EFFECT OF COBALT LAURATE ON THE PHOTO-DEGRADATION OF HIGH DENSITY POLYETHYLENE

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EFFECT OF COBALT LAURATE ON THE PHOTO-DEGRADATION OF HIGH
DENSITY POLYETHYLENE

ABDUL HISHAM BIN RUSLAN

Thesis submitted to the Faculty of Chemical and Natural Resources Engineering in
Partial Fulfillment of the Requirement for the
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Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

MAY, 2009

I declare that this thesis entitled "*Effect of Cobalt Laurate on the Photo-Degradation of High Density Polyethylene*" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Special Dedication of This Grateful Feeling to My…

Beloved father and mother;
Mr.Ruslan Mohammad and Mrs. Hasimah Hamzah

Loving brothers and sisters;
Norhafizah,Burhanuddin,Abdul Halim and Hamizah

Supportive families;
Uncles and Aunties

For Their Love, Support and Best Wishes.

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ABSTRACT

Plastics nowadays become something very needful in our packaging industry and its roles in our daily activities are irreplaceable. Plastics help make our life easier and better without any doubt. Plastics are polymer and it takes thousand of time to degrade to the environment. Plastic can degrade to the environment by several methods and photo-degradation is one of them. A common photo degradation reaction is oxidation. Then, oxidation agent that use in this research is cobalt laurate. There are 2 reactions involve in production of cobalt laurate. First reaction is sodium hydroxide with lauric acid, and then continues with cobalt chloride after that. The properties of cobalt laurate were measure like density, solubility, melting point and degradation point to analyze. To study the degradation process the polymer type high density polyethylene is used and it was mixed with cobalt laurate as the oxidation agent. The sample was produced by plastic injection molding. The amount of cobalt laurate in the sample is verified to study their effect on the degradation process. The sample was exposed to the sun light under normal and natural environment condition for two weeks to undergo the photo-degradation process. In this process, the sample will absorb the energy in the form of light to break the chain and bonding among polymer. To ensure the photo-degradation is taken place in the sample, it can reveal by determine differentiation and change in mechanical properties of sample before and after the photo-degradation. The mechanical properties are mass, density, tensile strength, elongation break and surface morphology. After this research is done, the conclusion is the degradation of polymer is faster as the amount of cobalt laurate in the sample increase.

ABSTRAK

Plastik kini menjadi sesuatu yang sangat diperlukan dalam industri pembungkusan dan peranannya dalam aktiviti seharian kita tidak dapat digantikan. Plastik membantu kita hidup lebih mudah dan lebih baik tanpa keraguan. Plastik adalah polimer dan ia mengambil ribuan masa untuk lerai ke alam sekitar. Plastik dapat dileraikan melalui beberapa cara dan foto-degradasi adalah salah satu daripadanya. foto degradasi yang biasa adalah reaksi pengoksidaan. Kemudian, agen pengoksidaan yang digunakan dalam kajian ini adalah kobalt laurat. Terdapat 2 reaksi yang terlibat dalam penghasilan kobalt laurat. Pertama adalah reaksi natrium hidroksida dengan asid laurik, dan kemudian disambung dengan kobalt klorida. Ciri-ciri kobalt laurat seperti kepadatan, keterlarutan, darjah kecairan dan darjah keleraian diukur untuk dianalisis. Untuk mempelajari proses keleraian, polimer jenis polyethylene yang kepadatn tinggi digunakan dan ia dicampur dengan kobalt laurat sebagai agen pengoksidaan. Sampel telah dihasilkan dengan menggunakan alat tusukan pembentukan plastik. Jumlah kobalt laurat di dalam sampel dibeza-bezakan untuk mempelajari kesannya terhadap proses leraian plastik. Sampel telah dibiarkan terkena cahaya matahari di bawah keadaan persekitaran yang normal selama dua minggu untuk menjalani proses foto-degradasi. Di dalam proses ini, sampel akan menyerap tenaga dalam bentuk cahaya untuk memutuskan rantai dan ikatan di antara polimer. Untuk memastikan foto-degradasi yang terjadi dalam sampel, ia dapat dilihat dengan menentukan perbezaan dan perubahan sifat mekanik sampel sebelum dan selepas foto-degradasi. Sifat mekanik adalah seperti jisim, kepadatan, kekuatan ketegangan, keputusan pemanjangan dan morfologi permukaan. Setelah kajian ini dijalankan, kesimpulannya adalah keleraian polimer adalah lebih cepat jika jumlah kobalt laurat di dalam sampel meningkat.

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Plastics that are being used every day in our life are become something very needful in our packaging industry and its roles in our daily activities are irreplaceable. Whether we are aware of it or not, plastics play an important part in our life. Plastics' versatility allows it to be used in everything, from transportation parts to doll parts, from soft drink bottles to the refrigerators they are stored in. Plastics help make our life easier and better without any doubt. Plastics are polymers, polymers are a long chains of atoms bonded to one another. These chains are made up of many repeating molecular units, known as "repeat units", derived from "monomers"; each polymer chain will have several 1000's of repeat units. There are so many types of polymer and polyethylene (PE) is one of them. The common polyethylenes are High Density Polyethylene (HDPE), Low Density Polyethylene (LDPE) and Linear Low Density Polyethylene (LLDPE). Polyethylene has high molecular weight and with its hydrophobic character, it is refuse to degrade to the environment, thus its can lead to the pollution. Polyethylene also harmful to the marine life and can make our drain system obstructed. Hence, using the degradable plastic will overcome this pollution problem. So, we can use the additive to allow the plastic undergoes degradation under the sun light and UV radiation. The involving reaction in the degradation process is photo degradation.

Photo degradation is degradation of a photodegradable molecule that caused by the absorption of photons. Photons is the elementary particle responsible for

electromagnetic phenomena. It is the carrier of electromagnetic radiation of all wavelengths, including gamma rays, X-rays, ultraviolet light, visible light, infrared light, microwaves, and radio waves or particularly we can say photons is wavelengths that found in sunlight, such as infrared radiation, visible light and ultraviolet light. However, other forms of electromagnetic radiation also can cause the photo degradation. Photo degradation is including photo dissociation, the molecules breakup into smaller pieces by photons. The shape of a molecule also will change to make it irreversibly altered such as the denaturing of proteins, and the addition of other atoms or molecules. A common photo degradation reaction is oxidation. Then, oxidation agent that use in this experiment is Cobalt Laurate.

1.2 Problem statement

Pollution, it has been existed for a long time and the intensity of pollution is in a high level and is waiting for an aggressive and effective action. Countless of pollution is involving everyday from the minor to major disastrous form, destructing our beloved living environment and as the time flow, causing imbalance to our equilibrium. One of the major pollutants is plastic. Nowadays, plastic have achieved an irreplaceable position in our packaging industry. Polyethylene or well known as plastic litter is ubiquitous in all over the world and due to its high molecular weight and its hydrophobic properties; it simply refuses to degrade thereby creating a very seriously environmental problem. So, one of the solution to this scenario is we produce the degradable plastic. The element that can make plastic degrade is pro-oxidant additive. In production of degradable plastic, we put pro-oxidant additive as a degradation agent. When polyethylene expose to the UV irradiation, pro-oxidant additive in the polyethylene chain plays its role to break the chain and bonding among polyethylene. Thus, it can make that polyethylene degrade in the natural environment.

1.3 Objectives of the study

  i.   To produce Cobalt Laurate as an additive for degradable plastic
  ii. To investigate the effect of verifying the amount of composition cobalt laurate on the degradation of High Density Polyethylene.

1.4 Scope of study

The scope of this experiment is to study the effect of different composition of cobalt laurate on degradation of High Density Polyethylene. To achieve the objectives of this experiment, the following aspects have been identified:

  i.   Synthesis of the Cobalt Laurate
  ii. Characterization of Cobalt Laurate.
  iii. Effect of different amount composition of Cobalt Laurate on Photo degradation of High Density Polyethylene.

1.5 Rationale and significance

According to Society of Plastic Engineers (SPE), over 200 million tonnes of plastics are manufactured annually around the world and in 2003, the Environmental Protection Agency (EPA) reported only 5.8% of those 26 million tons of plastic waste are recycled. We can't recycle the plastic waste continuously again and again because this can cause the reduction in the plastic quality. Thereby that's why we need to dispose these plastics by make it degradable. With this degradation, we can reduce the ubiquitous plastics waste, thus we can create the green environment. It is important in reducing one of sources of pollutions to ensure we can have a better living environment. By hook or by crook we need to save and maintain our environment for our future generation. The pollution getting worse day by day, so

this is grievous if our mistake will make our future generation can't get the pleasure from our peaceful environment.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Plastics due to their versatility become the essential ingredients to provide a quality to life. These are now rival metals in breadth of use and in severity of applications because of their flexibility, toughness, excellent barrier and physical properties and ease of fabrication. The accumulation of plastics in the environment is a matter of great concern leading to long-term environment, economic and waste management problems. Degradation of waste plastics through various means becomes one of the alternatives to deal with such problems. A wide variety of synthetic polymers absorbs solar ultraviolet (UV) radiation and undergoes photolytic, photo-oxidative, and thermo-oxidative reactions that result in the degradation of these materials. The propensity of plastic products to undergo solar UV radiation induced degradation/ozone-induced degradation has been increased by addition of some additives in these polymers. Besides these degradations, biodegradation offers another most efficient and attractive route to environmental waste management. The mechanisms involved in the biodegradation are complex due to the interaction of different oxidative processes which are caused by the oxygen present in the air either by the microorganisms or by the combination of the two.

On the other hand, sometime the product needs stability instead of degradation. Therefore, depending upon the product applications plastic needs controlled stability. In order to increase the outdoor uses of plastics, the development and production of polymers with increased weathering resistance is required

similarly for the use in high temperature applications, polymers need thermal stability. To control the stability, understanding of the mechanism is the primary requisite. Keeping in view the facts for the plastic degradation, in this review article, we have mainly discussed the various types of polymeric degradations (photo-oxidative degradation, thermal degradation, ozone-induced degradation, mechanochemical degradation, catalytic degradation and biodegradation) and mechanism followed by these degradations. We have also discussed the various methods used to study these degradations and various factors which affect these degradations.

2.2 Types of plastics

Plastics can be synthesized by the polymerization of small molecules and are in general classified into two groups which are thermoplastics and thermoset plastics. Thermoplastics are linear chain macromolecules where the atoms and molecules are joined end-to-end into a series of long, sole carbon chains. The bi-functionality necessary to form a linear macromolecule from vinyl monomers can be achieved by opening the double bond and reaction proceeds by a free radical mechanism. Such type of polymerization is known as addition polymerization, polyethylene and polypropylene are the examples. On the other hand, thermoset plastics are formed by step-growth polymerization under suitable conditions allowing bi-functional molecules to condense inter-molecularly with the liberation of small by-products at each reaction step. In this class, the monomers undergo some chemical changes (condensation) on heating and convert themselves into an infusible mass irreversibly.

2.3 Types of plastic degradation

Changes in polymer properties due to chemical, physical or biological reactions resulting in bond scissions and subsequent chemical transformations are categorized as polymer degradation. Degradation reflects changes in material

properties such as mechanical, optical or electrical characteristics in crazing, cracking, erosion, discoloration and phase separation. Depending upon the nature of the causing agents, polymer degradations have been classified as photo-oxidative degradation, thermal degradation, ozone-induced degradation, mechanochemical degradation, catalytic degradation and biodegradation (Baljit Singh and Nisha Sharma, 2007).

2.3.1 Photo-oxidative degradation

Photo-oxidative degradation is the process of decomposition of the material by the action of light, which is considered as one of the primary sources of damage exerted upon polymeric substrates at ambient conditions. Most of the synthetic polymers are susceptible to degradation initiated by UV and visible light. Normally the near-UV radiations (290–400 nm) in the sunlight determine the lifetime of polymeric materials in outdoor applications. Polymer degradation occurs mainly in the ether parts of the soft-segments, where photo-irradiation generates ester, aldehyde, formate and propyl end groups. UV radiations have sufficient energy to cleave C–C bond. The most damaging UV wavelength for a specific plastic depends on the bonds present and the maximum degradation therefore occurs at different wavelengths for different types of plastics. Photo-degradation changes the physical and optical properties of the plastic. The most damaging effects are the visual effect, the loss of mechanical properties of the polymers, the changes in molecular weight and the molecular weight distribution for the same. Plastic films when exposed to solar UV radiation readily lose their extensibility, mechanical integrity and strength along with decrease in their average molecular weight. For example, mechanical integrity of polystyrene (PS) is diminished through extensive chain scission during photo-degradation Another important study carried out on light-induced damage to PS plastics compounded with flame retardant additives has reduced the risk of fire when the plastics have been used as building construction materials. (Baljit Singh and Nisha Sharma, 2007).

At any given temperature and moisture content, the rate of weathering increases with an increase in UV flux. Tensile stressing of stabilized types of polymer in thermo-oxidative and photo-oxidative environment has accelerated embrittlement of the polymers. In one study, tensile stress has been applied at constant load by Baljit Singh and Nisha Sharma in 2007 to observe the behavior of stabilized and unstabilized types of isotactic polypropylene (PP) in the course of thermo-oxidative aging at 80–130 °C, photo-oxidative aging at 45°C and relative humidity of 65%. From kinetic evaluation of the temperature-dependence of weight changes of unstabilized PP during thermo-oxidative aging, it has been found that the weight losses of unstressed and tension-stressed specimens have obeyed the kinetic equations for a reaction of the first order. Along with stress, introduction of carbonyl group on polymeric backbone has also accelerated photochemical degradation. PS undergoes photochemical ring-opening reactions, which leads to backbone cleavage by subsequent Norrish Type II reactivity.

2.3.1.1 Mechanism of photo-degradation

According to Baljit Singh ana Nisha Sharma, 2007, the mechanisms of the degradation and oxidation reactions are determined by the extraneous groups and impurities in the polymer, which absorb light quanta and form excited states. Initially short-lived singlet state is transformed to long-lived triplet state. Excited triplet states may cleave the polymer chains and form radical pairs (Norrish Type I reaction) or form pairs of saturated and unsaturated chain ends by hydrogen transfer (Norrish Type II reaction). The polymer radicals thus formed may add molecular oxygen (in triplet ground state) to peroxy radicals, which abstract hydrogen and form hydroperoxide groups, which absorb UV light or become excited by energy transfer, the weak O–O bonds break and pairs of alkoxy and hydroxyl radicals are formed which may react in various ways, e.g. by hydrogen abstraction, chain scission, rearrangement, etc. and accelerate photo-degradation. Double bonds may add excited oxygen molecules in singlet state. In this reaction, the double bond is shifted to an adjacent C–C bond and a hydroperoxide group is formed. Some synthetic polymers, e.g. aromatic polyesters and polyamides, have inherent absorption of UV light,

causing excitation, radical formation, oxygen addition, splitting off small molecules, chain scission, etc. Some of these polymers are auto-stabilized towards photo-degradation by formation of an oxidized surface layer with high absorption of near UV and visible light of short wavelengths, preventing further penetration of light into deeper layers. In photo-oxidative degradation, mechanism involves auto-oxidation cycle comprising various steps shown by Scheme 1 in Figure 2.1

Initiation

Initiator $\longrightarrow$ $R_i^{\cdot}$

$R_i^{\cdot} + O_2 \longrightarrow R_iOO^{\cdot}$

$R_iOO^{\cdot} + R\!-\!H \longrightarrow R_iOOH + R^{\cdot}$

Propagation

$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$

$ROO^{\cdot} + R\!-\!H \longrightarrow ROOH + R^{\cdot}$

Termination

$R^{\cdot} + R^{\cdot} \longrightarrow R\!-\!R$

$R^{\cdot} + ROO^{\cdot} \longrightarrow ROOR$

Figure 2.1: Scheme 1

2.3.1.1.1 Initiation
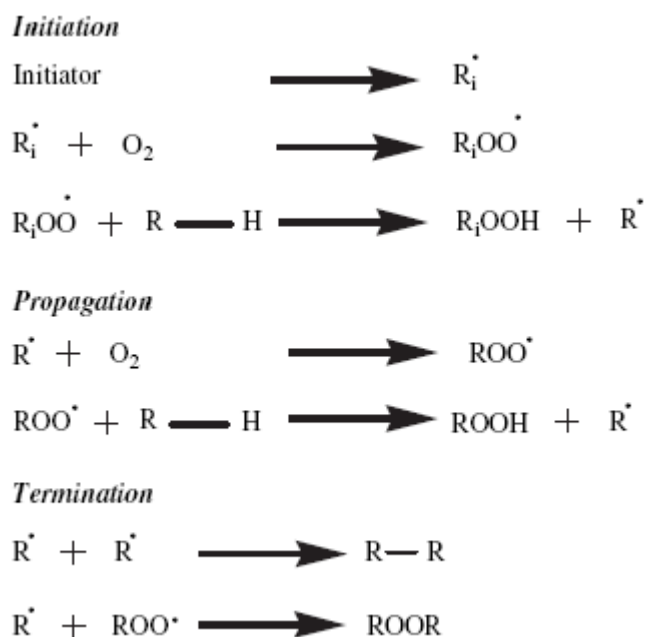
The absorption of UV light that has sufficient energy to break the chemical bonds in the main polymer chain leads to the initiation of mechanism responsible for polymer degradation. It involves a radical chain mechanism for the formation of initial radical. Different initiation steps under varied conditions have been undertaken in different polymers. (Baljit Singh and Nisha Sharma, 2007).

2.3.1.1.2 Direct UV initiated photolysis of C–C and C–H bond

Bond dissociation energy of C–C bond (375 kJ/mol) and C–H bond (420 kJ/mol) is equivalent to UV radiation of 320 nm and 290 nm (Baljit Singh and Nisha Sharma, 2007). Thus, direct photolysis of C–C and C–H bond is possible and the radical formed in these reactions become a source of initiation radicals as shown in Scheme 2 in Figure 2.2.

Figure 2.2: Scheme 2
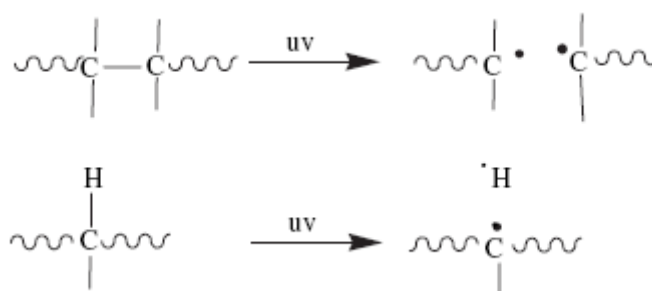
2.3.1.1.3 Photosensitized cleavage

Photosensitizers are highly photosensitive, readily get excited on exposure to light and are generally employed to bring about effective homolysis of the polymeric chains, which otherwise do not undergo sufficient photo-excitation at the frequency of light available to the system, Scheme 3 (Baljit Singh and Nisha Sharma, 2007).
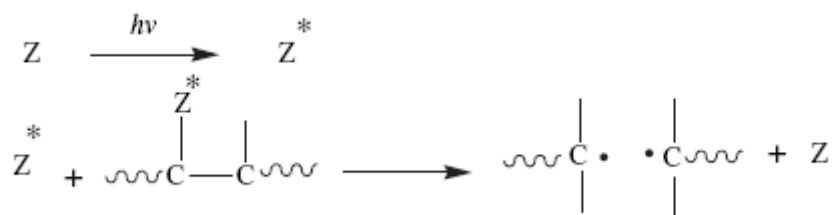
Figure 2.3: Scheme 3

2.3.1.1.4 Catalyst residues as source of generation of radical

Some metal salts and oxidation products of such residues when added to the polymers act as catalysts to generate initiation radicals, Scheme 4. Many commercial polymers contain metallic compounds as impurities or deliberately incorporated additives. The bulk of the latter types are pigments, whereas the former include polymerization catalyst residues or debris from processing equipment. Polymerization catalysts such as transition metals (Ti) may remain in polyolefins at 2–100 ppm, depending on workup and catalyst efficiency. These residues have been implicated in both photo- and thermal stability problems. For example, TiO_2 is a well-known photosensitizer for polyamide and polyolefin degradation and absorbs at 480 nm. Photosensitization involves the formation of highly reactive species including atomic oxygen, $^{\bullet}OH$, $^{\bullet}OOH$ and $O_2^{\bullet-}$. The primary process involves the promotion of the Ti electron to the conduction band of the semiconductor to form an electron-positive hole pair. The relative proportions of the reactive species depend on the presence of water. No TiO_2 sensitization will be observed unless both oxygen and water are present (Baljit Singh and Nisha Sharma, 2007).

$$TiCl_4 \xrightarrow{\text{hv}} TiCl_3 + Cl^{\bullet}$$

$$TiO_2 \xrightarrow{\text{hv}} TiO_2^{\bullet} \xrightarrow{O_2,\ RH} TiO_2 + HOO^{\bullet} + R^{\bullet}$$

Figure 2.4: Scheme 4

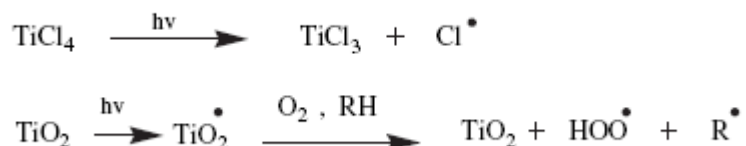**2.3.1.1.5 Incorporation of carbonyl groups**

Carbonyl groups formed by mild oxidation of polymer during synthesis or processing act as chromophores and become source of the initiation radicals. Carbonyl chromophore absorbs near-UV radiations and subsequently forms radicals following Norrish Type I, Norrish Type II and H-atom abstraction processes, Scheme 5 (Baljit Singh and Nisha Sharma, 2007).
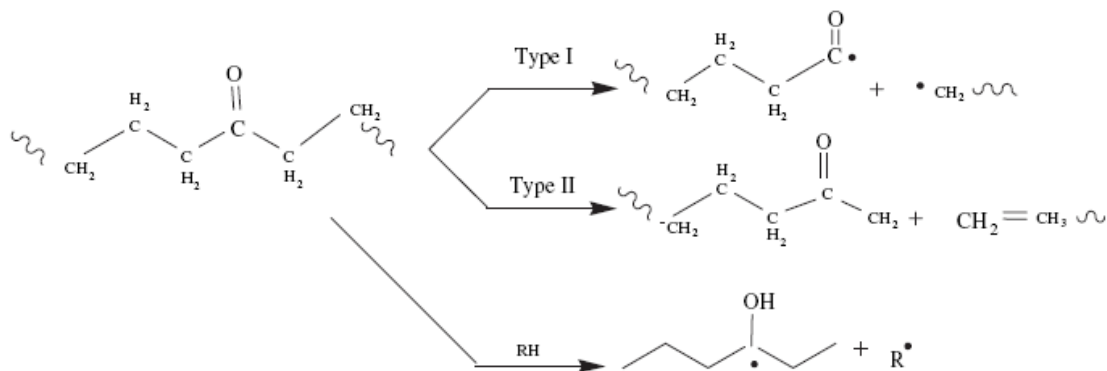
Figure 2.5: Scheme 5

2.3.1.1.6 Introduction of peroxides or site of Unsaturation

The peroxides or C$=$C sites become source of initiation radicals as shown in Scheme 6. The near UV component of sunlight (280–390 nm) is energetic enough to cleave C–C bond and C–heteroatom bonds provided that light of the appropriate wavelength is absorbed. Chain oxidation occurs in most of the polymers because of the labile O–O bond present in the macrohydroperoxide –C–OOH, the macroalkoxyl and hydroxyl radicals thus formed may abstract hydrogen from the surrounding polymer matrix to generate alcohol, water and new macroalkyl radicals which can then take part in many cycles of the chain-initiation reactions. In the case of unsaturated polymers, light generated singlet oxygen $^1O_2$ reacts with an unsaturated site by way of an "ene" reaction and starts chain oxidation, Scheme 6 (Baljit Singh and Nisha Sharma, 2007).
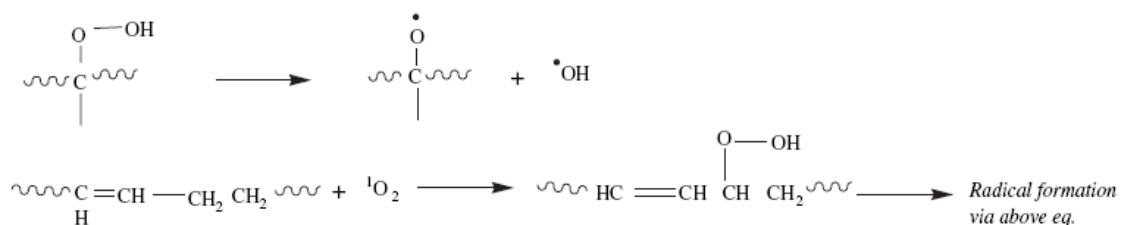
Figure 2.6: Scheme 6

2.3.1.1.7 Reactions of singlet and triplet stage

Reaction of a ketone in a triplet-excited state with ground state oxygen is another potential initiation reaction, Scheme 7 (Baljit Singh and Nisha Sharma, 2007). In these reactions, UV light is absorbed by carbonyl or other chromophoric groups and the energy of the excited groups is transferred to oxygen molecules. The resulting excited oxygen species react with vinyl or other unsaturated groups forming hydroperoxide which then initiate free radical reaction mechanism.
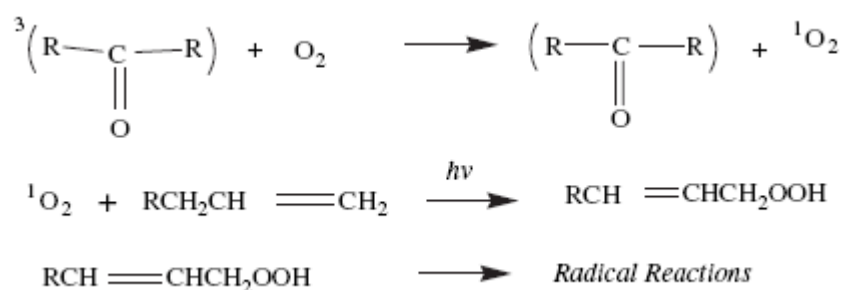
Figure 2.7: Scheme 7

2.3.1.1.8 Propagation reaction

The propagating reactions of auto-oxidation cycle are common to all carbon backbone polymers. These reactions lead to generation of hydroperoxide species, Scheme 8 and are not directly led to backbone cleavage but are the key intermediates to further reactions as shown in Scheme 1. Hydroperoxide species generated in propagating step lead to backbone degradation through cleavage of hydroperoxide O–O bond followed by β-scission, Scheme 9 (Baljit Singh and Nisha Sharma, 2007).
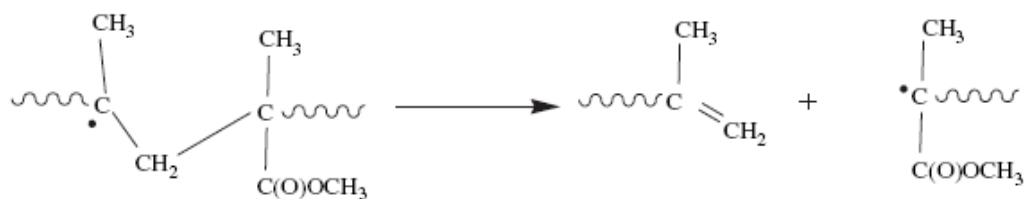
Figure 2.8: Scheme 8
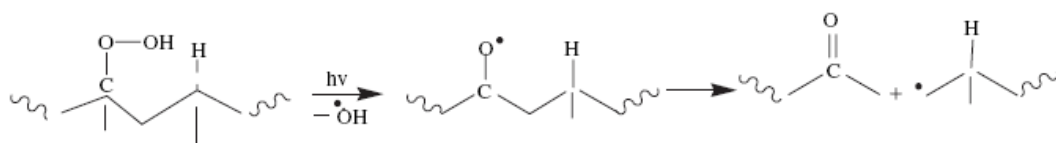
Figure 2.9: Scheme 9

Polymer backbone cleavage occurs through Norrish Type I and II reactions of chromophores (carbonyl) following β-scission route, which is a prevailing route for photo-oxidative degradation. In semi-crystalline polymers, this scission occurs in the amorphous domains. The scission process generates two chain ends that are free to restructure, and can often lead to increase in crystallinity as oxidative degradation proceeds. PS undergoes photo-oxidative bulk degradation via a free radical mechanism, Scheme 10 and Scheme 11 (Baljit Singh and Nisha Sharma, 2007). Oxidative process involves two steps: (1) formation of hydroperoxide and (2) decomposition of these hydroperoxides. Such oxidative reactions are initiated when hydrogen is removed through a photoreaction. The free radical formed on polystyrene reacts with oxygen to form peroxy radical, which can abstract a proton from some other labile positions, thereby forming hydroperoxides and a new radical site. The newly formed hydroperoxide group is subjected to decomposition and resulting ultimately in chain cleavage into ketones and olefins.
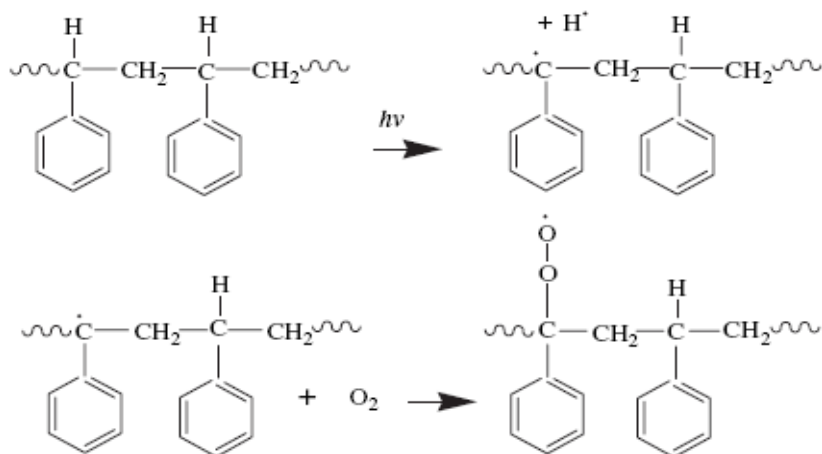
Figure 2.10: Scheme 10
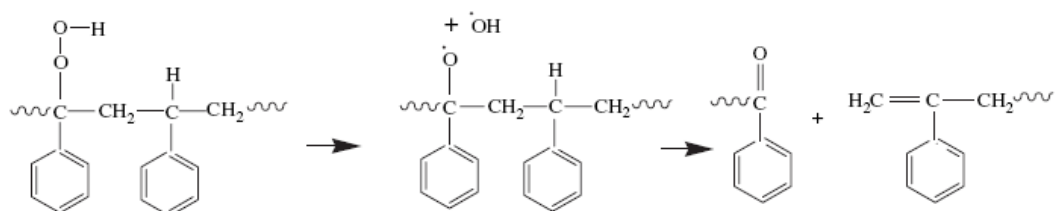
Figure 2.11: Scheme 11

2.3.1.1.9 Termination reaction

The termination of photo-degradation is achieved by 'mopping up' the free radicals to create inert products. This occurs naturally by combining free radicals or assisted by using stabilizers in the plastic. Macroalkyl radicals may combine to give a crosslinked, branched or disproportionated product. Peroxyl radicals eventually terminate by reaction with other radicals to give dialkyl peroxides, carbonyl species or alcohols.

2.3.1.2 Method for photo-degradation

2.3.1.2.1 Natural weathering method

Outdoor exposure can be performed on samples mounted on testing racks, oriented under standard conditions to expose the material to the full radiation spectrum besides the temperature and humidity of that location. In order to observe the aging of the material, it is characterized with respect to mechanical properties (elongation at break, tensile properties or impact strength) and visible characteristics, such as crack formation, chalking, and changes in color. The alterations in the polymeric materials on exposure can be characterized with FTIR spectroscopy and ultra violet/visible (UV/vis) spectroscopy.

2.3.1.2.2 Artificial weathering method/laboratory test

Pure laboratory testing involves using environmental chambers and artificial light sources to approximately replicate outdoor conditions but with a greatly reduced test time under highly controlled conditions. Laboratory testing can quickly assess the relative stability of plastics but has the major disadvantage that the quicker the test lower is the correlation to real behavior in the field. Lundin *et al.*,2002 have studied accelerated weathering of fiber-filled PE composites.

2.4 Factor affecting polymer degradation

Degradation is defined as a process which leads to a deterioration of any physical property of a polymer. In general, the degradation process affects the thermal stability, mechanical properties, crystallinity and lamellar thickness distribution and begins in the amorphous/crystalline interface. Degradations of plastic affected by various factors are given below.

2.4.1 Chemical composition

Chemical composition of the polymers plays a very important role in their degradation. Presence of only long carbon chains in the thermoplastic polyolefins makes these polymers non-susceptible to degradation by microorganisms. By the incorporation of the heterogroups such as oxygen in polymer chain makes polymers labile for thermal degradation and biodegradation. Presence of heteroatom in the polymer chain affects the strength of neighboring C–H bonds of the polymer and promotes carbanion formation in the presence of bases. Linear saturated polyolefins are resistant to oxidative degradation.

Presence of unsaturation in the polymer chain makes them susceptible to oxidation, for example natural rubber is more susceptible to degradation than PE. Amorphous regions in the polymer have been reported to be more labile to thermal oxidation as compared to crystalline areas because of their high permeability to molecular oxygen. Oxidation rates depend on the reactivity of the peroxy radicals formed and on the dissociation energies of available carbon–hydrogen bonds in the polymer substrate. A polymer with no hydrogen at all or with unreactive methyl and phenyl groups shows resistance to oxidation.

2.4.2 Molecular weight

Increase in molecular weight of the plastic decreases the rate of plastic degradation. It has been reported that some microorganisms utilize polyolefins with low molecular weight faster as compared to high molecular weight polyolefins. Linear polyolefins with molecular weight lower than 620 support microbial growth. It is easy to form the ozone adduct in low molecular weight olefins which rearranges to ozonide and during this operation, if the polymer chain is under tension during reaction, the broken chain ends separate out before rearrangement to ozonide occurs.

2.4.3 Hydrophobic character

Petrochemical-based plastic materials are not easily degraded into the environment because of their hydrophobic character and three-dimensional structure. Hydrophobicity of PE interferes with the formation of a microbial bio-film, thus decreases the extent of biodegradation.

2.4.4 Size of molecules

Size of the molecules in the polymers affects their mechanical degradation, thermal degradation and biodegradation. These degradations increase as the size of the molecule decreases.

2.4.5 Introduction of functionality

Introduction of carbonyl groups in polyolefins makes these polymers susceptible to photo-degradation. As the number of chromophores increases the rate of photo-degradation increases due to the more sites, which are available to absorb more photons and to initiate the reaction for degradation. The carbonyl chromophore absorbs near-UV radiation and form radicals by the Norrish Type I, II and H-abstraction processes for photochemical degradation. Chromophores other than carbonyl group $\diagup C \!\!=\!\! O$ such as metal–metal bond if incorporated in polymer backbone induce photo-degradability. In such a case, metal–metal bond cleaves homolytically on irradiation. Polyolefins undergo slow sulfonation and oxidative degradation by reagents based on concentrated sulfuric acid. In chromic acid, sulfonation results in more rapid oxidative degradation of PP with a slower attack on PE. Relative rates of attack on C–H sites are 4600:75:1 for tertiary:secondary:primary, Scheme 12 (Baljit Singh and Nisha Sharma, 2007).
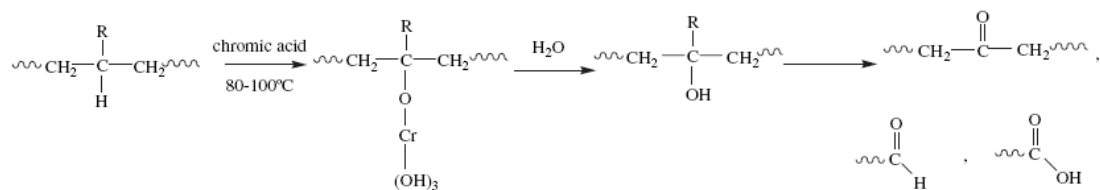
Figure 2.12: Scheme 12

To observe the effect of hydrophilic moieties on the degradations of the polymers, Singh and Sharma have carried out biodegradation study of pure PS and grafted PS that is [PS-*g*-poly(AAc)], [PS-*g*-starch] and [PS-*g*-poly(AAc)-*co*-starch] films by soil burial method. It has been observed that 37% degradation has occurred in PS when modified with starch after 160 days and no degradation has been seen in the case of PS grafted with poly(AAc). This is because starch is a natural hydrophilic polymer and has more susceptibility for bacterial and fungal degradations in soil as ambient environment available for their growth. This is possible due to scissoring caused by the microorganism in some chains at the site of grafting and polymer chains may get breakdown and decrease the number of carbon atom in the chains. It has also been observed by Wool and co-workers that the following exposure to soil test conditions, micrographs of thin films clearly showed the colonization of microorganisms within channels of the matrix that has been initially occupied by starch. Apart from weight loss, change in color of the starch modified PS films has also been observed. FTIR spectra have shown that with passage of time, the soil microorganisms have consumed starch portion of the grafted product.

2.4.6 Additives

Non-polymeric impurities (such as residues of polymerization catalysts, transformation products of additives), fillers or pigments affect the resistance to degradation. Yang *et al*.,2003 have reported that the thermal stability slightly decreases and the ash content increases when the ligno-cellulosic filler loading increases in the sample. The dispersion and interfacial adhesion between the ligno-cellulosic filler and thermoplastic polymer are the important factors affecting the

thermal stability of the composite system. Metals act as good pro-oxidants in polyolefins making polymer susceptible for thermo-oxidative degradation. For example, manganese (Mn) is a suitable metal participating in metal combination for pro-oxidant activity.

Upon activation by heat in the presence of oxygen, pro-oxidants have produced free radicals on the polyethylene chain which have undergone oxidation and have changed the physical properties of the polymers. In addition, the pro-oxidant catalyzes the reaction of chain scission in the polymer, producing low molecular mass oxidation products, such as –COOH, –OH, C$=$O group containing products. Traces of transition metals have accelerated thermal oxidative processes of polyolefins by inducing hydroperoxide decomposition. For example, TiO_2 delustrant has made the polyamides susceptible for heat- and light-induced oxidation. Oxidation of plastic (polyolefin) is influenced by the amount of pro-oxidant additives, chemical structure, morphology of plastic sample and the surface area. Chain-breaking (hindered phenol) antioxidants inhibit the oxo-biodegradation of the polyolefins under thermo-oxidative conditions during service. Photo-stabilizers decrease the chances of photodegradation of plastic materials. Effective light absorbers such as benzotriazoles, benzophenones, and phenyl esters, as well as hindered amine light stabilizers are presently used in plastic formulations intended for outdoor use (usually at a 0.05–2.0 wt.% level). Many transition metal ions are effective accelerators for peroxidation and hence for the biodegradation of the hydrocarbon polymers. Since the sequence of reactions shown in Scheme 20 leads to the rapid buildup of hydroperoxides in the polymer, peroxidation cannot be controlled by chain-breaking antioxidants such as the hindered phenols since the latter are rapidly destroyed by hydroxyl and peroxyl radicals, Scheme 13 (Baljit Singh and Nisha Sharma, 2007).
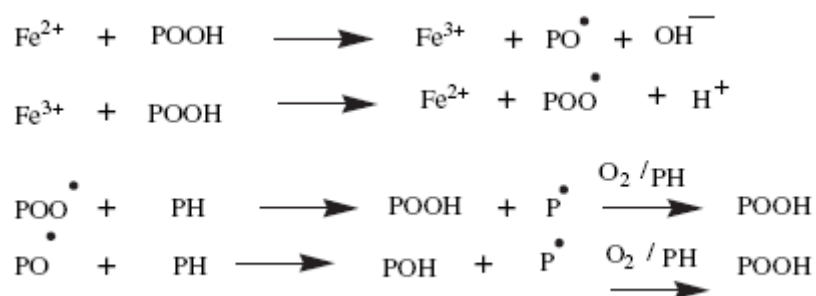
$$Fe^{2+} + POOH \longrightarrow Fe^{3+} + PO^\bullet + OH^-$$

$$Fe^{3+} + POOH \longrightarrow Fe^{2+} + POO^\bullet + H^+$$

$$POO^\bullet + PH \longrightarrow POOH + P^\bullet \xrightarrow{O_2/PH} POOH$$

$$PO^\bullet + PH \longrightarrow POH + P^\bullet \xrightarrow{O_2/PH} POOH$$

Figure 2.13: Scheme 13

As the antioxidants and the stabilizers make polyolefins resistant to degradation, the use of pro-oxidant additives can therefore make them oxo-biodegradable by making polymer hydrophilic and also catalyze breakdown of high molecular weight polyolefin to lower molecular weight product. Susceptibility towards biodegradation of polyolefins enhances by blending with starch or other polyesters and biodegradation depends upon the type of polymer and the blend composition. Along with this filler, pro-oxidants accelerate the process of biodegradation. Averous and co-workers have studied the effect of ligno-cellulosic fractions from wheat straw as natural fillers in composites of a polyolefin (a copolymer of PE and PP) and a biodegradable polyester [poly(butylenes adipate-*co*-terephthalate)]. It has been observed from the study that amount of natural composites affects the degradation of the composites. In another case grafting of the wheat starch had affected the tensile strength of the composites.

2.4.7 Chemical bonding

Linkage affects the degree of degradation in plastic. In thermoplastic, head-to-head addition of monomer units and tail-to-tail addition of monomer units during addition polymerization create weak points which make the plastic susceptible for degradation. Head-to-head linkage in PMMA enhances thermal degradation of the polymer. Branching in polymer chain increases thermal degradation. Crosslinking decreases the rate of photo-degradation by locking the polymer structure and

preventing lamellar unfolding because these actions prevent the separation of photo-produced radicals and favor the radical–radical combination.

2.4.8 Method of synthesis

Methods of synthesis show the noteworthy effect on the stability of the polymers. For example, anionic polymerized PS showed more photo-stability than free radically formed polymer due to the presence of peroxide residue in the latter, which is labile for photo-degradation. PP synthesized by bulk polymerization and by Ziegler–Natta catalyst is more susceptible towards photo-degradation as compared to copolymerized PP.

2.4.9 Effect of substances

Substituents effect the degradation processes in many polymers containing labile α-hydrogen in the repeating units and modify the reaction course profoundly even if the main-chain scission reactions prevail. For ethylene and 1-substituted ethylene, chain-end scission reactions are predominant, producing either little or up to 50% monomer as volatiles. In 1,1-Disubstituted ethylene, repeated units apparently favored 100% monomer yield, whereas chlorine as substituents did not favor chain end degradation route. Thermal stability of a polymer decreases as the number of substituents on polymer backbone increases. Phenyl group in styrene unit of PS makes C–C backbone labile for thermal degradation. Based on the same fact PE shows more thermal stability as compared to PP and polyisobutylene. The effect of substituent groups on the stability of the backbone C–C bond is apparent from the comparison of the bond dissociation energies for C–C bond (in kcal/mol), CH_3–CH_3 = 88, $CH_3CH_2CH_3$ = 85, $(CH_3)_3CCH_3$ = 80 and $C_6H_5CH_2CH_3$ = 70. In PVC, the presence of allylic positioned chlorine atom favored dehydrochlorination of the polymeric chain as double bond activated the release of chlorine radical as shown in Scheme 14 (Baljit Singh and Nisha Sharma, 2007).
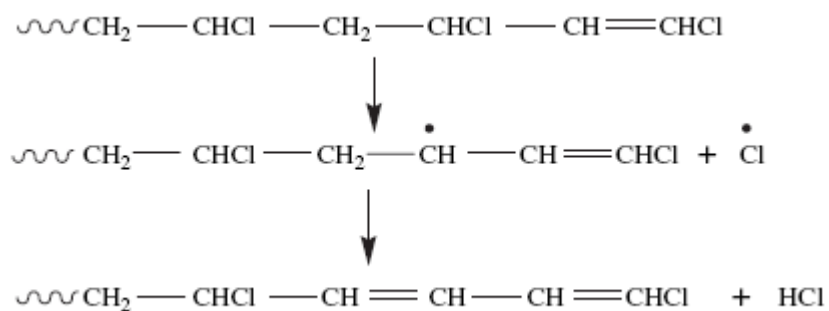
Figure 2.14: Scheme 14

The elimination of the first molecule of HCl and consequent formation of a double bond on PVC chain subsequently activates the neighboring chlorine atom which has assumed the nature of an allylic chlorine, causing elimination of another HCl molecule, with the process continuing to repeat itself finally producing a conjugated polyene structure by an autocatalytic effect. Contrary to this, all substituents not always reduce thermal stability of the polymeric systems. For example, the presence of electronegative groups as fluorine in teflon increases the thermal stability of the polymer due to high dissociation energy (108 kcal/mol) of C–F bond. Aromatic groups in a polymeric backbone increase the thermal stability.

2.4.10 Effect of stress

Stress has significant effect on polymer degradation. Tensile stress increases the rate of photo-degradation whereas compressive stress retards the photo-degradation rate. Stress changes the quantum yields of the reactions that lead to bond photolysis, the efficiency of radical recombination following homolysis, and changes the rate of the radical trapping reaction, Scheme 15 (Baljit Singh and Nisha Sharma, 2007).
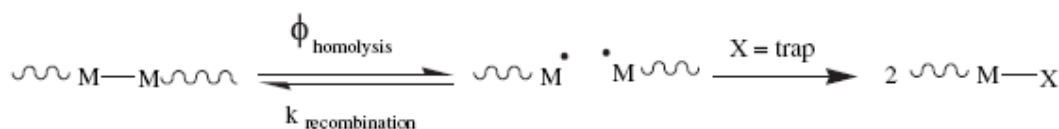
Figure 2.15: **Scheme 15**

The polymer morphology is one of the key factors to interpret the effect of stress on degradation rates. Higher stress causes significant morphological changes, including the straightening of the polymer chains in the amorphous regions. When stretched bonds are cleaved by light, the probability of radical recombination decreases as compared to non-stressed polymer because entropic relaxation of the chain drives the radicals apart and prevents their efficient recombination because of their increased separation. Stress induces a chain orientation that is more favorable for degradation, apparently due to chain conformation that becomes more susceptible to hydrogen abstraction. Stress also effects the thermo-oxidative degradation. Degradation of stressed specimens occurred with considerably higher rate as compared to the unstressed state and is marked by a decrease in apparent activation energy as well as by an increased rate of crack development. The cracks developed in the direction perpendicular to the tensile stress and have the shape of hollow funnels widening outward. An accelerated embrittlement of the polymer occurred due to the tensile stressing of stabilized types of PP in thermo-oxidative and photo-oxidative environments, manifested particularly by a marked decrease of elongation at break.

2.4.11 Environment condition

Biodegradation of polymer depends upon environmental conditions such as moisture, temperature, oxygen, and suitable population of microorganisms. In warm climates when the relative humidity exceeds above 70%, the rate of polymer degradation by the microorganisms increases. High temperature and high humidity enhance hydrolytic degradation of the polymers.

Temperature of the material and the presence of moisture show a considerable synergistic effect on the photodegradation of the polymeric materials. Moisture promotes the light-induced degradation due to the fact that under high humidity soluble photo-stabilizers might leach out of the plastic matrix, reducing the effectiveness of the light stabilizer and leading to degradation. The presence of high humidity, particularly at the higher temperatures tends to increase the photo-damage in polymers such as thermoplastic polyester elastomers. Even a small increase in solar UV level dramatically accelerates the deterioration processes in plastics at high temperature. It is the synergistic effect of high temperature and solar UV radiation that is responsible for the rapid degradation of the polyethylene films under these conditions. Weathering is a degradation process and as such is temperature dependent, i.e. it will occur more rapidly at higher temperatures. The general rule is that for every 10 °C increase in temperature the reaction rate will double. Tropical areas therefore suffer not only from an increase in UV exposure but also faster reaction rates because of the increased temperatures. Humidity also affects the degradation processes; most weathering processes are considerably slower in hot dry climates than in hot wet climates.

Oxygen affects the mechanochemical degradation of rubber at ambient temperature. For instance, degradation has been found to be almost absent when rubber is masticated in an atmosphere of nitrogen. However, when the process has been repeated in the presence of a small amount of oxygen or air, degradation has been observed very quick and significant. This is because during degradation free radicals are produced at the end of the scissor fragments of the chain. In nitrogen, however, the primary radicals formed under shear immediately recombine to give no effective chain breakage. Oxygen due to its radical scavenger nature readily reacts with the free radicals formed at the fragmented ends of the polymer molecule and renders the chain break permanent. Thermal dehydrochlorination of PVC in the presence of oxygen occurs faster than the inert atmosphere. During processing, carbon radicals are formed from chain scission because of strong shear forces. These radicals then react with oxygen to form peroxy radicals, and finally, hydroperoxides.

2.5 Effects of degradation on polymer

2.5.1 Mechanical properties

The degradation process can be reveal in the change of tensile strength and percentage elongation due to the UV exposure. Initially, the polymer will shows a slight increase, both in the tensile strength and elongation. However, the polymer containing additives exhibit a rapid loss in mechanical properties after a certain time of exposure. On absorption of energy in the form of light, the additive undergoes decarboxylation leading to the formation of free radicals. These generate radicals on the main chain of the polymer matrix leading to chain scission which finally affects the mechanical properties. This phenomenon is relatively slower in case of plastic films not containing additive, where UV irradiation leads to crosslinking and hence higher tensile strength. In almost all the cases, films containing additive retain 30% to 40% of their tensile strength but lose their elongation at break rapidly thereby rendering the film useless for practical applications. (P.K. Roy, P. Surekha, C. Rajagopal, V. Choudhary, 2006)

2.5.1.1 Tensile strength

All the formulations exhibit initial mechanical properties in the same range, thereby indicating that the additives do not lead to degradation during the process stage. Only changes in tensile yield strength and percentage loss in elongation at break have been reported here as they have been considered to be direct indicators of degradation. The polymer containing additive showed an increase in the tensile strength initially followed by a steady decrease till the failure of the sample. This initial increase in strength can be attributed to increase in the crystallinity of polymer and the latter decrease is a result of chain scission. (P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary, 2005)

2.5.1.2 Elongation at break

In a research conducted by P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary, 2005, they said that polymer films containing cobalt stearate, CS as the additive lose 90% of elongation within 100 h of UV exposure, while polymer films alone and containing cobalt stearate maleate, CSMA as the additive showed 60-70% loss even after 600 h of exposure. Films containing CS became completely fragile after 100 h of thermo-oxidative treatment and could not be tested any further. As a consequence of degradation the disordered phase is removed as a result of which modified surfaces with increased crystallinity are created.

2.5.1.3 Density

The apparent density of polymer has been reported to increase in the presence of heat and/or UV light. During the aging process, the material becomes denser due to tighter packing and incorporation of oxygen into the amorphous regions of the polymer rendering it heavier. In formulations containing additive, the increase in apparent density was found to be proportional to its amount. (P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary, 2005)

In other research showed the density of low density polyethylene, LDPE increases marginally from 0.92 to 0.93 g/cc after 600 h of UV exposure, while the density of LDPE containing additive increases to as high as 0.96 g/cc. This increase in density can be attributed to the increase in crytallinity as the matrix become dense due to tighter packing and also due to the incorporation of oxygen thereby rendering the polymer heavier and denser. (P.K. Roy, P. Surekha, C. Rajagopal, V. Choudhary, 2006)

2.5.2 Surface morphological

In surface morphology study as showed in Figure2.16, the plastic films had a smooth surface area before any degradation. However, after expose to the UV irradiation and degrade these plastic films' surfaces develop some cracks. The extent of damage was much more pronounced in the films containing additive as compared to neat plastic films. From the SEM test's result, the progressive deepening of the craters/grooves results in the formation of defects/or weaker points which in turn affects the mechanical properties. (P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary , 2007)
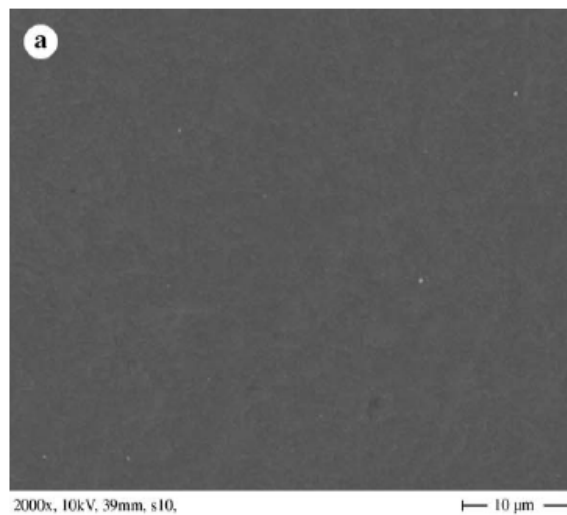

2000x, 10kV, 39mm, s10,   ⊢— 10 µm —⊣

Figure 2.16: Surface morphology of plastic before UV radiation.
(P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary ,
2007)

2000x, 10kV, 39mm, s1, ├── 10 µm ──┤

Figure 2.17: Surface morphology of plastic after 400 hours UV radiation.

(P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary , 2007)

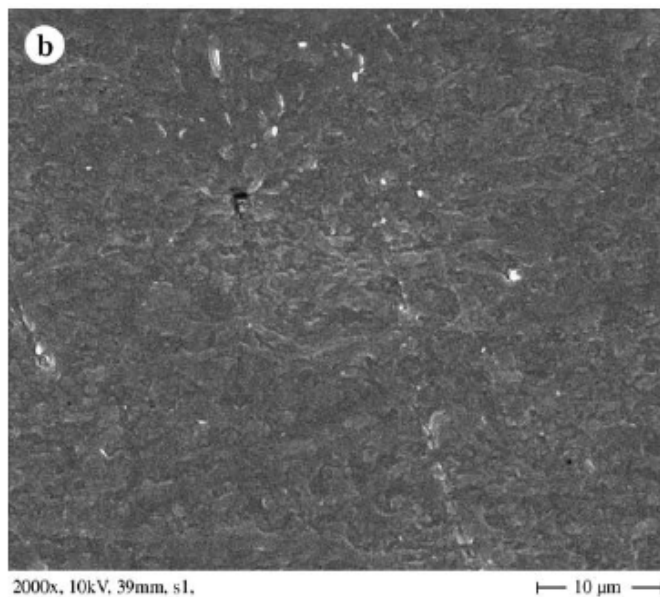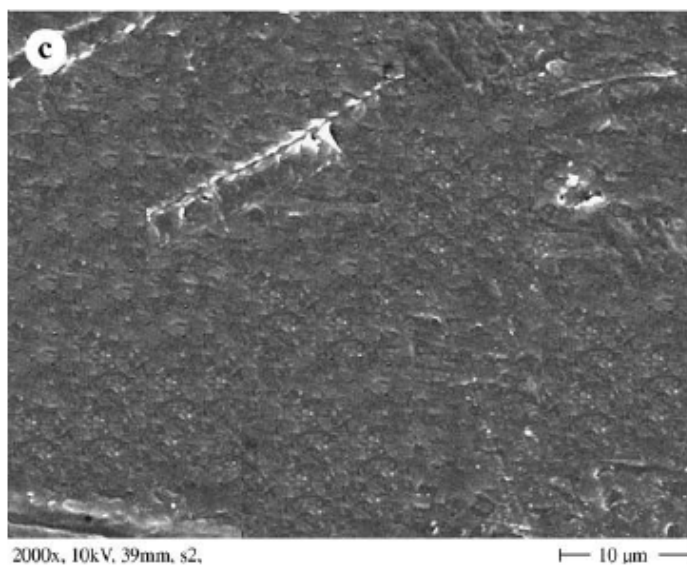2000x, 10kV, 39mm, s2, ├── 10 µm ──┤

Figure 2.18: Surface morphology of plastic after 600 hours UV radiation.

(P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary , 2007)

CHAPTER 3

METHODOLOGY

3.1 Introduction

Initially, the whole process for this research is quite simple. From the figure 3.4, there are six stages are taken to complete the overall research. It is start with the preparation of cobalt laurate then follows by the characterization of cobalt laurate, compounding, plastic molding, photo-degradation process, and finally end with evaluation of photo-degradation.

3.2 Material and equipments

In this research, there are several chemical that have been used which is sodium hydroxide (NaOH), lauric acid ($C_{12}H_{24}O_2$), cobalt chloride ($CoCl_2$), and the raw material is the high density polyethylene (HDPE). The equipment required in this research are analytical balance, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), plastic injection molding, oven, grinder, shaker, tensile testing machine and Scanning electron morphology (SEM).

3.3 Preparation of cobalt laurate

Cobalt Laurate is synthesis by two reactions. Firstly is the reaction of Lauric Acid with sodium hydroxide which produces sodium laurate, $Na(C_{12}H_{23}O_2)$. Then, sodium hydroxide will react with cobalt chloride to produce cobalt laurate, $Co(C_{12}H_{23}O_2)$.

3.3.1 Reaction of lauric acid with sodium hydroxide

In this initial reaction, the 0.25 mol of sodium laurate is needed to produce. First of all, from the figure, 1 mol of sodium hydroxide and 1 mol of lauric acid will produce 1 mol of sodium laurate and 1 mol of water. Proceed with the next step, the 10 gram of sodium hydroxide is weighed and it is dissolved in 500ml of water. The same step is goes for the lauric acid, 50.1 gram of lauric acid is weighed to make it 0.25 mol and it is left to melt down in 100 ml of water at 80^oC. The function of water here is just for the carrier of the chemical to make the reaction easier. The water did not take place in this reaction at all and furthermore at the end of this reaction the water will also be generated. After the lauric acid is completely melted and sodium hydroxide is completely dissolved, these two solutions were mix together at the temperature of 80^oC by using magnetic stirrer. The reaction is continued for one hour to ensure the reaction is complete. The temperature is set at 80^oC because of to prevent the lauric acid undergoes crystallization.
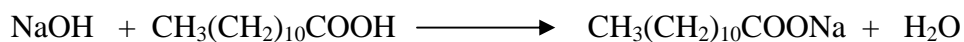
$$NaOH + CH_3(CH_2)_{10}COOH \longrightarrow CH_3(CH_2)_{10}COONa + H_2O$$

Figure 3.1: Reaction of lauric acid with sodium hydroxide

3.3.2 Reaction of sodium laurate with cobalt chloride

$$CoCl_2 \ + \ 2CH_3(CH_2)_{10}COONa \longrightarrow CH_3(CH_2)_{10}COOCo + \ 2NaCl$$
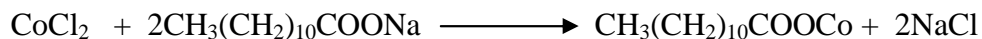
Figure 3.2: Reaction of sodium laurate with cobalt chloride

From the equation above, 1 mol of cobalt chloride will reaction with 2 mol of sodium laurate to produce 1 mol of cobalt laurate. For this step, 29.7413 gram of cobalt chloride is weighed and dissolved in 500ml of water at temperature $80^{o}C$. After ensure all the cobalt chloride is dissolved, the solution is mixed with sodium laurate at temperature $80^{o}C$ for another one hour.

3.3.3 Filtration

After the reaction is completed, the sample is filtrated to separate between cobalt laurate and sodium chloride. Cobalt laurate is in the form of solid and sodium chloride is in the liquid form.

3.3.4 Drying

The wet sample of cobalt laurate is place in the oven at temperature $70^{o}C$ until it dried. The oven model memert is used. The figure show the cobalt laurate before and after the drying process.

3.3.5 Grinding

In this step, grinder is used to produce cobalt laurate in the form of very fine powder.

3.4 Characterization of cobalt laurate

For the characterization of cobalt laurate, there are several characters need to be determine to ensure the sample produced is cobalt laurate.

3.4.1 Bulk Density

To measure the bulk density, the formula of density is used. Firstly, 5 gram of cobalt laurate is weighed and placed in the 75ml crucible. Then, it is burned at $200^{o}C$ for 2hours in a furnace. After the cobalt laurate is took out form the furnace, the crucible is filled up with water until it is full. Then the volume of crucible which is 75ml is minus with the volume of water that used to fill up the crucible to get the volume of cobalt laurate. Finally, the value is put in the formula to calculate the density.

$$Density = \frac{mass}{volume} \tag{3.1}$$

3.4.2 Solubility

The solubility of cobalt laurate was check in various solvents. The solvents chosen included polar and nonpolar. There are 4 solvents that used to determine the solubility of cobalt laurate. The solvents are as follow; water, benzene, toluene and acetone. For each solvent, 100ml is used to dissolve the cobalt laurate. 1 gram of cobalt laurate is weighed then placed in 250ml conical flask. Then, the solvent is poured in the conical flask and the shaker is used to shake the mixture at 150rpm for 1 hour.

3.4.3 Melting point

To measure the melting temperature, the differential scanning calorimetry, DSC model Q1000 is used with heating rate $10^{o}C$/min.

3.4.4 Degradation point

The measurement of degradation temperature of cobalt laurate is done by using the thermogravimetric analysis model Q500 in nitrogen condition with heating rate $20^{o}C$/min.

3.5 Compounding

This step is where the cobalt laurate is added to HDPE. Varying amounts of cobalt laurate (0.5%, 1.0%, 5.0% and 10%) were mixed with HDPE. The details of plastic preparation along with their designation are presented in Table 3.1.

Table 3.1: Preparation of samples

Plastic designation	Amount (g)		w/w percentage
	HDPE	Cobalt laurate	(%)
sample 1	190.901	0	0
sample 2	190.901	0.9545	0.5
sample 3	190.901	1.90901	1
sample 4	190.901	9.54505	5
sample 5	190.901	19.0901	10

3.6 Plastic molding

To produce the sample, Nissei injection molding machine model NS20 is used. The type of sample used in this study is Type 1 Tensile Bar for ASTM D638 with the dimension of width, length and thickness are 3mm, 60mm and 4mm respectively.

Figure 3.3: Type 1 Tensile Bar

3.7 Degradation process

For the degradation process, the samples were exposed to the sun light and natural weathering environment condition for 2 weeks.

3.8 Evaluation on degradation

There were several elements that are measured to study the degradation process. The elements recorded were as mass, density, tensile strength, elongation at break and surface morphology.

3.8.1 Mass

In this step, the mass of the samples were weighed before and after the degradation process by using the analytical balance.

3.8.2 Density

For the density measurement, firstly the mass of the samples before and after degradation were weighed. Then the samples were put in the 25 ml measuring cylinder which filled up with 15 ml of water. The differential of the volume of water in the measuring cylinder is the volume of the sample. After the value of mass and density were determined, the density is easily calculated using the equation 3.0.

3.8.3 Tensile testing

The tensile strength of the samples was measure using the tensile testing machine model INSTRON 3369.

3.8.4 Elongation at break

The elongation break measurement of the samples was done by the tensile testing model Instron 3369.

3.8.5 Scanning electron microscopic

The surface study of the samples was done by using the scanning electron microscopic machine model Zeiss Evo 50. The scale was set to 100µm and zoom to 35 times.
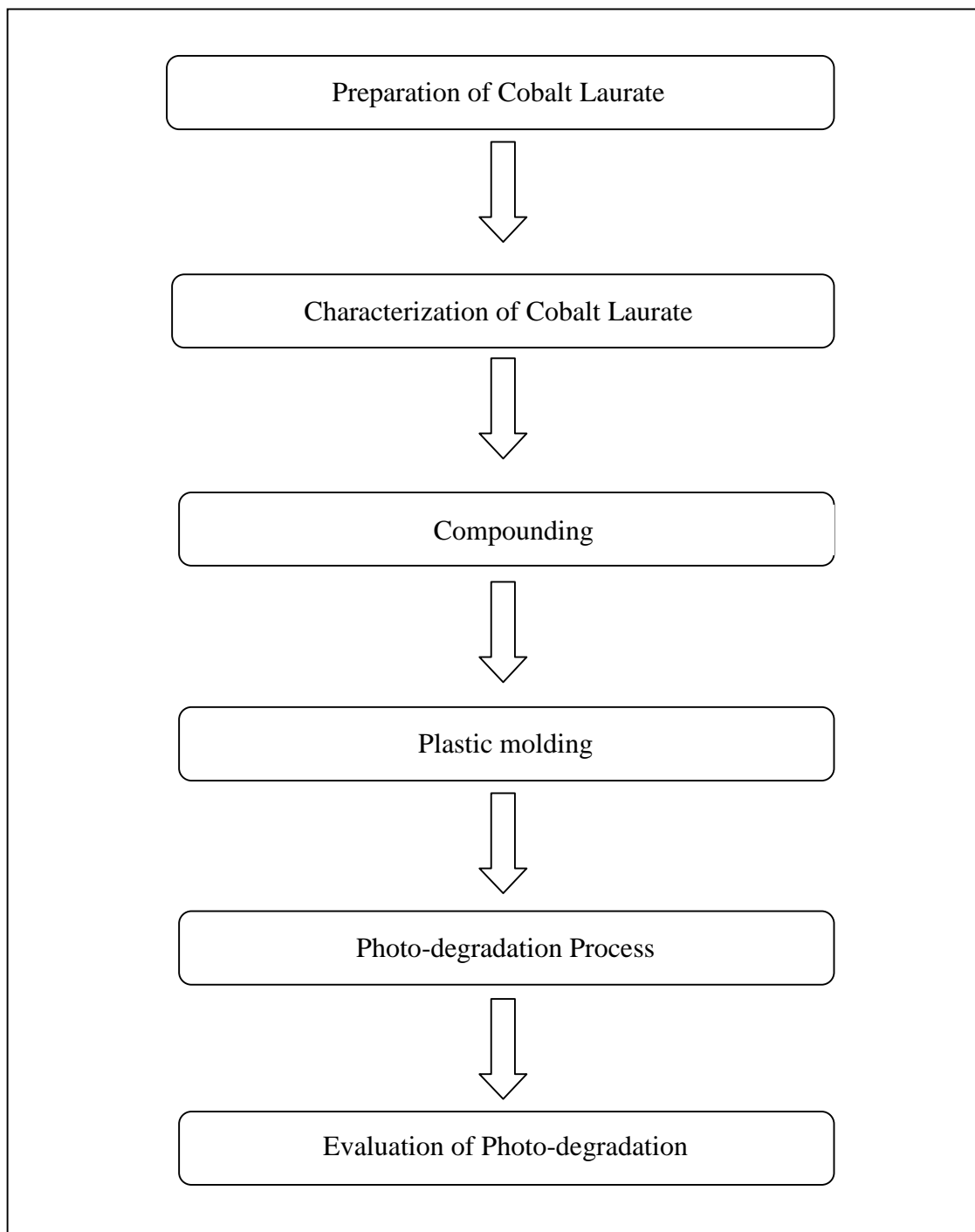
Figure 3.4: Methodology of Experiment

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

The experiment of effect of cobalt laurate in photo-degradation of high density polyethylene is completed. The procedure that used in this experiment was followed step by step to ensure that the best results will obtain.

4.2 Characterization of cobalt laurate result

4.2.1 Density

After the method to find the density was performed, the result was obtained like in the table 4.1;

Table 4.1: Volume of cobalt laurate

Trial	Mass of cobalt laurate(g)	Volume of water used (ml)		Volume of cobalt laurate (ml)
		Initial	Final	
1	5	75	67.8	7.2
2	5	75	65.7	9.3

| 3 | 5 | 75 | 64.8 | 10.2 |
| 4 | 5 | 75 | 66.9 | 8.1 |

From the table 4.1:

Average volume of cobalt laurate;

$$= \frac{7.2+9.3+10.2+8.2}{4} = 8.725 \; ml$$

$$density = \frac{mass}{volume} = \frac{5g}{8.725ml} = \frac{0.573g}{ml}$$

$$= \frac{0.573g}{ml} \times \frac{1ml}{1cm^3} = 0.573g/cm^3$$

By using the equation 3.1, the density of cobalt laurate was found about 0.573g/cm^3. The density of cobalt laurate is less than water because of the cobalt laurate is in the form of very fine powder.

4.2.2 Solubility

The solubility of the cobalt laurate was reveal in the table 4.2 below;

Table 4.2: Solubility result

Solvent	Observation
water	insoluble
acetone	insoluble
toluene	insoluble
benzene	insoluble

From the table 4.2, the result shows that the cobalt laurate does not soluble in all of those solvent. According to a research conducted by P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary in 2005 state that the insolubility of the additive in any of the solvents is contributed by the intermolecular crosslinking in the additive. The intermolecular crosslinking is stable mechanical and thermally, so once it is formed it is hard break.

4.2.3 Melting point

The result from the differential scanning calorimetry is obtained to measure the melting temperature. The figure 4.1 shows the melting temperature of the cobalt laurate.
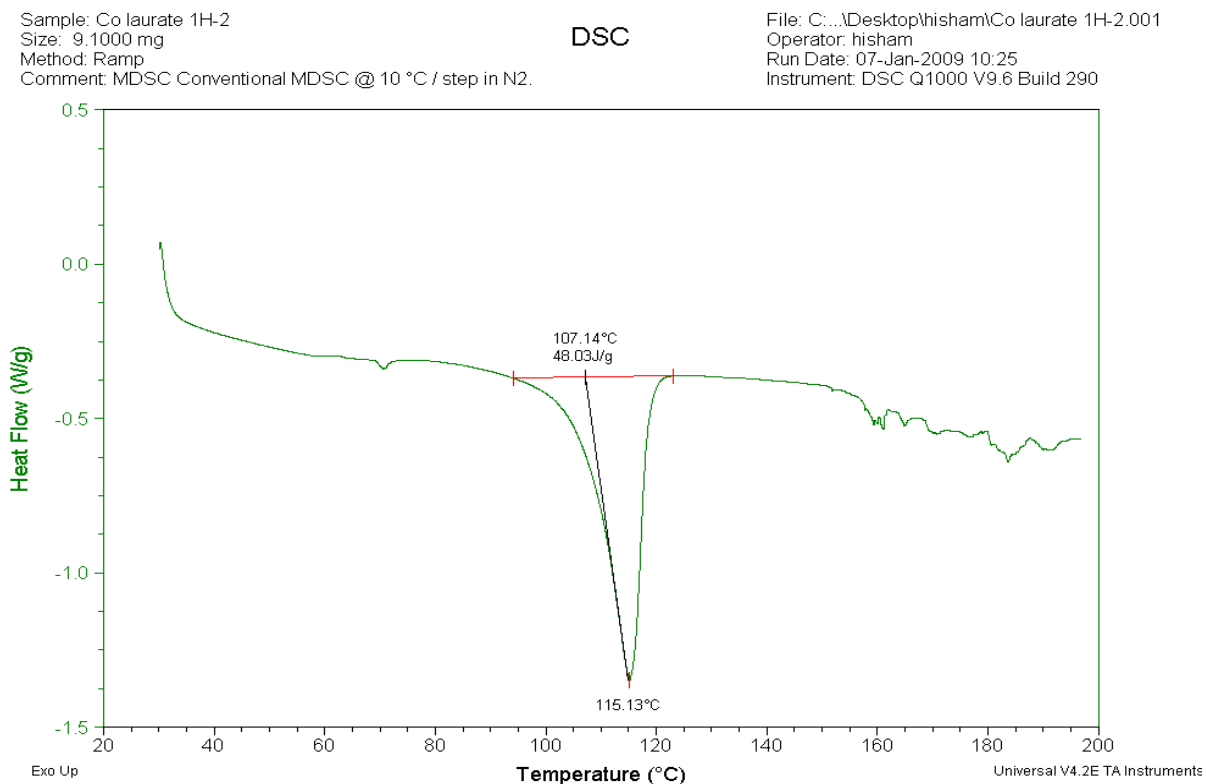

Figure 4.1: Melting temperature of cobalt laurate

From the figure 4.1, there is one major negative peak which is represented the cobalt laurate. The negative peak in the graph shows the melting process of the cobalt laurate. We can see the cobalt laurate is starting to melt at the temperature of 107.14^oC. After that, the graph decreased drastically until it reaches 115.13^oC. At this temperature the cobalt laurate is completely melting and it is shown the melting temperature of cobalt laurate is 15.13^oC.

4.2.4 Degradation point

The result from the thermal gravimetric analysis is shown in the figure 4.2;

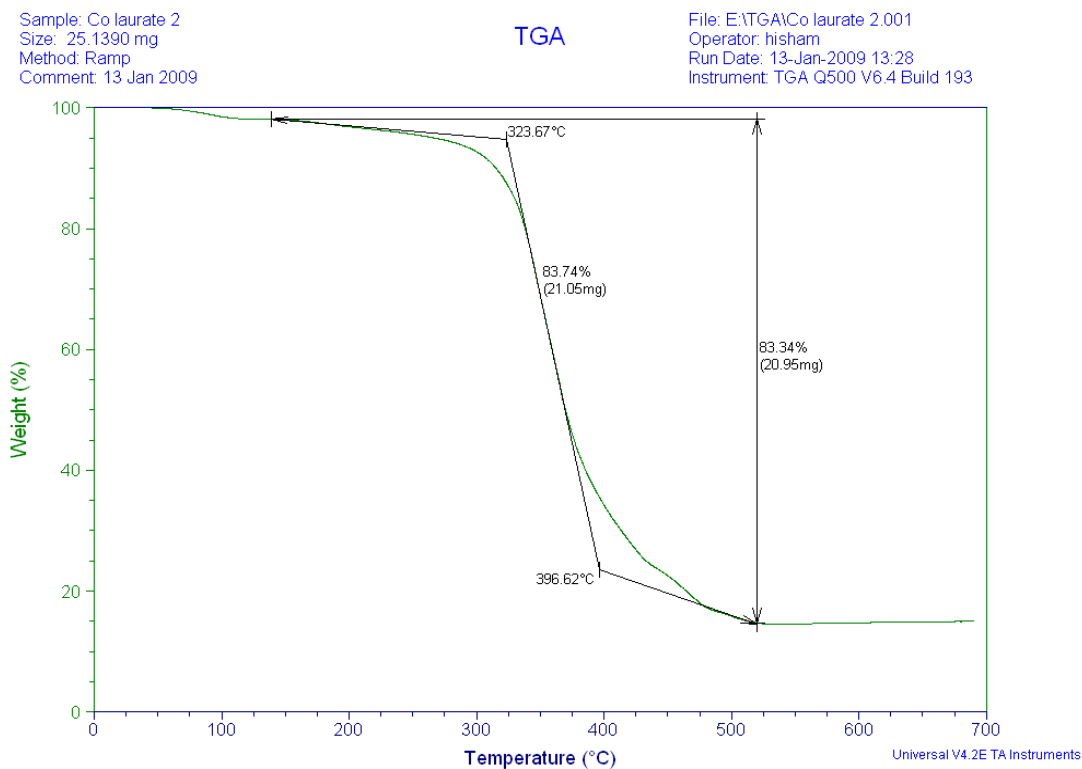**Figure 4.2**: Degradation temperature of cobalt laurate

The figure 4.2 shows the cobalt laurate is starting to degrade and lost it mass at $323.67^{o}C$ and at $396.62^{o}C$ the cobalt laurate lost the most of it mass. So, the degradation temperature of cobalt laurate is $396.62^{o}C$.

4.3 Evaluation of degradation process

4.3.1 Mass

In the mass study of the samples, the degradation process can be shown by the different of the sample before the degradation process and after the degradation process.

Table 4.3: Mass data result

sample	w/w percentage additive	Mass (g)		
		Before degrade	After degrade	Differential
1	0	1.5081	1.5081	0
2	0.5	1.5156	1.5152	0.0004
3	1	1.5156	1.5148	0.0008
4	5	1.5166	1.5157	0.0009
5	10	1.5294	1.5278	0.0016

From the table 4.3, we can see the mass after degradation is less than the sample before the degradation for each sample. The sample with the higher value of additive shows the highest value of mass differential. The sample number 5 with the 10% of the additive decreased its mass 0.0016 gram from 1.5294 gram to 1.5278 gram. The sample with the smallest percentage value of additive which is sample number 2 with only 0.5% of additive shows 0.0004 gram decreased from its original mass, from 1.5166 gram to 1.5152 gram. From the mass data result, without any additive the sample would not undergoes the degradation process. We can see it from the sample number 1 with the 0% of additive, it is nothing changed in its mass, the mass before the degradation process and after degradation process is the same. We can see the decreasing mass for each sample from the figure 4.3 which is the mass before the degradation process and after degradation process. We also can see the relation between the differential of the mass and percentage of the additive from the figure 4.4. From the figure 4.4, we can say that the differential of the mass is increasing as the percentage of additive is increased.
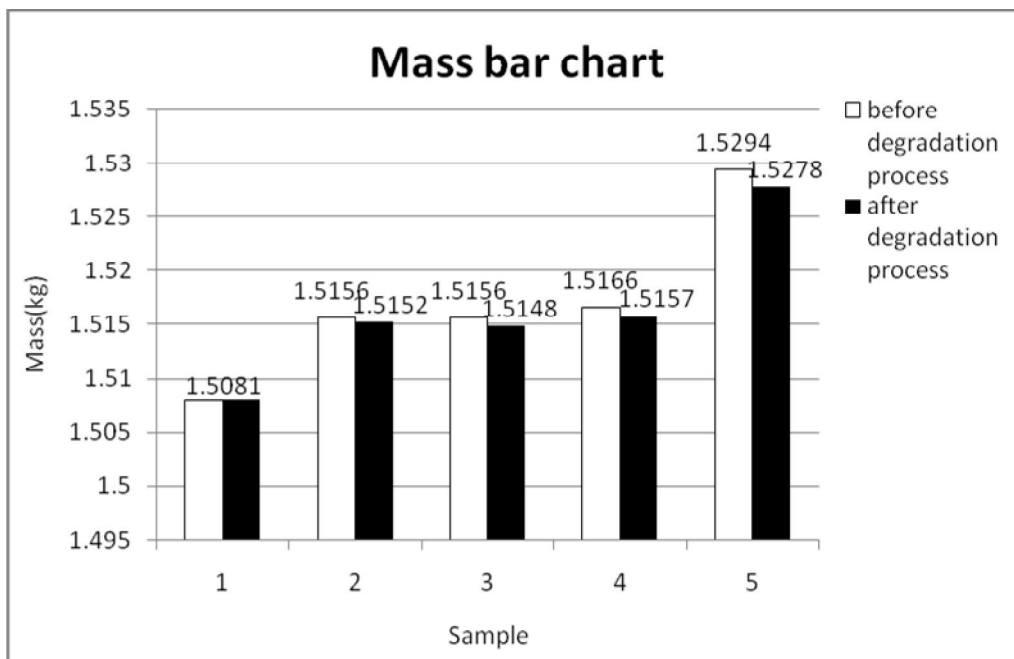
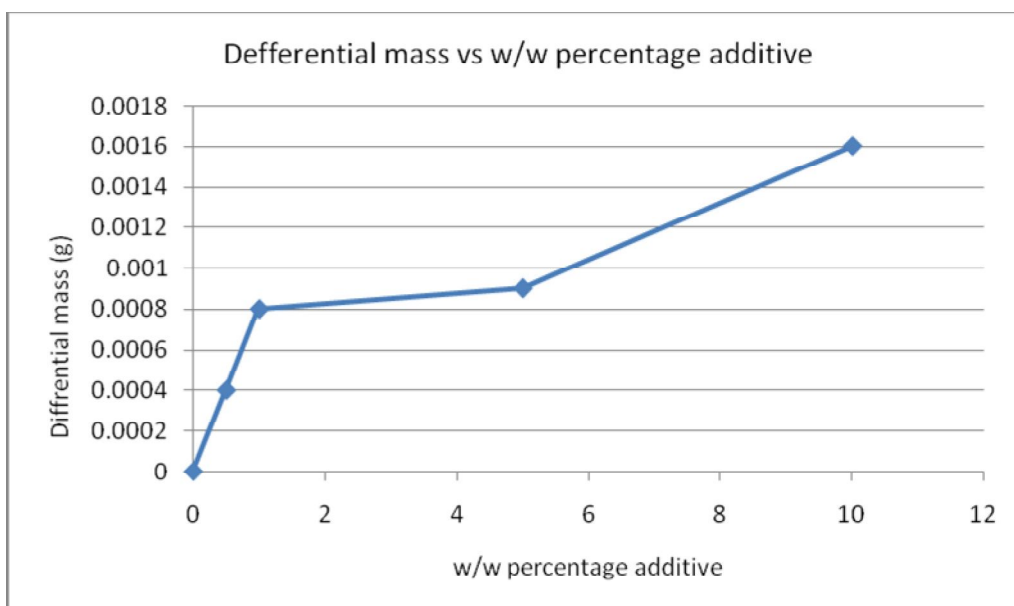**Figure 4.3**: Mass of samples before and after degradation process

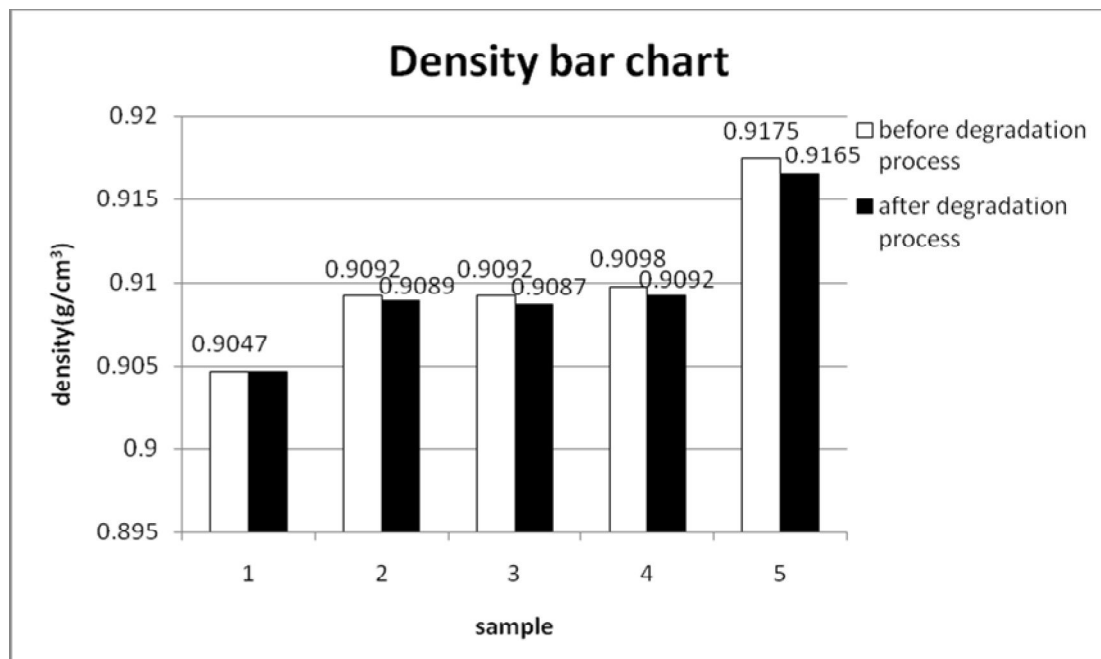**Figure 4.4**: Relation between differential mass and w/w percentage additive

4.3.2 Density

The density result of the samples is shown in the table 4.4.

Table 4.4: Density of samples before and after the degradation process

sample	w/w percentage additive	Density (g/cm^3)		
		Before	After	Differential
1	0	0.9047	0.9047	0
2	0.5	0.9092	0.9089	0.0003
3	1	0.9092	0.9087	0.0005
4	5	0.9098	0.9092	0.0006
5	10	0.9175	0.9165	0.001

From the table 4.4, we can see the density of the sample is decrease after the degradation process and it is decreasing as the percentage of the additive is increasing. The amount of density decrease is increase when additives composition is more in the sample. This can be seeing in the graph from figure 4.6. The sample number 2 with the 0.5% of additive show 0.0003 g/cm^3 different in the density but for the sample 5 with 10% of additive show the different in the density after degradation process is 0.001 g/cm^3. The amount of additive in the sample will affect the lost of density. The figure 4.5 shows the density of the sample before and after the degradation process and the figure 4.6 show the graph of different in density versus the percentage of additive in the sample.

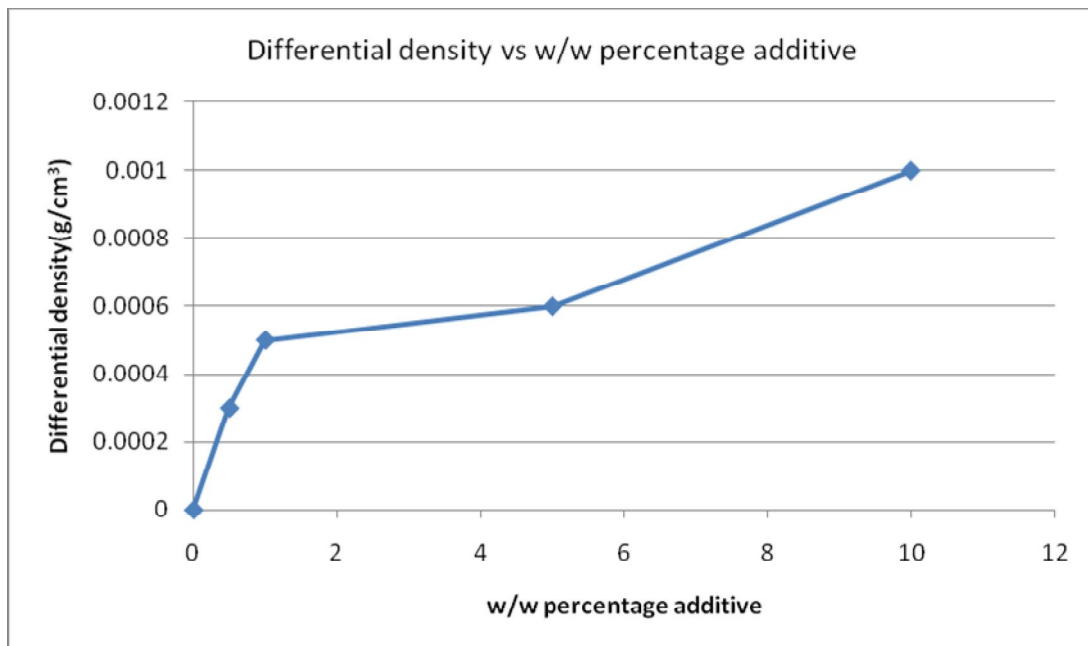**Figure 4.5**: Density of the samples before and after degradation process

Figure 4.6: Relation between density different and w/w percentage additive

4.3.3 Tensile strength

After the tensile testing is done, the tensile strength is reveal as in the table 4.5

Table 4.5: Tensile strength of samples before and after degradation process.

sample	w/w percentage additive	Tensile strenght(MPa)	
		before degradation	after degradation
1	0	31.415	31.415
2	0.5	28.949	26.989
3	1	27.815	26.53
4	5	21.149	15.6717
5	10	14.109	8.493

From the table 4.5, the original strength that the samples have is 31.415 MPa, but the strength is decreasing as the additive is put in the samples. Even before the degradation process is performed, the cobalt laurate is affecting the samples strength by reducing them. We can see in before the degradation process tensile strength is keep decreasing from 31.415, 28.949, 27.815, 21.149 and lastly 14.109 MPa as the

additive is increasing from 0, 0.5, 1.0, 5 and 10%. The sample number 5 shows the highest lost in tensile strength with 5.616 MPa. This is because sample number 5 is contain 10% of additive which is the highest among other samples. The further explanation can see in Figure 4.7.
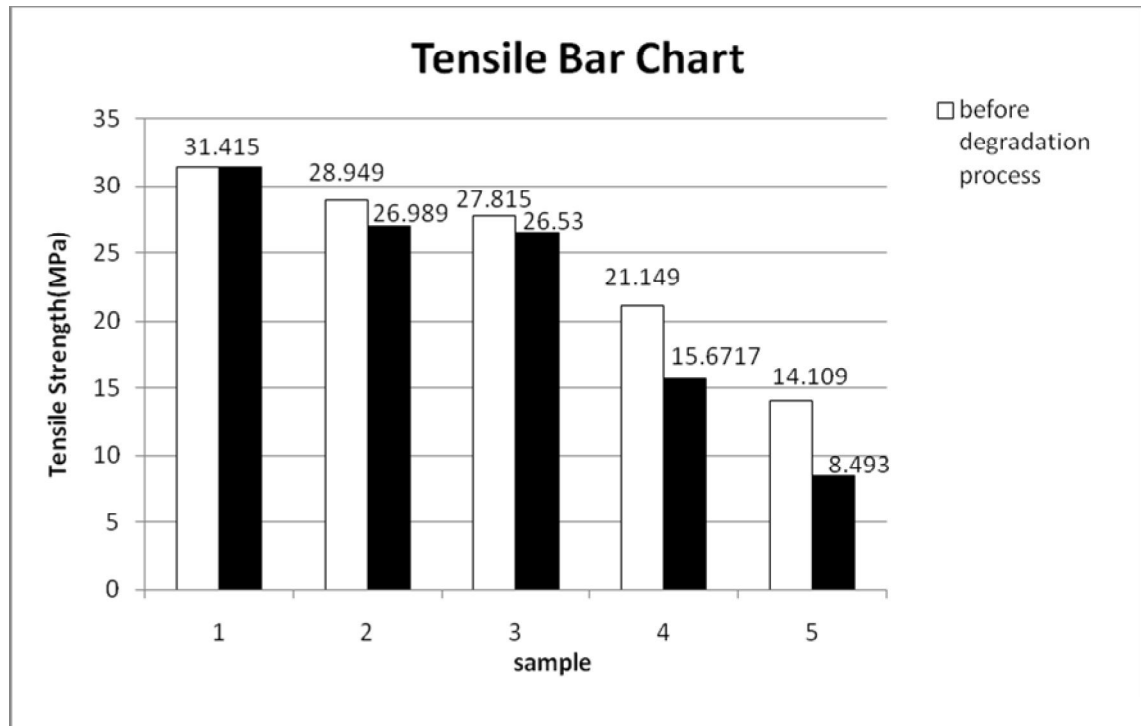

Figure 4.7: Tensile strength of samples before and after degradation process

4.3.4 Elongation at break

After the elongation break is tested, the result shows the maximum displacement of plastic will decrease as the percentage of additive is increase. As shown in the table 4.6, the maximum displacement of the sample without any additive is 4.405mm. After the samples were added with the additive the maximum displacement will become short. From the table, we take sample number 2 for an example. After the sample number 2 is added with 0.5% of additive, it maximum displacement is reduce to 3.71mm before the degradation process, and then after the degradation took place, the maximum displacement will reduce again to 3.47mm. Before the degradation process, the maximum displacement of sample 2 is already reduce 0.695mm. If we take the sample with the highest value of additive percentage,

the reducing in maximum displacement will become clearer. After the percentage of additive is added 10%, the maximum displacement of the sample went down from 4.405mm to 0.8597mm before the degradation and then after the degradation process, the maximum displacement reduced to 0.4099mm.

Table 4.6: Maximum displacement of samples before and after degradation process

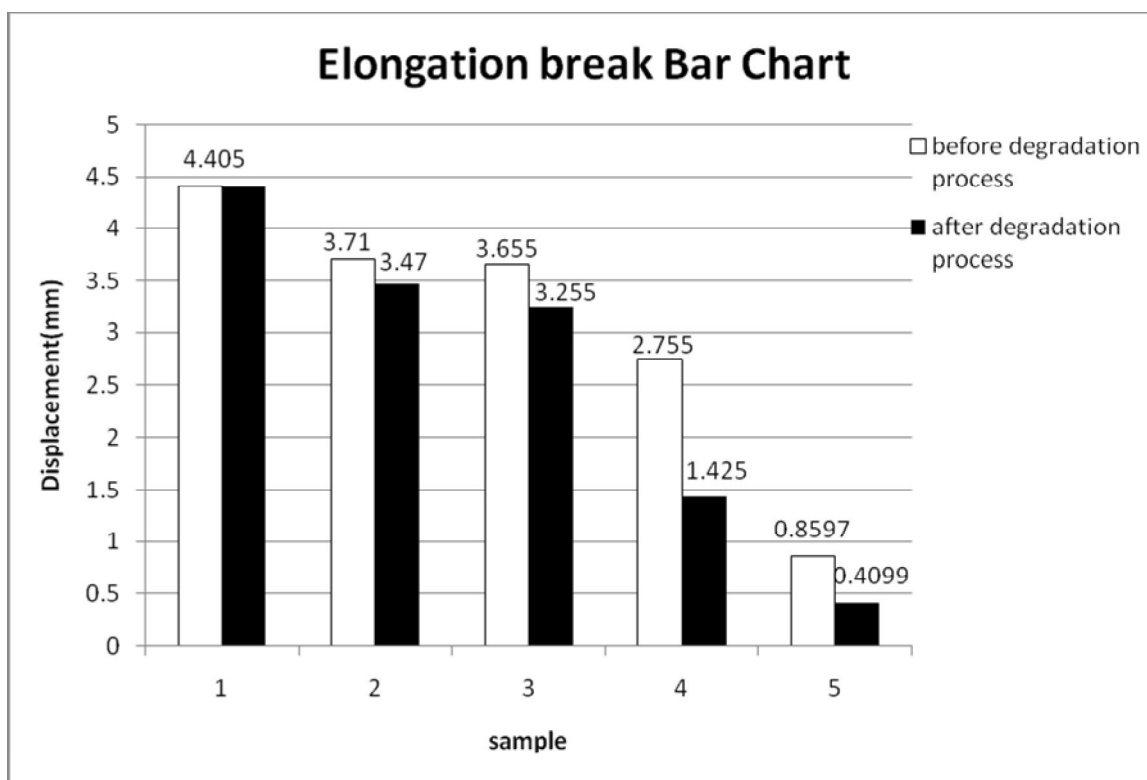| sample	w/w percentage additive	Elongation at break (mm)	
		before degradation	after degradation
1	0	4.405	4.405
2	0.5	3.71	3.47
3	1	3.655	3.255
4	5	2.755	1.425
5	10	0.8597	0.4099

Figure 4.8: Maximum displacement of samples before and after degradation process

4.3.5 Surface morphology

Figure 4.9 and 4.10 present a comparative of scanning electron micrographs of sample number 5 at uniform magnification of 35. As is apparent from figure 4.9, the surface of sample before degradation is smooth, without cracks and free from defect. Figure 4.10 shows the scanning electron microscopic of sample number 5 after 1 week of UV degradation. It was observed that the surface developed some cracks and grooves due to sun light exposure. However, in figure 4.11, the extent and expend of damage was much more revealed in the sample after 2 weeks of UV degradation.
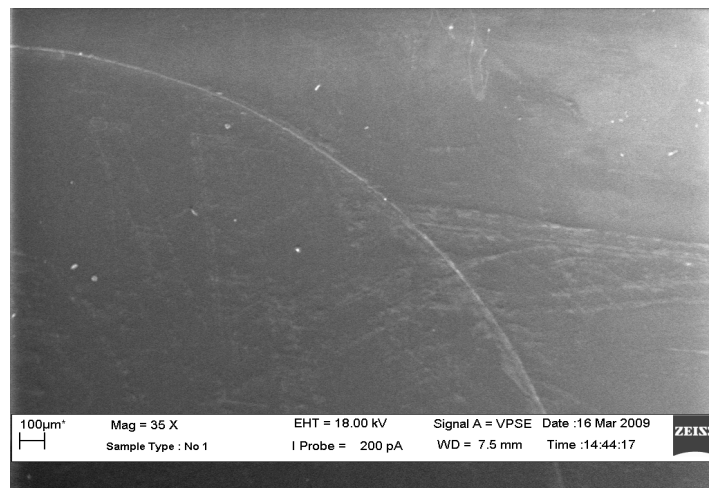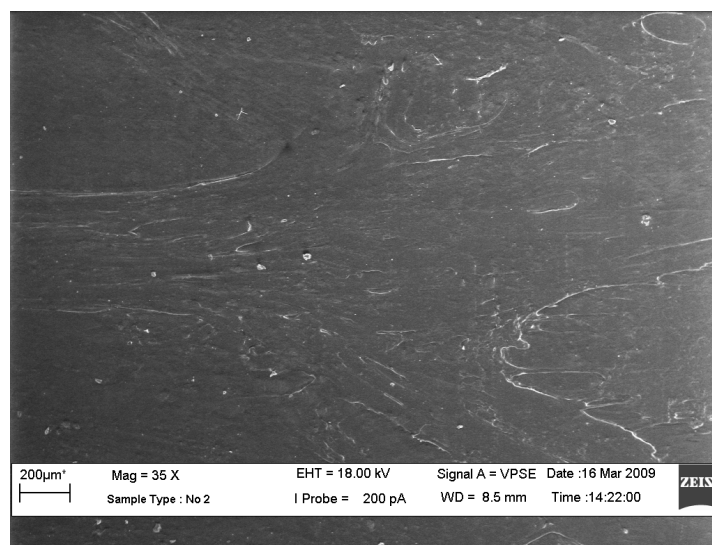

Figure 4.9: Nondegradable sample

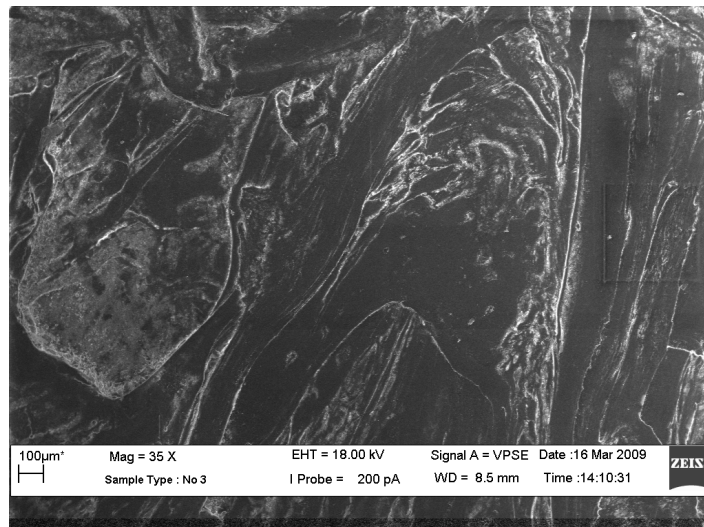**Figure 4.10**: After 1 week degradation process

Figure 4.11: After 2 weeks degradation process

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The effects of the cobalt laurate on the photo-degradation of high density polyethylene were evaluated by using TGA, DSC, tensile testing machine, and analytical balance. From the results of this study, the systematic knowledge of relationship between the properties of high density polyethylene and role of cobalt laurate on the photo-degradation process was obtained.

Back to the objectives of this research, the experiment was carry out to produce cobalt laurate as an additive for degradable plastic and to find out the effect of verifying the amount of composition cobalt laurate on the degradation of plastic. The high density polyethylene exhibit significant changes in their chemical structure after degrade under natural environment condition. These changes are accompanied with the formation of oxidation products and deterioration of mechanical properties.

The loss in mass, density, tensile strength and elongation break of the samples is significant in sufficient length of time. It is shown that the presence of cobalt laurate has an important role to allow the degradation of plastic. It is also found that the degradation process depends on amount of cobalt laurate, duration of time and exposure condition which includes the UV light as a key factor in this process.

5.2 Recommendation

From this research, some recommendations can be made to improve the result of the study. The recommendation is focus on the methodology of this research, first of all during the compounding step. There are some errors during this process. It was because of dry mixing. From the observation, the color of the sample is different between the initial sample to last sample even in the same batch due to the composition of the additive is a bit different. So, it is better if the wet mixing is used using the extruder. In the extruder, the polyethylene and additive will melt together and then will produce them in the form of pallet. Hence, by this method we can ensure that the composition of the additive is same in one batch.

The degradation process also can be improved by using the UV lamp. This is because under the UV lamp, the sample of HDPE will constantly absorb the UV radiation 24 hours per day. The conventional step which is the sample of HDPE will put under sun light of natural environment, the sample of HDPE cannot absorb the UV radiation constantly because of interruption of night period and raining. Hence, it can affect the degradation process.

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APPENDIXES

Figure A-1: Sample of Cobalt Chloride

Figure A-2: Sample of Cobalt Laurate After Grinding

Figure A-3: Sample of Cobalt Laurate Before Grinding

Figure A-4: Sample of HDPE mixed with Cobalt Laurate Before Degrade
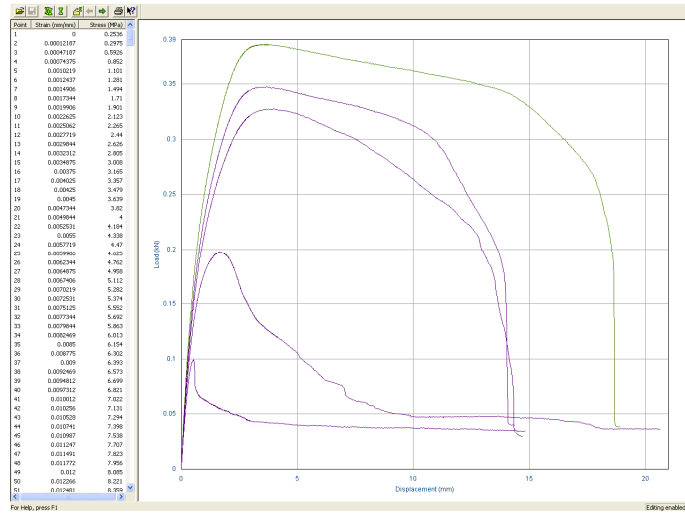

Figure A-5: Sample of HDPE mixed with Cobalt Laurate After Degrade

Figure A-6: Tensile Testing