EFFECT OF COBALT CARBOXYLATE ON THERMAL DEGRADATION OF POLYETHYLENE (HDPE)

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EFFECT OF COBALT CARBOXYLATE ON THERMAL DEGRADATION OF POLYETHYLENE (HDPE)

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A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
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APRIL 2010

I declare that this thesis entitled “Effect of Cobalt Carboxylate on Thermal Degradation of Polyethylene (HDPE)” is the result of my own research except as cited in 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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Date : 30 April 2010

Special Dedication to my family members,
my friends, my fellow colleague
and all faculty members

For all your care, support, encourage and believe in me.

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ABSTRACT

This study reports the effect of cobalt carboxylate on thermal degradation of polyethylene (HDPE). The purpose of this study is to gain knowledge and understand behaviour of HDPE film after adding cobalt carboxylate as additive after and before expose to the heating in the oven at 60^0C and also to investigate characteristics of cobalt carboxylate itself. The additives used were three cobalt carboxylate which are cobalt stearate, cobalt palmitate, and cobalt laurate and thin film HDPE containing these additives were prepared with different concentration (0.2% w/w, 0.5% w/w, and 1.0% w/w) by sheeting process. Seventy micron film of HDPE containing different concentration of additives and 3 types of cobalt carboxylate were subsequently exposed to heat and were observed. The characteristics of cobalt carboxylate were monitor by measuring the temperature degradation using TGA (Thermal Gravimetric Analyzer) and to measuring melting point using DSC (Different Scanning Calorimeter). While, the degradation was monitored by measuring the elongation break using tensile machine, changes of structure peak using FTIR and surface film using SEM. In DSC and TGA result, found that, cobalt stearate has high temperature of degradation and high melting point at 121.97^0C; 309.8^0C followed by cobalt palmitate and cobalt laurate at 84.06^0C; 282.74^0C and 69.04^0C; 182.97^0C, respectively. While for FTIR result, Carbonyl Index (CI), which in turn leads to an increase according to the increase of concentration of additives especially cobalt stearate and for tensile test, the percent of break strain decreased inversely proportional with increasing concentration additive present. Results on mechanical properties reveal that samples containing cobalt carboxylate, become mechanically fragile, embrittlement and flaking occurred for samples exposed to longer time periods in the oven for 480 hours. The effect of cobalt carboxylate on air oven aging, show that different behaviour of HDPE at different concentrations will increase proportionally with increasing chain length and follows order $CoSt_3$>$CoPal_3$>$CoLau_3$

ABSTRAK

Kajian ini melaporkan kesan kobat karbosilet terhadap perbuatan merendahkan terma plastik (HDPE). Tujuan kajian untuk mendapatkan pengetahuan dan memahami tabiat HDPE filem selepas menambahkan kobat karbosilet sebagai aditif selepas dan sebelum mendedahkannya kepada pemanasan oven yang bersuhu 60^0C dan juga untuk menyiasat sifat kobat karbosilet itu sendiri. Aditif ini menggunakan tiga kobat karbosilet iaitu kobat stearet, kobat palmitet, dan kobat lauret dan HDPE filem yang mengandungi aditif ini disediakan dengan berlainan kepekatan ((0.2% w/w, 0.5% w/w, and 1.0% w/w) melalui proses kepingan.Tujuh puluh mikron filem HDPE yang mengandungi aditif yang berbeza kepekatan dan 3 jenis kobat karbosilet berikutnya didedahkan kepada haba dan diperhatikan.Sifat kobat karbosilet dilihat dengan mengukur suhu pada perbuatan merendahkan menggunakan TGA dan mengukur takat kecairan menggunakan DSC. Sementara itu, perbuatan merendahkan diperhatikan dengan mengukur kepanjangan putus menggunakan alat mesin ketegangan, perubahan struktur pada kemuncak menggunakan FTIR, dan permukaan filem menggunakan SEM. Di dalam keputusan DSC dan TGA dijumpai, kobat stearet mempunyai suhu yang tinggi pada perbuatan merendahkan dan suhu takat kecairan pada 121.97^0C; 309.8^0C diikuti kobat palmitet dan kobalt lauret masing-masing pada 84.06^0C;282.74^0C and 69.04^0C;182.97^0C. Sementara itu, keputusan FTIR, bagi Indeks karbosil, meningkat berdasarkan peningkatan kepekatan aditif terutamanya kobat stearet dan untuk ujian ketegangan,peratusan putus ketegangan berkurang berkadar songsang dengan peningkatan kepekatan aditif yang hadir. Kajian pada sifat mekanikal mendedahkan, sampel yang mengandungi cobat karbosilet, menjadi rapuh secara mekanik dan mengelupas apabila sampel didedahkan terlalu lama di dalam oven untuk 480 jam. Kesan cobalt carboxylate di dalam oven terlalu lama, menunjukkan HDPE yang berbeza kepekatan aditif akan berkadar langsung dengan meningkatnya pemanjangan rantaian dan diikuti urutan $CoSt_3$>$CoPal_3$>$CoLau_3$.

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LIST OF ABBREVIATIONS

HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
SEM	Scanning Electron Microscopic
DSC	Different Scanning Calorimeter
TGA	Thermogravimetric Analyzer
FTIR	Fourier Transform Infrared Spectroscopy
CS	Cobalt stearate
CP	Cobalt palmitate
CL	Cobalt laurate
V	Volume
MW	Molecular Weight
W	Weight
Co	Cobalt
Mn	Manganese
Fe	Ferum
EAA	Ethylene Acrylic Acid Copolymer
PE	Polyethylene

PP	Polypropylene
DEET	diethyltoluamide
Cl	Carbonyl Index
OPE	Oxidized polyethylene
UV	Ultraviolet
ABS	Acrylonitrile butadiene styrene
DTG	Derivative thermogravimetry
PEO	Polyethylene Oxide
MT	Metric Tonne

LIST OF SYMBOL

$P(x')$	Molecular weight
k_d	Degradation coefficient
M_n	Number average molecular weight
$P^{\bullet}$.	formation
α	alfa
tf	time (days)
T	Temperature (^{0}C)
A	Area (cm)
%	Percentage

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CHAPTER 1

INTRODUCTION

1.1 Background of study

1.1.1 Polyethylene

Polyethylene has achieved a dominant position as a packaging material because of its relatively low cost, versatile properties including high tensile strength, elongation at break, good barrier properties against water borne organisms, lower cost, higher energy, effectiveness, light weight and good water resistance. The products from polyethylene are become famous in over the decade. However, it has been a target of much criticism due to its lack of degradability [1] especially the plastic bag, agriculture bag product and so on. So during the past two decades the quantity of plastic material used in the in packing application has increased annually at a phenomenal rate. At the present time something like 1000 square miles of polyethylene film are produced in the United Kingdom alone each year. Even if a large percentage of the population can be persuade to take care against creating litter and even if litter collection systems are reasonably efficient, a quantity of unsightly rubbish is bound to accumulate [2]. According to Guillet [3] the most effective way to deal with this litter problem is to reduce the “life time” of the littered objects. The meaning of ‘life time’ is to reduce for their chain ability of the polyethylene material to make it easier to decompose.

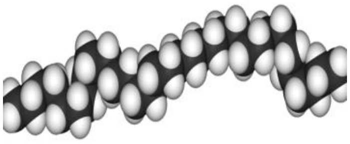

Figure 1.1: Space-filling model of a polyethylene

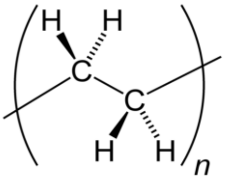

Figure 1.2: The repeating unit of chain showing its stereochemistry

The need to control the proliferation of plastic litter has been recognized for many years and has become increasingly pressing during the last few decades with the discovery by environmental scientists that discarded packaging is responsible for the death of a large number of mammals by ingestion and strangulation [4]. Polyethylene is relatively inert due to its hydrophobic chain and high molecular weight. It has been estimated that polyethylene biodegrades less than 0.5% in 100 years and about 1% if pre-exposed to sunlight for 2 years [5]. LDPE is extensively used for a variety of different applications, resulting in its increased production. Subsequently, the plastic fraction of the municipal solid waste stream has also increased leading to associated urban plastic litter problem. The hazardousness of polyethylene as a waste is associated with its excellent outdoor durability and its inherent resistance to hydrolysis and biodegradation in the environment.

Figure 1.3 Product from polyethylene

1.1.2 Degradability process

Degradability offers a complimentary strategy to deal with this litter problem. One of the simplest ways of modifying the existing polymer is to accelerate the rate of photo-degradation and thermal degradation process already taking place with using the additive such as transition metal corboxylates are particularly suitable for this purpose. Degradability also offers a complimentary strategy to deal with this litter problem. One of the simplest ways of modifying the existing polymer is to accelerate the rate of thermal/photodegradation process already taking place with using the additive such as transition metal corboxylates are particularly suitable for this purpose. Different approaches to develop thermal/photodegradable polyolefins have been adopted, including both copolymerization with ketone or CO groups and addition of thermal/photo initiating metal complexes [6]. Thermal/Prodegradant additives are used to enhance such oxo-biodegradation of polyolefins [7], [8], [9], [10], [11], [12], [13], and [14] and the additives preparation based on cobalt [15], [16], [17], [18] and [19] iron [20], [21], and [22], manganese [23] and [24] and cerium [25] have been commercialized. In addition, the formation of carbonyl groups on the surface increases its hydrophilicity. Consequently, the possibility of further degradation induces a significant enhancement towards mineralization of plastic material [26] and also leads to an increase in the surface area through embrittlement

1.1.3 Thermal Degradation

Thermal degradation of polymers is molecular deterioration as a result of overheating. At high temperatures the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. Thermal degradation can present an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss. Indeed unless correctly prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight and molecular weight distribution of the polymer and typical property changes include reduced ductility and embrittlement, chalking, color changes, cracking, general reduction in most other desirable physical properties [27].

1.1.4 Transition metal and carboxylic acid

Transition metal [28] and carboxylic acid containing polymers [29] individually have been reported to act as effective photo/thermal degradation initiators for polyethylene, although the mode of action of all the three is different. Transition metals especially Mn, Fe, Co possess a remarkable ability to decompose the hydroperoxides formed during the oxidation process of polymers. The prooxidant activity of carboxylate acid polymers like EAA can be attributed to ease of hydrogen abstraction from the acidic groups by peroxy radicals. [29]. Combination of all the two components i.e. metal and carboxylate acid based functionality would therefore be expected to show a strong thermal/photo initiating activity.

1.1.5 Cobalt Carboxylate

Cobalt stearate, cobalt palmitate and cobalt laurate are apart of carboxylates group and is also recognize as cobalt salt of stearic acid, palmitic acid and lauric acid. Transition metals like Co, Mn, Fe especially in the form of carboxylates, have been employed to initiate degradation in polyethylene films. The role of these metals/metallic compounds on the photo-degradation of polyethylene has been extensively studied by several authors [28]. However the effect of cobalt stearate, cobalt palmitate and cobalt laurate on the rates of thermal degradation of HDPE polyethylene has not been studied systematically. Although, cobalt stearate is the major additive in cobalt carboxylates group but another cobalt carboxylate additive like cobalt palmitate and cobalt laurate are used to make the comparison with cobalt stearate efficiency.

In this study, HDPE is used as the raw materials due to the significant disposal problem. Although it caused by major in bag plastic but the rest of litter it's contributes by product from HDPE material and become the pollution of the environment. The present of high temperature of light in HDPE polyethylene with a suitable additive are considered a real alternative to degrade or reduce molecule compound in HDPE polyethylene especially at their backbone.

So, in this thesis will give a systematic study on the effects induced by cobalt carboxylate, especially due to rate on the thermal degradation of HDPE.

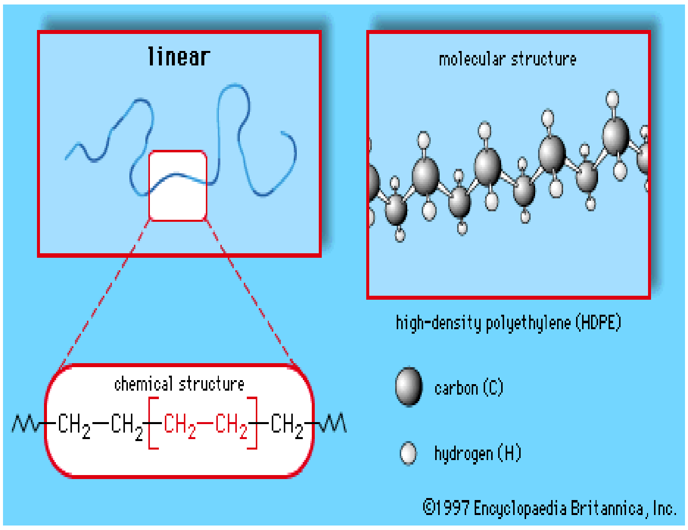

Figure 1.4: Structure of HDPE

1.2 Problem Statement

Nowadays all of component, furniture and also the packaging made from polyethylene as their main substance. For example, the wide application of plastics in agriculture has decisive influence on cultivation practices. Plastic films used as a growing aid in the form of mulch and tunnel covers have increased yield. The litter of this film left behind after the harvest poses serious disposal problem. Effect of the litter accumulation is become an environmental issues. If the problem is not preventing as soon as possible, the issues might become worst. For example, the most product of polyethylene used is plastic bag. Plastic bags are popular with consumers and retailers as they are a functional, lightweight, strong, cheap, and hygienic way to transport food and other products. Approximately 6.9 billion plastic bags are consumed annually in Australia:

- 6 billion of these are high density polyethylene (HDPE), such as supermarket singlet bags or supermarket checkout bags.
- 0.9 billion are low density polyethylene (LDPE), such as boutique bags.
- 67% of HDPE & 25% of LDPE bags are imported with the remainder locally produced.

Below is the two major environmental problem cause from our use of plastic bag [30]:

Firstly, plastic bags are one of the most damaging forms of litter.

- At least 80 million plastic bags end up as litter on our beaches, streets and parks each year
- While they are estimated to only be 2% of the litter stream, they have a significant environmental impact because they can take up to 1,000 years to break down.
- Their persistence in the environment means that they can entangle and harm marine life and other animals. In fact, the World Wide Fund for Nature estimates that more than 100,000 whales, seals, turtles, and birds die every year as a result of plastic bags.

- For example, on 24 August 2000, a Bryde's whale died in Trinity Bay, 2 km from central Cairns. An autopsy found that the whale's stomach was tightly packed with plastic, including supermarket bags, food packages, bait bags, three large sheets of plastic, and fragments of garbage bags. There was no food in its stomach. When the dead animal decays, the plastic bags are freed to be re-ingested by other animals in years to come.
- On land, plastic bag litter can block drains and trap birds. They also kill livestock. One farmer near Mudgee NSW carried out an autopsy on a dead calf and found 8 plastic bags in its stomach. The loss of this calf cost the farmer around $500.
- Cleaning up this litter is expensive. Australian local and state governments spend over $200 million a year picking up litter (all forms).

Secondly, the plastic shopping bag, a single use item, is a symbol of a wasteful society: [31]

- 20 million Australians used 6.7 billion plastic checkout bags this year (down from 6.9 billion the previous year). That's nearly 1 plastic bag per person per day or 345 bags per person per year.
- A person's use of a plastic checkout bag can be counted in minutes - however long it takes to get from the shops to their homes.
- The amount of petroleum used to make one plastic bag would drive a car about 115 metres. The 6.9 billion plastic checkout bags we use every year is enough to drive a car 800 million kilometres or nearly 20,000 times around the world - i.e. 4 round trips to the Sun.
- Less than 3% of Australia's plastic bags are currently being recycled, despite recycling facilities being available at major supermarkets.
- Only an estimated 19% of the 3.7 billion plastic supermarket shopping bags handed out in Australia every year, are being reused by households as kitchen bin liners.
- In many council areas, plastic bags are the single main contaminant of curbside recycling.

- Plastic bags are not free to consumers - they are actually adding an estimated $173 million a year to Australia's grocery bills.

The controlled photo degradation of plastic (polyethylene) afford a workable solution not only to this problem but open new possibilities of the new programmed removal of the film even during the growing period of time within the crops when this is desirable.

Solid waste disposal and litter like polyethylene are among the many problems that arise from the relationship between man or women and his or her environment whereby the litter is related with human inventor. The present generation commodity plastics, especially the packaging materials, contribute significantly to resolve the solid waste disposal problem. The use of plastic materials that can re-enter the biological life cycle, appear to be one of the most promising solution to this problem after the first photodegradation process is done. One of the most common techniques to decrease the lifetime of polyethylene with used to render a polyolefin degradable is to add prooxidants at the processing stage. The additives normally used for the initiation of degradation process are organosoluble transition metal ions, aromatic ketones, dithiocarbamates, acetyl acetonates, which act as thermal and/or photo-oxidant for the polymer also can effectively enhance the degradability of that material.

1.3 Objective and Scope

The objective of this research is to decrease the litter problem cause of polyethylene (HDPE) product and prevent it with use cobalt carboxylate as additives, also to determine the effective concentration of additive adding into HDPE to thermal degradation initiator with the scope of this research are:-

i. To investigate the characteristic of cobalt carboxylates.
ii. To investigate the thermal treatment effect before and after adding cobalt carboxylate additive into HDPE film including duration of thermal treatment exposed.
iii. To investigate the effect of increasing cobalt carboxylate's concentration in accelerating thermal degradation of polyethylene.
iv. To develop the effective additive preparation to increase the thermal degradtion process.

1.4 Research Contribution

This research can help in minimizing the environmental impact and aid by accelerate of thermal degradation of polyethylene when exposed to the heat at specific temperature. Whereas the decrease service life of typical plastic is strongly influence by the thermal degradation caused by high heating. So the additives such as cobalt carboxylate can be used to control the thermal stability and acceleration of thermal degradation process to make of polyethylene product easily to decompose.

1.5 Thesis Layout

This thesis has 5 chapters. Chapter 1 introduces a background of the study and also about the litter from polyethylene where become an environment issues and the way to solve that problem. It is also includes objective, scope and problem statement. Chapter 2 is about literature review which includes topic extensively researched of polyethylene; enhance a degradability process with use aid additive and variety of sources is cited. Literature research contains information relevant and directly related to research in this study. In Chapter 3, the methodology develops the steps needed to study about effect of cobalt carboxylate in strength of polyethylene will be discussed. Chapter 4 will be discussing about the results obtained from the experiment. It includes the efficiency concentration of used the cobalt carboxylate as the additive. Lastly Chapter 5 will conclude the thesis and provide recommendations on how to improve the way to make polyethylene especially High Density Polyethylene (HDPE) easier to decomposed and decrease the litter problem cause of polyethylene to importance of environmental issues.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Nowadays, the quantity of plastics material used in packaging application, furniture, and addition accessories of women has increased annually at a phenomenal rate. The quality is important but the more importance is to develop the effective additive to accelerate the photo degradation process and solve the litter problem from polyethylene which is decomposed it easily. Many of scientists doing their research to solve this problem and several of the research have been take as an initiative in the process to accelerate the degradability and resolve that problem.

2.2 Use High Density Polyethylene (HDPE) as Raw Material

The plastic industry plays a major role in the economy of the United States. The world's annual production of polymer resins has experienced a steady growth since the beginning of the century, with growth predicted way into the 21st century close to 1.5 million tons per year in 2000 [32]. Total resin consumption in Malaysia increased by 8% from 1.6 million MT in 2004 to 1.72 million MT in 2005, of which about 65% were polyolefins (PE and PP). Plastics production systematically increases, thus also plastics waste amount grows [33] .In the year 2000 and above, direct jobs in plastics accounted for 1.5 million employees while support/supply jobs added about 0.9 million. The total 2.4 million jobs accounted for more than 2 percent of the total workforce in the United States.

Between 1973 and 2000 above, the production of plastics in the United States grew at an average annual rate of 4.7 percent [34]. The total production included a number of various plastics. From the previous research about the production volume in 2000 for the major plastic, there increase to the year which accounted for 78 percent of the annual production:

Polypropylene (PP)	7,154
Polyvinyl chloride (PVC)	6,565
High Density Polyethylene (HDPE)	6,349
Low Density Polyethylene (LDPE)	3,443
Linear Low Density Polyethylene (LLDPE)	3,614
Polyester, thermoplastic (PETE)	3,195
Polystyrene (PS)	3,111
Phenolic	1,979
Total	35,410

Units: 1,000 metric tons

Table 2.1: U.S Production of Plastic

Acrylonitrile-butadiene-styrene	(ABS)
663	
Epoxy	
315	
Nylon	582
Phenolic	1,979
Polyester, thermoplastic	3.195
High Density Polyethylene	6,349
Low Density Polyethylene	3,443
Linear Low Density Polyethylene	3,614
Polypropylene	7,154
Polystyrene	3,111
Polyvinyl chloride	6,565
Styrene acrylonitrile	58

Urea and melamine	1,440
Others	7,010
Total	45,479
Units: 1,000 metric tons	

Based on the table above, the best raw material to choose in this research is polyethylene especially High Density Polyethylene type. HDPE Polyethylene also a famous base material to produce a bottle, plastic bag, furniture, toys and all the things in this decade we use a lot of bottle and plastic bag in our life and related to litter problem and environmental issues.

2.3 Characteristic of HDPE and LDPE Polyethylene

Polyethylene density is a characteristic used to distinguish between grades of polyethylene plastics that are expressed as g/cm^3. This measurement varies among petroleum-derived plastics due to differences in crystallization structure formed during the polymerization of ethene. In addition, density is affected by molecular weight of the final product. Branching, or the bonding of ethene monomers to hydrogen molecules to form polymers, also determines density. In fact, this last factor is the primary difference between high-density polyethylene (HDPE) and low-density polyethylene (LDPE).

Most people are familiar with HDPE and LDPE plastics. However, there are numerous other grades of polyethylene density. That’s because different types of polyethylene are obtained according to the methods employed to induce polymerization. For instance, material produced by the addition of a free-radical initiator (radical polymerization) often produces a different polyethylene density than one made by the use of a catalyst, such as chromium and/or silica. In addition, each type offers specific advantages.

HDPE possesses a density of at least 0.941 g/cm^3 and is used to produce various packaging materials, such as garbage bags, milk containers, and laundry detergent bottles. This type of plastic is also used in the construction of tanks to hold fuel and chemicals, as well as in plumbing pipes. HDPE films also used for special purposes as a result of the poor clarity, narrow heat-seal temperature range, high rigidity, and low tear strength. Grease and heat resistance, however, are higher than in the low and medium density varieties, and this advantage is exploited, for example, in the use of this film for boilable packages [35]. Its counterpart, LDPE, has a density of only 0.910 g/cm^3 and is primarily used to make plastic film, bags, and cling wrap. LDPE film, made by a high pressure process is inexpensive, easily heat-sealed, has good optical clarity and a balance of strength and optical properties [35]. LDPE also found that increasing the pressure increased the molecular weight of the product and accelerated polymerization and that increasing the temperature accelerated polymerization but gave the product of lower molecular weight [36]. Increasing the oxygen content also reduced the molecular weight [37].

As might be expected, polyethylene density affects the environmental impact of the product. Generally, plastics do not biodegrade, but linger in the environment intact for hundreds of years. However, most polyethylene plastics can be recycled to some degree. The best candidate for successful recycling is HDPE, which can be identified by the number “2” in the recycling symbol. LDPE, designated by the number “4,” can be recycled but, unfortunately, is not included in most residential collection programs and must be either returned to the store or the manufacturer for recycling [36].

Below is the characteristic and properties of low density and high density of polyethylene

Table 2.2: Characteristic Low Density and High Density Polyethylene [34] and [35]

Characteristic / Type	**Low Density**	**High Density**
Formula	$–(CH_2\text{-}CH_2)_n–$	$–(CH_2\text{-}CH_2)_n–$
Monomer	ethylene $CH_2{=}CH_2$	ethylene $CH_2{=}CH_2$
Properties	soft, waxy solid	rigid, translucent solid
Uses	film wrap, plastic bags	Electrical,insulation bottles, toys
T_m (ºC)	110	130
T_g (ºC	-110	-110
Properties Macromolecules	soft translucent solid which deforms badly above 75º C	rigid translucent solid which softens on heating above 100º C, and can be fashioned into various forms including films. It is not as easily stretched and deformed as is LDPE
Solubility	Insoluble in water but soften and swells on exposure to hydrocarbon solvent	Insoluble in water and most organic solvent
Melting Point	100^0C-120^0C	130^0C-135^0C
Molecular Weight	20000-40000	Up to 50000
Density	0.91	0.95-0.97
Pressure process	>500atm @ >200^0C	100atm
Specific gravity	0.910-0.925	0.941-0.965

2.4 Used Cobalt Stearate and another cobalt carboxylate as additive in Polyethylene

Cobalt stearate is the cobalt salt of stearic acid. Because cobalt is divalent, two stearic acid molecules are involved. The structural formula is CO(C~~H~~O). The cobalt salts of fatty acids, tall oil are more difficult to characterize chemically because the tall oil fatty acids are derived from the fractional distillation of crude tall oil, which is a by-product from the pulping of pine trees. The mixture of fatty acids in pine trees varies by species and even within species .The composition of a typical tall oil fatty acid includes oleic acid (48%), linoleic acid (35%), conjugated linoleic acid (7%), stearic acid (2%), palmitic acid (l%), and other acids and unsaponifiable matter Oleic acid and linoleic acid, like stearic acid, are Cl8 fatty acids with slightly differing degrees of saturation. Cobalt stearate and fatty acids, tall oil, cobalt salts are high molecular weight compounds [38].

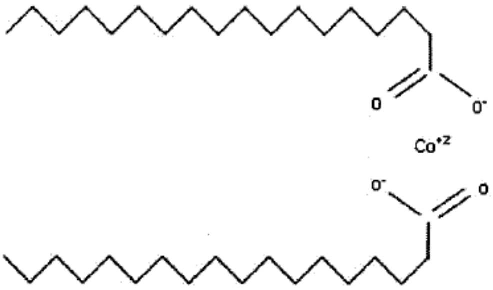

Figure 2.1: Cobalt stearate stereochemistry

The molecular weight for cobalt stearate is 625.9. The molecular weight of fatty acids, tall oil, cobalt salt is undefined due to the undefined nature of the acid component; however, the typical composition would be largely oleic and linoleic acid, both of which are Cl8 unbranched aliphatic acids, as is stearic acid. Thus the molecular weight of fatty acids, tall oil, cobalt salts would be similar to that of cobalt stearate.

Figure 2.1 provides the structure of cobalt stearate. The structures of oleic acid and linoleic acid, major components of fatty acids, tall oil have a quite different structure with cobalt stearate. The cobalt salts of fatty acids, tall oil consist of cobalt associated with the various acid moieties, similar to cobalt stearate.

Use Patterns for Metal Carboxylates The metal carboxylates function to deliver a metal ion into chemical reactions. The carboxylic acids (acids) are tailored for use in different products or chemical reactions.

In general the cobalt carboxylates are used as oxidative polymerization catalysts in many product areas. These areas include, but are not limited to ink and paint driers; unsaturated polyester resins, and hydrodesulfurization in their manufacturing; and the making of the insecticide DEET (diethyltoluamide). Some of these carboxylate compounds are used in oxygen scavenger plastics as well (for example, plastic bottles). The tire industry also uses cobalt carboxylate compounds as adhesion promoters in tire manufacturing. These compounds facilitate adhesion between the rubbers in the steel cords. The metal (not salt) loadings range from 0.01 -0.5% depending upon the application [38].

2.4.1 Comparison other additive types with cobalt stearate

The comparison provide between Cobalt Stearate and Fatty acids, Tall Oil, Cobalt Salts All the additive are two sponsored chemicals organized under the Metal Carboxylates Coalition (The Coalition), an HPV testing consortium managed by the Synthetic Organic Chemical Manufacturers Association's (SOCMA) VISIONS Department. The Coalition member companies sponsoring these compounds are OM Group (OMG) and The Shepherd Chemical Company.

The Metal Carboxylates Coalition has sponsored 19 compounds that are metal salts of carboxylic acids (metal carboxylates). These compounds readily dissociate to the corresponding metal and carboxylic acid. The HPV endpoints are fulfilled using a combination of data from the parent molecule, as well as for the dissociation products; that is, a metal salt and/or a carboxylic acid. Selected testing of the parent molecules has been proposed to further fulfill HPV endpoints [39]

All the data about comparison between cobalt stearate and other additive types had added in polyethylene and the reason why used cobalt stearate in this research.

Table 2.3: Summary of Available and Relevant Physical/Chemical Properties Data for Cobalt Stearate, Fatty Acids, Tall Oil, Cobalt Salt, and their Dissociation Products

Compound	**Physical/Chemical Properties**				
	Melting Point (deg C)	**Boiling Point (deg C)**	**Vapor Pressure (hPa)**	**Pertition coefficient (log Kow)**	**Water Solubility (mg/L)**
Dissociation Product: Cobalt chloride	735	1,049	NA	NA	450,000
Cobalt stearate	46.1-79.3	ND	-	NA	6.4@20^{0}C
Dissociation Product: Stearic acid	69-70	383	1.33@173.7	8.42	0.568@25^{0}C
Fatty acids,tall oil, cobalt salt	-38 to -39	ND	-	NA	1.49 @ 20^{0}C
Dissociation Product: Fatty acids, tall oil	NA	160-120 @ 6.6hPa	negligible	4.4-8.3@ pH2; 3.6-7.4 @ pH7.5	12.6

ND= no data testing did not yield results for boiling point

NA= no application due to substance properties

Table 2.4: Summary of Available Relevant Environment Fate Data for Cobalt Stearate, Fatty Acids, Tall Oil, Cobalt Salts, and their Dissociation Products

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Compound	**Environment Fate**			
	Stability in water	**Photo-degradation**	**Level III Fugacity Model**	**Biodegradation**
Dissociation Product: Cobalt chloride	(high water solubility)	NA	NA	NA
Cobalt stearate	Dissociates: pKa = 7.50 @ 20 C	-	-	-
Dissociation Product : Stearate acids	(low water solubility)	T1/2 = 0.5 days	Air: 0.676 Water : 7.19 Soil : 28.9 Sediment : 63.3	Readily biodegradable
Fatty Acids, tall oil cobalt salts	Dissociates : pKa= 5.82 @ 20	-	-	-
Dissociation Product: Fatty acids, tall oil	(low solubility)	T 1/2 = 2 hours or less	Air: <0.1 Water: 7-8 Soil: 28-29 Sediment: 63-64	Readily biodegradable

NA = not applicable due to substance properties

(1) Photo-degradation and fugacity results are averages of modeled result for oleic and linoleic acid, two components of fatty acids, tall oil

Table 2.5: Summary of Available and Relevant Environment Effect Data for Cobalt Stearate, Fatty acids, Tall oil, Cobalt Salt, and their Dissociation Product.

Compoound	**Environment Effect**		
	AcuteToxicity to Fish (mg/L)	Acute Toxicity to Daphnia (mg/L)	Acute Toxicity to Algae (mg/L)
Dissociation Product : Cobalt chloride	1.41-333 (96-h LC50)	1.52-5.5 (48-h EC50)	0.52 (96-h EC50)
Cobalt stearate	-	-	-
Dissociation Product: Stearate acid	LT50 data (marginally useful)	-	-
Fatty acids, tall oil, cobalt salts	-	-	-
Dissociation Product: Fatty acids, tall oil	10 (96-h LC50) to >1000 (96-h LL50)	55.7 (48-h EC50) to > 1000 (48-h 50)	0.79-9 (EC50) to 854 (72-h EL50)

Table 2.6: Summary of Available and Relevant Human Health Effect Data for Cobalt Stearate, Fatty Acids, Tall Oil, Cobalt Salt and their Dissociation Product.

Compound	**Human Health Effect**				
	Acute Toxicity (mg/L)	Repeat Dose Toxicity	Reproductive Effects	Developmental Effects	Genetic Toxicity
Dissociation Product : Cobalt chloride	LD50=42.4-190 (rat) LD50=89.3 (mouse)	NOAEL= 0.6 mg Co/kg; LOAELs 0.5-30.2	Effect in rats at 13.2-30.2 mg Co/kg/d; mice at 23-58.9mg Co/kg/d	NOAEL=24.8 mg/kg/d (mice); 81.7 mg Co/kg in screening study (mice)	Co (2+) generally non-mutagenic in bacteria assays; genotoxic/mutagenic/ clastogenic in mammalian system
Cobalt stearate	LD50= 9.82 gm/kg	-	-	-	-
Dissociation Product: Stearate acid	LD50=4600 (rat) LD50> 10,000	50 g/kg/d for 24 week produced	-	-	Not Mutagenic in bacteria assays

	(rat)	reversible lipogranulomas in rats; Severe effects in rats, including mortality at 3000 ppm			
Fatty acids, tall oil, cobalt salts	-	-	-	-	-
Dissociation Product: Fatty acids, tall oil	LD50 > 10,000 (rat)	NOEL= 2500 mg/kg/d (rat 90-d. diet)	NOEL= 5000 mg/kg/d (rat 2 gen study)	NOEL= 5000 mg/kg/d (rat 2 gen study)	Not mutagenic in bacterial assays; clastogenic to mammalian cells but at cytotoxic concentration

2.5 Degradation Mechanisms

Several of the more common bulk polymers like the polyolefins are susceptible to photo-oxidation. For a polymer like polyethylene, photo-oxidation lead to increasing amounts of carbonyl compounds. Some carbonyl groups act as sensitizers by UV light absorption. Figure 2.2 shows the mechanism for abiotic ester formation. By Norrish type I cleavage the radical formed can react with an alkoxyl radical on the polyethylene (PE) chain [40].

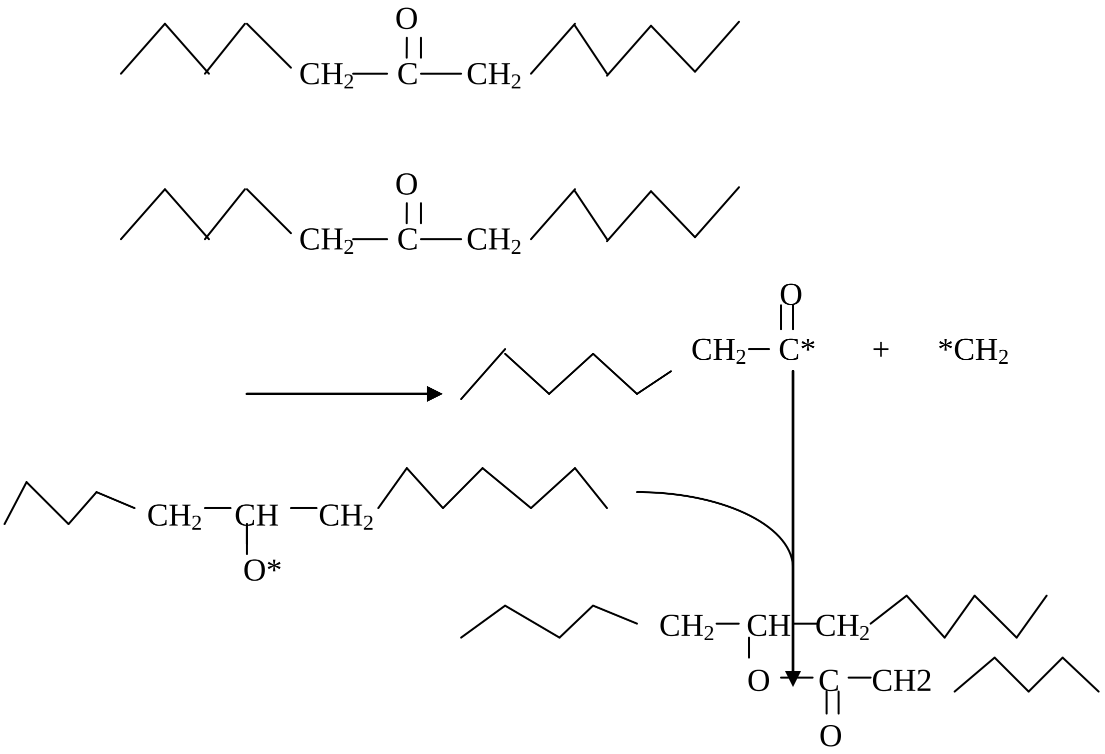

Figure 2.2: Abiotic ester formation in polyethylene

2.5.1 The factor influencing weathering

Response of a material to weathering is not a simple question to answer because of the complexity of the factors involved. Considering weathering involves considering the effects of solar radiation, temperature, humidity, pollutants and all the combinations of these factors. These major factors are shown in the diagram below [41]:

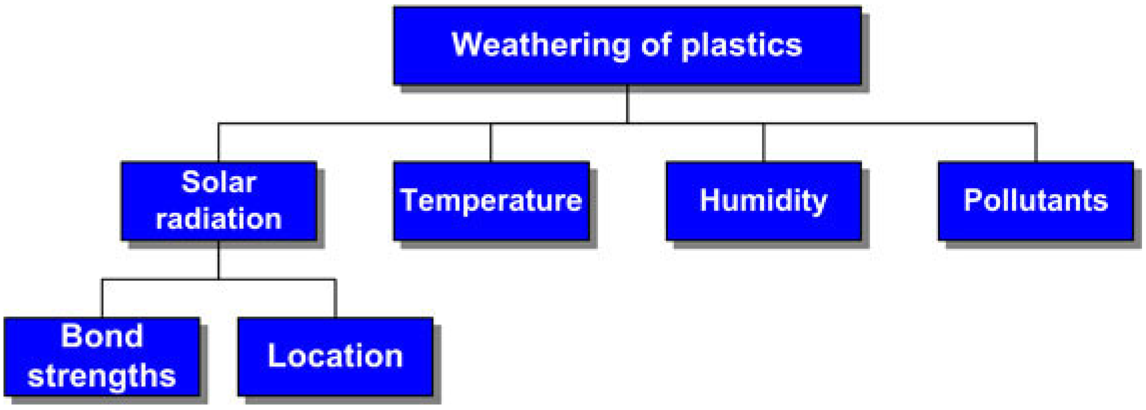

Figure 2.3: The factor influencing weathering

Rapid ultraviolet degradation resulting in several crazing is experienced by the unprotected material. A black-pigmented variety is recommended for exposure to direct sunlight. It is reported that as litter as 3% carbon black will absorb all the ultraviolet radiation in sunlight and will prevent its deleterious effect. Other ultraviolet absorbers may be employed if carbon black additions cannot be tolerated [42].

The weathering behavior of a plastic is one of the most important limiting factors in assessing and selecting a plastic for outdoor applications. The selection of a material by simple mechanical properties may well be sufficient in many cases but this is ineffective if the material loses strength or discolors in service. ABS may be more than adequate mechanically for many outdoor applications but the weathering response of ABS means that it is rarely selected for such applications. Asking and adequately answering the question '**How long will it last in service**?' must be a key factor in the selection of materials for external use [41].

2.5.2 Photos-Biodegradable

Photo-biodegradable is more concern of technical requirement of degradable plastic or decreasing of molecular substance in plastic with considered in the light of public and also use and misuse in waste and litter control. Essential requirement are that degradation process should be controllable and lead to lower molar mass oxidation products which can be assimilated by microorganisms to give biomass and ultimately carbon dioxide and water. It is shown that certain types of antioxidant, notably the transition metal dithiocarbamates, after fulfilling their stabilizing function during manufacturing and service life of the polymer based product [43].

The popular journal and scientist also belief that hydrocarbon polymer do not biodegrade at molar mass above 500 is shown to be based on a misinterpretation of earlier work. Bioerosion of carboxylatic acids, the oxidation products of polyolefin, occurs at the surface of polyethylene and these acts as nutrients for the growth of non-pathogenic bacteria and fungi in the absence of any source of carbon [43].

2.5.3 Thermal degrade and stability for another additive

Thermal stability for manganese carboxylate were investigated and reveal that the maximum degradation point relation between derivative weight change and temperature. The degradation of manganese carboxylate increase with increasing their chain length from manganese laurate, manganese palmitate and manganese stearate, respectively [44]. In aging studies for polymeric materials, the decrease in the decomposition and melting temperature is associated with shorter polymeric chains and a lower thermal stability of the material as reported by Colom *et al* (2003) [45]. The shorter chains of manganese carboxylates give the lower thermal stability

2.6 Theory of the degradation

Continuous distribution kinetics was applied to determine the kinetics of degradation of PEO and PAM. For a polymer of molecular weight $P(x')$, the random degradation of the polymer chain in solution is represented by

$$P(x')\rightarrow P(x)+P(x-x') \qquad (1)$$

The population balance equation with k_d as the degradation coefficient is

$$\delta p(x,t)/\delta \mathrm{t}=k_d(\mathrm{x})p(x,t)+ 2\int_x^\infty k_d(x')p\,(x',t)\,Q\,(x,x')dx' \qquad (2)$$

For random chain scission, the distribution of degraded products given by $\Omega(x,x')$ is $1/x'$ [46]. Assuming a linear dependence of k_d, $k_d(x) = k_d x$, the above equation reduces to

$$\delta p\,(x,\,t)/\delta t = \mathrm{k_d}\,x\,p\,(x,t) + 2\int_x^\infty k_d p(x',t)\,dx' \qquad (3)$$

Applying moment operation to Eq. (3) yields

$$\delta p^{(f)}/\delta \mathrm{t} = (\mathrm{j}\text{-}1)/\mathrm{j}+1)\mathrm{k_d}\,p^{(j+1)}\,(t) \qquad (4)$$

For $j = 0$ and $j = 1$

$$\delta p^{(f)}/\delta \mathrm{t} = \mathrm{k_d}p^{(1)}\,(t)$$
$$\delta p^{(f)}/\delta \mathrm{t} = 0 \qquad (5)$$

Solving the above equation with initial condition $p^{(0)}(t = 0) = p_0^{(0)}$ and using Eq. (4), the variation of number average molecular weight M_n, defined as $p^{(1)}/p^{(0)}$, with time

$$(M_{n0}/M_n)-1=k_d M_{n0}t=kt \qquad (6)$$

The degradation experiments were carried out both in the presence and absence of oxygen (by purging oxygen and nitrogen) and in atmospheric conditions.

It was observed that the polymer degraded only in the presence of oxygen and in atmospheric (contains both oxygen and nitrogen) conditions. In fact both the polymers were found to crosslink to a higher molecular weight polymer in an inert atmosphere of nitrogen (which has not been studied in detail here). The “oxygen effect” manifests in three different modes during the main chain degradation [34]. It can act as a promoter, inhibitor or fixing agent for the main chain breakage. For both PEO and PAM, oxygen promotes the degradation process by preventing cross linking. But nearly the same amount of degradation was observed when the study was carried in atmospheric conditions and in saturated condition where oxygen was purged continuously.

This indicates that though oxygen is required for degradation to occur, there is a saturation condition above which no further degradation is seen with increase in oxygen concentration. In aqueous solutions, hydrogen abstraction from polymer is by attack of $OH^{\bullet}$ radicals and the number of $P^{\bullet}$ formed by this indirect method exceeds the number of radicals formed by the direct scission of covalent bonds in polymer on irradiation [47]. Based on experimental observations it can be perceived that the degradation proceeds by the following sequential reactions.

$S + h\nu \rightarrow S^{*}$ solvent excitation (a)

$S^{*} \rightarrow 2X'$ solvent dissociation (a1)

$P' + X' \rightarrow XH + P'$ hydrogen abstraction from polymer (b)

$P' + O_2 \rightarrow PO'_2$ reaction of polymer radical with oxygen (c)

$2PO'_2 \rightarrow POOOOP \rightarrow 2PO' \rightarrow$ products main chain degradation (d1)

$PO'_2 \rightarrow P_1 + P'_2$ (d2)

$P' + P' \rightarrow PP$ termination reaction (e)

$P^{\bullet}+S\rightarrow P+X^{\bullet}$ (e1)

$P^{\bullet}+X^{\bullet}\rightarrow PX$ (e2)

$$P^{\bullet} + P_3 \rightarrow P_3^{\bullet} + P \qquad \text{(e3)}$$

The first step of polymer degradation is the abstraction of hydrogen from the polymer back bone by the solvent generated $OH^{\bullet}$ (b). The H–OH bond dissociation energy of H_2O is 5.118 ± 0.01 (≅242 nm) [48] which indicates that one photon excitation of water molecule at 266 nm (absorption coefficient = 0.01 cm^{-1}) cannot lead to the breakage of H–OH bond. However, consecutive two-photon absorption can provide the sufficient energy and lead to the breakage of H–OH bond. The hydroxyl radicals formed from solvent have high propensity for hydrogen abstraction from polymer, resulting in the formation of $P^{\bullet}$.

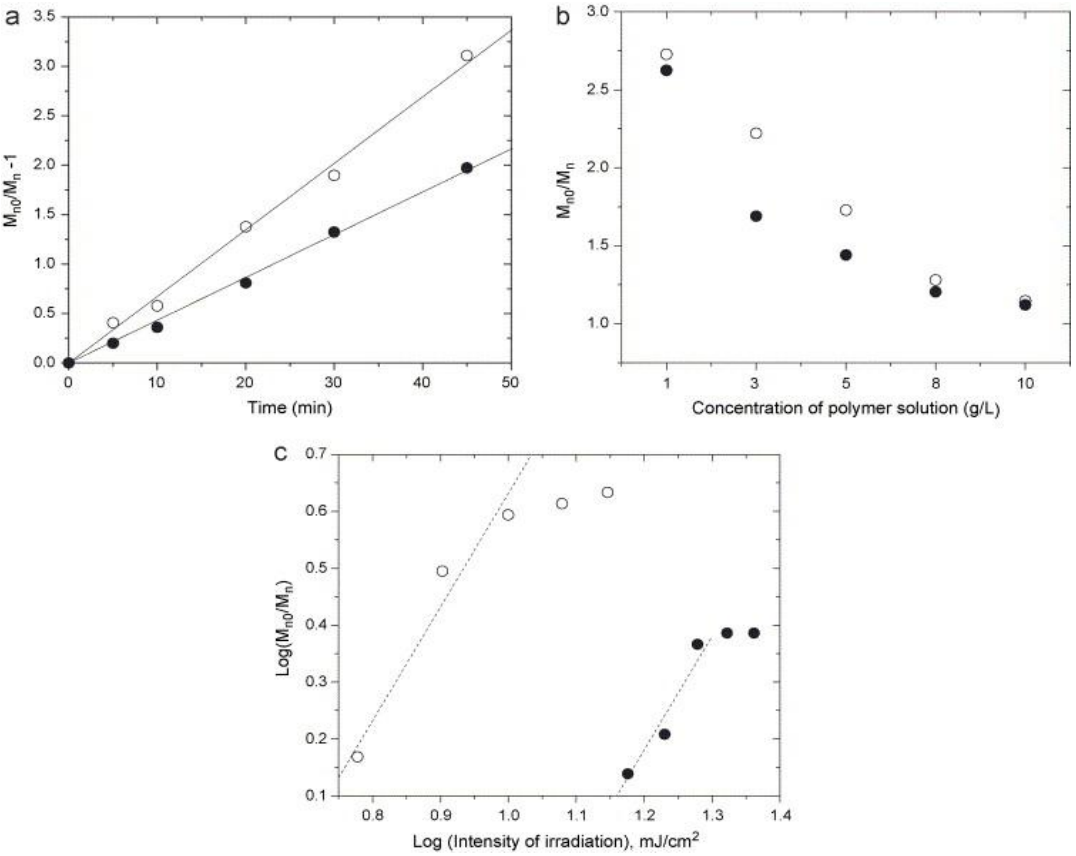

Figure 2.4: The effect of polymer concentration on the degradation rate

2.7 Lifetime predictions

Lifetime estimations are very useful in the development or selection of polymers for different applications. Usually the lifetime determined by accelerated aging, like air oven aging studies, require long time periods. The estimated lifetime of a formulation of a polymer to failure has been defined as the time when the mass loss reaches 5 wt%, example α = 0.05 [49, 50, and 51]. From the integration of Equation (7), the lifetime can be estimated by Equation (8):

$$\frac{d\alpha}{dt} = Ae^{\frac{E\alpha}{RT}}\,(1-\alpha)^{n} \tag{7}$$

$$tf = \frac{1-0.95^{1-n}}{A(1-n)}\,exp\frac{E\alpha}{RT} \qquad (n \neq 1) \tag{8}$$

The reaction order value (*n*) can be obtained directly from the symmetrical index of a derivative thermogravimetry (DTG) peak based on the second Kissinger technique [52], Equation (9):

$$n = 1.88\frac{\left|\frac{d^2\alpha}{dt^2}\right|}{\left|\frac{d^2\alpha}{dt^2}\right|} \tag{9}$$

Where, the indices *L* and *R* correspond to the left and right peak (d2α/d*t*2) values on the second derivative thermogravimetry (DTG) curve for the decomposition process.

Table 2.7: Result of lifetime as a function of service temperature in the presence of varying amount of cobalt stearate in air atmosphere

Sample designation	**Lifetime (minutes)**					
	25°C	**75°C**	**100°C**	**125°C**	**150°C**	**200°C**
F1	$2.1\text{x}10^{8}$	$2.7\text{x}10^{4}$	$4.2\text{x}10^{6}$	$7.3\text{x}10^{2}$	$1.6\text{x}10^{2}$	$1.5\text{x}10^{5}$
FCS5	$3.9\text{x}10^{6}$	$6.5\text{x}10^{3}$	$4.3\text{x}10^{3}$	$2.8\text{x}10^{2}$	79	14
FCS10	$4.5\text{x}10^{5}$	$3.6\text{x}10^{2}$	$1.2\text{x}10^{3}$	35	16	9
FCS15	$3.5\text{x}10^{3}$	$3.1\text{x}10^{2}$	$1.1\text{x}10^{2}$	11	14	5
FCS20	$8.9\text{x}10^{2}$	$2.1\text{x}10^{2}$	$1.1\text{x}10^{2}$	10	5	3

2.8 Technology of photodegradable plastic

Degradable plastic can be manufacture by variety of process [53]. An early approach to the problem was to add oxidation accelerators such as benzophenone to make ‘unstable’ plastics. As the technology development, more sophisticated system was devised since packaging materials must not only degrade, but must do so at controlled and predicted rate.

An alternative approach was adopted in Guillet’s laboratories at the University of Toronto. In this technology, small quantities of a sensitizing group are chemically attached to the macromolecular chains. When a plastic containing this sensitizing group expose to the natural sunlight, the group sensitizing will absorb radation which cause the chain to break at the point and thus form smaller segment. Since the physical properties of the plastic depend on the length of the chain, if the chain is broken, the plastic become very fragile [53].

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Introduction

Applied of equipment and fabricate the experimental work will been conducted throughout this study. Fabrication is done first by selecting the suitable chemical to prepared a chemical and develop an additive in this study. This paper also deals with the development of a thermal-degradable high-density polyethylene (HDPE) composition containing small amount of partially degraded oxidised polyethylene (OPE) as a degradation promoter. Films containing varying amounts of oxidised polyethylene were prepared and then exposed to heat in the oven for accelerated ageing studies. The degradation behaviour was monitored by measuring the changes in structure (by FTIR). For the equipment, FTIR are use to follow the time evolution of know the changes in the polyethylene present. Other equipment to measure the strength and stress (by tensile machine) and Scanning Electron Microscope (SEM) to observe surface change follow the time evolution, also for the thermal are (DSC) for measuring melting point of additive and Thermal Graphic Metric (TGA) for measuring thermal degradation of additive. The study was performed on HDPE keeping in mind its prime importance in the packaging field and its inherent resistance towards degradation and describes the preparation of polymer films having varying amounts of oxidized polyethylene and evaluation of its degradation behavior as a function of irradiation time.

3.2 The experiment flowchart

Figure 3.1 shows the flow of the experiment. It start from prepare the chemical solution for cobalt carboxylate (cobalt stearate, cobalt palmitate, cobalt laurate). After that follow with experimental work which consist about seven steps those are check the characteristic of neat polyethylene and cobalt carboxylates that have prepare, mixing or blending between polyethylene film and solution of cobalt carboxylate, and evaluate the characteristic of polyethylene film with the selected equipment after mixing, then expose polyethylene film to the heat about 20 days. After that, the final step is evaluate or analyzed the effect of heat or thermal into polyethylene and compare it between before and after the exposed.

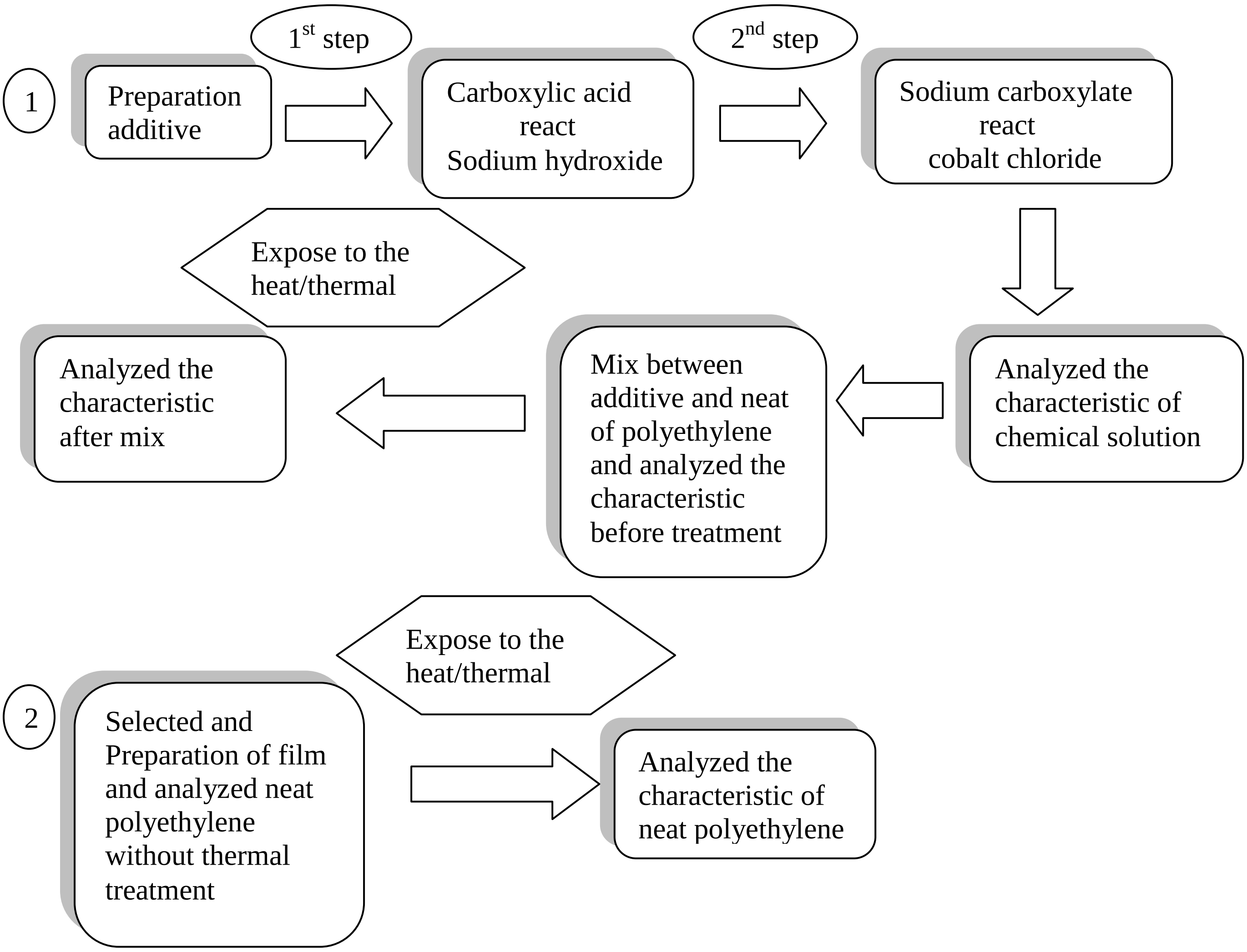

Figure 3.1: Experiment flowchart

3.3 Material

There are including sodium hydroxide (System), lauric acid, palmitic acid, stearic acid (AR grade E.Merck), cobalt chloride $COCI_2.6H_2O$, and resin High Density Polyethylene (HDPE) were used without further purification. General purpose film grade 'HDPE 24FSO40' has been used to prepared film. Cobalt stearate was prepared by double decomposition of cobalt acetate with sodium stearate according to procedure reported in the literature [54].

3.4 Experimental

In this experiment work, raw material must be selected to use a suitable type of High Density Polyethylene (HDPE). After that, prepare for the additive which is Cobalt Carboxylate (cobalt stearate, cobalt palmitate and cobalt laurate). There have two step reactions, the first step reaction sodium hydroxide will react with carboxylic acid then after the reaction is done, the reaction will continue with combine a chemical solution from first step with cobalt chloride. The chemical solutions were dissolved into homogenous solution in beaker. The solution were mixed together slowly in 1000 ml beaker under vigorous stirring. The pH of the mixture was kept constant at pH=10 throughout the reaction by careful adjustment of the solution flow rate stirring about 8rpm and keep it constant of their temperature during reaction around 80^0C to 85^0C and keep continuous stirrer about 2 or 4 hours. Then, wait until the solutions are mix well. Therefore, use the additive and add in the neat High Density Polyethylene (HDPE) based on the several concentration (0.2%, 0.5% and 1.0%) using injection molding machine. After all the process finish, insert all the different concentration's additive that have adding in HDPE film into oven an set the temperature at 60^0C. The sample can collect and observe based on their strength stress, surface change, and change of structure before and after expose to the heat with follow the time evolution within 20 days expose to the heat.

3.4.1 Synthesis of Cobalt Carboxylate

There have two steps to produce cobalt carboxylate. First step to produce sodium carboxylate (sodium stearate, sodium palmitate and sodium laurate) were synthesized by the reaction of carboxylate acid (stearic acid, palmitic acid and lauric acid) with sodium hydroxide. The reaction of carboxylate acid and sodium hydroxide (0.25M) must constant at temperature range 80^0C to 85^0C and mix well for 1 or 2 hour. Second step to produce cobalt carboxylate (cobalt stearate, cobalt palmitate and cobalt laurate) were synthesized by the reaction of sodium carboxylate with cobalt chloride respectively according to the procedure. Make sure the reaction temperature constant at range 80^0C to 85^0C with continuous stirring about 8 rpm. After that, filter the solution and wash it with hot water (range at 70^0C and above) to separate sodium chloride.

Varying amount of cobalt carboxylate (0.2%, 0.5% and 1.0%) were mixed with HDPE by mixing manually, then melt and molding it with injection molding to make easier for use tensile machine and measuring the stress and strain of the film, followed by sheeting process. The processing condition used for film preparation and chemical reaction preparation. The details of film prepared along with their designation are present in Table 3.1. HDPE film has been designated as F1, FCS, FCP, and FCL, respectively, follow by adding cobalt carboxylate concentration according with their percentage.

Figure 3.2: Cobalt Carboxylate as additive

3.4.2 Preparation films

A Brabender plasticorder Labstation with a 20 mm diameter screw of L:D = 25:1, extruder speed of 20 L/min associated with a roller having a draw speed of 3m/min was used for the preparation of film. HDPE chips were dry blended with varying amounts of cobalt carboxylate ranging from 0.2% to 1.0% w/w in a tumbler and fed to the Brabender. The temperature in the fed zone, 192^{0}C; compression zone, 195^{0}C; metering zone, 198^{0}C and die zone, 200^{0}C were used for extrusion. Neat HDPE film has been designated as H1 and films having cobalt carboxylate have been designated as HS1, HS2, HS3; HP1, HP2, HP3 and HL1, HL2, HL3. The details of films prepared along with their designation are presented in Table 3.3

Figure 3.3: Sample with different concentration of additive

Table 3.1: Details of formulation and the sample designation

Film designation	**Amount (g)**			
	HDPE	**Cobalt stearate**	**Cobalt palmitate**	**Cobalt laurate**
H1	400	-	-	-
HS1	399.2	0.8(0.2%)	-	-
HS2	398	2.0(0.5)	-	-
HS3	396	4.0(1.0%)	-	-
HP1	399.2	-	0.8(0.2%)	-
HP2	398	-	2.0(0.5%)	-
HP3	396	-	4.0(1.0%)	-
HL1	399.2	-	-	0.8(0.2%)
HL2	398	-	-	2.0(0.5%)
HL3	396	-	-	4.0(1.0%)

3.4.3 FTIR spectroscopy

Infrared (IR) spectroscopy is a chemical analytical technique, which measures the infrared intensity versus wavelength (wavenumber) of light. Based upon the wavenumber, infrared light can be categorized as far infrared (4 ~ 400cm^{-1}), mid infrared (400 ~ 4,000cm^{-1}) and near infrared (4,000 ~ 14,000cm^{-1}).

Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule. For example, the C=O stretch of a carbonyl group appears at around 1700cm^{-1} in a variety of molecules. Hence, the correlation of the band wave number position with the chemical structure is used to identify a functional group in a sample. The wave number positions where functional groups adsorb are consistent, despite the effect of temperature, pressure, sampling, or change in the molecule structure in other parts of the molecules. Thus the presence of specific functional groups can be monitored by these types of infrared bands, which are called group wave numbers [55].

The early-stage IR instrument is of the dispersive type, which uses a prism or a grating monochromator. The dispersive instrument is characteristic of a slow scanning. A Fourier Transform Infrared (FTIR) spectrometer obtains infrared spectra by first collecting an interferogram of a sample signal with an interferometer, which measures all of infrared frequencies simultaneously. An FTIR spectrometer acquires and digitizes the interferogram, performs the FT function, and outputs the spectrum.

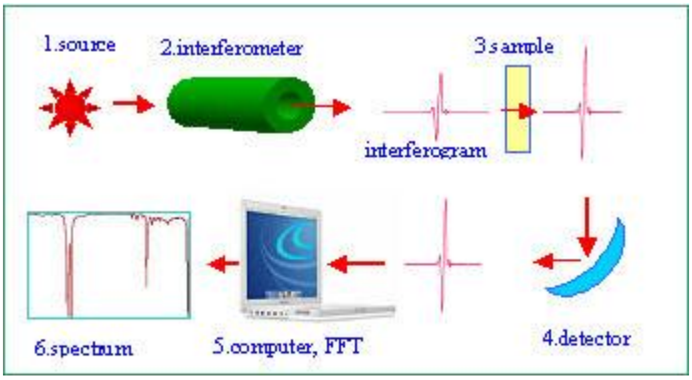

Figure 3.4 : Schematic flow of FTIR process

3.4.3.1 Schematic illustration of FTIR system

Characteristic bands around 3500 cm^{-1} and 1630 cm^{-1} are ascribed to atmospheric water vapor and the bands at 2350 cm^{-1} and 667 cm^{-1} are attributed to carbon dioxide. A background spectrum must always be run when analyzing samples by FTIR. When an interferogram is measured with a sample and Fourier transformed, a sample single beam spectrum is obtained. It looks similar to the background spectrum except that the sample peaks are superimposed upon the instrumental and atmospheric contributions to the spectrum. To eliminate these contributions, the sample single beam spectrum must be normalized against the background spectrum.

The absorbance spectrum can be calculated from the transmittance spectrum using the following equation.

The final transmittance/absorbance spectrum should be devoid of all instrumental and environmental contributions, and only present the features of the sample. If the concentrations of gases such as water vapor and carbon dioxide in the instrument are the same when the background and sample spectra are obtained, their contributions to the spectrum will ratio out exactly and their bands will not occur. If the concentrations of these gases are different when the background and sample spectra are obtained, their bands will appear in the sample spectrum [56].

3.4.4 Characterisation of cobalt carboxylate

The chemical properties and characteristic of the cobalt carboxylate especially cobalt stearate was checked. The characterization comprises include surface change, melting point and degradation temperature. The FTIR spectra of the cobalt carboxylates were recorded in KBr pallet in the wavelength range 400-4000 cm^{-1} on a BIORAD (FTS-40) spectrophotometer.

Evaluation of degradation temperatures were done using Thermogravimetric Analyzer (TGA) Q500 from TA Instruments, in N_2 atmosphere, ramp method, heating rate 10°C min^{-1} and final temperature 700°C [57,58]. While melting points were of cobalt carboxylate investigated using Differential Scanning Calorimeter (DSC) Q1000 from TA Instruments, in N_2 atmosphere; at heating rate 10°C min^{-1}, and load temperature range 50^0C to 200^0C.

3.5 Degradation studies

3.5.1 Thermo-oxidative tests

The thermo-oxidative test was carried out by placing the extruded in an air oven at 60^0C for extended period as report in the literature [59] and [60]. The changes due to thermo-oxidation were monitored using FTIR, tensile properties and Scanning Electron Microscope. There are expose to the thermal treatment at 20 days period

3.5.2 Evaluation of degradation

The tensile tests were performed on HDPE films according to ASTM 882-85 using a Universal testing machine (Model JRI-TT25). Films of 100 mm length and 10 mm width were cut out from the exposed films and subjected to a crosshead speed of 100 mm/min. The tests were undertaken in an air-conditioned environment at 27 °C and with a relative humidity of 60%. Five samples were tested for each experiment and the average value has been reported.

The structural changes occurring in the HDPE films upon exposure were investigated using FTIR spectroscopy. The FTIR spectra were recorded at regular intervals using a BIORAD (FTS-40) spectrophotometer. Carbonyl Index (CI) was used as a parameter to monitor the degree of photo-oxidation of polyethylene and has been calculated according to the baseline method [61].

Carbonyl Index (Cl)

$$\frac{Absorption\ at 1740\ cm^{-1}\ (the\ maximum\ of\ carbonyl\ peak)}{Absorption\ at\ 2020\ cm^{-1}\ (internal\ thickness\ \ band)}$$

Scanning electron microscopy (SEM) was performed to investigate the changes in the morphology due to heat irradiation. Sample surfaces were sputtered with gold using usual techniques and then analyzed in JEOL (JSM-840) electron microscope using a voltage of 10 kV. Photo-micrographs were taken at uniform magnification of 2000 fold.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The purpose of this study is to develop an additive and suitable percent of additive to add in HDPE to accelerated thermal degradation. In same time the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. From that matter polymer (HDPE) can easy to decompose. The result indicates an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss. Indeed unless correctly prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include reduced ductility and embrittlement, chalking, color changes, cracking, general reduction in most other desirable physical properties. [62]

4.2 Experiment

The purpose of this experiment is to determine the effectiveness amount of the additive added into the polymer (HDPE) based on the time ageing, so that it can be used as a pretreatment for accelerate decompose of HDPE.

4.2.1 Synthesis of cobalt carboxylate

Synthesis of cobalt carboxylate comprises two steps of reactions. The first step is to produce sodium carboxylate, same as below:

Stearic acid + sodium hydroxide → sodium stearate + water
Palmitic acid + sodium hydroxide → sodium palmitate + water
Lauric acid + sodium hydroxide → sodium laurate + water

The reaction will control with temperature at 80^0C to 85^0C until the reaction complete. The lower temperature would make the reaction process slower, since the melting points of carboxylic acid are quite high, in range 44^0C to 69^0C. The perfect aging is needed to make the reaction mixed well. While, if high temperature is used and close to the boiling point temperature, the mixture will cause formation foam and become lump.

The second step is to produce cobalt carboxylate and sodium chloride and the reaction are written as follow:

Sodium stearate+cobalt chloride → cobalt stearate +sodium chloride + water
Sodium palmitate+cobalt chloride→cobalt palmitate+sodium chloride+ water
Sodium laurate + cobalt chloride → cobalt laurate + sodium chloride+ water

This preparation are present in stoichiometric proportion. The yield term using for know to describe the degree to which a desired predominates over competing side reaction. The percent of complete reaction occur like table below:

Table 4.1: Percentage yield of complete reaction

	Additive		
	Cobalt stearate	Cobalt palmitate	Cobalt laurate
Yield	97%	84%	88%

From the table, show that percentage yield of cobalt carboxylate is higher than the rest of two cobalt carboxylate, it is because the reaction to produce cobalt stearate has reach complete reaction while the reaction occur. The reaction influence comes from the several aspects, which is cause of temperature, flow rate agitation, structure chain length and the amount of moles. In fact if the parameter not consistent, the result of yield for cobalt palmitate and cobalt laurate react at 84% and 88%, respectively.

4.2.2 Characteristic of cobalt carboxylate

4.2.2.1 Melting Point using (DSC equipment)

The melting point of cobalt carboxylate is determined from the peak of endothermic melting transition in the DSC trace.

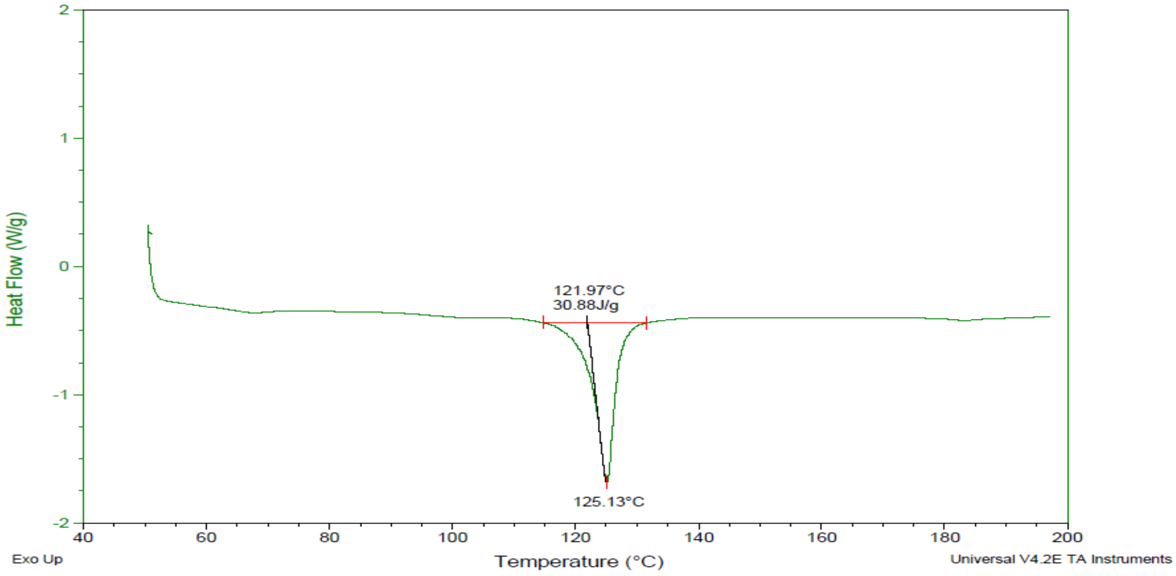

Figure 4.1 : Melting point of Cobalt Stearate

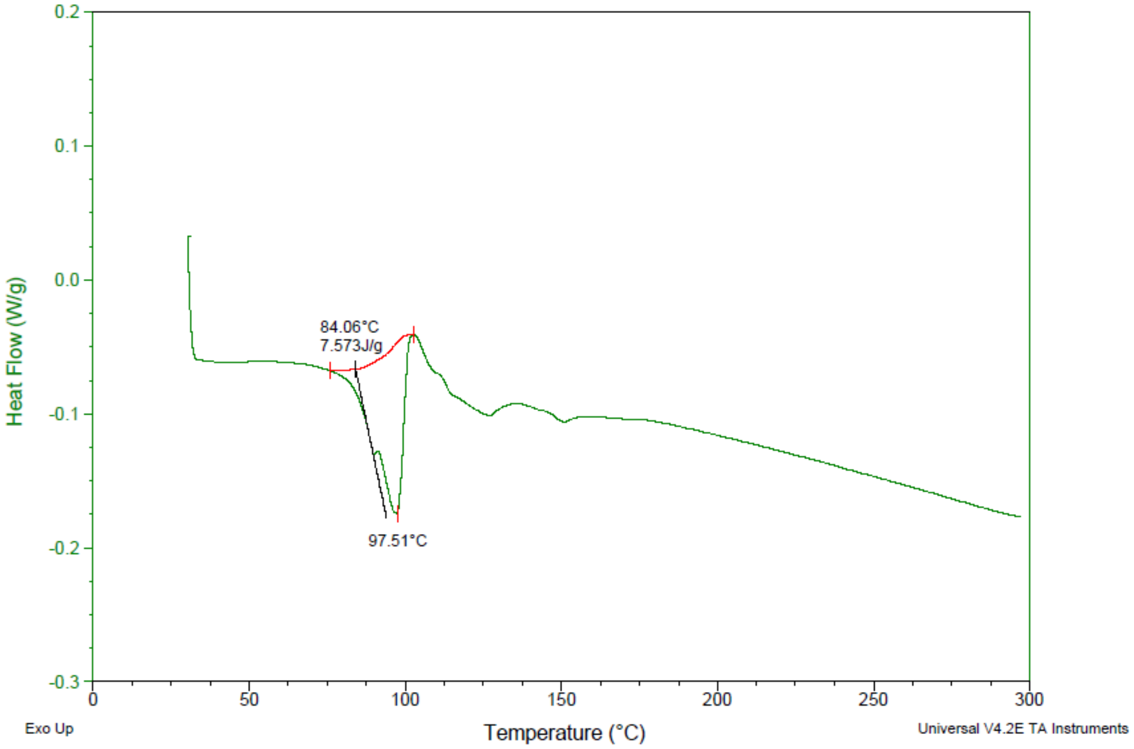

Figure 4.2: Melting point cobalt palmitate

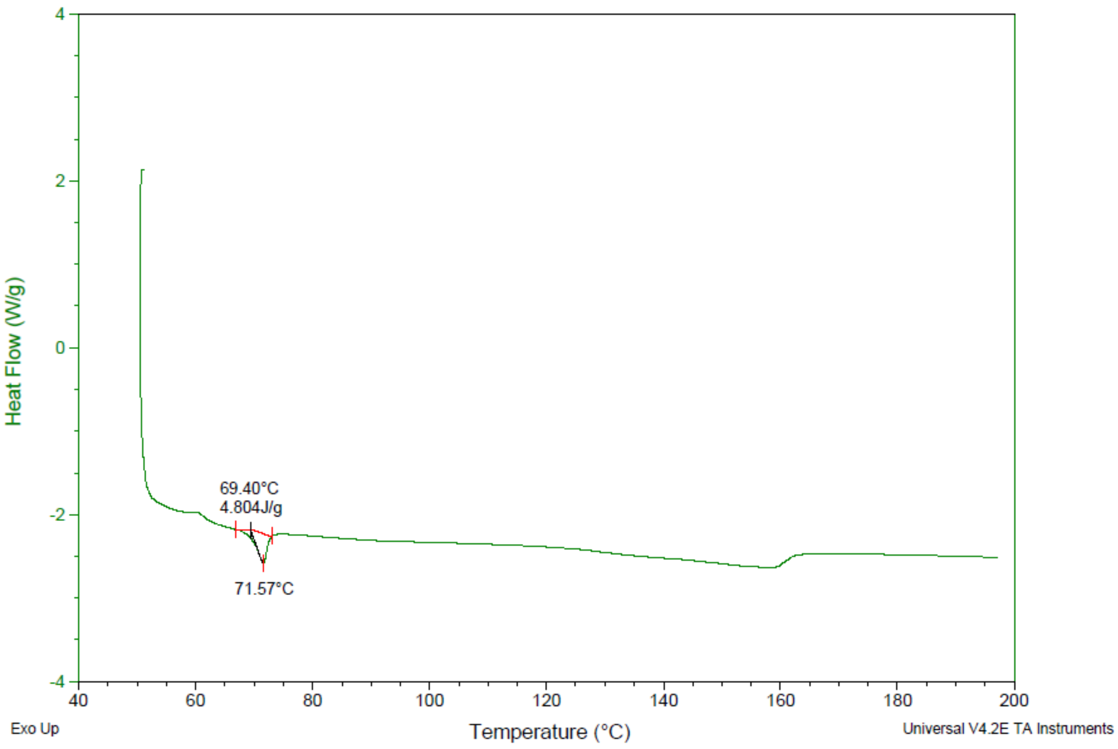

Figure 4.3: Melting point of cobalt laurate

From the figure 4.1, 4.2, and 4.3 show that melting point of the three additives that had prepared. From the figure, melting point of cobalt stearate is higher than cobalt palmitate and cobalt laurate whereas 121.97^{0}C, 84.06^{0}C, and 69.04^{0}C, respectively. While, additive's melting point is importance expect and must lower than melting point of HDPE itself, which is 190^{0}C to 200^{0}C. In order to make HDPE to accelerate thermal degrade, additive are use to help attached to the side of backbone inside the HDPE. After held by bonds which are weaker than bond connecting the chain, it can easier to decompose. Under thermal effect, the end of polymer chain departs, and forms low free radical which has low activity. Then according to the chain reaction mechanism, the polymer loses the monomer one by one. However, the molecular chain doesn't change a lot in a short time.

4.2.2.2 Temperature degrade (TGA equipment)

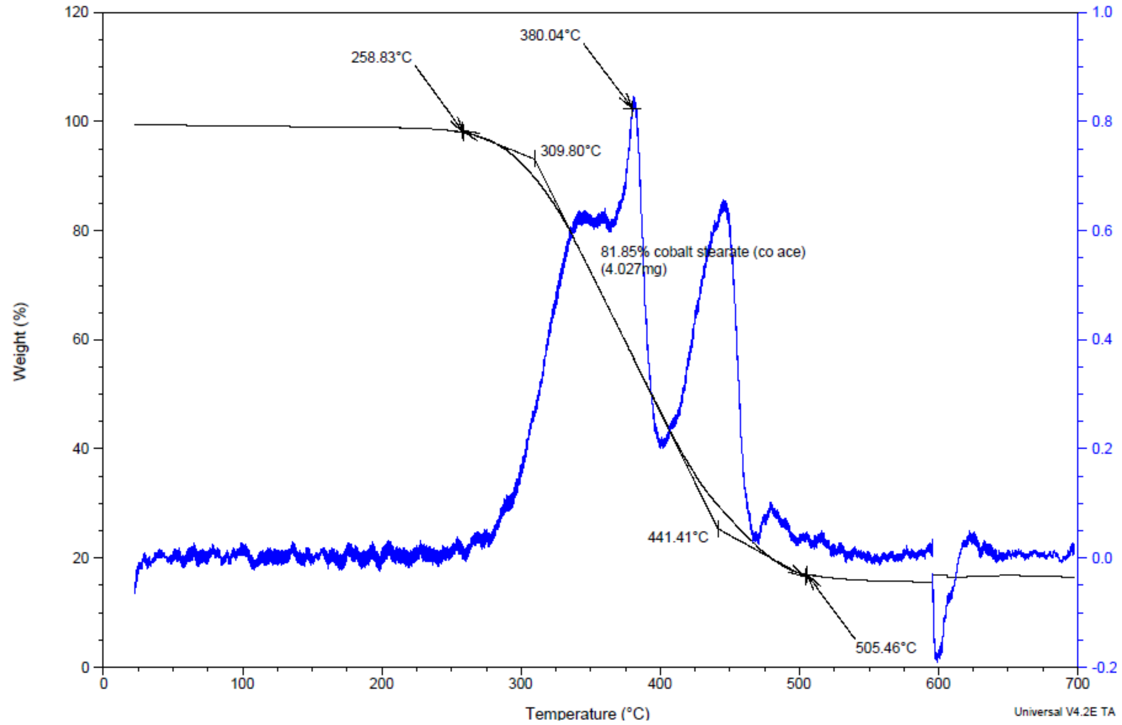

Figure 4.4: Temperature degradation of cobalt stearate

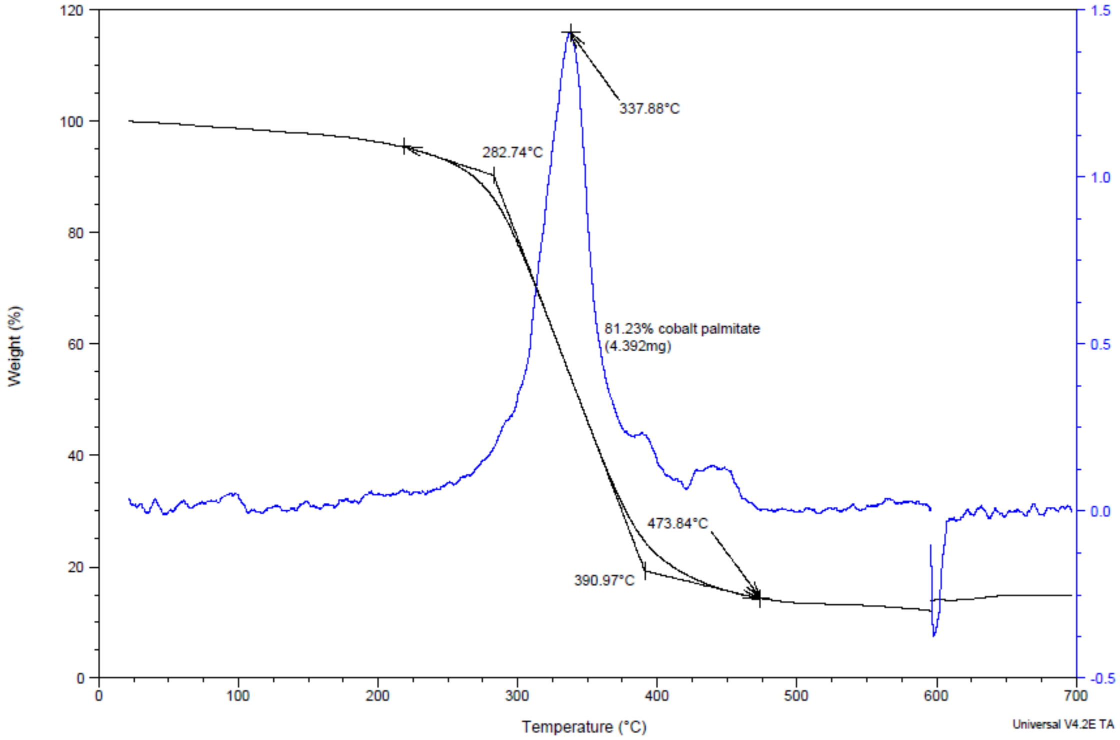

Figure 4.5: Temperature degradation of cobalt palmitate

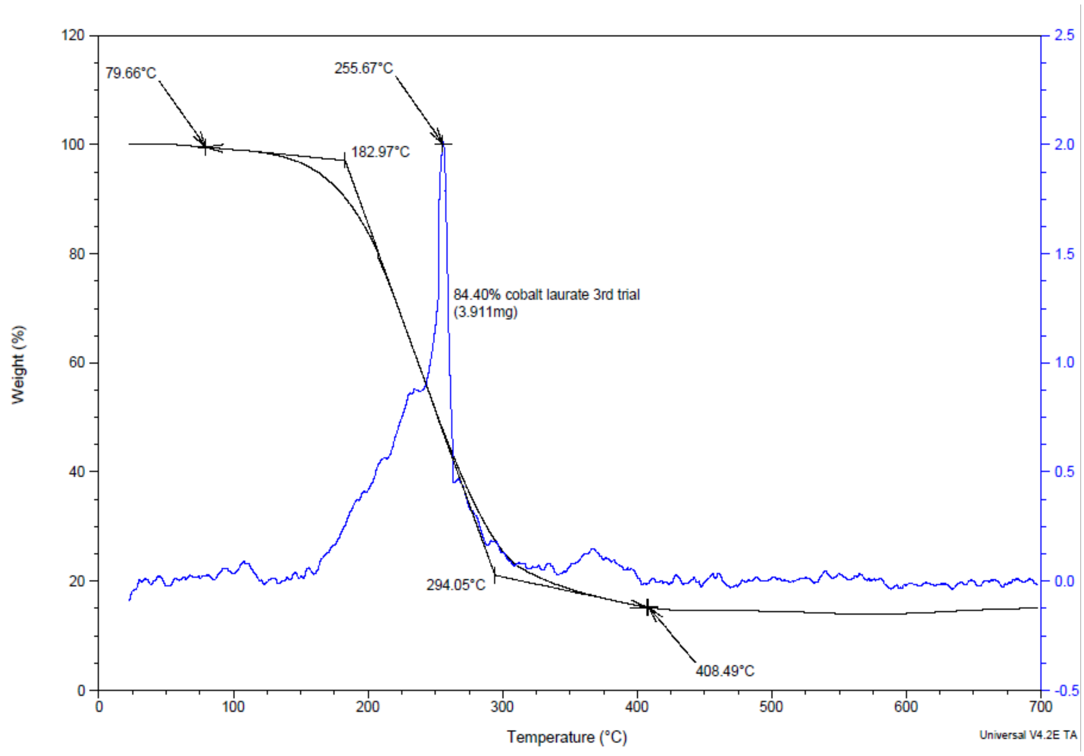

Figure 4.6: Temperature degradation of Cobalt laurate

Table 4.2: Thermal characterization of cobalt carboxylate

Additive	**T_{melt} [^{0}C]**	**T_{onset} [^{0}C]**	**T_{max}[^{0}C]**	**T_{end}[^{0}C]**	**ΔT[^{0}C]**
Cobalt Stearate	121.97	309.80	390.04	441.41	131.61
Cobalt Palmitate	84.06	282.74	337.88	390.97	108.23
Cobalt Laurate	69.04	182.97	255.67	294.05	111.08

From the figure and table above, show that the TGA traces single step decomposition for all the carboxylates. The melting temperature (T_{melt}), initial temperature of degradation (T_{onset}), maximum temperature of degradation (T_{max}) and final temperature of degradation (T_{end}) are reported in Table 4.2. As is evident, the thermal stability increased with increasing chain length as indicated by T_{onset}, T_{end} and T_{max}. The figure also reveal that cobalt stearate have high temperature point than cobalt palmitate and cobalt laurate, its indicate that the decrease in the decomposition and melting temperature or temperature degradation are associated with short polymeric chain and lower thermal stability of the material as report by Colom *et.al* [45]. Besides, cobalt stearate starts to degrade at temperature 309.80^{0}C and have higher degradation temperature than cobalt palmitate and cobalt laurate. Mixing of additive with polyethylene are usually performed around 170^{0}C-190^{0}C [12, 56, 63, 57]. It means that, all cobalt carboxylate have good thermal stability, especially in application for polyethylene, since the temperature of polyethylene processing is lower than their degradation temperatures.

4.2.2.3 Structure change by (FTIR)

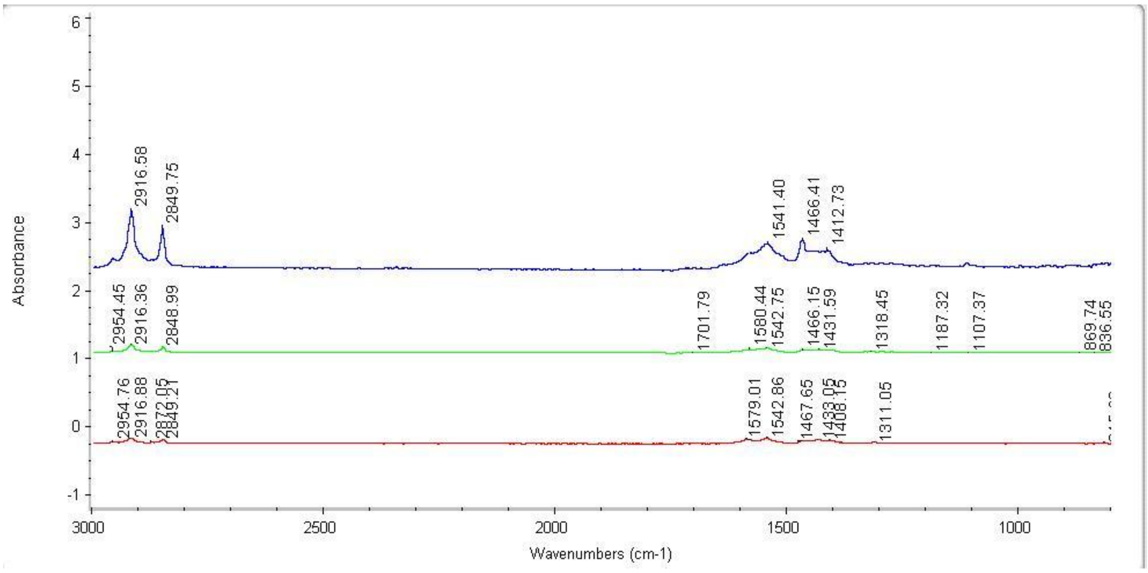

Figure 4.7: Combination peak of cobalt carboxylate where cs(blue), cp(green), cl(red)

The highest percent of contain polyethylene low density and ketone groups is cobalt stearate , 85% followed by cobalt laurate 81% and cobalt palmitate 24%. From the figure 4.7 show the FTIR spectra peak of all the cobalt carboxylates exhibited absorbance at 2916.58 cm^{-1} from cobalt stearate due to asymmetric vibration stretching of the hydroxyl regions. While cobalt palmitate at 2954 cm^{-1} and cobalt laurate at 2954.76 cm^{-1}. There have no carbonyl group region yet because these carboxyalate not doing thermal treatment.

4.2.3 Thermo-oxidative aging study

4.2.3.1 Before and after thermal treatment

4.2.3.1.1 Tensile test studies

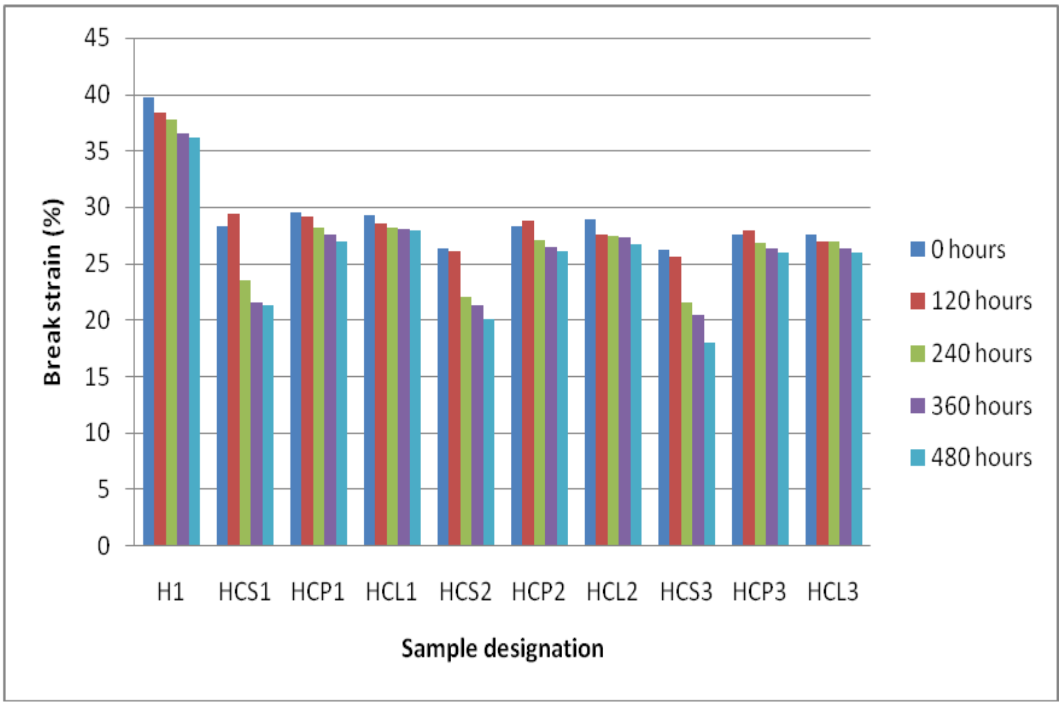

Figure 4.8: Break Strain of HDPE with thermal exposure

Figure .4.8 represents the effect of thermal exposure by time in air oven at 60 ^{0}C on mechanical properties (tensile strength and break strain) of HDPE films in the presence of additives and neat HDPE film. It should be noted that the initial values of break strain were not affected by the incorporation of these additives thereby implying that these additives do not lead to degradation in the processing stage.

For the sake of brevity, only percentage loss in elongation or break strain have been taken into consideration, which have been reported to be direct indicators of degradation as reported in the literature [64, 65 and 66]. It is well documented that during thermal treatment, heat and oxygen will initiate free radical reaction to degrade polyethylene [67 and 68].

Films containing cobalt stearate, the percent of break strain decrease inversely proportional with increasing concentration additive present. It also followed by time ageing where more time needed to loss the strength. In the early or initial stages, there are increases followed by a steady decrease till the failure of the sample. The initial increase in strength can be attributed to increase in the crystallinity of films and the later decrease can be attributed to chain scission.

The difference contain additive in each HDPE film sample indicate the difference enhance of brittle. After cobalt stearate additive, it followed by cobalt palmitate and cobalt laurate additive where the percent of break strain decrease by time ageing increase. The rate have being much faster in the case of samples containing cobalt stearate than another additive like cobalt palmitate and cobalt laurate.

The decrease in elongation or break strain is basically due to the increase in the degree of cross-linking with aging, which finally lead to the embrittlement of the sample. The polymer chains take up oxygen and lead to the formation of hydroperoxide which breakdown to give oxygenated products. Further, effects like chalking, loss of gloss, embrittlement and flaking occurred for samples exposed to longer time periods.

4.2.3.1.2 FTIR studies

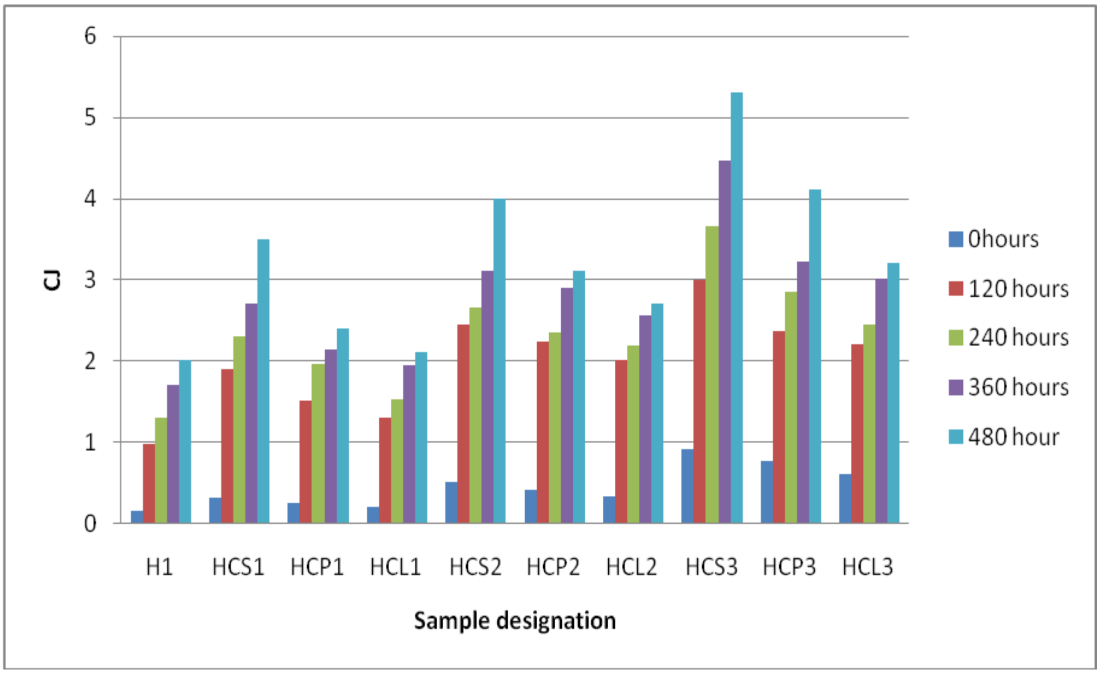

Figure 4.9: Variation of Carbonyl Index due to thermal exposure

From the figure 4.9 above, show that the Carbonyl Index of HDPE designation due to thermal exposure and indicate that pure HDPE did not reach this stage even after 480 hours exposure to the heat. While, the sample containing CS however, had undergone significant degradation follow the rest of two additive, CP and CL respectively as apparent from a large increase in Cl during the initial period of thermo-oxidation and sample will completely broke off after extend more than 480 hours because there have reported that polyethylene film enter into decay stage at Cl greater than 6 [69]. The increase in Cl also found to be proportional to the concentration of cobalt carboxylate in the formulation especially cobalt stearate additive.

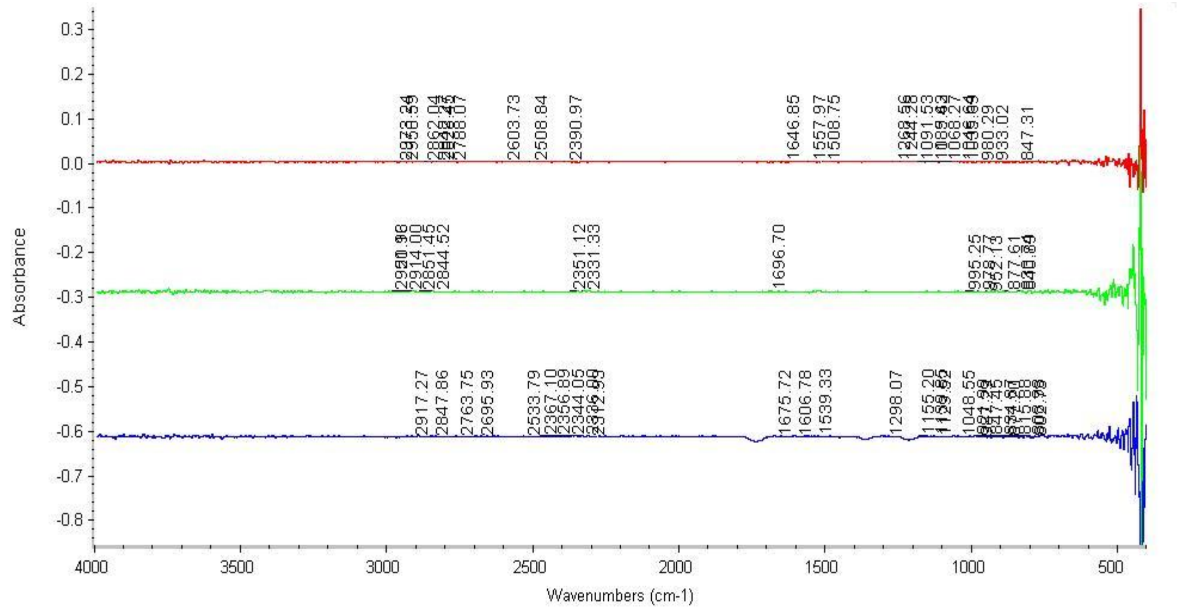

Figure 4.10: FTIR data for cobalt stearate at concentration 0.2% (red), 0.5% (green), 1.0% (blue) after 20 days treatment

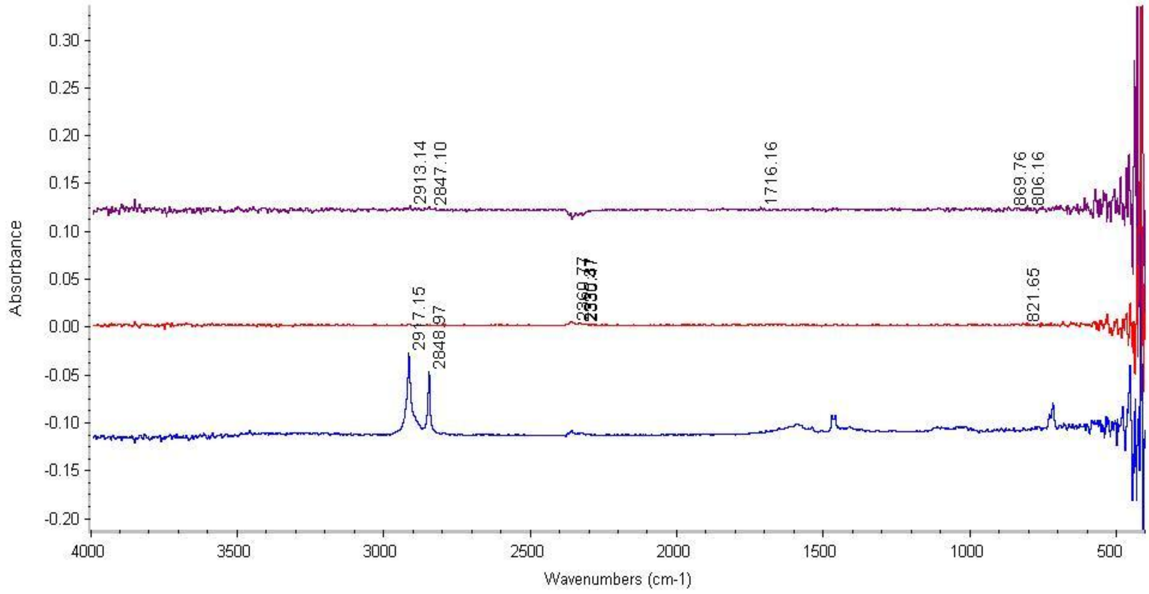

Figure 4.11: FTIR data for cobalt palmitate at concentration 0.2% (purple),0.5% (red), 1.0% (blue) after 20 days treatment.

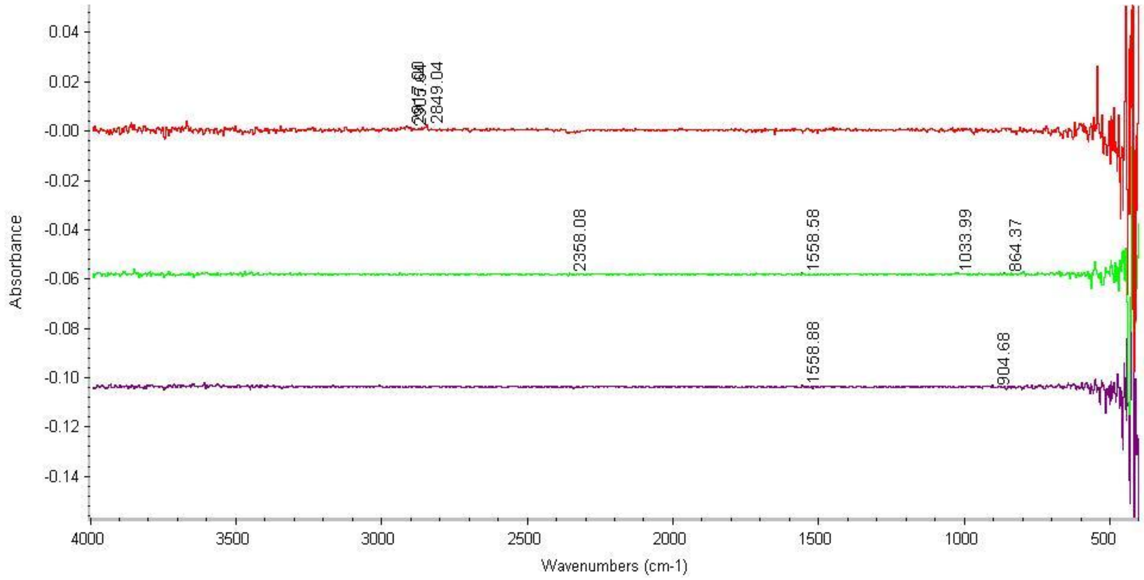

Figure 4.12 **:** FTIR data for cobalt laurate at concentration 0.2% (red), 0.5% (green),1.0% (purple) after 20days treatment

Figure 4.10, Figure 4.11, Figure 4.12 shows the change in the FTIR spectra of HDPE films as well as films containing cobalt stearate, cobalt palmitate and cobalt laurate at difference concentration of additive due the sample of exposure, with thermal degradation. Carbonyl Index has been used as a parameter to monitor the degradation. As can be seen from the FTIR spectra, HDPE films containing cobalt stearate at 1.0% concentration show significant changes in the carbonyl (1700 cm^{-1} 1780 cm^{-1}), amorphous (1200 cm^{-1}) and hydroxyl regions (3500 cm^{-1}).

The absorption band due to stretching of carbonyl group, which is centered around 1730 cm^{-1} grow in intensity and at the same time, a band broadening is stage even after 480 hours of exposure. Samples containing CS, however, had undergone significant degradation as apparent from a large increase in CI during the initial period of thermo-oxidation and the samples completely broke off after more 500 hours of exposure. The increase in CI was found to be proportional to the amount of concentration CS in the formulation. While HDPE films containing cobalt palmitate and cobalt laurate at 1.0% concentration show significant changes in the carbonyl just only (1200 cm^{-1}),(1320 cm^{-1}), and hydroxyl regions (2917 $cm^{=1}$),(2700cm^{-1}).

With an aim to investigate the chemical changes taking place in the polyethylene films due to thermal-oxidation and after added additive, the evolution of the FTIR spectra was studied with respect to exposure time. Similar changes in the FTIR spectra were observed in all the samples, the extent of change depends on the concentration of additive and nature of carboxylate. Some new features that show increased intensity with thermal exposure are reported below.

The increase in the absorbance of these bands was however more pronounced for samples containing cobalt carboxylates than neat HDPE. As far as the band shape is concerned, a progressive broadening of the carbonyl band was observed. This carbonyl band is a result of overlapping of absorption bands due to several functional groups like ketones, carboxylic acids, aldehydes, esters and peroxycarboxylic acids, etc. The overlap of all these bands results in the observed band broadening [68] and [70].

4.2.3.1.3 SEM studies

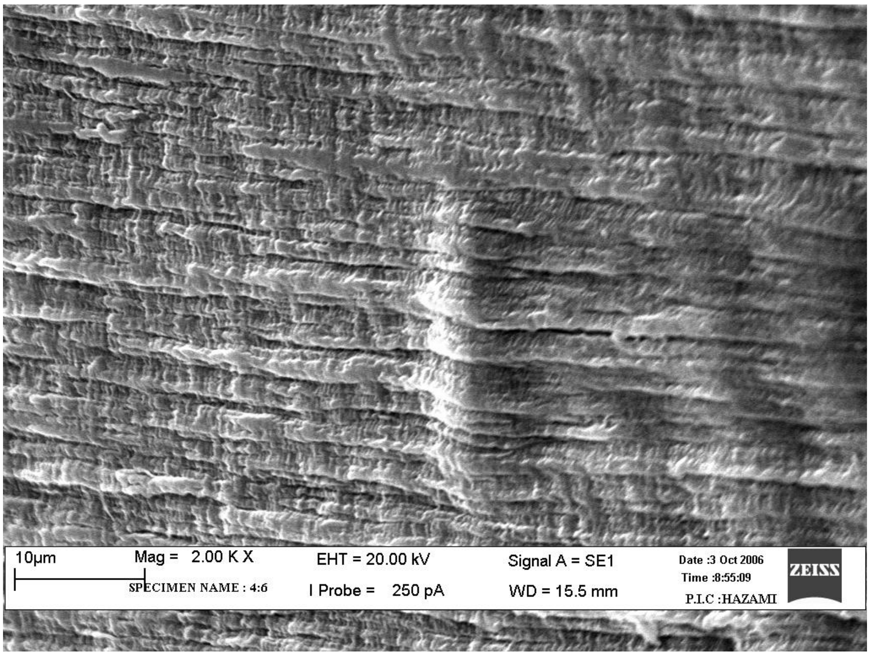

Figure 4.13: Neat HDPE surface

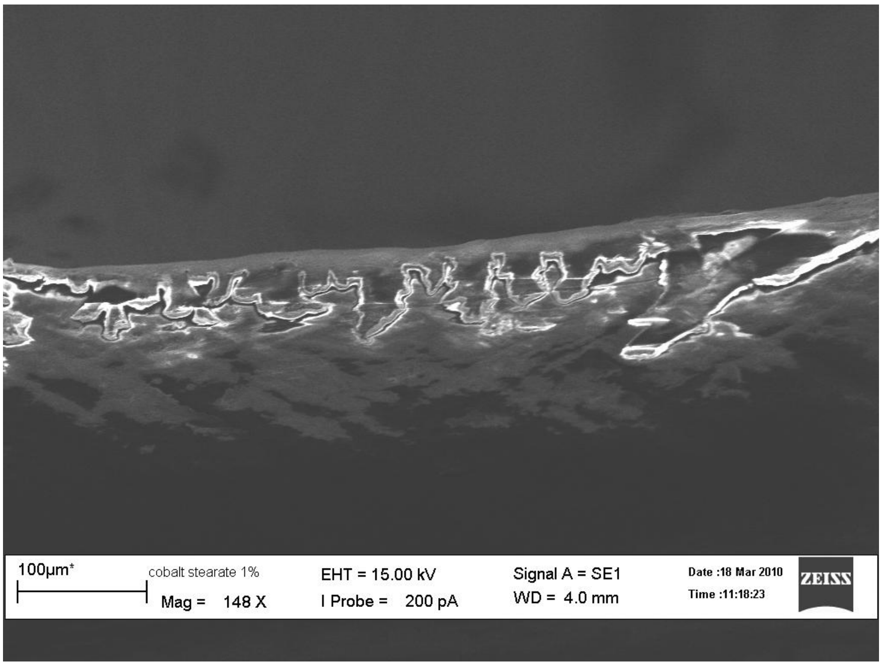

Figure 4.14: HDPE surface contain cobalt stearate at 1% concentration after thermal expose at 480 hours

From the figure above show that surface of HDPE neat and surface HDPE contain 1% concentration additive of cobalt stearate that have thermal expose at 480 hours. From another result before reveal an effective additive is more to cobalt stearate than another additive like cobalt palmitate and laurate. Because of that, for Scanning Electron Micrographs (SEM) measuring, only cobalt stearate at 1% concentration is show.

So from the figure 4.13 and figure 4.14 present a comparative compilation of scanning electron micrographs of two samples (neat HDPE and HS3) at uniform magnification of 2000 and 148. As it apparent from figure 4.14, the surface of nondegraded HDPE is smooth, without cracks and free from defect.

While for figure 4.14 shows the SEM of HDPE after 480 hours of thermal degradation was observed that the surface developed some cracks and grooves due to thermal exposure. However, the extent of damage was much more pronounced in the samples containing cobalt stearate. The damage is more evident in this case and sample after 480 hours showed extensive grooves and pits as a result of thermal irradiation.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The present study reveals that additive of Cobalt Stearate (CS) at higher concentration (1%) more efficient to added in neat of HDPE, although containing three different cobalt carboxylate and also three different concentration (0.2%,0.5%. and 1.0%), each individually capable of initiating degradation, namely carboxyl based functionality, cobalt palmitate and cobalt laurate , was less impression of initiating degradation in HDPE films. Then they also indicate that all the cobalt carboxylates studied, namely stearate, palmitate and laurate promote thermal degradation of HDPE. Although the three of cobalt carboxylate almost same of the composition but the different structure and chain length make their have different characteristic. The results also reveal the high concentration of cobalt carboxylate additive would make the structure in the polyethylene leak and stretch. Besides, the effect of high concentration of additive and long duration of thermal treatment expose formed to fictionalization of the carbon backbone and chain scission simultaneously. The following order of thermal degradation was observed: $CoSt_3$ > $CoPal_3$ > $CoLau_3$. It can be concluded that besides metal content, the chain length of carboxylate also plays a vital role in polyethylene thermal degradation.

5.2 Recommendation

In this research work there is only for 0.2%, 0.5% and 1.0% of concentration additive has been investigated and also just use for three type of cobalt carboxylate or concentrate to the thermal treatment. If this research work is continued with the high concentration like limit 1.5% and used different sources of additive like manganese carboxylate or ferum carboxylate or used photo or biodegradable it might be many other parameters that can be manipulated. This experiment is only on the fabrication of the effective amount of additive to make polymer accelerated to decompose or degrade and may be next time the suitable additive added in polymer will make polymer easier to decompose in short time.

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APPENDIX A

EXAMPLE CALCULATION OF SYNTHESIS COBALT CARBOXYLATES

a) Cobalt Stearate

Step 1

Stearic acid + sodium hydroxide → sodium stearate + water

$C_{18}H_{36}O_2$	$NaOH$	$C_{18}H_{35}NaO_2$	H_2O
0.1 mole	0.1 mole	0.1 mole	0.1 mole
0.25 M	0.25 M		

i) For NaOH

$$V= \frac{0.1\ mole}{0.25\ mole/L}$$

= 0.4 L @ 400 ml

W= MW x mole

= 40 g/mole x 0.1 mole

= 4 g

ii) For $C_{18}H_{36}O_2$

$$V= \frac{0.1\ mole}{0.25\ mole/L}$$

= 0.4 L @ 400 ml

W= MW x mole

= 284.48 g/mole x 0.1 mole

= 28.448 g

Step 2

Sodium stearate + cobalt chloride → cobalt stearate+sodium chloride + water

$C_{18}H_{35}NaO_2$	$\frac{1}{2}CoCl_2.6H_2O$	$\frac{1}{2}C_{36}H_{70}COO_4$	NaCl	$3H_2O$
0.1 mole	0.05 mole	0.05 mole	0.1 mole	0.3 mole
0.25 M	0.25 M			

iii) For $CoCl_2.6H_2O$

$$V= \frac{0.05\ mole}{0.25\ mole/L}$$

= 0.2 L @ 200 ml

W= MW x mole

= 237.93 g/mole x 005 mole

= 11.9 g

b) Cobalt Palmitate

Step 1

Palmitic acid + sodium hydroxide → sodium palmitate + water

$C_{16}H_{32}O_2$	NaOH	$C_{12}H_{23}NaO_2$	H_2O
0.1 mole	0.1 mole	0.1 mole	0.1 mole
0.25 M	0.25 M		

i) For NaOH

$$V=\frac{0.1\ mole}{0.25\ mole/L}$$

= 0.4 L @ 400 ml

W= MW x mole

= 40 g/mole x 0.1 mole

= 4 g

ii) For $C_{16}H_{32}O_2$

$$V=\frac{0.1\ mole}{0.25\ mole/L}$$

= 0.4 L @ 400 ml

W= MW x mole

= 256.42 g/mole x 0.1 mole

= 25.642 g

Step 2

Sodium palmitate + cobalt chloride → cobalt palmitate + sodium chloride+ water

$C_{12}H_{23}NaO_2$	$\frac{1}{2}CoCl_2.6H_2O$	$\frac{1}{2}C_{30}H_{62}CO_4O_2$	NaCl	$3H_2O$
0.1 mole	0.05 mole	0.05 mole	0.1 mole	0.3 mole
0.25 M	0.25 M			

iii) For $CoCl_2.6H_2O$

$$V=\frac{0.05\ mole}{0.25\ mole/L}$$

= 0.2 L @ 200 ml

W= MW x mole

= 237.93 g/mole x 005 mole

= 11.9 g

c) Cobalt Laurate

Step 1

Lauric acid + sodium hydroxide → sodium laurate + water

$C_{12}H_{24}O_2$	NaOH	$C_{12}H_{23}NaO_2$	H_2O
0.1 mole	0.1 mole	0.1 mole	0.1 mole
0.25 M	0.25 M		

i) For NaOH

$$V=\frac{0.1\ mole}{0.25\ mole/L}$$

= 0.4 L @ 400 ml

W= MW x mole

= 40 g/mole x 0.1 mole

= 4 g

ii) For $C_{12}H_{24}O_2$

$$V=\frac{0.1\ mole}{0.25\ mole/L}$$

= 0.4 L @ 400 ml

W= MW x mole

= 200.3177 g/mole x 0.1 mol

= 20.03 g

Step 2

Sodium laurate + cobalt chloride → cobalt laurate + sodium chloride+ water

$C_{12}H_{23}NaO_2$	$\frac{1}{2}CoCl_2.6H_2O$	$\frac{1}{2}$C22H46COO$_4$	NaCl	$3H_2O$
0.1 mole	0.05 mole	0.05 mole	0.1 mole	0.3 mole
0.25 M	0.25 M			

iii) For $CoCl_2.6H_2O$

$$V= \frac{0.05\ mole}{0.25\ mole/L}$$

= 0.2 L @ 200 ml

W= MW x mole

= 237.93 g/mole x 005 mole

= 11.9 g

APPENDIX B

EXAMPLE CALCULATION OF PERCENTAGE YIELD FOR COMPLETE REACTION

Weight after dry the cobalt carboxylates

i) Cobalt stearate

Weight dry = 28.8 g
MW of cobalt stearate = 594 g/mole

$$\text{Yield} = \frac{mole\ desired}{mole\ formed}$$

$$\text{Mole desired} = \frac{Weight\ dry}{MW}$$

$$= \frac{28.8\ g}{594\ g/mole} = 0.0487 \text{ mole}$$

$$\text{Yield} = \frac{0.0487\ mole}{0.05\ mole} \text{ x } 100\% = 97\%$$

ii) Cobalt palmitate

Weight dry = 22.3 g

MW of cobalt palmitate= 530 g/mole

Yield = $\frac{mole\ desired}{mole\ formed}$

Mole desired = $\frac{Weight\ dry}{MW}$

$= \frac{22.3\ g}{530\ g/mole}$ = 0.042 mole

Yield = $\frac{0.042\ mole}{0.05\ mole}$ x 100% = 84%

iii) Cobalt laurate

Weight dry = 18.8 g

MW of cobalt laurate = 426 g/mole

Yield = $\frac{mole\ desired}{mole\ formed}$

Mole desired = $\frac{Weight\ dry}{MW}$

$= \frac{18.8\ g}{426\ g/mole}$ = 0.044 mole

Yield = $\frac{0.044\ mole}{0.05\ mole}$ x 100% = 88%

APPENDIX C

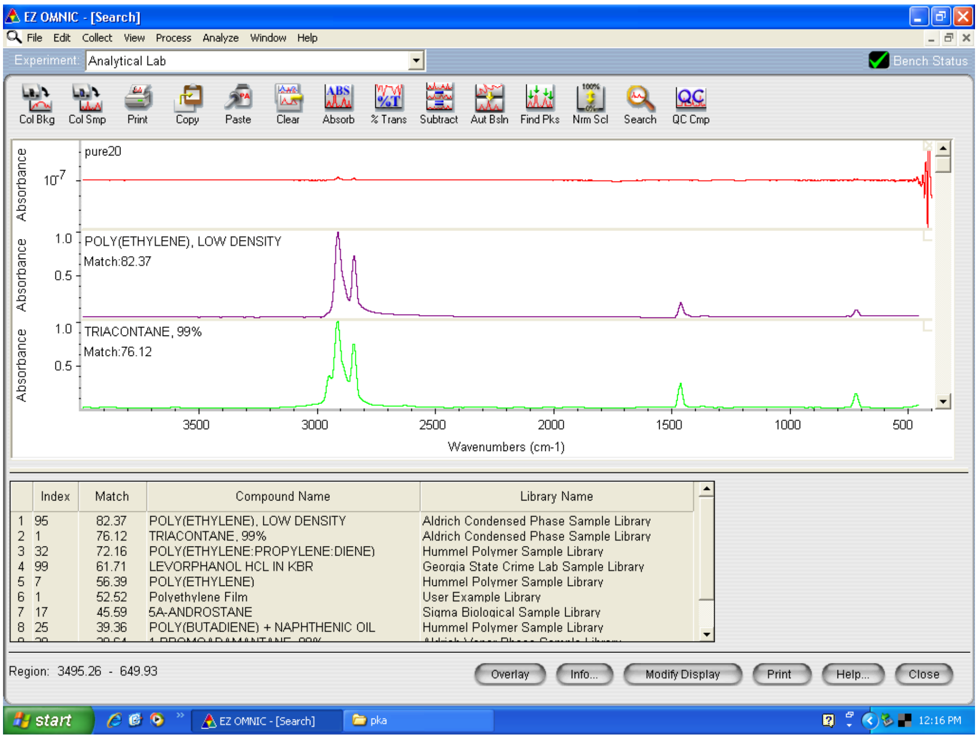
FTIR result

C1) Table of Carboxyl Index

Table B.1: Carboxyl Index

Sample designation	0 hours	120 hours	240 hours	360 hours	480 hour
H1	0.15	0.97	1.3	1.7	2
HCS1	0.3	1.9	2.3	2.7	3.5
HCP1	0.24	1.5	1.95	2.13	2.4
HCL1	0.2	1.3	1.52	1.94	2.1
HCS2	0.5	2.45	2.65	3.1	4
HCP2	0.41	2.23	2.34	2.89	3.1
HCL2	0.32	2.01	2.18	2.56	2.7
HCS3	0.9	2.99	3.66	4.47	5.3
HCP3	0.76	2.36	2.85	3.22	4.1
HCL3	0.6	2.2	2.45	3	3.2

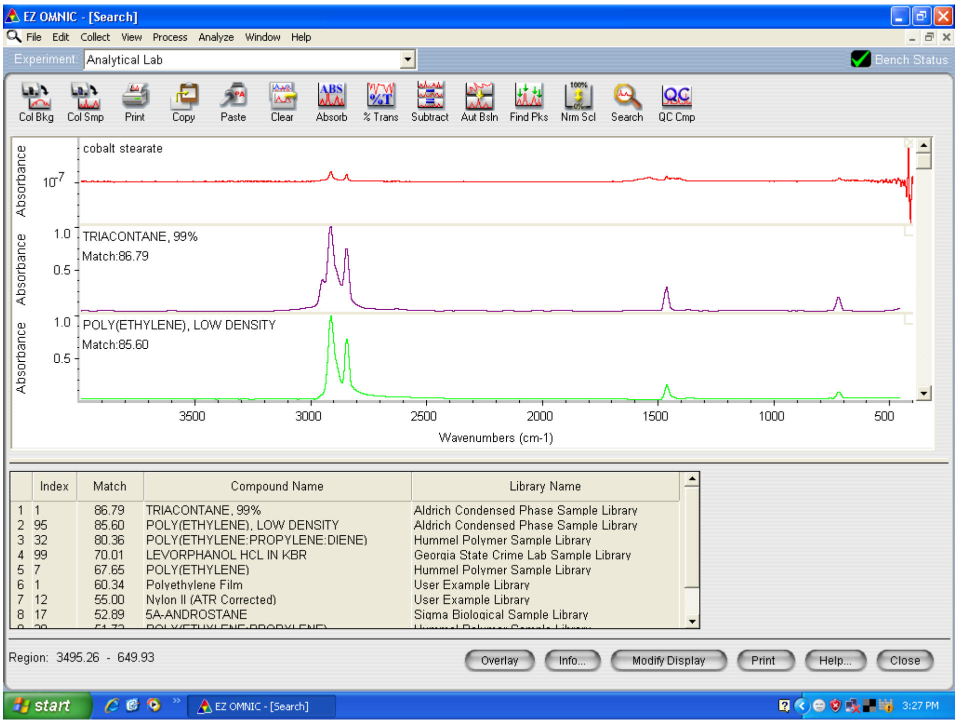
C2) Funtional group cobalt carboxylate and pure of polyethylene



	Index	Match	Compound Name	Library Name
1	95	82.37	POLY(ETHYLENE), LOW DENSITY	Aldrich Condensed Phase Sample Library
2	1	76.12	TRIACONTANE, 99%	Aldrich Condensed Phase Sample Library
3	32	72.16	POLY(ETHYLENE:PROPYLENE:DIENE)	Hummel Polymer Sample Library
4	99	61.71	LEVORPHANOL HCL IN KBR	Georgia State Crime Lab Sample Library
5	7	56.39	POLY(ETHYLENE)	Hummel Polymer Sample Library
6	1	52.52	Polyethylene Film	User Example Library
7	17	45.59	5A-ANDROSTANE	Sigma Biological Sample Library
8	25	39.36	POLY(BUTADIENE) + NAPHTHENIC OIL	Hummel Polymer Sample Library

Region: 3495.26 - 649.93

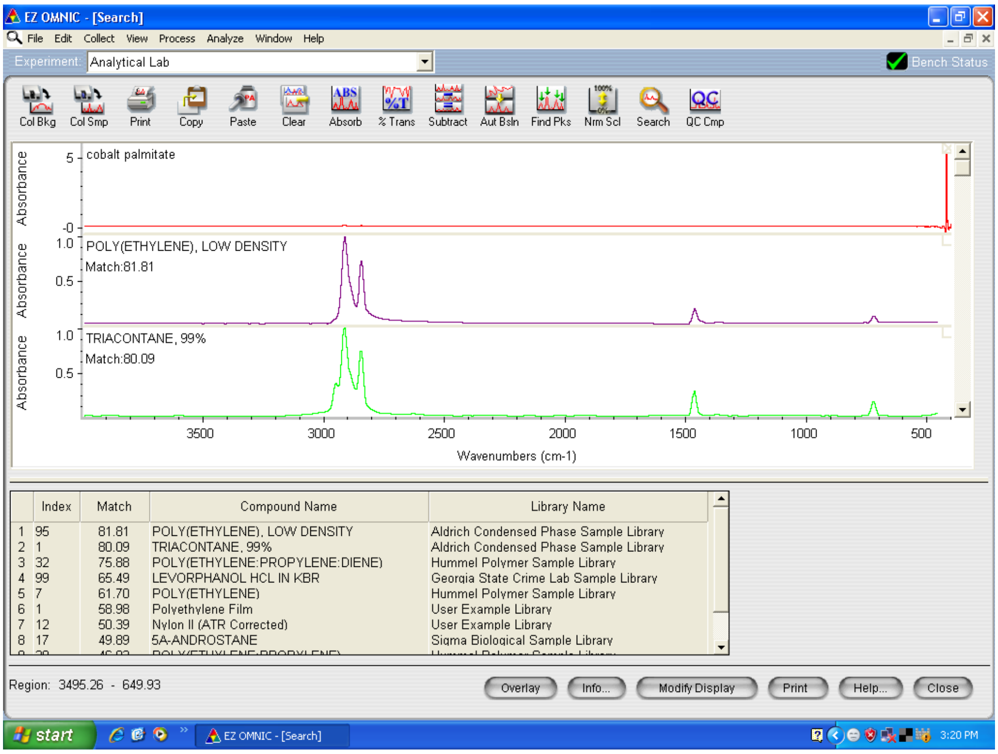
Figure B.2: Pure polyethylene



	Index	Match	Compound Name	Library Name
1	1	86.79	TRIACONTANE, 99%	Aldrich Condensed Phase Sample Library
2	95	85.60	POLY(ETHYLENE), LOW DENSITY	Aldrich Condensed Phase Sample Library
3	32	80.36	POLY(ETHYLENE:PROPYLENE:DIENE)	Hummel Polymer Sample Library
4	99	70.01	LEVORPHANOL HCL IN KBR	Georgia State Crime Lab Sample Library
5	7	67.65	POLY(ETHYLENE)	Hummel Polymer Sample Library
6	1	60.34	Polyethylene Film	User Example Library
7	12	55.00	Nylon II (ATR Corrected)	User Example Library
8	17	52.89	5A-ANDROSTANE	Sigma Biological Sample Library

Region: 3495.26 - 649.93

Figure B.3: Cobalt stearate



Experiment: Analytical Lab

cobalt palmitate

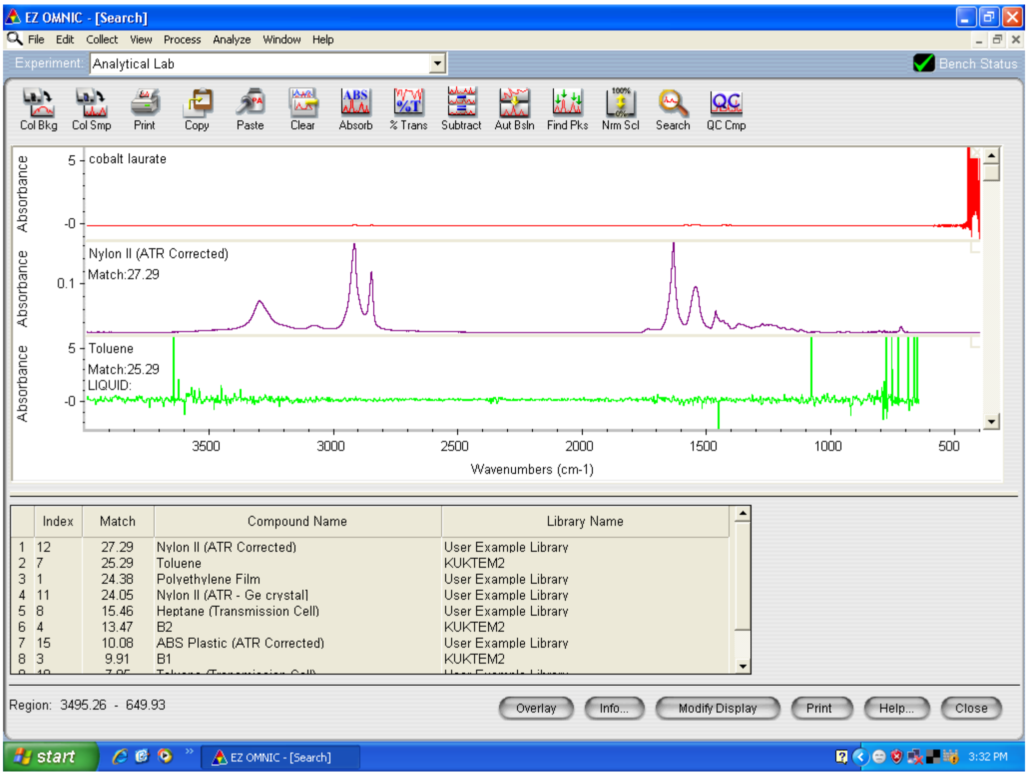
POLY(ETHYLENE), LOW DENSITY
Match:81.81

TRIACONTANE, 99%
Match:80.09

	Index	Match	Compound Name	Library Name
1	95	81.81	POLY(ETHYLENE), LOW DENSITY	Aldrich Condensed Phase Sample Library
2	1	80.09	TRIACONTANE, 99%	Aldrich Condensed Phase Sample Library
3	32	75.88	POLY(ETHYLENE:PROPYLENE:DIENE)	Hummel Polymer Sample Library
4	99	65.49	LEVORPHANOL HCL IN KBR	Georgia State Crime Lab Sample Library
5	7	61.70	POLY(ETHYLENE)	Hummel Polymer Sample Library
6	1	58.98	Polyethylene Film	User Example Library
7	12	50.39	Nylon II (ATR Corrected)	User Example Library
8	17	49.89	5A-ANDROSTANE	Sigma Biological Sample Library

Region: 3495.26 - 649.93

Figure B.4: Cobalt palmitate



Experiment: Analytical Lab

cobalt laurate

Nylon II (ATR Corrected)
Match:27.29

Toluene
Match:25.29
LIQUID:

	Index	Match	Compound Name	Library Name
1	12	27.29	Nylon II (ATR Corrected)	User Example Library
2	7	25.29	Toluene	KUKTEM2
3	1	24.38	Polyethylene Film	User Example Library
4	11	24.05	Nylon II (ATR - Ge crystal]	User Example Library
5	8	15.46	Heptane (Transmission Cell)	User Example Library
6	4	13.47	B2	KUKTEM2
7	15	10.08	ABS Plastic (ATR Corrected)	User Example Library
8	3	9.91	B1	KUKTEM2

Region: 3495.26 - 649.93

Figure B.5: Cobalt laurate

C3) Graph of peak cobalt carboxylate before treatment

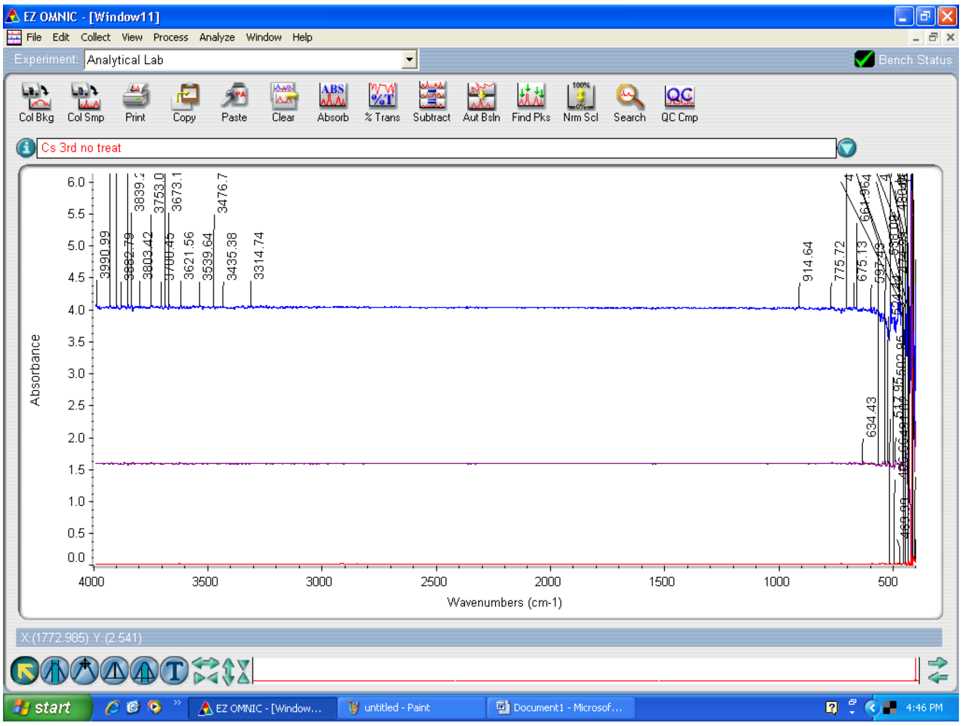


Figure B.6: Cobalt stearate

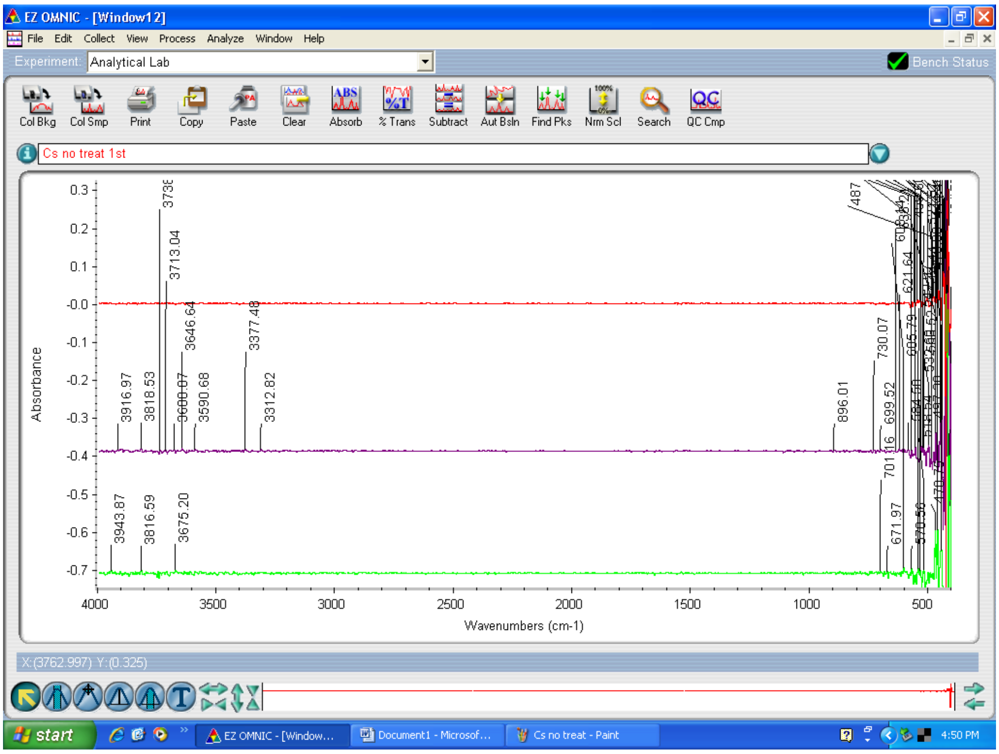
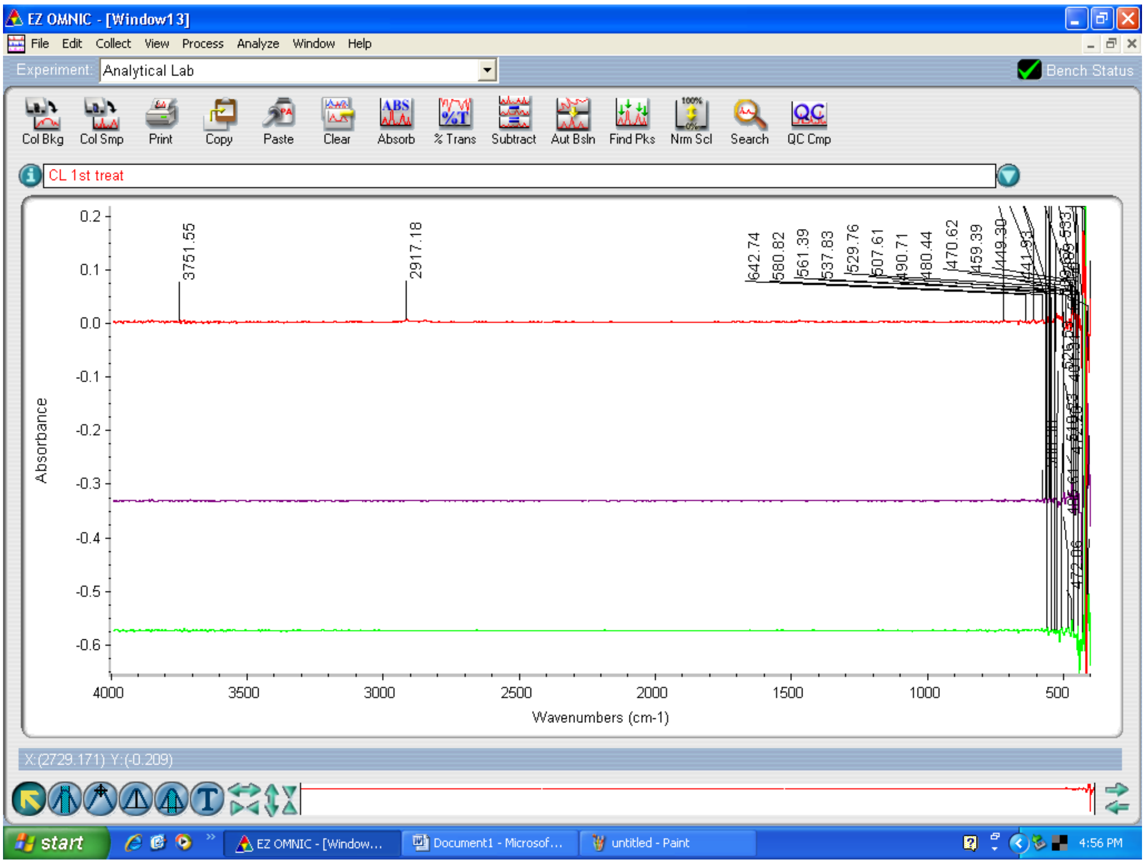


Figure B.7: Cobalt palmitate



Experiment: Analytical Lab

CL 1st treat

X:(2729.171) Y:(-0.209)

Figure B.8: Cobalt laurate

APPENDIX C

Tensile Test Result

Table C.1: Break strain percentage

Film designation	0 hours	120 hours	240 hours	360 hours	480 hours
H1	39.762	38.3378	37.762	36.5686	36.1553
HCS1	28.3454	29.3865	23.598	21.6226	21.3021
HCP1	29.5123	29.1696	28.1501	27.6424	26.9376
HCL1	29.3277	28.6003	28.2013	28.0504	27.9213
HCS2	26.3534	26.1646	22.0935	21.3215	20.1267
HCP2	28.3312	28.7787	27.1327	26.5129	26.1213
HCL2	28.9865	27.6242	27.4401	27.3038	26.7854
HCS3	26.2244	25.6231	21.5908	20.4902	18.001
HCP3	27.5449	27.921	26.8479	26.3427	25.9422
HCL3	27.5454	27.0131	26.9321	26.3757	26.003

EFFECT OF COBALT CARBOXYLATE ON THERMAL DEGRADATION OF POLYETHYLENE (HDPE)

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Abstract

This study reports the effect of cobalt carboxylate on thermal degradation of polyethylene (HDPE). The purpose of this study is to gain knowledge and understand behavior of HDPE film after adding cobalt carboxylate as additive after and before expose to the heating in the oven at 60^0C and also to investigate characteristics of cobalt carboxylate itself. The additives used were three cobalt carboxylate which are cobalt stearate, cobalt palmitate, and cobalt laurate and thin film HDPE containing these additives were prepared with different concentration (0.2% w/w, 0.5% w/w, and 1.0% w/w) by sheeting process. Seventy micron film of HDPE containing different concentration of additives and 3 types of cobalt carboxylate were subsequently exposed to heat and were observed. The characteristics of cobalt carboxylate were monitor by measuring the temperature degradation using TGA (Thermal Gravimetric Analyzer) and to measuring melting point using DSC (Different Scanning Calorimeter). While, the degradation was monitored by measuring the elongation break using tensile machine, changes of structure peak using FTIR and surface film using SEM. In DSC and TGA result, found that, cobalt stearate has high temperature of degradation and high melting point at 121.97^0C; 309.8^0C followed by cobalt palmitate and cobalt laurate at 84.06^0C; 282.74^0C and 69.04^0C; 182.97^0C, respectively. While for FTIR result, Carboxyl Index (CI), which in turn leads to an increase according to the increase of concentration of additives especially cobalt stearate and for tensile test, the percent of break strain decreased inversely proportional with increasing concentration additive present. Results on mechanical properties reveal that samples containing cobalt carboxylate, become mechanically fragile, embrittlement and flaking occurred for samples exposed to longer time periods in the oven for 480 hours. The effect of cobalt carboxylate on air oven aging, show that different behaviour of HDPE at different concentrations will increase proportionally with increasing chain length and follows order $CoSt_3$>$CoPal_3$>$CoLau_{3.}$

Abstrak

Kajian ini melaporkan kesan kobat karbosilet terhadap perbuatan merendahkan terma plastik (HDPE). Tujuan kajian untuk mendapatkan pengetahuan dan memahami tabiat HDPE filem selepas menambahkan kobat karbosilet sebagai aditif selepas dan sebelum mendedahkannya kepada pemanasan oven yang bersuhu 60^0C dan juga untuk menyiasat sifat kobat karbosilet itu sendiri. Aditif ini menggunakan tiga kobat karbosilet iaitu kobat stearet, kobat palmitet, dan kobat lauret dan HDPE filem yang mengandungi aditif ini disediakan dengan berlainan kepekatan ((0.2% w/w, 0.5% w/w, and 1.0% w/w) melalui proses kepingan.Tujuh puluh mikron filem HDPE yang mengandungi aditif yang berbeza kepekatan dan 3 jenis kobat karbosilet berikutnya didedahkan kepada haba dan diperhatikan.Sifat kobat karbosilet dilihat dengan mengukur suhu pada perbuatan merendahkan menggunakan TGA dan mengukur takat kecairan menggunakan DSC. Sementara itu, perbuatan merendahkan diperhatikan dengan mengukur kepanjangan putus menggunakan alat mesin ketegangan, perubahan struktur pada kemuncak menggunakan FTIR, dan permukaan filem menggunakan SEM. Di dalam keputusan DSC dan TGA dijumpai, kobat stearet mempunyai suhu yang tinggi pada perbuatan merendahkan dan suhu takat kecairan pada 121.97^0C; 309.8^0C diikuti kobat palmitet dan kobalt lauret masing-masing pada 84.06^0C;282.74^0C and 69.04^0C;182.97^0C. Sementara itu, keputusan FTIR, bagi Indeks karbosil, meningkat berdasarkan peningkatan kepekatan aditif terutamanya kobat stearet dan untuk ujian ketegangan,peratusan putus ketegangan berkurang berkadar songsang dengan peningkatan kepekatan aditif yang hadir. Kajian pada sifat mekanikal mendedahkan, sampel yang mengandungi cobat karbosilet, menjadi rapuh secara mekanik dan mengelupas apabila sampel didedahkan terlalu lama di dalam oven untuk 480 jam. Kesan cobalt carboxylate di dalam oven terlalu lama, menunjukkan HDPE yang berbeza kepekatan aditif akan berkadar langsung dengan meningkatnya pemanjangan rantaian dan diikuti urutan $CoSt_3$>$CoPal_3$>$CoLau_{3.}$

Keywords: thermal degradation, cobalt carboxylate, thermal stability,pro-degradation additives

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1.0 Introduction

Polyethylene has achieved a dominant position as a packaging material because of its relatively low cost, versatile properties including high tensile strength, elongation at break, good barrier properties against water borne organisms, lower cost, higher energy, effectiveness, light weight and good water resistance. The products from polyethylene are become famous in over the decade. However, it has been a target of much criticism due to its lack of degradability [Guillet J,1995] especially the plastic bag, agriculture bag product and so on. So during the past two decades the quantity of plastic material used in the in packing application has increased annually at a phenomenal rate. At the present time something like

1000 square miles of polyethylene film are produced in the United Kingdom alone each year. Even if a large percentage of the population can be persuade to take care against creating litter and even if litter collection systems are reasonably efficient, a quantity of unsightly rubbish is bound to accumulate [John A. Brayson,1995,199]. According to [Guillet, 2003] the most effective way to deal with this litter problem is to reduce the "life time" of the littered objects. The meaning of 'life time' is to reduce for their chain ability of the polyethylene material to make it easier to decompose.

The need to control the proliferation of plastic litter has been recognized for many years and has become increasingly pressing during the last few decades with the discovery by environmental scientists that discarded packaging is responsible for the death of a large number of mammals by ingestion and strangulation [J. Guillet, 1995]. Polyethylene is relatively inert due to its hydrophobic chain and high molecular weight. It has been estimated that polyethylene biodegrades less than 0.5% in 100 years and about 1% if pre-exposed to sunlight for 2 years [F. Khabbaz, 2001]. LDPE is extensively used for a variety of different applications, resulting in its increased production. Subsequently, the plastic fraction of the municipal solid waste stream has also increased leading to associated urban plastic litter problem. The hazardousness of polyethylene as a waste is associated with its excellent outdoor durability and its inherent resistance to hydrolysis and biodegradation in the environment.

Degradability offers a complimentary strategy to deal with this litter problem. One of the simplest ways of modifying the existing polymer is to accelerate the rate of photodegradation process already taking place with using the additive such as transition metal corboxylates are particularly suitable for this purpose. Degradability also offers a complimentary strategy to deal with this litter problem. One of the simplest ways of modifying the existing polymer is to accelerate the rate of thermal/photodegradation process already taking place with using the additive such as transition metal corboxylates are particularly suitable for this purpose. Different approaches to develop thermal/photodegradable polyolefins have been adopted, including both copolymerization with ketone or CO groups and addition of thermal/photo initiating metal complexes [M. A. Villetti, 2002]. This study also attempts to investigate characteristic of cobalt carboxylate and thermal behavior of HDPE containing additive.

2.0 Methodology

2.1. Materials and Equipment

Stearic acid, palmitic acid, lauriac acid (Merck), sodium hydroxide, and cobalt chloride were used without any treatments.For the equipment, FTIR are use to follow the time evolution of know the changes in the polyethylene present. Other equipment to measure the strength and stress (by tensile machine) and Scanning Electron Microscope (SEM) to observe surface change follow the time evolution, also for the thermal are (DSC) for measuring melting point of additive and Thermal Graphic Metric (TGA) for measuring thermal degradation of additive

2.2. Process Description

It start from prepare the chemical solution for cobalt carboxylate (cobalt stearate, cobalt palmitate, cobalt laurate). After that follow with experimental work which consist about seven steps those are check the characteristic of neat polyethylene and cobalt carboxylates that have prepare, mixing or blending between polyethylene film and solution of cobalt carboxylate, and evaluate the characteristic of polyethylene film with the selected equipment after mixing, then expose polyethylene film to the heat about 20 days. After that, the final step is evaluate or analyzed the effect of heat or thermal into polyethylene and compare it between before and after the exposed.

2.3. Experiment and Sampling Methodology

This paper also deals with the development of a thermal-degradable high-density polyethylene (HDPE) composition containing small amount of partially degraded oxidised polyethylene (OPE) as a degradation promoter. Films containing varying amounts of oxidised polyethylene were prepared and then exposed to heat in the oven for acclerated ageing studies. The degradation behaviour was monitored by measuring the changes in structure (by FTIR). For the equipment, FTIR are use to follow the time evolution of know the changes in the polyethylene present. Other equipment to measure the strength and stress (by tensile machine) and Scanning Electron Microscope (SEM) to observe surface change follow the time evolution, also for the thermal are (DSC) for measuring melting point of additive and Thermal Graphic Metric (TGA) for measuring thermal degradation of additive. The study was performed on HDPE keeping in mind its prime importance in the packaging field and its inherent resistance towards degradation and describes the preparation of polymer films having varying amounts of oxidized polyethylene and evaluation of its degradation behaviour as a function of irradiation time. The steps in experimental work are as follows

i) Synthesis of cobalt carboxylate

There have two step to produce cobalt carboxylate. First step to produce sodium carboxylate (sodium lauric, sodium palmitate and sodium stearate) were synthesized by the reaction of carboxylate acid (lauric acid, palmitic acid and stearic acid) with sodium hydroxide. The reaction of carboxylate acid and sodium hydroxide (0.25M) must constant at temperature 80^0C-85^0C and mix well for 1 or 2 hour. Second step to produce cobalt carboxylate (cobalt lauric, cobalt palmitate and cobalt stearate) were synthesized by the reaction of sodium carboxylate with cobalt chloride respectively according to the procedure. Make sure the reaction temperature constant at 80^0C-85^0C with continuous stirring about 8 rpm. After that, filter the solution and wash it with hot water (range at 70^0C and above) to separate sodium chloride or sodium acetate.

Varying amount of cobalt carboxylate (0.2%-1.0%) were mixed with HDPE by mixing manually, then melt and molding it with injection molding to make easier for use tensile machine and measuring the stress and strain of the film, followed by sheeting process. The processing condition used for film preparation and chemical reaction preparation. The details of film prepared along with their designation are present in Table 3. HDPE film has been designated as F1, FCS, FCP, and FCL, respectively, follow by adding cobalt carboxylate concentration according with their percent

ii) Preparation films

A Brabender plasticorder Labstation with a 20 mm diameter screw of L:D = 25:1, extruder speed of 20L/min associated with a roller having a draw speed of 3m/min was used for the preparation of film. HDPE chips were dry blended with varying amounts of cobalt carboxylate ranging from 0.2-1.0% w/w in a tumbler and fed to the Brabender. The temperature in the fed zone, 192^0C; compression zone, 195^0C; metering zone, 198^0C and die zone 200^0C were used for extrusion. Neat HDPE film has been designated as H1 and films having cobalt carboxylate have been designated as HS1, HS2, HS3; HP1, HP2, HP3 and HL1, HL2, HL3. The details of films prepared along with their designation are presented in Table 1.1

Table 1.1: Details of formulation and the sample designation

Film designation	Amount (g)			
	HDPE	Cobalt stearate	Cobalt palmitate	Cobalt laurate
H1	400	-	-	-
HS1	399.2	0.8(0.2%)	-	-
HS2	398	2.0(0.5)	-	-
HS3	396	4.0(1.0%)	-	-
HP1	399.2	-	0.8(0.2%)	-
HP2	398	-	2.0(0.5%)	-
HP3	396	-	4.0(1.0%)	-
HL1	399.2	-	-	0.8(0.2%)
HL2	398	-	-	2.0(0.5%)
HL3	396	-	-	4.0(1.0%)

iii) Characterisation of cobalt carboxylate

The chemical properties and characteristic of the cobalt carboxylate especially cobalt stearate was checked. The characterization comprises include surface change, melting point and degradation temperature. The FTIR spectra of the cobalt carboxylates were recorded in KBr pallet in the wavelength range 400-4000 cm^{-1} on a BIORAD (FTS-40) spectrophotometer. Evaluation of degradation temperatures were done using Thermogravimetric Analyzer (TGA) Q500 from TA Instruments, in N_2 atmosphere, ramp method, heating rate 10°C min^{-1} and final temperature 700°C [Bajer *et al.*, 2007; Rimez *et al.*, 2008]. While melting points were of cobalt carboxylate investigated using Differential Scanning Calorimeter (DSC) Q1000 from TA Instruments, in N_2 atmosphere; at heating rate 10°C min^{-1} , and load temperature range 50^0C to 200^0C.

2.3.1 Degradation studies

i) Thermo-oxidative test

The thermo-oxidative test was carried out by placing the extruded in an air oven at 60^0C for extended period as report in the literature [Sharma N, 2001] and [M.U. Amin, 1974]. The changes due to thermo-oxidation were monitored using FTIR, tensile properties and Scanning Electron Microscope. There are expose to the thermal treatment at 20 days period

ii) Evaluation of degradation

The tensile tests were performed on HDPE films according to ASTM 882-85 using a Universal testing machine (Model JRI-TT25). Films of 100 mm length and 10 mm width were cut out from the exposed films and subjected to a crosshead speed of 100 mm/min. The tests were undertaken in an air-conditioned environment at 27 °C and with a relative humidity of 60%. Five samples were tested for each experiment and the average value has been reported.

The structural changes occurring in the HDPE films upon exposure were investigated using FTIR spectroscopy. The FTIR spectra were recorded at regular intervals using a BIORAD (FTS-40) spectrophotometer. Carbonyl Index (CI) was used as a parameter to monitor the degree of photo-oxidation of polyethylene and has been calculated according to the baseline method [J. Brandrup, 1986].

Carboxyl Index

$$\frac{Absorption\ at 1740\ cm^{-1}\ (the\ maximum\ of\ carbonyl\ peak)}{Absorption\ at\ 2020\ cm^{-1}\ (internal\ thickness\ band)}$$

Scanning electron microscopy (SEM) was performed to investigate the changes in the morphology due to heat irradiation. Sample surfaces were sputtered with gold using usual techniques and then analyzed in JEOL (JSM-840) electron microscope using a voltage of 10 kV. Photo-micrographs were taken at uniform magnification of 2000 fold.

3.0 Results and Discussion

i) Synthesis of cobalt carboxylate

Synthesis of cobalt carboxylate comprises two steps of reactions. The first step is to produce sodium carboxylate, same as below:

Stearic acid + sodium hydroxide → sodium stearate + water
Palmitic acid + sodium hydroxide → sodium palmitate + water
Lauric acid + sodium hydroxide → sodium laurate + water

The reaction will control with temperature at 80^0C-85^0C until the reaction complete. The lower temperature would make the reaction process slower, since the melting point of carboxylic acid are quit high, in range 44^0C-69^0C. The perfect aging are needed to make the reaction mixed well. While, if high temperature is used and it's close to the boiling point, the mixture will cause formation foam and become lump.

The second step is to produce cobalt carboxylate and sodium chloride and the reaction are written as follow

Sodium stearate + cobalt chloride → cobalt stearate + sodium chloride
Sodium palmitate + cobalt chloride → cobalt palmitate + sodium chloride
Sodium laurate + cobalt chloride → cobalt laurate + sodium chloride

This preparation are present in stoichiometric proportion The yield term using for know to describe the degree to which a desired predominates over competing side reaction. The percent of complete reaction occur like table below:

Table 1.2: Percentage yield of complete reaction

	Additive		
	Cobalt stearate	Cobalt palmitate	Cobalt laurate
Yield	97%	79%	88%

From the table, show that percentage yield of cobalt carboxylate is higher than the rest of two cobalt carboxylate, it is because the reaction to produce cobalt stearate has reach complete reaction while the reaction occur. The reaction influence comes from the several aspects, which is cause of temperature, flow rate agitation, structure chain length and the amount of moles.

ii) Characteristic of cobalt carboxylate

From the table below show that melting point of the three additives that had prepared. From the figure melting point of cobalt stearate is higher than cobalt palmitate and cobalt laurate whereas 121.97^{0}C, 84.06^{0}C, and 69.04^{0}C, respectively. While as additive, melting point is importance expect and must lower than melting point of HDPE itself, which is 190^{0}C-200^{0}C. In order to make HDPE to accelerate thermal degrade, additive are use to help attached to the side of backbone inside the HDPE. After held by bonds which are weaker than bond connecting the chain, it can easier to decompose. Under thermal effect, the end of polymer chain departs, and forms low free radical which has low activity. Then according to the chain reaction mechanism, the polymer loses the monomer one by one. However, the molecular chain doesn't change a lot in a short time.

Table 1.3: Thermal characterization of cobalt carboxylate

Additive	**T_{melt} [^{0}C]**	**T_{onset} [^{0}C]**	**T_{max}[^{0}C]**	**T_{end}[^{0}C]**	**ΔT[^{0}C]**
Cobalt Stearate	121.97	309.80	390.04	441.41	131.61
Cobalt Palmitate	84.06	282.74	337.88	390.97	108.23
Cobalt Laurate	69.04	182.97	255.67	294.05	111.08

While from the table above, show that the TGA traces single step decomposition for all the carboxylates. The melting temperature (T_{melt}), initial temperature of degradation (T_{onset}), maximum temperature of degradation (T_{max}) and final temperature of degradation (T_{end}) are reported in **Table 1.3**. As is evident, the thermal stability increased with increasing chain length as indicated by T_{onset}, T_{end} and T_{max}. The figure also reveal that cobalt stearate have high temperature point than cobalt palmitate and cobalt laurate, its indicate that the decrease in the decomposition and melting temperature or temperature degradation are associated with short polymeric chain and lower thermal stability of the material as report by *Colom et.al* (2003). [*Colom, 2003*]. Besides, cobalt stearate starts to degrade at temperature 309.80^{0}C and have higher degradation temperature than cobalt palmitate and cobalt laurate. Mixing of additive with polyethylene are usually performed around 170^{0}C-190^{0}C [Albertson *et al*,1992; Bikiaris *et al*, 1997, Xia *et al*,2006; Bajer *et al*, 2007]. It means that, all cobalt carboxylate have good thermal stability, especially in application for polyethylene, since the temperature of polyethylene processing is lower than their degradation temperatures.

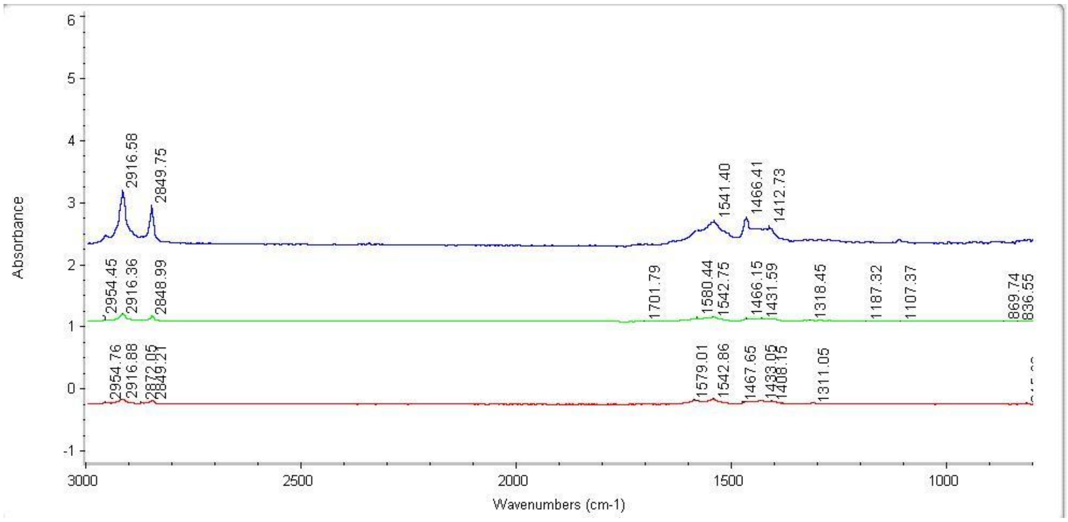

Figure 1.1: Combination peak of cobalt carboxylate where cs(blue),cp(green), cl(red)

The highest percent of contain polyethylene low density and ketone group is cobalt stearate , 85% follow by cobalt laurate 81% and cobalt palmitate 24%. While The FTIR spectra of all the cobalt carboxylates exhibited absorbance at 2916.58 cm^{-1} from cobalt stearate due to asymmetric vibration stretching of the hydroxyl regions. While cobalt palmitate at 2954 cm^{-1} and cobalt laurate at 2954.76 cm^{1} . There have no carbonyl group region yet because these carboxyalate not doing thermal treatment.

iii) Thermo-oxidative aging study

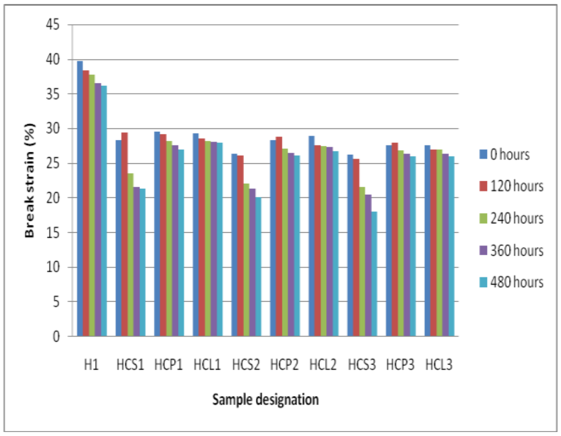

Figure 1.2: Break Strain of HDPE with thermal exposure

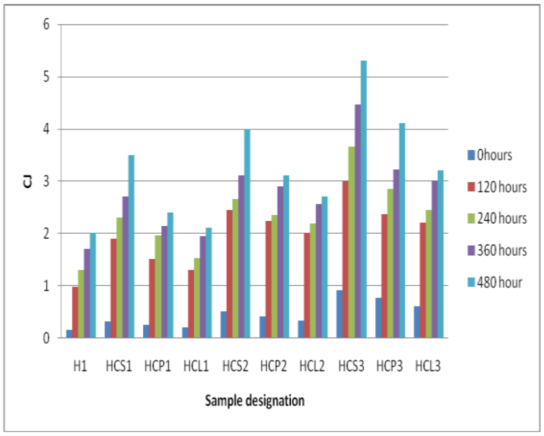

Figure 1.3: Variation of Carbonyl Index due to thermal exposure

Figs.1.2 represents the effect of thermal exposure by time in air oven at 60 ^{0}C on mechanical properties (tensile strength and break strain) of HDPE films in the presence of additives and neat HDPE film. It should be noted that the initial values of break strain were not affected by the incorporation of these additives thereby implying that these additives do not lead to degradation in the processing stage. For the sake of brevity, only percentage loss in elongation or break strain have been taken into consideration, which have been reported to be direct indicators of degradation as reported in the literature [Qureshi FS (1990), Madfa H-Al(1998), Tavares AC(2003)]. It is well documented that during thermal treatment, heat and oxygen will initiate free radical reaction to degrade polyethylene [*Epacher E (1999), Gulmine JV(2003*)]. Films containing cobalt stearate, the percent of break strain decrease inversely proportional with increasing concentration additive present.

It also followed by time ageing where more time needed to loss the strength. In the early or initial stages, there are increases followed by a steady decrease till the failure of the sample. The initial increase in strength can be attributed to increase in the crystallinity of films and the later decrease can be attributed to chain scission. The difference contain additive in each HDPE film sample indicate the difference enhance of brittle. After cobalt stearate additive, it followed by cobalt palmitate and cobalt laurate additive where the percent of break strain decrease by time ageing increase. The rate have being much faster in the case of samples containing cobalt stearate than another additive like cobalt palmitate and cobalt laurate. The decrease in elongation or break strain is basically due to the increase in the degree of cross-linking with aging, which finally lead to the embrittlement of the sample. The polymer chains take up oxygen and lead to the formation of hydroperoxide which breakdown to give oxygenated products. Further, effects like chalking, loss of gloss, embrittlement and flaking occurred for samples exposed to longer time periods.

From the fig. 1.3 above show that the Carbonyl Index of HDPE designation due to thermal exposure and indicate that pure HDPE did not reach this stage even after 480 hours exposure to the heat. While, the sample containing CS however, had undergone significant degradation follow the rest of two additive, CP and CL respectively as apparent from a large increase in Cl during the initial period of thermo-oxidation and sample will completely broke off after extend more than 480 hours because there have reported that polyethylene film enter into decay stage at Cl greater than 6 [Khabbaz F, 2001]. The increase in Cl also found to be proportional to the concentration of cobalt carboxylate in the formulation especially cobalt stearate additive.

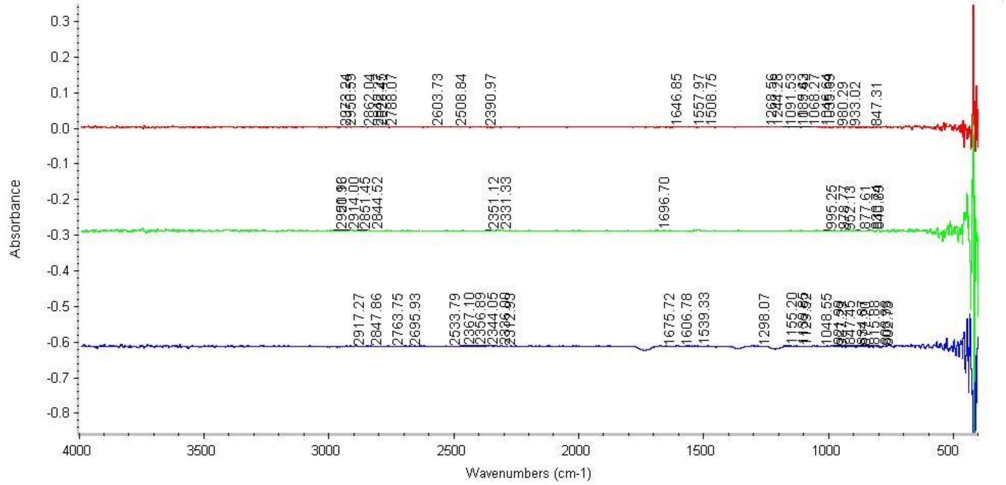

Figure 1.4 : FTIR data for Cobalt stearate at concentration 0.2% (red), 0.5% (green), 1.0% (blue) after 20days treatment

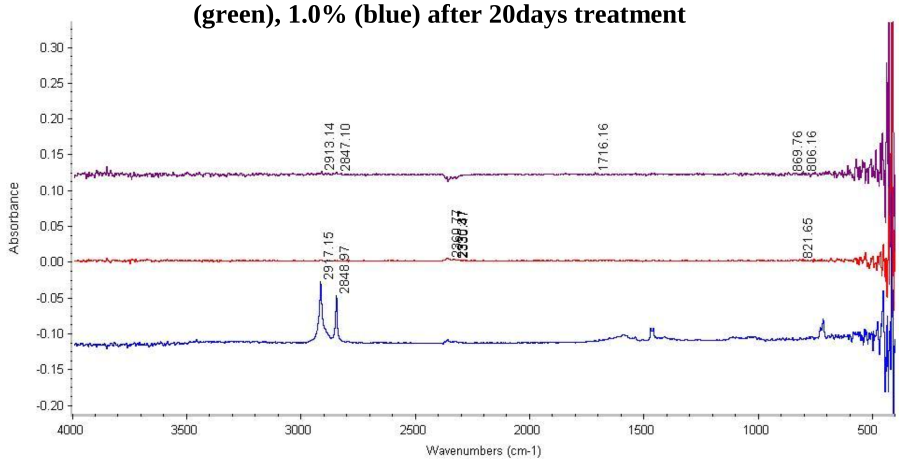

Figure 1.5: FTIR data for Cobalt palmitate at concentration 0.2% (purple), 0.5% (red), 1.0% (blue) after 20days treatment.

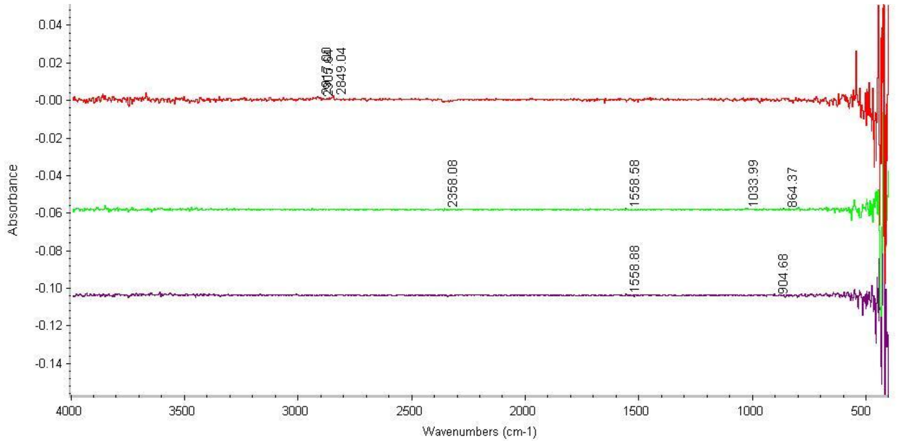

Figure 1.6 : Cobalt laurate at concentration 0.2% (red), 0.5% (green), 1.0% (purple) after 20days treatment

Fig. 1.4, Fig. 1.5, Fig 1.6 shows the change in the FTIR spectra of HDPE films as well as films containing cobalt stearate, cobalt palmitate and cobalt laurate at difference concentration of additive due the sample of exposure, with thermal degradation. Carbonyl Index has been used as a parameter to monitor the degradation. As can be seen from the FTIR spectra, HDPE films containing Cobalt Stearate at 1.0% concentration show significant changes in the carbonyl (1700-1780 cm_1), amorphous (1200 cm_1) and hydroxyl regions (3500 cm_1). The absorption band due to stretching of carbonyl group, which is centered around 1730 cm_1 grow in intensity and at the same time, a band broadening is stage even after 480 h of exposure. Samples containing CS, however, had undergone significant degradation as apparent from a large increase in CI during the initial period of thermo-oxidation and the samples completely broke off after more 500 h of exposure. The increase in CI was found to be proportional to the amount of concentration CS in the formulation. While HDPE films containing Cobalt Palmiate and cobalt laurate at 1.0% concentration show significant changes in the carbonyl just only (1200 cm_1),(1320 cm_1), and hydroxyl regions (2917 cm_1),(2700cm_1). With an aim to investigate the chemical changes taking place in the polyethylene films due to thermal-oxidation and after added additive, the evolution of the FTIR spectra was studied with respect to exposure time. Similar changes in the FTIR spectra were observed in all the samples, the extent of change depends on the concentration of additive and nature of carboxylate. Some new features that show increased intensity with thermal exposure are reported below. The increase in the absorbance of these bands was however more pronounced for samples containing cobalt carboxylates than neat HDPE. As far as the band shape is concerned, a progressive broadening of the carbonyl band was observed. This carbonyl band is a result of overlapping of absorption bands due to several functional groups like ketones, carboxylic acids, aldehydes, esters and peroxycarboxylic acids, etc. The overlap of all these bands results in the observed band broadening [Gulmine JV, 2003] and [Khabbaz F, 1999]

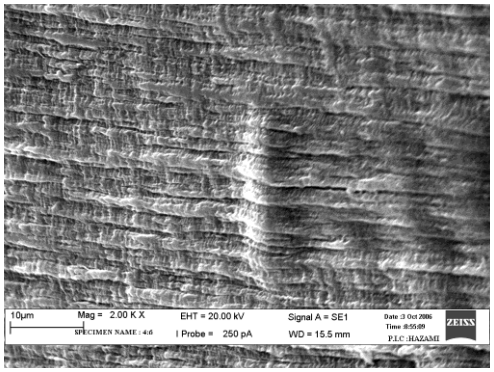

Figure 1.7 : neat HDPE surface

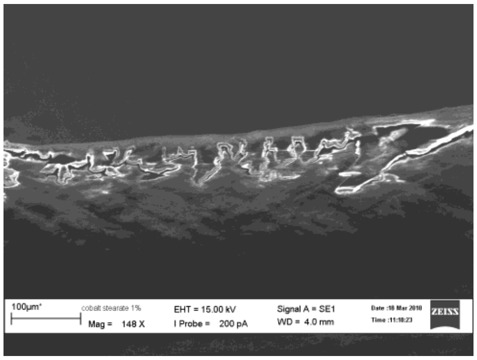

Figure 1.8: HDPE surface contain cobalt stearate at 1% concentration after thermal expose at 480h

From the figure above show that surface of HDPE neat and surface HDPE contain 1% concentration additive of cobalt stearate that have thermal expose at 480 hours. From another result before reveal an effective additive is more to cobalt stearate than another additive like cobalt palmitate and laurate. Because of that, for Scanning Electron Micrographs measuring, only cobalt stearate at 1% concentration is show. So from the figure 1.7 and figure 1.8 present a comparative compilation of scanning electron micrographs of two samples (neat HDPE and HS3) at uniform magnification of 2000 and 148. As it apparent from Fig. 14.4, the surface of nondegraded HDPE is smooth, without cracks and free from defect. While for Fig. 1.8 shows the SEM of HDPE after 480 h of thermal degradation was observed that the surface developed some cracks and grooves due to thermal exposure. However, the extent of damage was much more pronounced in the samples containing cobalt stearate. The damage is more evident in this case and sample after 480 h showed extensive grooves and pits as a result of thermal irradiation

4.1. Conclusion

The present study reveals that additive of Cobalt Stearate (CS) at higher concentration (1%) more efficient to added in neat of HDPE, although containing three different cobalt carboxylate and also three different concentration (0.2%,0.5%. and 1.0%), each individually capable of initiating degradation, namely carboxyl based functionality, cobalt palmitate and cobalt laurate , was less impression of initiating degradation in HDPE films. Then they also indicate that all the cobalt carboxylates studied, namely stearate, palmitate and laurate promote thermal degradation of HDPE. Although the three of cobalt carboxylate almost same of the composition but the different structure and chain length make their have different characteristic. The results also reveal the high concentration of cobalt carboxylate additive would make the structure in the polyethylene leak and stretch. Besides, the effect of high concentration of additive and long duration of thermal treatment expose formed to fictionalization of the carbon backbone and chain scission simultaneously. The following order of thermal degradation was observed: $CoSt_3 > CoPal_3 > CoLau_3$. It can be concluded that besides metal content, the chain length of carboxylate also plays a vital role in polyethylene thermal degradation.

4.2 Recommendations for Future Study

In this research work there is only for 0.2%, 0.5% and 1.0% of concentration additive has been investigated and also just use for three type of cobalt carboxylate or concentrate to the thermal treatment. If this research work is continued with the high concentration like limit 1.5% and used different sources of additive like manganese carboxylate or ferum carboxylate or used photo or biodegradable it might be many other parameters that can be manipulated. This experiment is only on the fabrication of the effective amount of additive to make polymer accelerated to decompose or degrade and may be next time the suitable additive added in polymer will make polymer easier to decompose in short time.

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