt is with the properties maintain in Table (3.3) [29].

Table 3.2: Properties of the used NaCl

Propriety	Data
Chemical formula	NaCl
Appears	Colorless crystals
Molecular weight	58.44 g/mol
Boiling Point	1,413° C (2,575° F)
Melting Point	801° C (1,474° F)

3.2.4 Tap Water (H₂O)

It was the chemist Henry Cavendish (1731 – 1810), who discovered the composition of water, when he experimented with hydrogen and oxygen and mixed these elements together to create an explosion (oxyhydrogen effect).

Tap water (also known as faucet water, running water, or municipal water) is water supplied through a tap, a water dispenser valve. Tap water is commonly used for drinking, cooking, washing, and toilet flushing

Tap water used with the properties maintain in Table (3.4) [30].

Table 3.4: Properties of the used water

Propriety	Data
Chemical formula	H ₂ O
Appears	White crystalline solid, almost colorless liquid with a hint of blue, colorless gas
Molar mass	18.01528(33) g/mol
Boiling Point	99.98 °C (211.96 °F; 373.13 K)
Melting Point	0.00 °C (32.00 °F; 273.15 K)

3.3 Sample Preparation

In order to subject HDPE polymer to a chemical degradation, rectangular sheets (40 x 20 x 2 mm) of HDPE immersed in three different solutions for two interval times; 28 and 56 days. Two types of chemical degradation studied. In hydrolysis degradation, HDPE immersed in tap water, while in solvolysis degradation, HDPE immersed in 36% HCl acidic solution and in 3.5 wt% saline solution separately. The HDPE samples immersed in 50 mm distilled water, dried in 90°C for 45 min, weighted with sensitive balance, then tested.

The weighting process carried out before and after each immersion duration and achieved by accurate balance with 0.0001 mg tolerances (Figure 3.1).

The immersion process achieved by immersion the rectangular HDPE samples in containers containing 50 mm distilled water for 28 and 56 days (Figure 3.2). The drying process carried out in a vacuum oven at a 90°C temperature for 45 minutes(Figure 3.3).



Fig.3.1 : Sensitive balance



Fig.3.2: Immersion process



Fig.3.3 : Vacuum oven

3.4 Tests

To evaluate the effects of immersion durations upon these sheets, many tests were carried out, such as morphological tests, swelling, hardness and contact angle.

Morphological tests were carried out by two devices, which are optical and digital microscopes

3.4.1 Hardness test

Shore Durometer device (Figure 3.5) used to achieve the hardness tests. It measures the depth of an indentation in the material created by a given force on a standardized presser foot. This depth is dependent on the hardness of the material, its viscoelastic properties the shape of the presse foot; and the duration of the test ASTM D2240 durometers allows for measurement of the initial hardness, Or the indentation hardness after given period of time. The basic test requires applying the force in consistent manner; without shock; and measuring the hardness (depth of the indentation timed hardness is desired, force is applied for the required time and then read [31].



Fig.3.5 : Shore durometer device

3.4.2 Optical Microscope

The optical microscope model (1280 XEQ-MM 300TUSB), which shown in figure 3.6 used in order to monitoring the microstructure[32] for HDPE samples. The device where connects with the camera and computer to show the picture. This test was conducted in the laboratories of the Department of metallic Engineering of Materials Engineering University of Babylon.



Fig.3.6 : Optical microscope device

3.4.3 Wettability test (Contact Angle Approach)

This test was carried out to evaluate effects solution type as well as the immersion durations on the wettability HDPE samples. The used device is SL 200C - Optical Dynamic I Static Interfacial Tensiometer & Contact Angle Meter which manufactured in KINO Industry Co., Ltd., USA with contact angle range from 0° to 180° (Figure 3.7). This device makes calculation and comparison of left and right contact angle as well as calculate their average value giving a Real-time data graph monitoring changes of contact angle with video recording[33]. This test was conducted in the laboratories of the Department of Ceramic Engineering of the Materials Engineering University of Babylon.

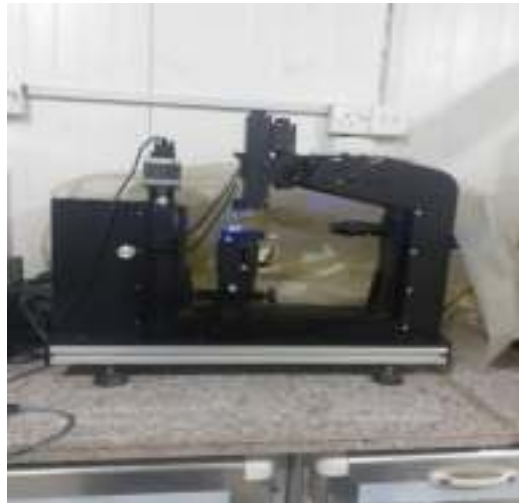


Fig.3.7: Contact angle device

3.4.4 Digital Microscope

This microscope (Figure 3.8) is also used to study the morphology of the HDPE samples by evaluating their surface roughness [34]. The calibration of the three samples was found 7 mm. This test was conducted in the laboratories of the Department of Polymer and petrochemical industries Engineering of the Materials Engineering University of Babylon.



Fig.3.8: Digital microscope device

CHAPTER FOUR

RESULT & DISCUSSIONS

4.1 Introduction

This chapter follows results of two types of the chemical degradation of High Density Poly Ethylene (HDPE) polymer. These degradation types are hydrolysis (degradation by water) and solvolysis (degradation by saline and acidic solutions).

PE samples were subjected to chemical degradation for 28 and 56 days and their properties were measured and compared with its initial properties. These properties are hardness, wettability, swelling capacity and the surface morphology. The later property (surface morphology) was studied by two techniques; digital and optical microscopes.

4.2 Result of hydrolysis degradation (immersion in water)

4.2.1 Hardness Result

Figure 4.1 shows the relationship between immersion time in water and hardness. It is clear that hardness decreased with immersion time (by 2.45 %) due the penetration of water molecules within the high density Polyethelne structure. That means that water molecules enters among PE chains, reducing the secondary forces (crosslinking) which leads to decreases the cohesive energy density (CED), which resulted finally in decreasing the crystallinity degree and increase the amorphous portion in the HDPE network. As the polymeric chains be apart, the indenter will penetrates the network easily.

$$\begin{aligned}\Delta \text{Hardness} &= \frac{55.6 - 57}{57} * 100 \% \\ &= - 2.45 \%\end{aligned}$$

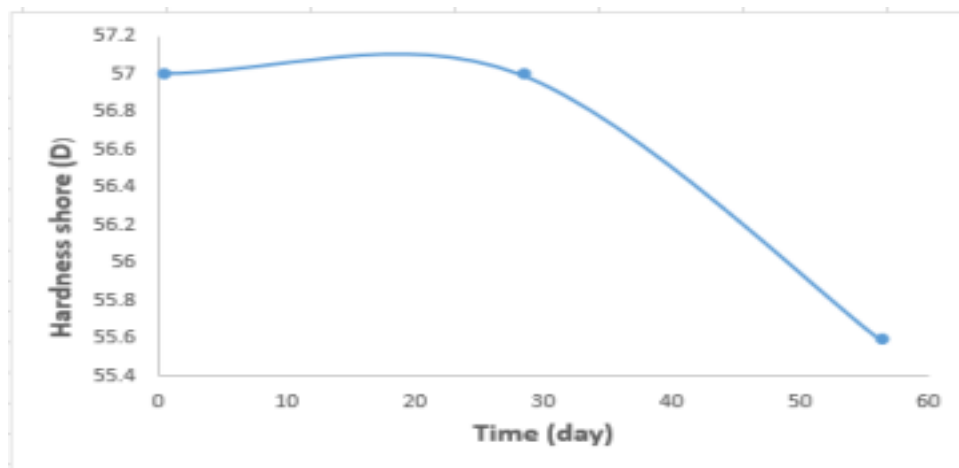


Fig.4.1: Effect of water immersion on hardness property

4.2.2 Wettability Results

Figure 4.2 shows that the contact angle (CA) decreased with time from 71.807° to 50.409° after 56 days, which means increasing the wettability by 29.79%. That means that PE network tend to be more hydrophilic than the sample before immersion. The wettability increased as immersion time increased due to penetration effect. This result coincides with the previous result (hardness reduction).

$$\Delta CA = \frac{50.409 - 71.807}{71.807} * 100\%$$
$$= - 29.79 \%$$

Or + 29.79% in wettability

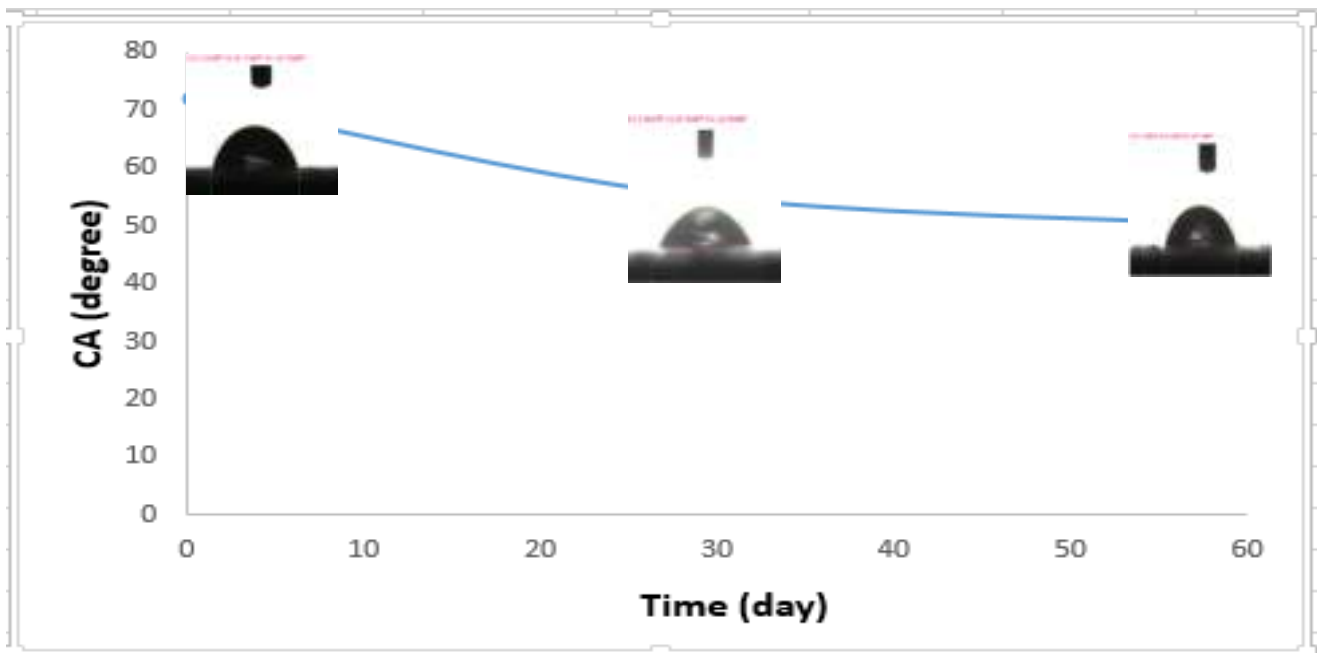


Fig.4.2 : Effect of water immersion on contact angle

4.2.3 Swelling Results (or weight loss)

Hydrolysis degradation occurs in two stages; swelling (weight gain) followed by weight loss stage. In the current case (figure 4.3), slight weight loss occurs due swelling effect after immersion to 28 days as well as after 56 days. This low reduction in weight happened linearly, which means that the hydrolysis action continue slowly with time with missing of some parts of the polymeric chains. After 56 days, only 0.14 % of the PE weight will missed. That means the possibility of using PE cans can be used to store liquid water.

$$\begin{aligned}\text{Weight loss} &= \frac{W_2 - W_1}{W_1} * 100\% \\ &= \frac{0.8930 - 0.8936}{0.8936} * 100\% \\ &= -0.067\%\end{aligned}$$

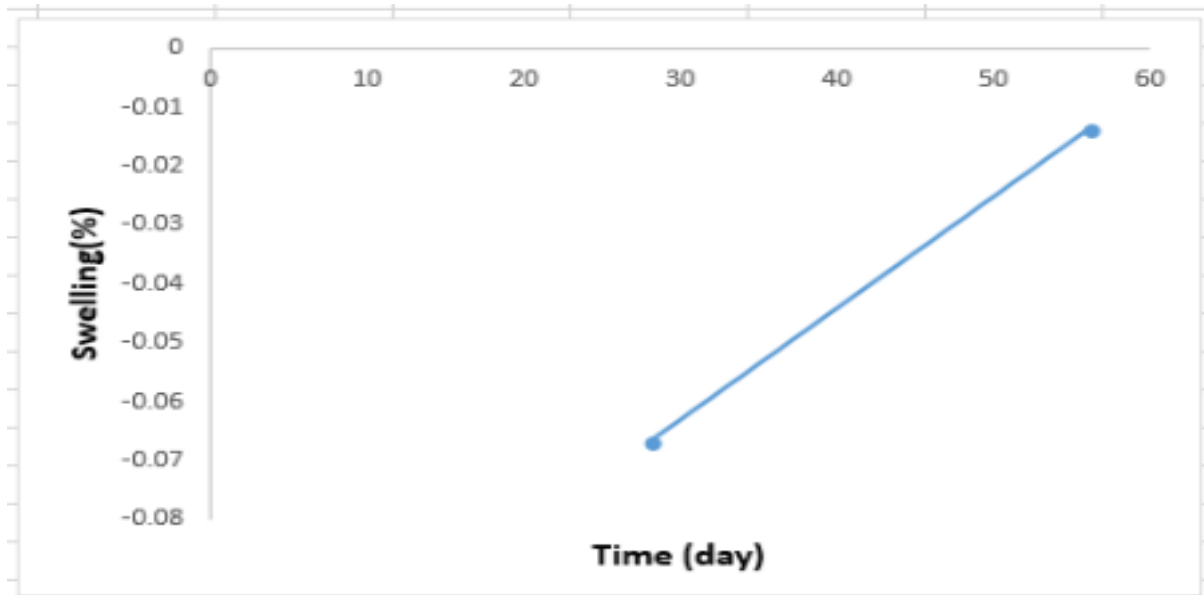


Fig.4.3 : Effect of water immersion on swelling capacity

4.2.4 Morphology results

The morphology of the HDPE samples were studied by monitoring digital and optical images before immersion in water and after 28 and 56 days.

Figure 4.4 shows the surface morphology of the PE samples when immersed in water for 28 days. These pictures include internal and external surfaces. It is clear that the morphology of both sides altered with immersion time, so these surfaces become smoother and their roughness reduced clearly. This finding coincides with the previous result, which is weight loss because of weathering action to the rough parts of the surface.



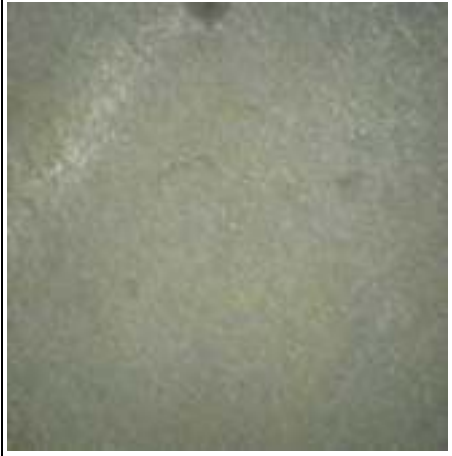
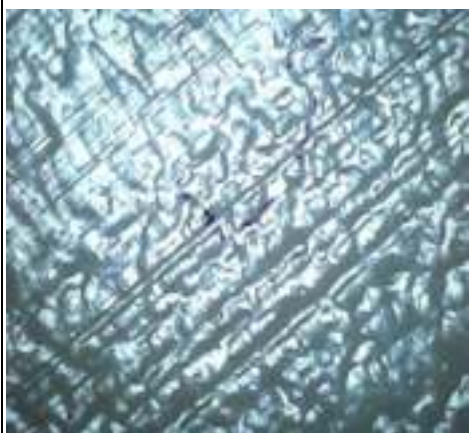


At 0 (day)	At 28 (day)	At 56 (day)
The surface of sample	The surface of sample	The surface of sample
		
The bottom of sample	The bottom of sample	The bottom of sample
		

Fig.4.4 : Digital microscope images of HDPE samples immersed in water

Fig.4.5 : shows the morphology using optical microscope, where the same findings obtained. The roughness decreased and the grooves disappeared.

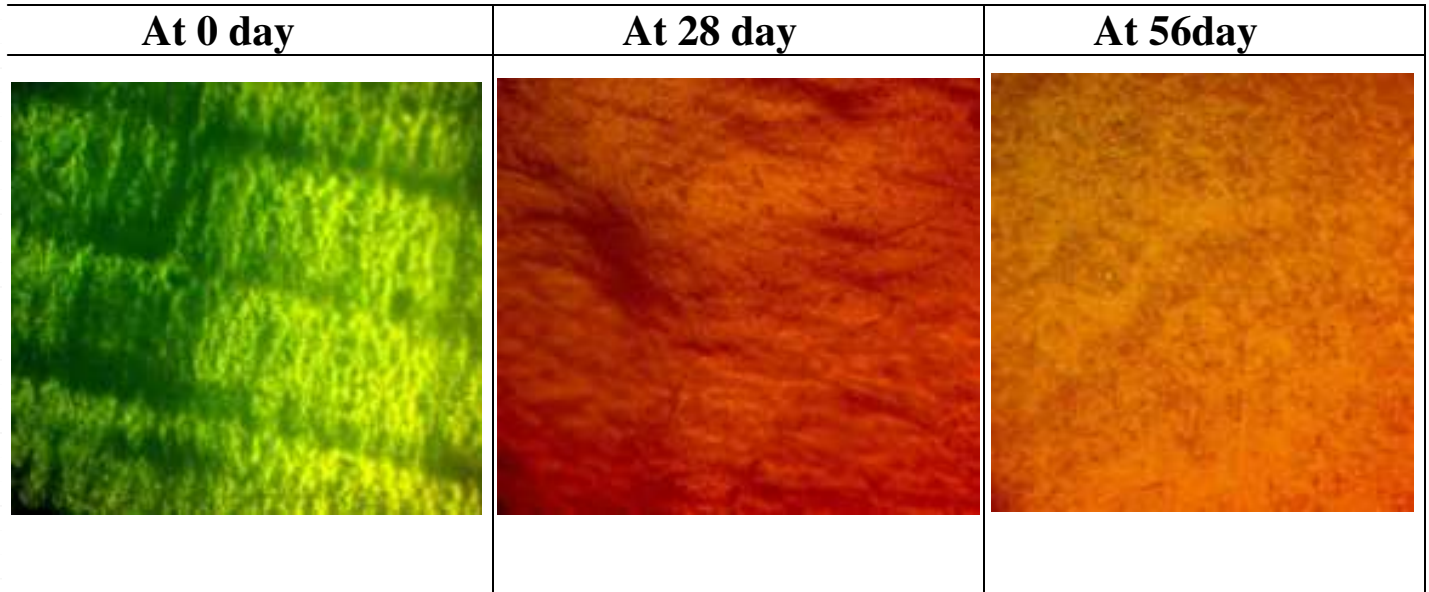


Fig.4.5 : Optical microscope images of HDPE samples immersed in water

4.3 Result of acidic solvolysis degradation (immersion in 36 % HCl acid)

4.3.1 Hardness Result

Figure 4.2 shows the effect of immersion in (36% HCl) acidic solution on the hardness property. It is clear that there is a decline in the hardness property with the immersion duration. Hardness is a surface property, not bulk property, therefore this property is high sensitive to the environmental media. So that immersion PE sample in acidic media causes slight surface degradation to the upper PE chains due to the failure of some secondary forces among these polymeric chains.

This hardness reduction is not exceed 2.9%, therefore HDPE material can be suggested to store acids.

$$\begin{aligned} \Delta \text{Hardness} &= \frac{56.8-58.5}{58.5} * 100\% \\ &= - 2.90\% \end{aligned}$$

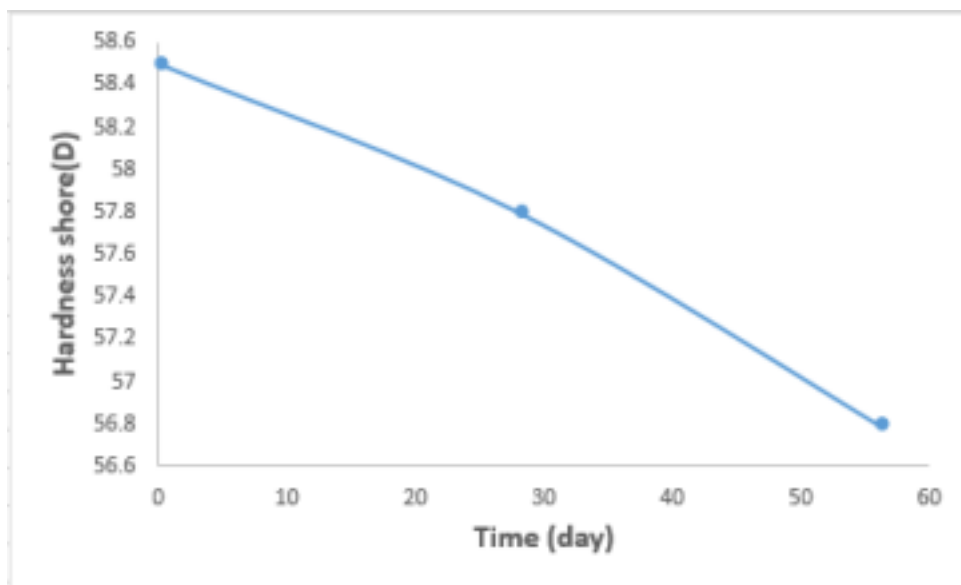


Fig.4.6 : Effect of immersion of HCl 36% on hardness property

4.3.2 Wettability Results

Figure 4.7 shows that, the contact angle (CA) increase with time from 40.21° to 74.005° after 56 days, which means increase by 84.04%.

$$\Delta CA = \frac{74.005 - 40.211}{40.211} * 100\%$$

$$= 84.04\%$$

That means that PE network tend to be more hydrophobic (less wettability) than the sample before immersion in HCl acid, where this is a desirable property in acids and food packaging. This finding confirms using PE in store the acidic materials. Also, the interaction between environmental humidity and food be minimal. This will minimize the food hydrolysis and keep food for long times.

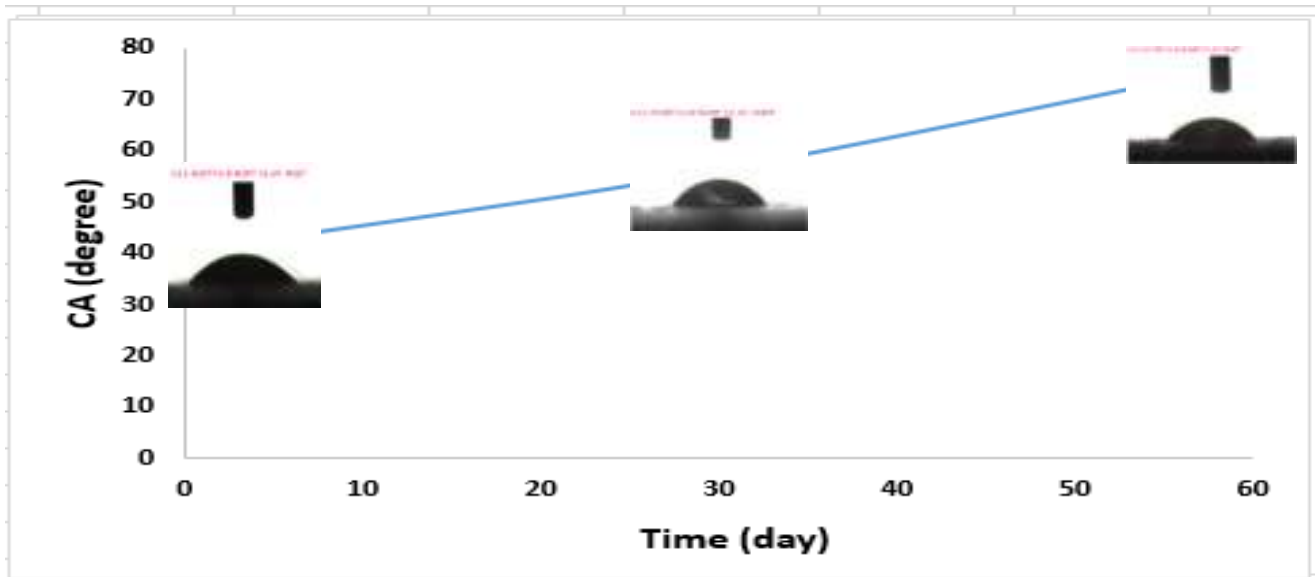


Fig.4.7 : Effect of 36%HCl immersion on contact angle

4.3.3 Swelling Results

The immersion of HDPE in acid (figure 4.8) resulted in swelling stage only (weight gain) and don't reached to the dissolution stage (weight loss) as happened with water immersion. This result agreed with the previous wettability result (increasing contact angle). Swelling calculations showed that, the HCl penetration takes place largely in the first period (28 days), reaching to 10%, and increased slightly (only 1%) during the second period, which means, that with time, the wettability decreased and the HDPE sample tends to be less hydrophilic. This result, agreed also with the slight decreasing in the hardness property (-2.9%).

$$\begin{aligned}
 \text{Swelling after 28 day} &= \frac{W_2 - W_1}{W_1} * 100\% \\
 &= \frac{0.9742 - 0.9732}{0.9732} * 100\% \\
 &= 0.10\%
 \end{aligned}$$

$$\text{Swelling after 56 day} = 0.11\%$$

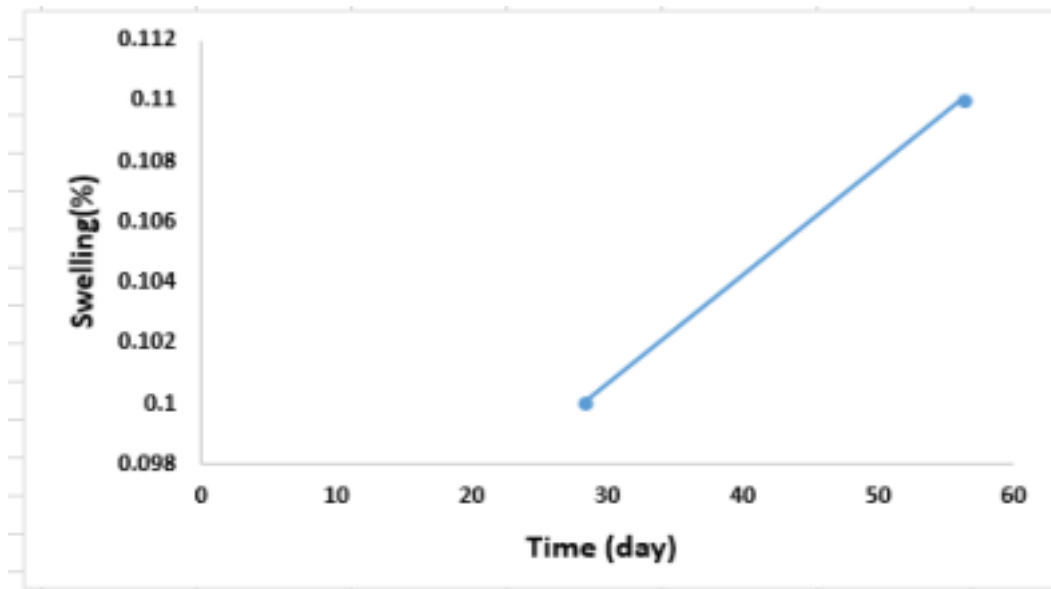
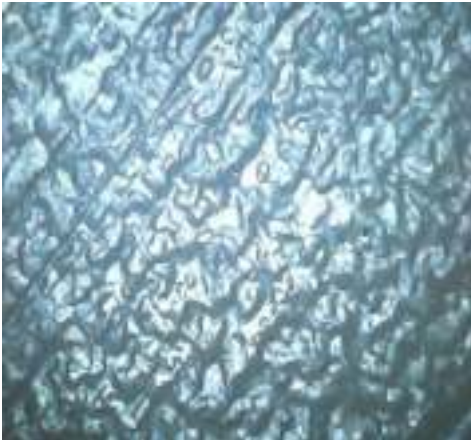







Fig.4.8 : Effect of HCL immersion on swelling capacity

4.3.4 Morphological Results

Figures 4.9 and 4.10 show the morphological properties of HDPE sample before and after immersion in HCl acid by two techniques; digital and optical microscopes. Both techniques showed that the surface morphology altered after immersion. At the first period, the roughness decreased (the surface be smoother) and after the second period the roughness increased again. This is means that, at the first immersion period, there is a swelling in the amorphous regions so that the grooves filled with the swollen parts, which resulted in the smooth surface. At the second period, these swollen amorphous parts continue in swelling so that the surface retain to be rough again.

At 0 day	At 28 day	At 56 day
<p>The surface of sample</p> 	<p>The surface of sample</p> 	<p>The surface of sample</p> 
<p>The bottom of sample</p> 	<p>The bottom of sample</p> 	<p>The bottom of sample</p> 

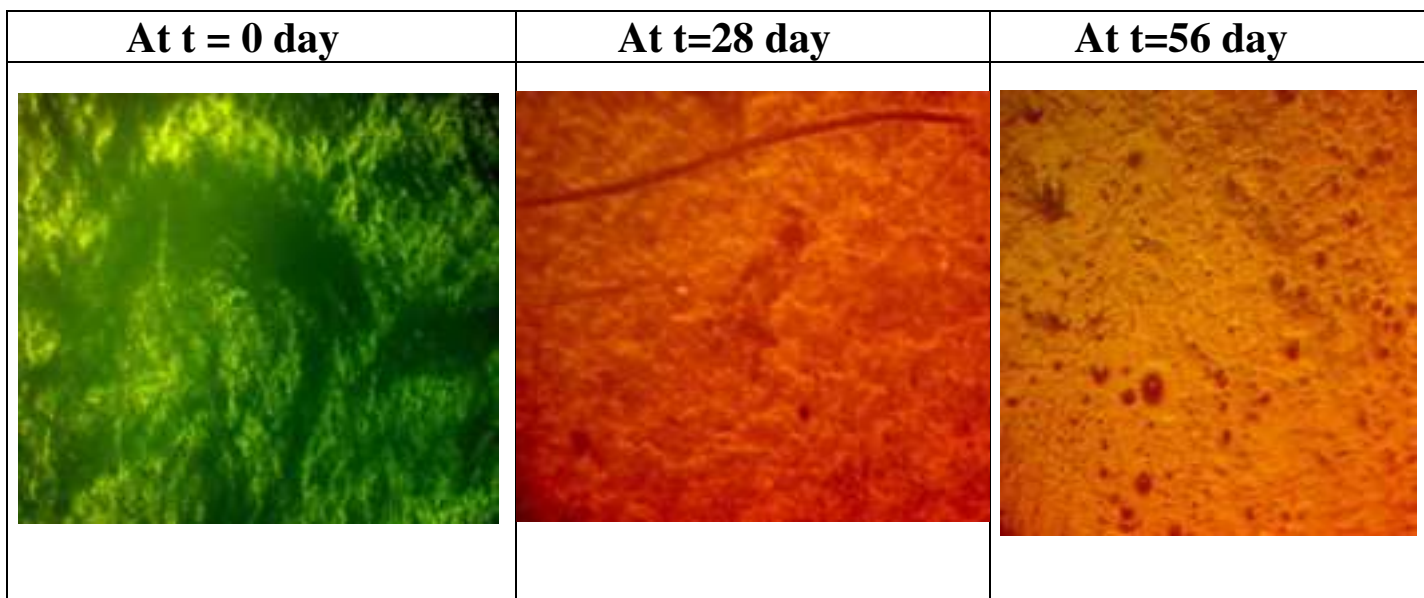


Fig.4.9 : Optical microscope images of HDPE samples immersed in HCL acid

4.4 Immersion in Saline Solution

4.4.1 Result Hardness

Figure 4.11 shows the relationship between immersion in saline solution and hardness, where hardness increased by 4.76%. This finding indicates that chlorine atoms occupy the voids among PE chains, which reduces the free volume and resists the indenter penetration. Also, this increment in the hardness can be attributed to the strong ionic bonding (Na – Cl) in the saline solution compared with covalent bonds and secondary forces in the PE.

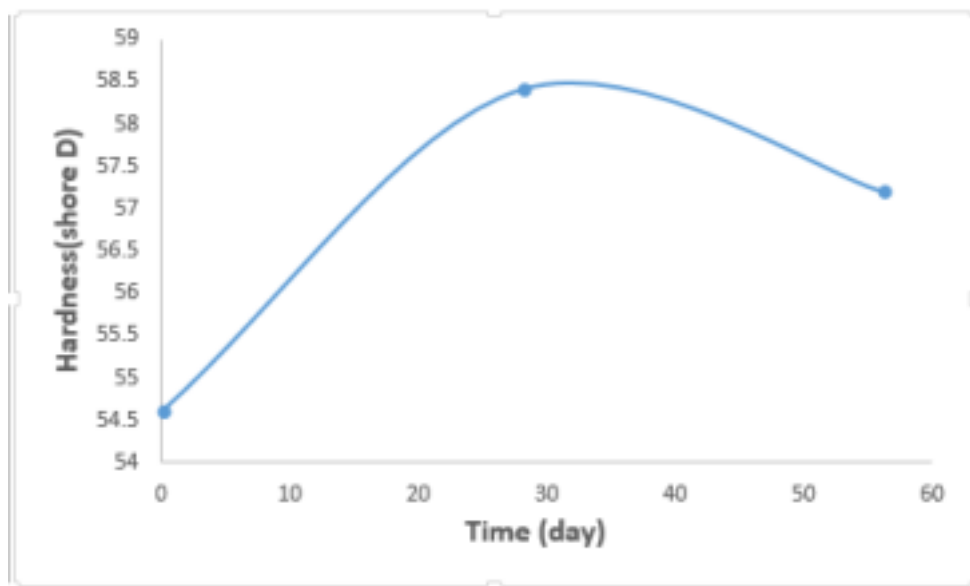


Fig.4.10 : Effect of saline solution immersion on hardness property

$$\Delta \text{Hardness} = \frac{57.2-54.6}{54.6} * 100\%$$

$$= 4.76\%$$

4.4.2 Wettability Results

Figure 4.12 shows that the contact angle (CA) decrease with time from 57.33⁰ to 56.908⁰ when a PE sample is immersed in saline solution; changed only by 0.73%.

$$\Delta \text{CA} = \frac{56.908-57.33}{57.33} * 100\%$$

$$= - 0.73\%$$

That means that the penetration of the saline solution was restricted to some extent, so that there is only new few voids added to the neat PE network. These few additional voids absorb very little amount of water and caused slight increment in the wettability property.

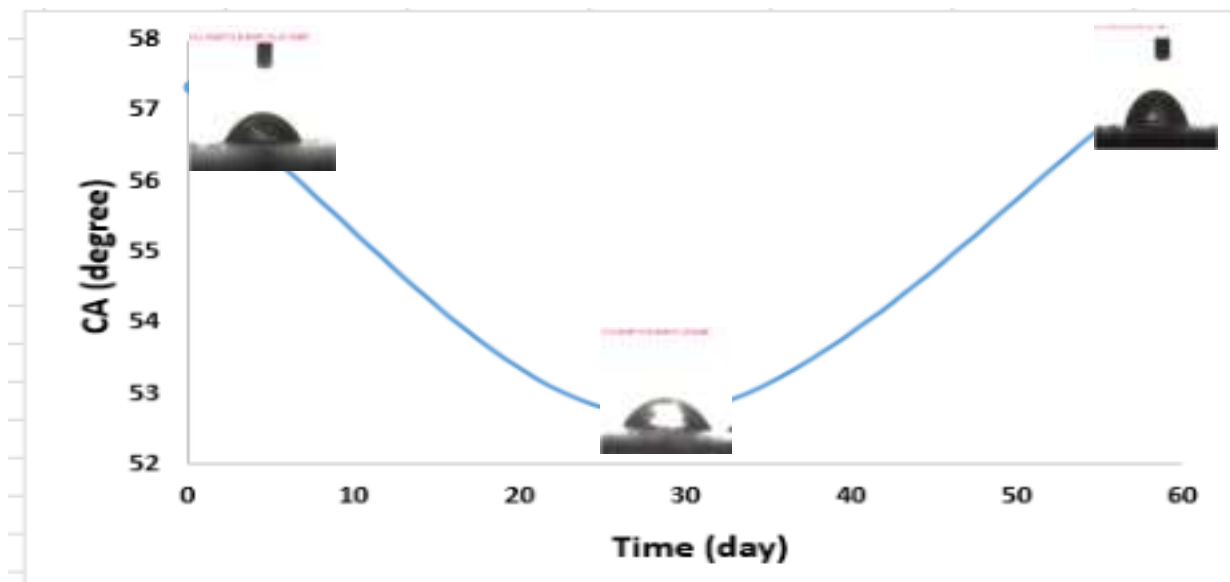


Fig.4.11: Effect of saline solution immersion on contact angle

4.4.3 Swelling Results

When PE sample was immersed in the saline solution, a noticeable swelling was found (especially after 56 day). This volume increment is a result of the penetration of the saline solution molecules into the sample. At the first immersion period, only 0.13% swelling occurs, and this rate increased up to 0.35% in the second period, which means that the absorption capacity is time-dependent property.

$$\begin{aligned} \text{Swelling after 28 day} &= \frac{w_2 - w_1}{w_1} * 100\% \\ &= \frac{0.8648 - 0.8636}{0.8636} * 100\% \\ &= 0.13\% \end{aligned}$$

$$\text{Swelling after 56 day} = 0.35\%$$

In both these two periods, only gain weight happened and there is no loss weight, which means that there is slight chemical degradation occurs. This finding suggests using PE in the saline environments, such as in marine applications (coating ships bottom with PE material).

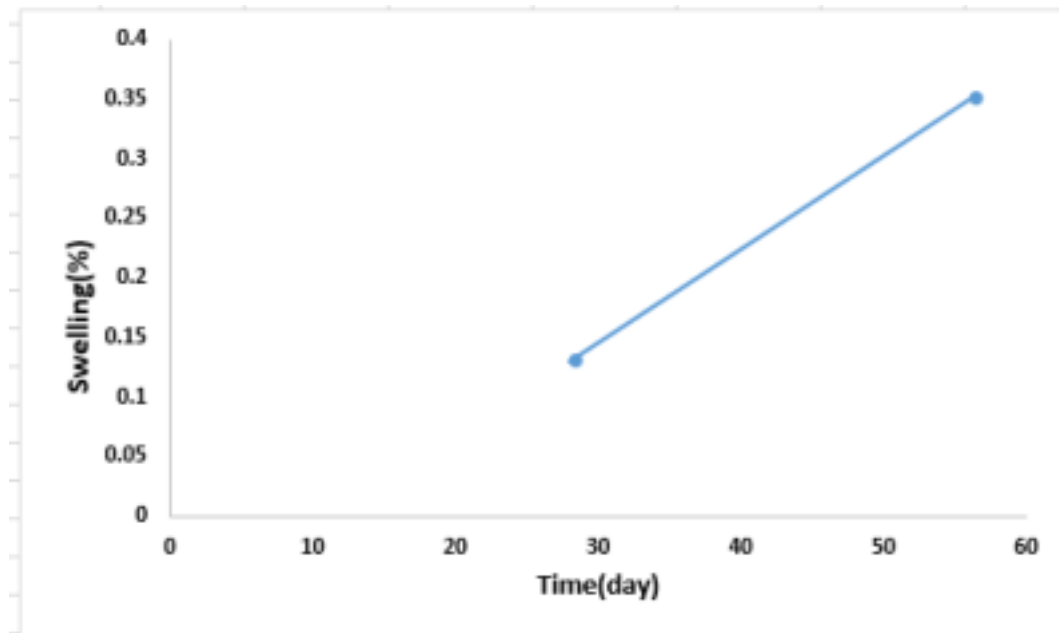


Fig.4.12 : Effect of saline solution immersion on swelling capacity

4.4.4 Morphology Results

Figures 4.14 and 4.15 show the surface morphology of PE sample before and after immersion in saline solution by two techniques; digital and optical microscopes.

Before immersion, the surface is generally rough, after that the surface become softer during 28 day. This is because the swelling in the amorphous regions in the polymer network (the crystalline regions don't be affected by saline solution). After 56 day these amorphous regions continued in swelling and get out from the surface making it rougher.





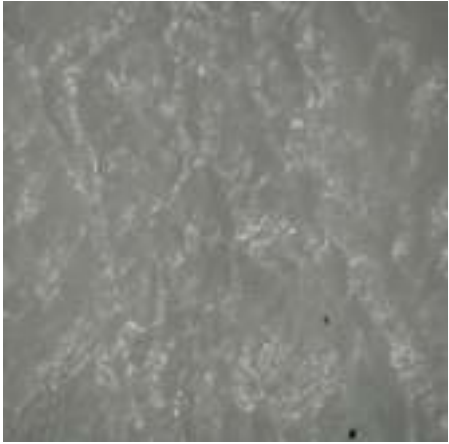

At 0 day	At 28 day	At 56 day
<p>The surface of sample</p> 	<p>The surface of sample</p> 	<p>The surface of sample</p> 
<p>The bottom of sample</p> 	<p>The bottom of sample</p> 	<p>The bottom of sample</p> 

Fig.4.13 : Digital microscope images of HDPE samples immersed in saline solution


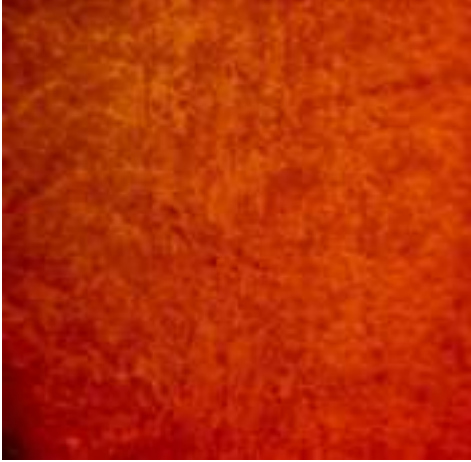
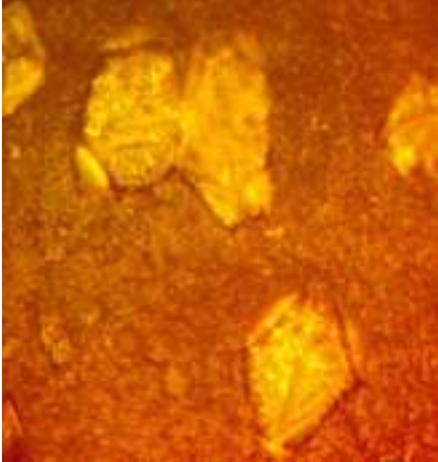
At t = 0 day	At t=28 day	At t=56 day
		

Fig.4.14 : Optical microscope images of HDPE samples immersed in saline solution

CHAPTER FIVE

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

The following findings can be concluded from subjecting HDPE to the chemical degradation (Table 4.1) :

- 1- After 56 days of hydrolysis degradation, PE experiences slight weight loss, slight hardness reduction, announced wettability and its surface become smoother and their roughness reduced clearly.
- 2- In the acidic solvolysis degradation, weight gain happened, moderate hardness reduction, announced reduction in the wettability. Its surface morphology showed two different actions, where at the first immersion period (28 days), there is a swelling in the amorphous regions so that the grooves filled with the swollen parts, which resulted in the smooth surface. At the second period, these swollen amorphous parts continue in swelling so that the surface retain to be rough again.
- 3- In the saline solvolysis degradation, the hardness increased clearly, the wettability increased slightly, moderate weight gain and its surface morphology altered in two stages likes what happened with acidic solvolysis degradation.

Property	Hydrolysis Degradation	Acidic solvolysis degradation	Saline solvolysis degradation
Hardness (Shore D)	- 2.45	- 2.9	+ 4.76
Contact Angle (degree)	- 29.79	+ 84.04	- 0.73
Swelling Capacity (%)	- 0.067	+ 0.11	+ 0.35

Table 4.1: Summary of chemical degradation effects on HDPE

5.2 Recommendations

- 1- Study another types of chemical degradation upon HDPE, such as "Oxidation" and "Ozonoziation" degradation.
- 2- Achieve an a comparison between the chemical degradation of HDPE and LDPE to evaluate the effect of crystallinity on degradation.
- 3- Using another techniques to study the degradation, such as AFM, SEM and DSC (T_g parameter). Also, another mechanical properties can be studied, such as tensile strength, Yong modulus and so on.
- 4- Study the effects of HDPE recycling conditions (temperature, time and extrusion parameters) on the oxidation degradation. And calculate the number of times that HDPE polymer can be recycled without sacrificing its mechanical properties.
- 5- Study the solvolysis chemical degradation under alkaline conditions, such as NaOH base.
- 6- Extending the immersion time more than 56 days.
- 7- Subject the HDPE samples to two parameters simultaneously, such as acids and heat or base and ozone and so on.

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