DEVELOPMENT AND INVESTIGATION OF

ENVIRONMENTALLY DEGRADABLE

PLASTIC BAGS IN SAUDI ARABIA

BY

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In

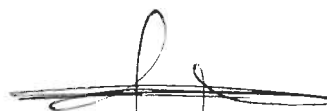# CHEMICAL EENGINEERING

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This dissertation, written by   **MUHAMMAD RUHUL AMIN** under the direction of his dissertation advisor and approved by his dissertation committee, has been presented to and accepted by Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING.**

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DISSERTATION ABSTRACT

Full Name	**MUHAMMAD RUHUL AMIN**
Title of Study	**DEVELOPMENT AND INVESTIGATION OF**
	ENVIRONMENTALLY DEGRADABLE
	PLASTIC BAGS IN SAUDI ARABIA
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Owing to their low production cost, good physical properties and lightweight, plastic objects have slowly substituted glass, paper and metals in several fields of application. The current huge global production of plastics (200 million tons/year) has generated enormous environmental concerns, mainly related to the waste generation by plastic packaging, which are responsible for 35—40% share of annual plastics consumption. If plastic bags are dumped in the city and go into drainage and sewage lines, causing blockages, if disposed of by landfill, the plastics worsen the shortage of landfill sites. If the plastics are incinerated, they can emit green house gases as well as poisonous gases such as dioxins. So making plastic bags degradable is one way to try to ease the task of waste reduction.

We study the influence of adding photodegradable additives to film grade polyethylene under natural weathering conditions in Saudi Arabia. We investigated the degradation products and determine the time required to convert the material into gases or low molecular weight hydrocarbons. Plastic films were prepared by first premixing the film grade polyethylene pellets with different amounts of additives. The films were exposed in outdoor environments located in Dhahran, Saudi Arabia. Samples of the films were drawn at regular intervals and evaluated for degradation.

الخلاصة

الاسم : محمد روح الامين

عنوان الرسالة: تطوير والتحقق من التحلل البيئي للاكياس البلاستيكية في المملكة العربية السعودية

التخصص: هندسة كيميائية

بسبب كلفة إنتاجها المنخفضة و خصائصها الفيزيائية الجيدة وخفة وزنها ,أخذت المواد البلاستيكية دورالزجاج والورق والمعادن في العديد من التطبيقات .

إن الإنتاج العالمي الضخم الحالي للبلاستيك (200 مليون طن / سنة) ولد مخاوف بيئية هائلة، تتعلق بشكل رئيسي بالنفايات الناتجة عن التغليف البلاستيكي، الذي يعتبر مسؤول عن 35-40 % من الاستهلاك السنوي للبلاستيك . إذا تم التخلص من الأكياس الاستيكية في المدن فأنها تدخل خطوط مياه المجاري والتصريف مسببة انسدادها ،و إذا تم التخلص منها في مواقع دفن النفايات تسبب العديد من المشاكل,واذا تم حرق المواد البلاستيكية تنبعث العديد من الغازات الضارة والسامة. لذلك فأن جعل المواد البلاستيكية قابلة للتحلل هو احد الطرق لتسهيل مهمّة تقليل النفايات.

في هذه الدراسة درسنا تأثير إضافة photodegradable لي polyethylene تحت الظروف الجوية الطبيعية في المملكة العربية السعودية. درسنا تحلل المواد البلاستيكية والزمن المطلوب لتحويل هذه المواد الى غازات ومواد هيدروكربونية ذات وزن جزيئي منخفض.

CHAPTER ONE

1 INTRODUCTION

1.1 Background

Owing to their low production cost, good physical properties and lightweight, plastic objects have slowly substituted glass, paper and metals in several fields of application (Miertus, 2002). At the same time, the current huge global production of plastics (200 million tons/year) has generated enormous environmental concerns, mainly related to the waste generation by plastic packaging, which are responsible for 35—40% share of annual plastics consumption (Miertus, 2004). Where recovery of plastics is not economically feasible, plastics often remain as litter. This is the case in most of agricultural and plastic bag applications of polymeric materials. The market for biodegradable polymers is at this moment focusing on products in which biodegradability provides beneficial effects (*e.g.* waste-disposal, recycling) and a number of biodegradable materials are already being marketed or are close to market introduction and customer acceptance.

Environmental degradability is the ability of materials to break down, by bacterial (biodegradable), thermal (oxidative) or ultraviolet (photodegradable) action. In order to use degradable polymers for making functional plastic bags they must meet the following criteria:

Be able to be formed into film;

Have adequate tensile strength and elongation;

Have adequate puncture resistance;

Have adequate tear resistance; and

Generally possess properties that resemble low-density polyethylene (LDPE) or high density polyethylene (HDPE) in overall physical properties and rheological characteristics (ExcelPlas, 2003). It is also necessary that degradable plastics for bags are required to degrade rapidly at the end of their useful life. On the other hand, it is equally important that their mechanical properties remain essentially unchanged during use (ExcelPlas, 2003).

In order to be considered environmentally degradable, a plastic must disintegrate mechanical, which means that the molecular weight of the molecules must be reduced, and then these molecular fragments must be microbially susceptible (Wiles 1998). Given that polyethylenes are microbially inert, other degradation mechanisms must be called into play, at an appropriate time, to convert hydrophobic, high-molecular-weight polymeric materials into water-wettable, friable substances containing much smaller molecules. It is known that the abiotic oxidative degradation of polyethylene film to produce oxidized molecular fragments having, on average, a molar mass reduced by a factor of ten or more can be accelerated without altering the products (Wiles 1998). It is also known that such products are biodegradable by aerobic micro-organisms.

In summary, there are three essential criteria for biodegradation of plastic bags:

They must disappear and leave no visible trace;

This disintegration must occur in a reasonable timeframe (e.g. 3 months or 6 months); and

They must not leave behind any toxic residues.

1.2.1 Types of plastic bags

A Plastic bag is a bag flexible packaging made of thin, flexible, blown poly film. Plastic bags are used for containing waste for packaging, disposal, and for storing and transporting foods, produce, powders, ice, chemicals, etc.

There are 4 main types of poly bags in widespread use:

High density polyethylene (HDPE)

Low density polyethylene (LDPE)

Oriented Polypropylene (OPP)

Complex structure (two or more plastics bonded together for better mechanical or barrier properties as Nylon and LDPE for vacuum packaging.

Polyethylene is an economical and versatile plastic so it is commonly used for disposable and general use bags. Poly bags are made by melting the resin in a blown machine. Plastic bags were first introduced in 1977 and now account for four out of every five bags handed out at grocery stores. Polyethylene or polyethene is one of the simplest and most inexpensive polymers.

Bags made of HDPE (High Density Polyethylene) range from 0.941 to 0.965 g/cm3 density, typically haze, typical application in supermarket and grocery stores, due to his strength even in low thickness, compared to other films. Bags made out of LDPE (Low Density Polyethylene) range from 0.910 to 0.925 g/cm3 density, can be clearer than HDPE and are used worldwide in general applications, usually for its cheap and versatile advantages, from sugar, grains, bread to ice, oranges, apples and carrot bags.

HDPE and LDPE bags are manufactured from resin pellets, from ethylene gas, a by-product of the oil industry.

OPP bags are made from Polypropylene film, usually are preferred when you look for transparency, bright, water vapour barrier and gift-look and sound, as in candies, confectionery, pasta and flour products, imported wine packaging, recordable media, etc. When a usually white OPP film is woven, the bag is a woven sack.

1.2.2 Shapes and Sizes of Plastic Bags

Many plastic bags are shaped like two identically-sized rectangular plastic sheets welded or folded together on 1, 2 or 3 sides, with one side open. This type of shape allows for simple, economic manufacturing and compact storage of the bags before use. Sizes vary from a few centimeters on a side, to several meters on a side, depending the need. Typical properties manufacturers look for when determine the bag material are impact strength, flexibility, low or high temperature properties, cristallinity, resistance to environmental stress cracking, lower melting points and wide processing ranges.

Bags are also made with carrying handles, hanging holes, tape attachments, security features, paper and other laminations, heavy sacks, pouch and standup pouch and other shapes. Some bags have provision for resealable hermetic or non-hermetic closing; others are sealed, often by heating the open edge, once filled, and can only be opened by destroying the packaging.

The thickness or gauge of the film is expressed in Mil - A unit of measurement in thousandths of an inch, (i.e., .001 = one thousandth of an inch or 1.0 mil), generally used to designate the thickness of LDPE products; or Mic - Short for micron, one thousandth of a millimeter, generally used to designate the thickness of HDPE products.

1.2.3 Shopping bags

Open bags with carrying handles are used in large numbers worldwide. A common size for general shopping is about 35 x 40cm, but sizes range from a bag to hold a couple of greeting cards, to bags which can hold large appliances. Bags are often supplied without charge by retail outlets, and usually printed with the store's identity, to serve as mobile advertising. Shopping bags may be reused for their original purpose, although there is little incentive to do so as new ones are usually supplied without charge. Used shopping bags are used for a multitude of other purposes, from reuse as rubbish bags, to manufacture of craft items, but ultimately the overwhelming majority are discarded. Taxes on bags are being introduced and discussed in several countries; once there is a cost, albeit small, associated with bags, the number used drops drastically.

1.2.4 Rubbish bags

Plastic bags are a convenient and sanitary way of handling rubbish, and are widely used. Plastic rubbish bags are fairly lightweight and are particularly useful for messy or wet rubbish, as is commonly the case with food waste, and are also useful for wrapping up rubbish to minimize odor. Plastic bags are often used for lining litter or waste containers or bins. This serves to keep the container sanitary by avoiding container contact with the rubbish. After the bag in the container is filled with litter, the bag can be pulled out by its edges, closed, and tied with minimal contact with the waste matter.

Plastic bags for rubbish or litter are sold in a number of sizes at many other stores in packets or rolls of a few tens of bags. Wire twist ties are sometimes supplied for closing the bag once full. In the mid-1990s rubbish bags with draw strings for closure were

introduced. Some bags have handles which may be tied, or holes through which the neck of the bag can be pulled. Most commonly, the rather soft, flexible plastic used to make rubbish bags is LDPE (Low Density Polyethylene) or, for strength, LLDPE (Linear Low Density Polyethylene). HDPE (High Density Polyethylene) is sometimes used.

1.3.1 Types of Degradable Polymer

Conventionally, plastics are made of fossil fuel. These conventional types of plastics are heavily used worldwide – mainly in packaging and household applications. The benefits of low production costs, light weight, strength, relative imperviousness to gas and water, clarity, and printability are highly regarded, but the final disposal of used flexible plastics causes problems. The ever increasing use of plastics, particularly in packaging, has become a significant source of environmental pollution (litter) and created problems in waste management. If disposed of by landfill, the plastics worsen the shortage of landfill sites. If the plastics are incinerated, they can emit poisonous gases such as dioxins. These problems motivate the public to take more care of the environment. Making plastic bags biodegradable is one way to try to ease the task of waste reduction.

Degradable bags can be classified in two ways (ExcelPlas 2003):

According to their degradation mechanism: biodegradable, or require the action of heat, ultraviolet light, mechanical stress or water in order to degrade.

According to their materials: natural starch polymers, synthetic polymers or a blend of a conventional polymer with an additive to facilitate degradation.

1.3.2 Types of Degradable Polymer

1.3.2.1 Biodegradable polymers

These are polymers that undergo decomposition into carbon dioxide, methane, water, inorganic compounds or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standardized tests, in a specified time, reflecting available disposal conditions.

Biodegradation is the chemical breakdown of materials by a physiological environment. The term is often used in relation to ecology, waste management and environmental remediation (bioremediation). Organic material can be degraded aerobically with oxygen, or anaerobically, without oxygen. A term related to biodegradation is biomineralisation, in which organic matter is converted into minerals. Biosurfactant, an extracellular surfactant secreted by microorganisms, enhances the biodegradation process.

Some microorganisms have the astonishing, naturally occurring, microbial catabolic diversity to degrade, transform or accumulate a huge range of compounds including hydrocarbons (e.g. oil), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), pharmaceutical substances, radionuclides and metals. Major methodological breakthroughs in microbial biodegradation have enabled detailed genomic, metagenomic, proteomic, bioinformatic and other high-throughput analyses of environmentally relevant microorganisms providing unprecedented insights into key biodegradative pathways and the ability of microorganisms to adapt to changing environmental conditions.

1.3.2.2 Biodegradable Polymer Types

There are two main types of biodegradable plastics in the market: hydro-biodegradable plastics (HBP) and oxo-biodegradable plastics (OBP). Both will first undergo chemical degradation by hydrolysis and oxidation respectively. This results in their physical disintegration and a drastic reduction in their molecular weight. These smaller, lower molecular weight fragments are then amenable to biodegradation.

Oxo-biodegradable and other degradable plastic bags have certain useful applications when used as rubbish bags. Organic waste can be put into oxo-biodegradable plastic sacks and put straight into the composting plant, unopened, thus reducing smells, disease transmission by insects, and handling hazards. The resulting compost may be used by farmers and growers. Since oxo-biodegradable plastic (unlike the starch-based alternative) releases its carbon slowly, it produces high quality compost. Oxo-biodegradable plastic does not degrade quickly in low temperature "windrow" composting, but it is suitable for "in-vessel" composting at the higher temperatures required by new animal by-products regulations. Oxo-biodegradable plastics become peroxidised and embrittled, and behave like natural waste. It is bio-assimilated by the same bacteria and fungi, which transform the degraded plastic products to cell biomass, like lignocellulosic materials. Oxo-biodegradable plastic is designed to fragment by a process which includes both photo-oxidation and thermo-oxidation, so it can degrade in the dark. This article or section is in need of attention from an expert on the subject.

OBPs are made by adding a small proportion of compounds of specific transition metals (iron, manganese, cobalt and nickel are commonly used) into the normal production of polyolefin (PE & PP) and polystyrene. The additives act as catalysts* in speeding up the

normal oxidative degradation, with the overall process increased by up to several orders of magnitude (factors of 10). The products of the catalyzed oxidative degradation of the polyolefins are precisely the same as for conventional polyolefins because, other than a small amount of additive present, the plastics are conventional polyolefins. Many commercially useful hydrocarbons (e.g., cooking oils, polyolefins, many other plastics) contain small amounts of additives called antioxidants that prevent oxidative degradation during storage and use. Antioxidants function by 'deactivating' the free radicals that cause degradation. Lifetime (shelf life + use life) is controlled by antioxidant level and the rate of degradation after disposal is controlled by the amount and nature of the catalyst.

Since there are no existing corresponding standards that can be used directly in reference to plastics that enter the environment in other ways other than compost - i.e. as terrestrial or marine litter or in landfills, OBP technology is often attacked by the HBP industry as unable to live up to the standards (which are actually the standards for composting). It has to be understood that composting and biodegradation are not identical. OBP can however be tested according to ASTM D6954, and (as from 1.1.2010) UAE 5009:2009.

HBPs tend to degrade and biodegrade somewhat more quickly than OBP, but they have to be collected and put into an industrial composting unit. The end result is the same - both are converted to carbon dioxide (CO_2), water (H_2O) and biomass. OBP are generally less expensive, possess better physical properties and can be made with current plastics processing equipment. HBP emits methane in anaerobic conditions, but OBP does not.

Polyesters play a predominant role in hydro-biodegradable plastics due to their potentially dydrolysable ester bonds. HBP can be made from agricultural resources such as corn, wheat, sugar cane, or fossil (petroleum-based) resources , or blend of thee two. Some of the commonly-used polymers include PHA (polyhydroxyalkanoates), PHBV (polyhydroxybutyrate-valerate), PLA (polylactic acid), PCL (polycaprolactone), PVA (polyvinyl alcohol), PET (polyethylene terephthalate) etc. It would be misleading to call these "renewable" because the agricultural production process burns significant amounts of hydrocarbons and emits significant amounts of CO_2. OBPs (like normal plastics) are made from a by-product of oil or natural gas, which would be produced whether or not the by-product were used to make plastic.

HBP technology claims to be biodegradable by meeting the ASTM D6400-04 and EN 13432 Standards. However, these two commonly quoted standards are related to the performance of plastics in a commercially managed compost environment. They are not biodegradation standards. Both were developed for hydro-biodegradable polymers where the mechanism including biodegradation is based on reaction with water and state that in order for a production to be compostable, the following criteria need to be met:

Disintegration, the ability to fragment into non-distinguishable pieces after screening and safely support bio-assimilation and microbial growth;

Inherent biodegradation, conversion of carbon to carbon dioxide to the level of 60% and 90% over a period of 180 days for ASTM D6400-04 and EN 13432 respectively; There is therefore little or no carbon left for the benefit of the soil, but the CO_2 emitted to atmosphere contributes to climate-change.

Safety, that there is no evidence of any eco-toxicity in finished compost and soils can support plant growth; and

Toxicity, that heavy metal concentrations are less than 50% regulated values in soil amendments.

1.3.2.3 Methods of measuring biodegradation

Biodegradation can be measured in a number of ways. The activity of aerobic microbes can be measured by the amount of oxygen they consume or the amount of carbon dioxide they produce. Biodegradation can be measured by anaerobic microbes and the amount of methane or alloy that they may be able to produce.

1.3.2.3.1 Measurement of aerobic decomposition

The DR4 test or 4-day dynamic respiration index test is a test to measure the biodegradability of a substance over 4 days. The substance is aerated by passing air through it. This definition is used to determine the method from those where aeration is by diffusion of air into and out of the test material which is referred to as the SRI or static respiration index test. Microbes are introduced to the test material while incubating it under aerobic conditions by aerating the mixture in a vessel through which air is blown. The microbes degrade the material producing CO_2 as the product of biodegradation. This CO_2 production can be monitored as a measure of the biodegradability of the test material and converted into oxygen consumption units.

1.3.2..2 Measurement of anaerobic decomposition

BMP100 test, 100 day biogenic methane potential test, is a test method that determines the potential biodegradability of biodegradable wastes under anaerobic conditions by measuring the production of biogas. The test has not been peer-reviewed by the international community and no known official publication exists for it. Other published tests that accomplish this in shorter time are the GB21 protocol (DIN 38414).

Under anaerobic methanogenic conditions the decomposition of organic carbon proceeds by producing biogas (containing methane and carbon dioxide)from the organic carbon. The amount of biogas production therefore measures directly the carbon which is mineralised. The test is set up in a small vessel containing the test substrate, a mineral aqueous medium and an inoculum of methanogenic bacteria taken from an active anaerobic digester. The test is monitored by collecting and measuring the biogas produced. The test is incubated for an extended period until gas production ceases which may be up to 100 days or more; for all practical purposes most organic materials reach the majority of decomposition in less than 45 days. By being run so long, however, the BMP100 test therefore measures the complete degradation of the waste.

1.3.3 Compostable polymers

These are polymers that degradable under composting conditions. To meet this definition they must break down under the action of microorganisms (bacteria, fungi, algae), achieve total mineralization (conversion into carbon dioxide, methane, water, inorganic compounds or biomass under aerobic conditions) and the mineralization rate must be high and compatible with the composting process.

1.3.4 Bioerodable polymers

These are polymers that undergo controlled degradation through the incorporation of 'prodegradation' additives (additives that can trigger and accelerate the degradation process). These polymers undergo accelerated oxidative degradation initiated by natural daylight, heat and/or mechanical stress, and embrittle in the environment and erode under the influence of weathering.

1.3.5 Photodegradable polymers

These are polymers that break down through the action of ultraviolet (UV) light, which degrades the chemical bond or link in the polymer or chemical structure of the plastic. This process can be assisted by the presence of UV-sensitive additives in the polymer.

Photodegradation is degradation of a molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, such as infrared radiation, visible light and ultraviolet light. However, other forms of electromagnetic radiation can cause photodegradation. Photodegradation includes photodissociation, the breakup of molecules into smaller pieces by photons. It also includes the change of a molecules shape to make it irreversibly altered, such as the denaturing of proteins, and the addition of other atoms or molecules. A common photodegradation reaction is oxidation. This type of photodegradation is used by some drinking water and wastewater facilities to destroy pollutants.

1.3.6 Thermoplastic starch-based polymers

These are polymers made with at least 90% starch from renewable resources such as corn, potato, tapioca or wheat.

1.4 Ways of making biodegradable film

There are two main options for making normal polythene into a biodegradable film:

1.4.1 Starch based or Biobased (Hydrodegradable)

It is made from corn (maize), potatoes, wheat. This form of biodegradable films meets the ASTM standard (American Standard for Testing Materials) and European norm EN13432 for compostability as it degrades at least 60% within 180 days or less.

Examples of polymers with which starch is commonly used:

Polycaprolactone (PCL)

Polyvinyl alcohol (PVA)

Polylactic acid (PLA)

These materials predominantly require a controlled microbial environment such as an industrial compost facility before they will degrade. The heat, moisture and aeration one gets in a compost pile are vital to this type of biodegradable film working well.

Poorer mechanical strength than additive based example – filling a starch bag with wet leaves and placing curbside can result in the bottom falling out when a hauler picks it up.

Limited Shelf life

Can only be composted in a special composting facility.

Typical Application area

Industrial Compostable Facility, Please visit your local city government's website to see if you have an industrial composting facility that accepts residential compost.

1.4.2 Additive based

These films are made by blending an additive to provide a UV / oxidative and/or biological mechanism to degrade them. This typically takes 6 months to 2 years in a landfill site and/or standard composting system. In these films, biodegradation is a two stage process; first the plastic is converted by reaction with oxygen (light, heat and/or stress) to molecular fragments that water can wet, and then these smaller oxidized molecules are biodegraded, i.e. converted into carbon dioxide, water and biomass by microorganisms.

Cheaper & Proven

Controlled degradation

These films look, act and perform just like their non-degradable counterparts, except they break down after being discarded.

Made using fossil fuel

Degradation depends on conditions of heat, light, stress, air etc

Typical Applications

Trash Bags, Garbage Bags, Compost Bags, Carrier bag, Agricultural Film, Mulch Film

Films made by blending an additive to provide a mechanism to attract microbes to biodegrade them. This typically takes in 1 year to 5 years in a landfill site and/or standard composting system.

Cheaper & Proven

Useful shelf life until discarded in a landfill or microbial environment

These films look, act and perform just like their non-degradable counterparts, except they break down after being discarded.

Is not affected by light, heat, mechanical stress, or moisture.

1.5 Polymer Options and Scope of Work

While the potential list of degradable polymer types is extensive there are certain degradable

plastic systems that are preferred for the manufacture of plastic bags on the basis of their favorable property profile. In addition, based on the available locally manufactured plastics, this investigation will be limited to:

Starch + film grade polyethylene blends

Film grade polyethylene + controlled degradation master batch additives combinations (e.g. TDPA™)

Film grade polyethylene + prooxidant additives that turn the polymer into CO_2 and H_2O.

1.6 Degradable bags in Compost

Composting is a specific type of microbiological treatment and is used to describe several distinct technologies (ExcelPlas, 2003):

Aerobic composting;

Anaerobic treatment / gasification; or

A combination of aerobic and anaerobic treatment.

These technologies can be applied to either municipal solid waste (MSW) or separated waste. Various studies have shown that starch-based plastics do biodegrade under controlled composting conditions. The degradation of polyethylene (PE) modified with TDPA. Pro oxidant additives from EPI has been assessed by a variety of laboratory-scale and field-scale tests. One study by Chiellini (2003) found that the resin did undergo ultimate biodegradation (i.e. mineralization) in simulated soil burial but not readily in composting conditions. He noted, however, that the completeness of biodegradation and the time for oxidation are still unanswered questions.

There is little evidence to prove that polymer residues in the soil are harmful (ExcelPlas, 2003). Some results suggest that pure polymeric fragments may provide useful properties as a soil additive. However, many of the additives in plastic material, for example, plasticizers, coloring pigments, stabilizers, and degradation promoters-can contain heavy toxic metals, which can make the entire compost unusable (Garthe and Kowal 2002). The analysis of the heavy metal content of five different biodegradable garbage bags showed that the polymers themselves contained very low amounts of heavy metals. However, the printing with green and blue colours with copper pigments was increasing the copper content in all products (Kaiser 2001).

1.7 Problems of Plastic Bags

Plastic bags have advantages and disadvantages when compared to alternatives such as paper bags and cardboard boxes. The durability, strength, low cost, water and chemicals resistance, welding properties, lesser energy and heavy chemicals requirements in manufacture, fewer atmosphere emissions and light weight are advantages of plastic

bags. Plastic polymers including poly bags, bottles, foam cups, pipes, toys, TV and PC cases and more, account for about 20 percent (by volume) of landfill space. However, non-biodegradable bags fill landfill sites and make for long-lasting litter, which in particular is dangerous to wildlife away from centers of human population, due mostly to virgin resin cheap price when compared to other flexible packagings and this low price tend to be under-enthusiastic to recyclers. As the global climate crisis deepens consumers are starting to take responsibility for their actions and to use resusable cloth bags and other bags like backpacks etc in place of the proverbial one time use plastic shopping bag.

Many studies comparing plastic versus paper for shopping bags show that plastic bags have less net environmental effect than paper bags, requiring less energy to produce, transport and recycle; however these studies also note that recycling rates for plastic are significantly lower than for paper[citation needed]. Paper is also made from a renewable resource (trees), whereas plastic is non-renewable (petroleum-based). Additives have been developed that allow plastic to degrade and biodegrade within a few months in landfill (as opposed to an estimated 500-1000 years for non-degradable plastic). Plastics made with these additives are called oxobiodegradable, and have been adopted by many 'ethical' retailers, e.g., the Co-op in the UK. However, some argue that oxo-biodegradable plastics contribute more to global warming as they release their carbon as carbon dioxide and methane far more quickly than plastics in landfill. In April 2002, the Marine Conservation Society reported that a dead Minke whale that had washed up on the coast of Normandy was found to have had 800 kg of plastic bags and packaging (including two U.K supermarket bags) inside its stomach. In the other hand, bags are made from

Polylactic acid (PLA) a biodegradable polymer derived from lactic acid. It is a highly versatile material and is made from 100% renewable resources like corn, sugar beets, wheat and other starch-rich products. Polylactic acid exhibits many properties that are equivalent to or better than many petroleum-based plastics, which makes it suitable for a variety of applications, emits fewer greenhouse gases, and contains no toxins.

Data released by the United States Environmental Protection Agency shows that somewhere between 500 billion and a trillion plastic bags are consumed worldwide each year. (National Geographic News September 2, 2003)

The plastic bags are dumped in the city and go into drainage and sewage lines, causing blockages. It was discovered that due to the drainage congestion – by polythene shopping bags, water could not go down. This was the cause of increasing water born diseases and air pollution-related environmental degradation.

Plastic bags are everywhere! Everyday, we are handed countless plastic bags: when we go to the grocery store, retail clothing store, book store, restaurants, etc. Yes, sometimes, plastic bags are convenient, as they are water resistant and light and inexpensive compared to paper bags. Most of the time, plastic bags are superfluous and avoidable.

Most of them go straight to our landfill and a very small percentage of plastic bags are actually recycled. A reduction in our use of plastic bags is essential in solving the environmental problems stemming from them.

Plastic bags and packaging account for a major part of our waste in landfills. More importantly, plastic bags are one of the top items of litter on our community beaches, roads, sidewalks, and vegetation along with cigarette butts and Styrofoam. Plastic bags are light and hard to contain. Because of their light weight, plastic bags fly easily in wind,

float along readily in the currents of rivers and oceans, get tangled up in trees, fences, poles, and so forth, and block the drainage.

Plastic bags are made from a non-renewable natural resource: petroleum. Consequently, the manufacturing of plastic bags contributes to the diminishing availability of our natural resources and the damage to the environment from the extraction of petroleum. At the same time, plastics are hazardous to produce; the pollution from plastic production is harmful to the environment. Finally, most plastic bags are made of polyethylene - more commonly known as polythene - they are hazardous to manufacture and are said to take up to 1,000 years to decompose on land and 450 years in water.

The fact that plastics are not biodegradable means that the plastic bags in circulation and future production of plastic bags will stay with us for a long time: in our landfills, oceans, streets, and so forth.

Countless plastic bags end up in our ocean and cause harm to our marine wildlife. Many marine animals and birds mistakenly ingest plastic or become entangled and choke in plastic bags that is floating around. For instance, environmentalists have pointed out that turtles often mistake plastic bags for jellyfish and invariably swallow them. It is estimated 100,000 marine mammals die each year because of plastic litter in our ocean in the North Pacific. (www.algalita.org)

Land animals seem to be victims as well. In countries such as India, cows are mistakenly ingesting plastic bags on the streets as they are scavenging for food and end up choking or starving to death, as the plastic cannot be digested.

Polyethylene materials are not bio-degradable. Whenever a polyethylene bag is thrown away, it does not decompose through natural process. It contributes to the accumulation

of non-destructive waste of permanent nature. If anybody looks at any garbage dumping site, he will observe this fact that although other garbage matter get decomposed and merged into the soil but polyethylene bags remain intact with their different colours especially the black coloured polyethylene bags. Polyethylene remains intact in the soil and disturbs the flow of nutrients to the soil and hinders entering sunlight. It destroys the beneficial bacteria of soil and losses soil fertility. It hinders the way of soil compaction, which in the long run effects the construction of foundation of the different structure.

The use of polyethylene is not environment friendly. Medical reports find it as an agent of cancer, skin diseases and other health problems. The users are more exposed to these types of health hazards when polyethylene is used to pack bread, biscuits, potato chips or other food items. In the developed countries, food is wrapped in food-graded plastic or polyethylene, but in Bangladesh this was not strictly followed and sometimes colorants are used, some of which may be carcinogenic.

1.8 Many Countries in the World Banned the Use of Plastic Bags

The international crisis, which plastic bags are creating, is indicated by the fact that most nations recognize the problem and are making strong attempts to eliminate the use and productions of plastic bags. Many countries in Europe and Asia are attempting to eradicate plastic bags. Some are banning plastic bags altogether while others are implementing a tax on plastic bags to decrease their use. In Bangladesh, plastic bags have been banned completely since early 2002. They were found to have been the main culprit during the 1988 and 1998 floods that submerged two-thirds of the country. The problem was that discarded bags were choking the drainage system.

In 2001, Bombay council also eliminated the use of plastic bags to prevent them from littering the streets and clogging up the city's sewerage system. As a result, merchants have switched to recycled paper bags and litter in the city has been reduced considerably.

In Ireland, a tax on plastic bags was introduced. Essentially, each plastic bag handed out costs the consumer an extra 15 cents. After the tax scheme began in March 2002, it is estimated the plastic bags available at stores have been decreased by 90%.

These are great success stories from various countries working out the problem of plastic bags. They have set examples on how a ban or a tax on plastic bags may work. Consequently, other nations such as the United Kingdom are considering implementing similar regulations.

Taiwan is moving to ban the free distribution of plastic bags, while, next month, the government in Singapore will launch a campaign to discourage their use.

In India, cows are ingesting plastic bags as they forage for food on the street. They then end up choking or starving to death. The same happens to turtles, which commonly mistake plastic bags for jellyfish, say environmentalists.

In South Africa, they have been dubbed the "national flower" because so many can be seen flapping from fences and caught in bushes.

They are even big in America, despite all those Hollywood films featuring "moms", returning from the supermarket, overburdened with paper bags. Four out of five grocery bags in the US are now plastic.

The Department of the Environment of Bangladesh organised a discussion session. Speaking as chief guest, Minister for Environment and Forest said the government is

determined to stick to its decision to ban use of polythene shopping bags in the Dhaka City and would not consider any appeal from any quarter.

The plastic bag situation has taken a serious turn across the country, due to billions of the bags being dumped into rivers and other water bodies, as well as drains, over the years, causing a serious environmental threat.

From the beginning of January 2002, the Bangladesh government banned the use of plastic bags. China has banned free plastic bags. Ireland took the lead in Europe, taxing plastic bags in 2002 and have now reduced plastic bag consumption by 90%. (BBC News Aug. 20, 2002)

In 2005 Rwanda banned plastic bags. (Associated Press)

Israel, Canada, Western India, Botswana, Kenya, Tanzania, South Africa, Taiwan and Singapore have also banned or are moving toward banning the plastic bag. (PlanetSave.com Feb. 16, 2008)

On March 27th 2007, San Francisco becomes first U.S city to ban plastic bags. (NPR.org National Public Radio)

Oakland and Boston are considering a ban. (The Boston Glove May 20, 2007)

China will save 37 million barrels of oil each year due to their ban of free plastic bags. (CNN.com/asia Jan. 9,2008)

1.9 Benefits of Banning Plastic Bags

It can be said that, banning of polyethylene has achieved its success with a little residues left. People in general has accepted it. Now the city bins and garbage dumping sites are almost free from polythene shopping bags. They look much cleaner now. The city drains

are no longer clogged with polyethylene shopping bags. Jute growers are particularly happy to see that demand for jute products in the domestic markets is going up. Polyethylene shopping bags manufacturers have now been engaged in the production of alternative bags and an additional huge number of jobs have been created in this sector.

The historic decision for banning polythene shopping bags not only ensured environmental benefits for the country it also created a great opportunity for generation of more employment and alleviating poverty in rural areas. The rejection of a non-biodegradable product by an entire nation is probably a unique example Bangladesh has set with peoples' participation under a popular government. This pro-environment decision can be repeated in other arenas of nation building activities in other parts of the world to turn our only planet, the Earth, habitable for human beings.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 *Overview of degradable polymers*

In this section we present an overview of degradable polymers useful in the manufacture of plastic bags and relevant to the local industries in Saudi Arabia.

2.1.1 *Starch-based polymers*

Thermoplastic starches are based on gelatinized starch from different sources, for example, potato, corn, wheat or tapioca. With the use of specific plasticizing solvents can be converted into thermoplastic materials with good performance properties and with inherent biodegradability. Most importantly, thermoplastic starch compounds can be processed on existing plastics fabrication equipment. Three types of starch-based polymers have been developed (ExcelPlas, 2003). The first type consists of a synthetic polymer, usually polyethylene (PE), and the starch is only present as a filler. These bags are not fully biodegradable and consist of mainly non-biodegradable synthetic polymers like polyethylene or polypropylene and only 5-50 percent starch. The starch biodegrades and the plastic disintegrates into small particles. Many manufacturers of starch based additives describe their product as being 'photo-biodegradable'. One example of a refined first type products is the Willow Ridge products such as PolyStarch N, a masterbatch of 55% cornstarch with LLDPE. The product includes a processing aid and 3-10% levels of a desiccant (trade-named Aquanil) that ensures moisture control prior to use. PolyStarch N is suitable for LDPE and LLDPE garbage bags, agricultural films, and injection and

blow molded parts intended for disposal in conditions able to sustain microbes. In the second type, the thermoplastic starch is used as a polymeric materials and not only as an additive. It is usually blended with hydrophilic synthetic polymers (e.g. a polyester or a polycaprolactone) and contributes to the strength of the material when used an a percentage of 50-80%. The third type is a truly biodegradable plastic that does not contain synthetic polymers at all. To improve some of the properties of the plastic, the starch is modified, but no synthetic materials is necessary. An example of this type of polymer is Novon, which is starch (90-95%) plus additives.

2.1.2 Controlled degradation master-batch additives

Totally Degradable Plastic Additive (TDPA™) formulations have been developed by Ecosoft (ExcelPlas, 2003). When compounded with conventional polymers at appropriate levels, these additives control the lifetimes of plastic films and articles. Stability is maintained during processing, storage and short-term end use. Once the material is discarded, oxidative degradation (initiated by heat, UV light or mechanical stress in the environment) is accelerated by as much as several orders of magnitude. The oxidized molecular fragments are hydrophilic, have low molecular weight and are biodegradable. Prodegradants include additives based on transition metal ions (Mn, Cu, Fe, Co, Ni, Ce4) and metal complexes (e.g. cobalt stearate, cerium stearate), which render polyethylene susceptible to hydroperoxidation (ExcelPlas, 2003). Only trace quantities of Mn, Cu, Fe, Co, Ni and Ce are added to the polymer and the quantities of these elements are equivalent to the trace elements present in soil. These additives are typically incorporated into the final formulation as additives at levels of a few percent. They are a well dsigned

combinations of additives, which, with appropriate compositional adjustments, allow for a wide range of storage, use, and degradation times, depending on the end use and the environment. Polyolefin pellets which have been compounded with these additives are processed on conventional equipment at normal speeds (ExcelPlas, 2003). An important feature of these additives is that they are activated both by the action of sunlight and by heat.

2.1.3 Photodegradable polymers

'Photodegradable polymers' are synthetic polymers incorporating light-sensitive chemical additives or copolymers for the purposes of weakening the bonds of the polymer in the presence of ultraviolet radiation (ExcelPlas, 2003). Photosensitizers used include diketones, ferrocene derivatives (aminoalkyferrocene) and carbonyl-containing species. A new approach to making photodegradable plastics is adding metal salts to initiate the breakdown process. Many photodegradable polymers are a combination of PE and controlled degradation masterbatch additives.

One of the manufacturers of these additives is Evergreen Environmental, a South African company, which developed an additive system that causes plastic litter to degrade rapidly into water and carbon dioxide in the outdoors under the influence of UV radiation. By introducing a prodegradant into plastic bag production, the life of the plastic bag is reduced which would ultimately reduce the build-up of litter in the environment. A second manufacturer is Willow Ridge (Willow Ridge (Erlanger, Ky. USA) which produces a master-batch that simultaneously triggers photodegradation and thermal-oxidative breakdown in PE. The product is typically used at a 3% level (Leaversuch

2002). Willow Ridge also supplies a photodegradable master-batch designated UV-H that accelerates UV degradation by creating free radicals that sever the polymer chains into smaller fragments that can be consumed by microbes.

2.2 Current Status of Research

Swift classified the environmentally degradable polymers into 5 classes: degradable plastic, biodegradable plastic, hydrolytically degradable plastic, oxidatively degradable plastic, and photodegradable plastic. Potential applications for the environmentally degradable polymers were described and test protocols for the biodegradability were given and countless synthetic routes for the prepn. of these materials were outlined. The key issues of terminology and test methodology of polymers that are biodegradable, photodegradable, oxidatively degradable, and hydrolytically degradable are also addressed (Swift, 1995, 1997).

Photodegradation of poly(isobutylene oxide) was investigated by observing the degradation and photodegradation of the polymer observed (Lee 1997). Additives, especially organic acids, accelerate photodegradation. One of the degradation products is acetone. A possible degradation mechanism, via a hydroperoxide pathway, is suggested.

The artificial and natural aging of foil made from a 60/40 mixture of LDPE/LLDPE extrudates containing degradation additive, UV stabilizer, and carbon black was investigated (Sanchez-Valdez et al 1996). The experimental results verified that with proper mixing of previous mentioned additives, polyethylene-based soil mulch foils can be manufactured which preserve their mechanical properties for the planed duration and decomposition after the cultivation period.

Iwasa reviewed the current trends in degradable plastics and technologies of two types of photodegradable plastics and the benzophenone-based additive (Iwasa et al 1990). Characteristic properties of modified polyethylene and polypropylene resins were shown. A mechanism of degradation was described briefly.

Hakozaki et al. reviewed the background and the present status of the technology of biodegradable and photodegradable plastics (Hakozaki et al 1990). In his section on biodegradable plastics, copolyesters of 3-hydroxybutyrate prepared by fermentation with microorganism, natural polymers such as cellulose, typical synthetic polymers such as polycaprolactone and polyvinyl acetate, and cornstarch-blended polyethylenes are described. In the section on photodegradable plastics, the addition of sensitizing additives and the introduction of a sensitizing group, e.g., the carbonyl group, in the polymer main chain are described. Ethylene-CO copolymers and ethylene-vinyl ketone and styrene-Ph vinyl ketone copolymers are exemplified.

Hakozaki et al reviewed the photochemical properties of ethylene-CO copolymer and photodegradable polyethylene DXM 439 and additive-effected photodegradable plastics (Hakozaki et al, 1990b).

Scott reviewed different types plastics designed to undergo photodegradation, with discussions on mechanisms of degradation, current additives used to both prevent and enhance degradation, synergistic effects of certain additives, and how such additives impact on the useful lifetime of plastic products (Scott, 1990). Special emphasis is placed on the current problem of plastics recycling vs. biodegradable plastics.

The mechanism of polymer photodegradation and the effect of ketone copolymer formulations and metal salts as photodegradation catalysts were discussed by Perrone for

environmental protection (Perrone, 1987). The highest photodegradation rate was observed for polyolefins, especially polyethylene and polypropylene, and for polystyrene. Use of PVC and poly(ethylene terephthalate) as photodegradable materials was not recommended due to the lack of appropriate additives promoting the degradation.

The effect of the method of disposal on degradation was investigated. Special attention is paid to possible reuse of plastics and several examples are given (Stepic et al, 1981). Introduction of photosensitizer additives (metal dithiocarbamates, used originally as heat stabilizers of polymers and S vulcanization accelerators) support the photodegradation after a certain induction period. However, plastics with such additives behave differently in various climates. Light radiation causes the polymers to form a brittle network, which decomposes into powder within several weeks and improves the quality of soil. Results obtained with cellophane, polyethylene and polypropylene with various sensitizers are described.

2.2.1 Effect of the Structure of Additives

Freedman investigated the relation between the structure of additives (arylmethyl halides, phenacyl halides, haloalkenes) and their effectiveness in promoting photodegradation of polystyrene (I), polypropylene (II), and polyethylene (III) (Freedman, 1976 a,b). The order of degradation by a 275 W sunlamp is I > II > III. Molecular weight degradation of irradiated I is significantly greater in the presence of additives than in their absence.

Freedman and Diamond also investigated the effect of adding 1.0% of N-halogen compds. to polystyrene polypropylene and polyethylene and found that it enhanced the photodegradability of the polymers in film form (Freedman, Diamond, 1976). The

effectiveness of the additives varied with their structure and with the polymer. A comparison of N-bromosuccinimide (II) with a number of known photoinitiators showed that it was superior in effectiveness to all but cobalt stearate. The films were irradiated with a 275 W RS sunlamp for 66-200 hr. Degradation was measured by determining the increase in carbonyl absorption at 1750-1695 cm-1 using ir spectroscopy and by the change in viscosity. Viscosity measurements showed that I containing II underwent a greater molecular weight loss than unmodified I after UV exposure.

2.2.2 Compostability Studies

Otto et al investigated the biodegradability of 4 selected, compostable waste bag types in a respirometer test (Otto et al, 2003). The bags consisted of aliph.-arom. copolyester (1), starch/polycaprolactone (2), and polyester-amide/polycaprolactone. The respirometer was filled with a synthetic, aquatic material and inoculated. Bag foil snippets were the sole Carbon source. The degradation was measured by O consumption and CO_2 production. All types were biologically decomposed with degradation rates of 25-76% within 42 days. The differences are attributed to the material composition of the bags. Additives for the improvement of manufacturing and mechanical stability may influence the biodegradability. Degradation rates of 2-11% within 7 days guarantee the use in presorting vessels without loss of mechanical stability.

Hill reported fully degradable plastic bags from polyethene that contain a degradable compostable plastic additive technology that induces reduction of the plastic to carbon dioxide and water in just a few weeks (Hill, 1999). The polyethylene plastic has the same mechanical properties and processing characteristics as regular polyethene and so can be

used in the same way to make products and the additive acts as a catalyst for the degradation of polyethene.

Chiellini et al. designed a straightforward experimental set-up derived from the Biometer Flask previously utilized for experiments of pesticides biodegradation, for testing the ultimate biodegradability of natural, synthetic and semi-synthetic polymeric materials on solid substrates such as soil and mature compost (Chiellini, 2003). The use of these whole substrates as incubation media in respirometric experiments, may negatively affect the accuracy of the test due to the large amount of carbon dioxide developed from the blanks, especially in the presence of specimen degrading at low or moderate rates. In the present test procedure soil and compost samples are diluted with perlite, a naturally occurring inert aluminum silicate widely utilized in horticultural applications, in order to ensure optimal conditions for the microbial growth while reducing the carbon dioxide emissions from the blanks. The results so far reported clearly indicate that the adopted procedure is extremely valuable and versatile for the appreciation of even subtle differences in the biodegradation rate of different polymeric materials, as well as for long-term degradation experiments.

2.2.3 Additive packages for UV and Biodegradation

Wiles et al. devised additive packages which, when added to polyolefins, can be used to fabricate films which are suitable for landfill covers, refuse sacks, etc., or, in a different manifestation, are suitable for compost bags (Wiles et al, 1998). Sensitivity to near UV light is one characteristic but, more importantly, sensitivity to heat is achieved. Complete compostability within a few weeks has been observed reproducibly. The time of the

onset of degradation is defined by the end use, and is controlled by adjusting the components in the additive formulations.

Rodlan-Carrillo et al. studied starch metabolites and enzymes during starch-based plastic polymer biodegradation by the white rot fungus Phanerochaete chrysosporium, grown in sugarcane bagasse pith in tubular reactors [Roland et al, 2003). Various metabolites, amylase, ligninase and cellulase production were measured during P. chrysosporium growth on sugarcane bagasse pith with added glucose and starch polymer. On-line respirometric analyses followed during 32 days confirmed the P. chrysosporium capability of growing on sugarcane bagasse pith with starch polymer degradation. Enzyme activity during secondary metabolism increased, and a 70% and 74% starch degradation was reached with and without glucose addition, generating low molecular weight metabolites (e.g.) dextrin, maltotriose, maltose and glucose that were detected by high performance liquid chromatography.

Kulshreshtha et al. reviewed some commercially available environment-friendly plastics (Kulshreshtha et al, 1998). The biodegradable plastics reviewed were available as starch-filled thermoplastics, such as LDPE, LLDPE, HDPE, ethylene-acrylic acid copolymers, starch-g-PAN graft copolymer, polyester based polyurethanes, etc.   These bear the following trade names: Ecostar, Ecostar plus, Super Slurper, Ecolan, Novon, Mater-Bi & PBHV. Bio-degradability was found to be relevant to landfill conditions since burial and moisture are required. Photodegradability was found to be relevant to litter from plastics cups and packaging and depends upon exposure to UV radiation.   Com. available photodegradable plastics are: E/CO, Ecolyte, PS2005, PE3006, PP4006 (Environmer) and Plastigone. "REXflex" flexible polyolefin and Biofine is available as a substitute for

PVC and plasticized PVC. "Poly-Grade" is a proprietary additive containing masterbatch for making polyolefins degradable. ICI's polyester BIOPOL used in shampoo bottles is made by fermentation.

The environmental degradation of polyethylene was reviewed by Hakkarainen & Albertsson (Hakkarainen & Albertsson, 2004). Degradation of polyethylene proceeds by synergistic action of photo- and thermo-oxidative degradation and biologically activity. Since biodegradation of com. high molecular weight polyethylene proceeds slowly, abiotic oxidation is the initial and rate-determining step. Enhanced environmentally degradable polyethylene is prepared by blending with biodegradable additives or photo-initiators or by copolymerization. One of the key questions for successful development and use of environmentally degradable polymers is to understand the interaction between degradation products and nature. Polymer fragments and degradation products should be environmentally assimilable and should not accumulate or negatively affect the environment. Determination of abiotic and biotic oxidation products is an important step towards establishing the environmental degradation mechanism and environmental impact of the material. More than 200 different degradation products including alkanes, alkenes, ketones, aldehydes, alcs., carboxylic acid, keto-acids, dicarboxylic acids, lactones and esters were identified in thermo- and photo-oxidized polyethylene. In biotic environment these abiotic oxidation products and oxidized low molecular weight polymer can be assimilated by microorganisms. In future we will probably see a development of new polyethylenes with tailor-made structures specially designed for environmental degradation through different pathways. Paralleled with the development of these new materials we need to obtain better understanding of the environmental impact of

degradable polymers and the interactions between nature and degradation products in a dynamic system.

2.2.4 Effect of light Stabilizers

The effect of various types of light stabilizers, i.e., Diacetam 5, Polyacetam 81, and Benazol P, on the fluorescence intensity of Eu(III) complexes in polyethylene (I) in the course of its processing and as a result of UV irradiation was studied (Mirochink et al, 1998). The study is of interest with respect to the use of films for agricultural purposes with Eu(III) complex luminescent additives simulating growth of plants covered with such films. It was shown that all the above stabilizers suppress the fluorescence of both Eu(NO3)3.2Phen and Eu(HFAA) 3.2TPhPO (where Phen = 1,10-phenanthroline, HFAA = hexafluoroacetylacetonate, TPhPO = triphenylphosphine oxide).

2.2.5 Starch-Plastic films

Kenneth et al. investigated the photodegradation of com. starch-polyethylene plastic compost bags (Kenneth et al., 1993). Bags differed in starch content (5-9%) and prooxidant additives (transition metals and unsaturated vegetable oil). All materials containing transition metals demonstrated rapid thermal oxidative degradation at 70°C (dry) and high-temp., high-humidity (steam chamber) treatments. Compost site was seeded with test strips (200-800 of each type) taped together, which were recovered periodically over an 8- to 12-mo period. At each sampling date, the compost row temp. was measured (65 to 95 $^{\circ}$C), the location of the recovered test strip was recorded (interior or exterior), and at least 4 strips were recovered for evaluation. Degradation was

followed by measuring the change in polyethylene molecular weight distribution via high-temp. gel permeation chromatography. The initial 8-mo study indicated that materials recovered from the interior of the compost row demonstrated very little degradation, whereas materials recovered from the exterior degraded well. In the 2nd-year study, however, degradation was observed in several plastic materials recovered from the interior of the compost row by month 5 and almost every material by month 12. Sitohy et al investigated degradability of different phodphorylated starch types (corn, rice, potato, corn amylose, and corn amylopectin) (Sitohy, 2001). Starches were phosphorylated to varying degrees of substitution (DS) and tested both for acid hydrolysis during 3 h in a boiling bath and for enzymic hydrolysis with a thermostable bacterial a-amylase (II) (Bacillus licheniformis) for 30 min at $95^{o}C$. Generally, phosphorylated I samples showed a decreased degree of acid hydrolysis during the entire time of hydrolysis (3 h), as well as decreased susceptibility to II hydrolysis. The enzyme action was inhibited by the presence of phosphate groups in the modified I molecules, and the extent of inhibition increased with increasing degree of phosphate substitution, regardless of the I type. Thermoplastic films were fabricated by blending modified corn I samples of different DS with polyacrylate, urea, and water at a ratio of 4:5:1:50, heating for 30 min at 95 ^{o}C before casting, and allowing to cool, stand, and dry at room temp. The plastic films prepared from phosphorylated corn I showed both higher disintegration rate and a greater degradability by thermostable bacterial II than the ones prepared from non-phosphorylated I. These newly acquired properties can meet the increasing demand for biodegradable disposable plastic bags.

The compostability of 9 lawn and leaf bags made from environmentally degradable plastics was assessed using a 3-tiered approach involving both standard lab.-scale tests and field studies (Farrell et al, 2001). Results obtained for the test plastics were compared to those obtained for both positive (Kraft paper) and negative (LLDPE) controls. Statistical analyses were used to rank the test materials in terms of their overall degradation; the degree of agreement in the relative rankings was then assessed using Kendall's coeff. of concordance (W). The calculated coefficient of concordance was 0.724 (significant at the 1% level of probability), indicating that the comparative biodegradability of the test/ref. materials was relatively unaffected by variations in the test conditions. Five of the test plastics exhibited significantly more degradation than the pos. control, with plastics whose degradation pathway included a significant abiotic contribution having an apparent advantage.

Roper et al. reviewed the chemical modification of classical polymers into photo- and chemo-degradable materials (Roper et al., 1990). The study included physical mixing of 6-20% granular starch with polyethylene or polypropylene, coprocessing of more than 50% disintegrated starch with hydrophilic polymers like polyacrylate or polyvinylalcohol to biodegradable films for agricultural mulch or carrying bags, thermoplastic extruded starch with plasticizer containing >90% starch for blister packaging and disposables for fast food, and finally biodegradable polyesters like poly(hydroxybutyric acid) and polylactic acid, produced by fermentation processes.

Biodegradation of polythene bags and plastic cups was analyzed by Kathiresan after 2, 4, 6, and 9 months of incubation in the mangrove soil (Kathiresan, 2003). The biodegradation of polythene bags was significantly higher (up to 4.21% in 9 months) than

that of plastic cups (up to 0.25% in 9 months). Microbial counts in the degrading

materials were recorded up to 79.67 x 10(4) per gram for total heterotrophic bacteria, and

up to 55.33 x 10(2) per gram for fungi. The microbial species found associated with the

degrading materials were identified as five Gram positive and two Gram negative

bacteria, and eight fungal species of Aspergillus. The species that were predominant

were Streptococcus, Staphylococcus, Micrococcus (Gram +ve), Moraxella, and

Pseudomonas (Gram -ve) and two species of fungi (Aspergillus glaucus and A. niger).

Efficacy of the microbial species in degradation of plastics and polythene was analyzed

in shaker cultures. Among the bacteria, Pseudomonas species degraded 20.54% of

polythene and 8.16% of plastics in one-month period. Among the fungal species,

Aspergillus glaucus degraded 28.80% of polythene and 7.26% of plastics in one-month

period. This work reveals that the mangrove soil is a good source of microbes capable of

degrading polythene and plastics.

2.2.6 Thermal Characterization

The thermal properties of a series of commercially degradable polymers were studied

using thermogravimetry and differential scanning calorimetry (Day et al., 1998). The

polymers in com. biodegradable plastics include polycaprolactones, polyesters,

polyethylenes, poly(lactic acid), and starch polymers. While the results of the

thermogravimetry expts. suggest that the thermal stability of the polymers should not

pose any problems at the temps. that can be expected in a com. composting process

($60^{o}C$), phase changes associated with some of the polymers studied may cause problems

in the interpretation of data from composting degradation studies. Several biodegradable

polymers were observed to have melt transitions at temperatures similar to those found in a composting environment. Consequently, under the controlled composting conditions used to evaluate biodegradable polymers, degradation of a polymer may be inferred, while actually the polymer has merely undergone a phase change.

2.2.7 Spectroscopic Characterization

Fourier-transform IR spectra of polyethylene film bags were used to monitor the rate and extent of biodegradation of com. products. The products were composites of I with starch film, Ecostar. Biodegradability was tested using the modified Sturm method: the material as a powder suspension is inoculated with biologically sludge, CO_2 evolution is measured periodically for 28-day cycles adjusting pH re-inoculating for each cycle, and data are compared with a paper standard The combination of the Sturm method and the IR spectra allows for systematic analytical control of the test. The combined method is thus highly reliable, to be used by manufacturers to ensure quality and biodegradability claims and by regulatory agencies to establish compatibility with the environment.

Blends, based on waste gelatin (WG) and poly(vinyl alc.) (PVA), formulated for agroindustrial applications (mulching) are investigated (Miertus & Chiellini, 2002). Characterization of the belnds by thermogravimetry (TG) and differential scanning calorimetry (DSC) is reported. The results obtained are compared with those of analogous blends based on "virgin" gelatin (VG). Whereas these last tended to phase segregate, the blends based on WG were compatible due to the presence of glycerol in WG and its inherent destructurization caused by former thermal and mechanical treatment.

For the purpose of increasing degradability of polystyrene (PS) and poly(vinyl chloride) (PVC), they were modified by means of introducing 1-5% addition of ketone (acetophenone or benzophenone) (Kaczmarek 2004). The influence of UV radiation on thin films of polymers modified in this way was studied. The changes in chem. structure of PS and PVC were studied using UV-vis and FTIR spectroscopy, the degradation reactions were monitored by determining the average molecular weights and polydispersity by gel chromatog., and the crosslinking reactions were estimated by determining the weight content of insoluble gel. The mechanical properties were studied by using standard tensile testing measurements. It was found that the ketones used, acting as sensitizers and/or initiators, caused some considerable changes of photochemical stability of both polymers. The oxidative photodegradation of PS, carried out in the same conditions and presence of the same quantity of modifying additives, is accelerated by a considerably higher rate in comparison to the analogous processes occurring in PVC. The differences in the course of photochemical processes of both irradiated polymers are related to the different miscibility of components. At the same time the limited efficiency of photocrosslinking and only slight deterioration of mechanical properties in PS with added acetophenone or benzophenone suggest the possibility of using such compounds for the manuf. of plastics degradable in natural environment.

2.2.8 Totally Degradable Plastic Additives (TDPA)

R. Mohee et al (2006) investigated biodegradability of plastic materials under controlled and natural composting environments. They examine the biodegradability of two

different types of plastic, namely Willow Ridge Plastics – PDQ-H additive (Plastic A) and Ecosafe Plastic – TDPA additive (Plastic B) under controlled and natural composting environments. The results obtained from the controlled composting environment showed that the cumulative carbon dioxide evolution for Plastic A was much higher than that for Plastic B. Plastic A therefore showed a higher level of biodegradation in terms of CO_2 evolution than Plastic B.

Billingham reviewed some studies and applications of oxo-biodegradable additives that can be incorporated into conventional hydrocarbon polymers inducing accelerated oxidation on exposure to light or heat (Billingham, 2000). The effects of TDPA formulations (TDPA: totally degradable plastic additive) on mechanical properties and degradation behavior of polyolefins are discussed.

CHAPTER THREE

OBJECTIVE

The objective of this dissertation is to develop and investigate the degradability of environmentally degradable plastic bags. The specific objectives are:

(1) To study the influence of adding starch and photodegradation additives to film grade polyethylene under the natural weathering conditions in Saudi Arabia.

(2) To determine the time required to convert the material into gases or low molecular weight hydrocarbons.

3) To find out the optimum formulation for commercial production.

4) Economic feasibility study for commercial production of environmentally degradable plastic bags.

CHAPTER FOUR

4 WORK PLAN

To achieve the objectives, the work was carried out in the following groups of activities:

4.1 Materials

Materials utilized in this investigation include film grade low density polyethylene obtained from SABIC, Saudi Arabia, and were used without any purification. Biodegradation will be enhanced by blending with starch or modified starch products. The samples for tests were prepared using the following additives that enhance photo-degradation and biodegradation, supplied by Willow Ridge Co., USA., in their received form:

PDQ-H, Polystarch N and Polystarch Plus H.

4.1.1 PDQ-H

A non-starch based additive. This additive uses photo (UV) and oxidative methods to reduce the molecular weight of the plastic. After the molecular weight is reduced to a certain level, the biological process begins. The end product manufactured with this additive will be clear. The recommended loading of this additive is 1-3% by weight, depending on the end product requirements. This additive when used with PP and PE, has been tested and found to be acceptable for food contact applications.

Figure 1 PDQ-H, non-starch based additive

4.1.1.2 Advantages to Using PDQ-H

Using PDQ-H can make clear film. Moisture is not a problem because it contains no starch. Degradation can be made fast or slow by adjusting the percentage of additive. This product is a Masterbatch additive to be used with your PE or PP. UV-H has many of the above capabilities, but utilize ultra violet rays for degradation.

This additive is not made with cornstarch. It is made with proprietary ingredients to disintegrate plastic by oxo-bio degradation oxidation and photodegradation.

4.1.2 Polystarch N

For making degradable film which require no additional prodegradants. "N" stands for nothing added. Mix ratio 25% POLYSTARCH N • 75% PE Printing Use water base solution result Degradation by bacteria only.

4.1.2.1 Properties of Starch

Starch is a complex carbohydrate which is insoluble in water, it is used by plants as a way to store excess glucose. Starch (in particular cornstarch) is used in cooking for thickening

sauces. In industry, it is used in the manufacture of adhesives, paper, and textiles. It is a white powder, and is tasteless and odorless.

Biochemically, starch is a combination of two polymeric carbohydrates (polysaccharides) called amylose and amylopectin. Amylose is constituted by glucose monomer units joined to one another head-to-tail forming alpha-1,4 linkages. Amylopectin differs from amylose in that branching occurs, with an alpha-1,6 linkage every 24-30 glucose monomer units. The overall structure of amylopectin is not that of a linear polysaccharide chain since two glucose units frequently form a branch point, so the result is the coiled molecule most suitable for storage in starch grains. Both amylopectin and amylose are polymers of glucose, and a typical starch polymer chain consists of around 2500 glucose molecules in their varied forms of polymerisation. In general, starches have the formula $(C_6H_{10}O_5)_n$, where "n" denotes the total number of glucose monomer units.

Structurally, the starch forms clusters of linked linear polymers, where the alpha-1,4 linked chains form columns of glucose units which branch regularly at the alpha-1,6 links. The relative content of amylose and amylopectin varies between species, and between different cultivars of the same species. For example, high-amylose corn (maize) has starch consisting of about 85% amylose, which is the linear constituent of starch, while waxy corn starch is more than 99% amylopectin, or branched starch. The primary function of starch in plants, is to act as an energy storage molecule for the organism. In plants simple sugars are linked into starch molecules by specialized cellular organs called amyloplasts.

Starches are insoluble in water. They can be digested by hydrolysis, catalyzed by enzymes called amylases, which can break the glycosidic bonds between the 'alpha-

glucose' components of the starch polysaccharide. Humans and other animals have amylases, so they can digest starch. Digestion of starches consists of the process of the cleavage of the starch molecules back into their constituent simple sugar units by the action of the amylases. The resulting sugars are then processed by further enzymes (such as maltase) in the body, in the same manner as other sugars in the diet.

Starch is often found in the fruit, seeds, rhizomes or tubers of plants. The four major resources for starch production and consumption in the USA are corn, potatoes, rice, and wheat. Pasta is an important dietary source of starch which is commonly prepared from wheat, rice or beans. Bread is another important source of starch and is commonly prepared from wheat.

As an additive for food processing, arrowroot, guar gum, locust bean, and tapioca are commonly used as well. Commonly used starches around the world are: arracacha, buckwheat, banana, barley, cassava, konjac, kudzu, oca, sago, sorghum, sweet potato, taro and yams. Edible beans, such as favas, lentils and peas, are also rich in starch.

When starch is used in cooking it is normally prepared with ingredients such as lemon, tomato, vinegar, hot pepper, onion or garlic to change its characteristic 'starchiness.' An example of this would be the use of ketchup or vinegar in the presentation of french fries or chips.

When a starch is pre-cooked it can then be used to thicken chilled foods. This is referred to on packaging as modified food starch. Agar, carrageenan, gelatins and pectins are used in very much the same way.

4.1.2.2 Physical Properties of Starch

Table 1 Properties of Starch

Properties	
Molecular formula	$(C_6H_{10}O_5)_n$
Appearance	white powder
Density	1.5 g/cm3
Melting point	decomp.
Solubility in water	None
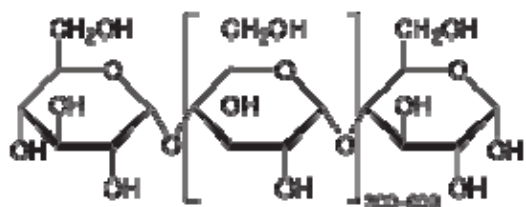
Figure 2 Structure of the amylose molecule.
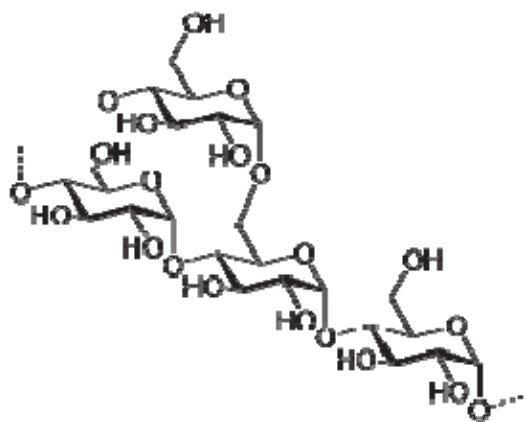
Figure 3 Structure of the amylopectin molecule.

Starch or amylum is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. This polysaccharide is produced by all green plants as an

energy store. It is the most important carbohydrate in the human diet and is contained in such staple foods as potatoes, wheat, maize (corn), rice, and cassava.

Pure starch is a white, tasteless and odorless powder that is insoluble in cold water or alcohol. It consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin.[Brown and Poon 2005] Glycogen, the glucose store of animals, is a more branched version of amylopectin.

Starch is processed to produce many of the sugars in processed foods. When dissolved in warm water, it can be used as a thickening, stiffening or gluing agent, giving wheatpaste.

The word "starch" is derived from Middle English sterchen, meaning to stiffen. "Amylum" is Latin for starch, from the Greek "amulon" which means "not ground at a mill". The root amyl is used in biochemistry for several compounds related to starch.

In photosynthesis, plants use light energy to produce glucose from carbon dioxide. The glucose is stored mainly in the form of starch granules, in plastids such as chloroplasts and especially amyloplasts. Toward the end of the growing season, starch accumulates in twigs of trees near the buds. Fruit, seeds, rhizomes, and tubers store starch to prepare for the next growing season.

Glucose is soluble in water, hydrophilic, binds much water and then takes up much space; glucose in the form of starch, on the other hand, is not soluble and can be stored much more compactly.

Since starch is a reserve sugar for the plant, glucose molecules are bound in starch by the easily hydrolyzed alpha bonds. The same type of bond can also be seen in the animal reserve polysaccharide glycogen. This is in contrast to many structural polysaccharides

such as chitin, cellulose and peptidoglycan, which are bound by beta-ties and are much more resistant to hydrolysis.

Starch molecules arrange themselves in the plant in semi-crystalline granules. Each plant species has a unique starch granular size: rice starch is relatively small (about 2μm) while potato starches have larger granules (up to 100μm). Although in absolute mass only about one quarter of the starch granules in plants consist of amylose, there are about 150 times more amylose molecules than amylopectin molecules. Amylose is a much smaller molecule than amylopectin.

Starch becomes soluble in water when heated. The granules swell and burst, the semi-crystalline structure is lost and the smaller amylose molecules start leaching out of the granule, forming a network that holds water and increasing the mixture's viscosity. This process is called starch gelatinization. During cooking the starch becomes a paste and increases further in viscosity. During cooling or prolonged storage of the paste, the semi-crystalline structure partially recovers and the starch paste thickens, expelling water. This is mainly caused by the retrogradation of the amylose. This process is responsible for the hardening of bread or staling, and for the water layer on top of a starch gel (syneresis).

Some cultivated plant varieties have pure amylopectin starch without amylose, known as waxy starches. The most used is waxy maize, others are glutinous rice, waxy potato starch. Waxy starches have less retrogradation, resulting in a more stable paste. High amylose starch, amylomaize, is cultivated for the use of its gel strength.

The enzymes that break down or hydrolyze starch into the constituent sugars are known as amylases.

Alpha-amylases are found in plants and in animals. Human saliva is rich in amylase, and the pancreas also secretes the enzyme. Individuals from populations with a high-starch diet tend to have more amylase genes than those with low-starch diets; chimpanzees have very few amylase genes. It is possible that turning to a high-starch diet was a significant event in human evolution.[Myers 2008]

Beta-amylase cuts starch into maltose units. This process is important in the digestion of starch and is also used in brewing, where the amylase from the skin of the seed grains is responsible for converting starch to maltose (Malting, Mashing).

If starch is subjected to dry heat, it breaks down to form pyrodextrins, in a process known as dextrinization. Pyrodextrins are brown in color. This process is partially responsible for the browning of toasted bread.

4.1.3 Polystarch Plus H

A composite of LLDPE and food grade corn Starch. UV and oxidative prodegradants are added to enhance the degradation process. This additive uses photo (UV), and oxidative methods to reduce the molecular weight of the plastic. After the molecular weight is reduced to a certain level the biological degradation process begins. The end product manufactured with this additive will be clear. The recommended loading of this additive is 10-25% by weight, depending on the end product requirements.

Figure 4 Polystarch Plus H, starch based additive

Polystarch Additives are hygroscopic materials and will absorb moisture from the atmosphere when opened. This product can be handled in conventional resin conveying and feeding systems. Adequate filters for the removal of fines and dust present in all resins should be used. Equipment should be properly maintained to prevent leaks, and adequately grounded at all times. Good housekeeping practices should be followed at all times.

4.1.4.1 Polyethylene
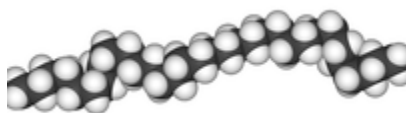
Figure 5 Space-filling model of a polyethylene chain.
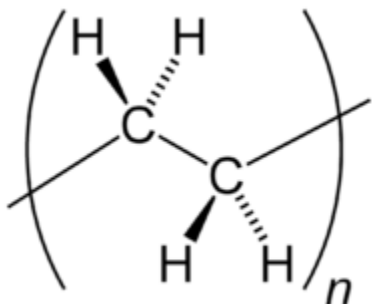
Figure 6 The repeating unit of polyethylene, showing its stereochemistry.
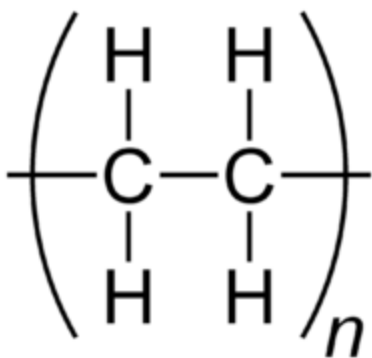
Figure 7 A simpler way of representing the repeating unit. Note, however, that the C−H bond angles are not 90° as this diagram would indicate, but are approximately 110°, since each carbon atom is tetrahedral (sp3).

Polyethylene or polythene (IUPAC name polyethene or poly(methylene)) is the most widely used plastic, with an annual production of approximately 80 million metric tons.[Piringer and Baner 2008] Its primary use is within packaging (notably the plastic shopping bag).

Polyethylene is a thermoplastic polymer consisting of long chains of the monomer ethylene (IUPAC name ethene). The recommended scientific name polyethene is systematically derived from the scientific name of the monomer.[Blackwell 1993] [Kahovec et al 2002].

In certain circumstances it is useful to use a structure-based nomenclature; in such cases IUPAC recommends poly(methylene) (poly(methanediyl) is an non-preferred alternative [Henri and Powell 2005]. The difference in names between the two systems is due to the opening up of the monomer's double bond upon polymerisation.

The name is abbreviated to PE in a manner similar to that by which other polymers like polypropylene and polystyrene are shortened to PP and PS respectively. In the United Kingdom the polymer is commonly called polythene, although this is not recognized scientifically.

The ethene molecule (known almost universally by its common name ethylene) C_2H_4 is $CH_2=CH_2$, Two CH_2 groups connected by a double bond, thus:
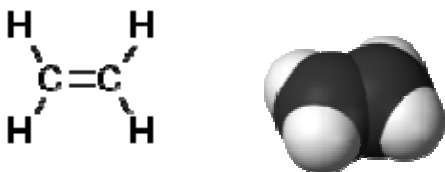
Figure 8 Polyethylene contains the chemical elements carbon and hydrogen.

Polyethylene is created through polymerization of ethene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization. This is because ethene does not have any substituent groups that influence the stability of the propagation head of the polymer. Each of these methods results in a different type of polyethylene.

4.1.4.2 Classification of Polyethylene

Polyethylene is classified into several different categories based mostly on its density and branching. The mechanical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight.

Ultra high molecular weight polyethylene (UHMWPE)

Ultra low molecular weight polyethylene (ULMWPE or PE-WAX)

High molecular weight polyethylene (HMWPE)

High density polyethylene (HDPE)

High density cross-linked polyethylene (HDXLPE)

Cross-linked polyethylene (PEX or XLPE)

Medium density polyethylene (MDPE)

Linear low density polyethylene (LLDPE)

Low density polyethylene (LDPE)

Very low density polyethylene (VLDPE)

UHMWPE is polyethylene with a molecular weight numbering in the millions, usually between 3.1 and 5.67 million. The high molecular weight makes it a very tough material, but results in less efficient packing of the chains into the crystal structure as evidenced by densities of less than high density polyethylene (for example, 0.930–0.935 g/cm3). UHMWPE can be made through any catalyst technology, although Ziegler catalysts are most common. Because of its outstanding toughness and its cut, wear and excellent chemical resistance, UHMWPE is used in a diverse range of applications. These include can and bottle handling machine parts, moving parts on weaving machines, bearings, gears, artificial joints, edge protection on ice rinks and butchers' chopping boards. It

competes with Aramid in bulletproof vests, under the tradenames Spectra and Dyneema, and is commonly used for the construction of articular portions of implants used for hip and knee replacements.

HDPE is defined by a density of greater or equal to 0.941 g/cm3. HDPE has a low degree of branching and thus stronger intermolecular forces and tensile strength. HDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. The lack of branching is ensured by an appropriate choice of catalyst (for example, chromium catalysts or Ziegler-Natta catalysts) and reaction conditions. HDPE is used in products and packaging such as milk jugs, detergent bottles, margarine tubs, garbage containers and water pipes.

PEX is a medium- to high-density polyethylene containing cross-link bonds introduced into the polymer structure, changing the thermoplast into an elastomer. The high-temperature properties of the polymer are improved, its flow is reduced and its chemical resistance is enhanced. PEX is used in some potable-water plumbing systems because tubes made of the material can be expanded to fit over a metal nipple and it will slowly return to its original shape, forming a permanent, water-tight, connection.

MDPE is defined by a density range of 0.926–0.940 g/cm3. MDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. MDPE has good shock and drop resistance properties. It also is less notch sensitive than HDPE, stress cracking resistance is better than HDPE. MDPE is typically used in gas pipes and fittings, sacks, shrink film, packaging film, carrier bags and screw closures.

LLDPE is defined by a density range of 0.915–0.925 g/cm3. LLDPE is a substantially linear polymer with significant numbers of short branches, commonly made by

copolymerization of ethylene with short-chain alpha-olefins (for example, 1-butene, 1-hexene and 1-octene). LLDPE has higher tensile strength than LDPE, it exhibits higher impact and puncture resistance than LDPE. Lower thickness (gauge) films can be blown, compared with LDPE, with better environmental stress cracking resistance but is not as easy to process. LLDPE is used in packaging, particularly film for bags and sheets. Lower thickness may be used compared to LDPE. Cable covering, toys, lids, buckets, containers and pipe. While other applications are available, LLDPE is used predominantly in film applications due to its toughness, flexibility and relative transparency.

LDPE is defined by a density range of 0.910–0.940 g/cm3. LDPE has a high degree of short and long chain branching, which means that the chains do not pack into the crystal structure as well. It has, therefore, less strong intermolecular forces as the instantaneous-dipole induced-dipole attraction is less. This results in a lower tensile strength and increased ductility. LDPE is created by free radical polymerization. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap.

VLDPE is defined by a density range of 0.880–0.915 g/cm3. VLDPE is a substantially linear polymer with high levels of short-chain branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins (for example, 1-butene, 1-hexene and 1-octene). VLDPE is most commonly produced using metallocene catalysts due to the greater co-monomer incorporation exhibited by these catalysts. VLDPEs are

used for hose and tubing, ice and frozen food bags, food packaging and stretch wrap as well as impact modifiers when blended with other polymers.

Recently much research activity has focused on the nature and distribution of long chain branches in polyethylene. In HDPE a relatively small number of these branches, perhaps 1 in 100 or 1,000 branches per backbone carbon, can significantly affect the rheological properties of the polymer.

4.1.4.3 Physical properties

Depending on the crystallinity and molecular weight, a melting point and glass transition may or may not be observable. The temperature at which these occur varies strongly with the type of polyethylene. For common commercial grades of medium- and high-density polyethylene the melting point is typically in the range 120 to 130 °C (248 to 266 °F). The melting point for average, commercial, low-density polyethylene is typically 105 to 115 °C (221 to 239 °F).

Most LDPE, MDPE and HDPE grades have excellent chemical resistance and do not dissolve at room temperature because of their crystallinity. Polyethylene (other than cross-linked polyethylene) usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene, or in chlorinated solvents such as trichloroethane or trichlorobenzene.

4.2 Sample Preparation

Plastic films were prepared by first premixing the film grade polyethylene pellets with different amounts of additives. Additive loadings were 10, 20, 30, 40 and 50 percent mixed with pure polyethylene. Subsequently, the mixer was placed between the plates of a manually operated CARVER PRESS to produce the film.


Figure 9 Manually operated CARVER PRESS

4.3.1 Outdoor Degradation Studies

The degradability of the films in outdoor environment was determined in this study. The films were exposed in outdoor environments at the exposure site located in Dhahran, Saudi Arabia. The films were exposed for one year and samples were drawn at regular intervals and evaluated for degradation. Figure 2 shows the photograph of the films at the time of exposure and Figure 3 show the photographs of sample taken after 9 months.

Figure 10 Exposing plastic samples in natural weathering condition. Films are fixed on plexy glasses and oriented in a steel rack at 45 degree angle with the basement and facing to east so that maximum amount of sunlight fall on the film in all time.
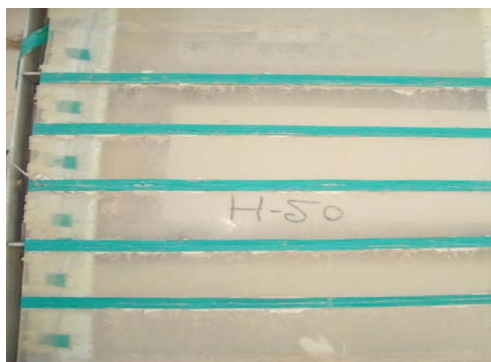
Figure 11 Photographs of sample containing 50 percent Polystarch-plus-H additive. It was taken after 9 months which shows that all the exposed parts were severely degraded

and were taken away by air. Only small amount of sample which are attached by the tapes are left.

4.3.2 Climatic Conditions

Location: RIYADH : {N 24° 42'} {E 46° 47'} {GMT +3.0 Hours}

 Elevation --   612m above sea level

 Standard Pressure at Elevation -- 94186Pa

 Data Source**:** http://www.climate-charts.com/Locations/s/SD40438.php

In general conditions in Riyadh are dry and hot, but the city does receive about four inches (102mm) of rain a year, most of it falling between January and May. In summer hot winds can send temperatures soaring up to 113F (45C). In winter it can be surprisingly chilly, however, particularly at night when the thermometer can plunge below freezing. The best months in Riyadh, when days are pleasantly tolerable and nights are cool, are between October and May.

Table 2 Annual Climatic Condition of Riyad

Statistic	Units	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Average
Temperature Mean Value	C	14.0	16.4	21.1	25.7	31.5	34.2	35.0	35.1	31.9	26.8	20.7	15.4	25.65
High Temperature Mean Daily Value	C	20.2	22.9	27.6	32.3	38.7	41.5	42.8	42.5	40.1	34.6	27.4	21.7	32.69
Low Temperature Mean Daily Value	C	8.2	10.3	14.4	18.9	24.2	26.2	27.4	27.0	24.1	19.2	14.3	9.4	18.63
Precipitation Mean Monthly Value	mm	11.3	10.1	24.0	29.4	7.8	.1	.4	.6	.1	1.2	5.6	10.7	8.44
Snowfall Mean Monthly Value	cm	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	0.00
Relative Humidity Mean Value	%	50	40	35	33	22	14	15	14	18	24	37	46	29.00
Relative Humidity Mean Daily Maximum Value	%	100	100	100	100	98	63	80	77	94	98	100	100	92.50
Relative Humidity Mean Daily Minimum Value	%	7	0	3	1	1	1	2	2	2	3	2	4	2.33

4.4 Biodegradability Study

The biodegradability of the degradable polymeric materials were carried out in cylindrical glass vessels of 1000 ml capacity containing a 20g of sandy soil.

Figure 12 Biodegradation set-up

Soil collected from KFUPM date palm garden were sieved at 0.6 mm and mixed with 20g perlite and 25 ml of 0.1% (NH4)2HPO4 solution. The polymer sample were kept between two layers of 10g perlite mixed with 30 ml distilled water. The vessels were kept in the dark at room temperature. Each vessel was equipped with a beaker containing 50 ml of 0.05 N KOH solution. The solution was taken out of the vassel after 30 days and titrated with 0.1 N HCl by using phenolphthalein as an indicator to estimate the CO_2

content evolved from the polymeric sample. The percentage biodegradation was calculated from the CO_2 production on the basis of the determined carbon content of the samples.

CHAPT FIVE

5   SAMPLE ANALYSIS

5.1.1 Morphological: Scanning electron microscopy (SEM)

The morphology of the blends retrieved from degradation experiments was investigated by studying the fractured surfaces using Scanning Electron Microscope (Model: JEOL JSM 5800LV). Samples were coated with a thin layer of Carbon using a Carbon Evaporator in order to avoid sample charging during imaging. The imaging was performed at varying magnifications in a secondary electron mode using an accelerating voltage of 10kV. The chemical composition of samples was analyzed using an energy dispersive X-ray spectrometer fitted with an ultra-thin Be window.

Figure 13 Scanning Electron Microscopy

Figure 14 SEM opened sample chamber

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more

than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally-assisted Schottky type, using emitters of zirconium oxide.

The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron

column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronised with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disc.

5.1.2 Magnification

Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Unlike optical and transmission electron microscopes,

image magnification in the SEM is not a function of the power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Provided the electron gun can generate a beam with sufficiently small diameter, a SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution. In a SEM, as in scanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power.

5.1.3 Sample preparation

All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of SEM can examine any part of a 6-inch (15 cm) semiconductor wafer, and some can tilt an object of that size to 45°.

For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated

with an ultrathin coating of electrically-conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Conductive materials in current use for specimen coating include gold, gold/palladium alloy, platinum, osmium,[5] iridium, tungsten, chromium and graphite. Coating prevents the accumulation of static electric charge on the specimen during electron irradiation.

Two reasons for coating, even when there is enough specimen conductivity to prevent charging, are to increase signal and surface resolution, especially with samples of low atomic number (Z). The improvement in resolution arises because backscattering and secondary electron emission near the surface are enhanced and thus an image of the surface is formed.

5.2 Spectroscopic Characterization

Original and degraded polymeric materials, as well as the relevant extractable fractions were characterized by FTIR. Carbonyl and double bond indexes will be calculated on the basis of the relative intensities of the carbonyl band at 1715 cm^{-1} and the double-bond band at 1650 cm^{-1} to that of methylene scissoring band at 1465 cm^{-1}, respectively.

IR Spectra were recorded on a NicoletTM 6700 FT-IR spectrometer from a thermo-electron by using a smart orbit for net samples. The results were reported in wave numbers (cm-1) (Spectral resolution, 4 cm-1; Number of scans, 4).

Figure 15 Nicolettm 6700 FT-IR Spectrometer

A beam of infrared light is produced and split into two separate beams. One is passed through the sample, the other passed through a reference which is often the substance the sample is dissolved in. The beams are both reflected back towards a detector, however first they pass through a splitter which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained.

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint".

FTIR is a failure analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. It is used in failure

analysis to identify unknown materials present in a specimen, and is usually conducted to complement EDX analysis.

The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials in the FTIR library.

Unlike SEM inspection or EDX analysis, FTIR spectroscopy does not require a vacuum, since neither oxygen nor nitrogen absorb infrared rays. FTIR analysis can be applied to minute quantities of materials, whether solid, liquid , or gaseous. When the library of FTIR spectral patterns does not provide an acceptable match, individual peaks in the FTIR plot may be used to yield partial information about the specimen.

Single fibers or particles are sufficient enough for material identification through FTIR analysis. Organic contaminants in solvents may also be analyzed by first separating the mixture into its components by gas chromatography, and then analyzing each component by FTIR.

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR

instruments are computerized which makes them faster and more sensitive than the older dispersive instruments.

5.2.1 Qualitative Analysis

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum.

By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. We have several infrared spectral libraries including on-line computer libraries. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by

the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E0) and the first excited state (E1)].

The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum.

Difference in Energy States= Energy of Light Absorbed

E1 - E0= h c / l

Where   h=Planks constant

             C=speed of light, and

             L=the wavelength of light.

5.2.2 Sample Preparation

Samples for FTIR can be prepared in a number of ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt). Salt is transparent to infrared light. The drop forms a thin film between the plates. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a cast film, and is frequently used for polymer identification.

Solutions can also be analyzed in a liquid cell. This is a small container made from NaCl (or other IR-transparent material) which can be filled with liquid, such as the extract for

EPA 418.1 analysis. This creates a longer path length for the sample, which leads to increased sensitivity. Sampling methods include making a mull of a powder with a hydrocarbon oil (Nujol) or pyrolyzing insoluble polymers and using the distilled pyrolyzate to cast a film. Matrials can be placed in an Attenuated Total Reflectance (ATR) cell and gases in gas cells.

Table 3 Characteristic IR Band Positions

Group	Frequency Range (cm-1)
OH stretching vibrations	
Free OH	3610-3645 (sharp)
Intramolecular H bonds	3450-3600 (sharp)
Intermolecular H Bonds	3200-3550 (broad)
Chelate Compounds	2500-3200 (very broad)
NH Stretching vibrations	
Free NH	3300-3500
H bonded NH	3070-3350
CH Stretching vibrations	
=-C-H	3280-3340
=C-H	3000-3100

C-CH3	2862-2882, 2652-2972
O-CH3	2815-2832
N-CH3 (aromatic)	2810-2820
N-CH3 (aliphatic)	2780-2805
CH2	2843-2863,2916-2936
CH	2880-2900
SH Stretching Vibrations	
Free SH	2550-2600
C=-N Stretching Vibrations	
Nonconjugated	2240-2260
Conjugated	2215-2240
C=-C Stretching Vibrations	
C=-CH (terminal)	2100-2140
C-C=-C-C	2190-2260
C-C=-C-C=-CH	2040-2200
C=O Stretching Vibrations	
Nonconjugated	1700-1900

Conjugated	1590-1750
Amides	~1650
C=C Sretching Vibrations	
Nonconjugated	1620-1680
Conjugated	1585-1625
CH Bending Vibrations	
CH2	1405-1465
CH3	1355-1395, 1430-1470
C-O-C Vibrations in Esters	
Formates	~1175
Acetates	~1240, 1010-1040
Benzoates	~1275
C-OH Stretching Vibrations	
Secondary Cyclic Alcohols	990-1060
CH out-of-plane bending vibrations in substituted ethylenic systems	

-CH=CH2	905-915, 985-995
-CH=CH-(cis)	650-750
-CH=CH-(trans)	960-970
C=CH2	885-895

5.3 Differential Scanning Calorimetry

Cooling curves of polymer/fiber/processing aid mixtures will provide a measure of the crystallinity and relative molecular weight of the degradable polymer blend. Differential scanning calorimetry (DSC) will be used to quantify the extent of miscibility of the polymers with the additives. DSC analysis will be performed by utilizing a differential scanning calorimeter (TA dynamic DSC).

Figure 16 Differential Scanning Calorimetry

5.4 GPC Analysis

Gel permeation chromatography (GPC) is a term used for when the separation technique size exclusion chromatography (SEC), that separates analytes on the basis of size, is applied to polymers in particular. As a technique, SEC was first developed in 1955 by Lathe and Ruthven.[Lathe and Ruthven 1956] The term gel permeation chromatography can be traced back to J.C. Moore of the Dow Chemical Company who investigated the technique in 1964.[Moore 1964] While polymers can be synthesized in a variety of ways, it is often necessary to separate polymers, both to analyze them as well as to purify the desired product.

When characterizing polymers, it is important to consider the polydispersity index (PDI) as well the molecular weight. Polymers can be characterized by a variety of definitions for molecular weight including the number average molecular weight (Mn), the weight average molecular weight (Mw) (see molar mass distribution), the size average molecular weight (Mz), or the viscosity molecular weight (Mv). GPC allows for the determination of PDI as well as Mv and based on other data, the Mn, Mw, and Mz can be determined. GPC separates based on the size or hydrodynamic volume (radius of gyration) of the analytes. This differs from other separation techniques which depend upon chemical or physical interactions to separate analytes. [Skoog 2006] Separation occurs via the use of porous beads packed in a column (see stationary phase (chemistry)).
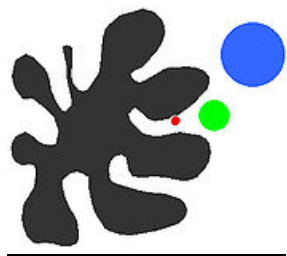
Figure 17 Schematic of pore vs. analyte size

The smaller analytes can enter the pores more easily and therefore spend more time in these pores, increasing their retention time. Conversely, larger analytes spend little if any time in the pores and are eluted quickly. All columns have a range of molecular weights that can be separated.

If an analyte is either too large or too small it will be either not retained or completely retained respectively. Analytes that are not retained are eluted with the free volume outside of the particles (Vo), while analytes that are completely retained are eluted with volume of solvent held in the pores (Vi). The total volume can be considered by the following equation, where Vg is the volume of the polymer gel and Vt is the total volume: $Vt = Vg + Vi + Vo$

As can be inferred, there is a limited range of molecular weights that can be separated by each column and therefore the size of the pores for the packing should be chosen according to the range of molecular weight of analytes to be separated. For polymer separations the pore sizes should be on the order of the polymers being analyzed. If a sample has a broad molecular weight range it may be necessary to use several GPC columns in tandem with one another to fully resolve the sample.

GPC is often used to determined the relative molecular weight of polymer samples as well as the distribution of molecular weights. What GPC truly measures is the molecular volume and shape function as defined by the intrinsic viscosity. If comparable standards are used, this relative data can be used to determine molecular weights within ± 5% accuracy. Polystyrene standards with PDI of less than 1.2 are typically used to calibrate the GPC. [Sandler 1998] Unfortunately, polystyrene tends to be a very linear polymer

and therefore as a standard it is only useful to compare it to other polymers that are known to be linear and of relatively the same size.

Figure 18 The inside of sample holder of Waters GPC instrument

Gel permeation chromatography is conducted almost exclusively in chromatography columns. The experimental design is not much different from other techniques of liquid chromatography. Samples are dissolved in an appropriate solvent, in the case of GPC these tend to be organic solvents and after filtering the solution it is injected onto a column. A Waters GPC instrument is shown above. The separation of multi-component mixture takes place in the column. The constant supply of fresh eluent to the column is accomplished by the use of a pump. Since most analytes are not visible to the naked eye a detector is needed. Often multiple detectors are used to gain additional information about the polymer sample. The availability of a detector makes the fractionation convenient and accurate.

5.4.1 Gel

Gels are used as stationary phase for GPC. The pore size of a gel must be carefully controlled in order to be able to apply the gel to a given separation. Other desirable

properties of the gel forming agent are the absence of ionizing groups and, in a given solvent, low affinity for the substances to be separated. Commercial gels like Sephadex, Bio-Gel (cross-linked polyacrylamide), agarose gel and Styragel are often used based on different separation requirements. [Helmut 1969]

5.4.2 Eluent

The eluent (mobile phase) should be a good solvent for the polymer, should permit high detector response from the polymer and should wet the packing surface. The most common eluents in for polymers that dissolve at room temperature GPC are tetrahydrofuran (THF), o-dichlorobenzene and trichlorobenzene at 130–150 °C for crystalline polyalkines and m-cresol and o-chlorophenol at 90 °C for crystalline condensation polymers such as polyamides and polyesters.

5.4.3 Detector

In GPC, the concentration by weight of polymer in the eluting solvent may be monitored continuously with a detector. There are many detector types available and they can be divided into two main categories. The first is concentration sensitive detectors which includes UV absorption , differential refractometer (DRI) or refractive index (RI) detectors, infrared (IR) absorption and density detectors. Molecular weight sensitive detectors include low angle light scattering detectors (LALLS), multi angle light scattering (MALLS).[Trathnigg 1995] The resulting chromatogram is therefore a weight distribution of the polymer as a function of retention volume.

The most sensitive detector is the differential UV photometer and the most common detector is the differential refractometer (DRI). When characterizing copolymer, it is necessary to have two detectors in series. For accurate determinations of copolymer composition at least two of those detectors should be concentration detectors. The determination of most copolymer compositions is done using UV and RI detectors, although other combinations can be used. [Pasch 2000]

5.4.4 Sample Analysis by GPC

The molecular weight and molecular weight distribution of the polyolefin films were determined as a function of thermal, photo and biodegradation time. Samples withdrawn in the degradation tests were characterized using a high temperature GPC. Two mixed bed columns (Plgel 10 micron, Polymer laboratories) were used at 150 C. sample solution of 0.100 % by weight was prepared. The resulting solution (200 micro liter) was stabilized, dissolved in TCB and injected at 145 ^{o}C. The GPC is equipped with four detectors: RI, viscosity, static and dynamic light scattering. Broad molecular weight distribution PE and narrow molecular weight distribution polystyrene samples will be used as reference materials. The total run time was 30 minutes.

Figure 19 Waters Alliance GPC 2000 system

5.4.5 Calibration of GPC

The chromatogram data were acquired and analyzed using millenium32 software. The instrument was calibrated using narrow molecular weight polystyrene standards. The polystyrene based calibration curve was converted to universal calibration curve using the Mark Houwink constants (K and alpha values) of polystyrene and polyethylene.

Table 4 Mark Houwink constants of polystyrene and polyethylene.

Polymer	K	Alpha
Polystyrene	0.000121	0.707
Polyethylene	0.000406	0.725

5.5 Mechanical Strength Measurement

Mechanical strength of the polymer film was measured by Instron 5560 Tensile Testing Machine.

Figure 20 Instron 5560 Tensile Testing Machine

Film thickness was 1 mm, width 3.14 mm and length of each specimen was 19 mm.

Figure 21 Measuring Stess-strain of plastic sample.

CHAPTER SIX

6 RESULTS & DISCUSSION

6.1 Tensile Properties

The stress-strain curves for the LLDPE and its blends as a function of Polystarch N is given in the Figure 22.
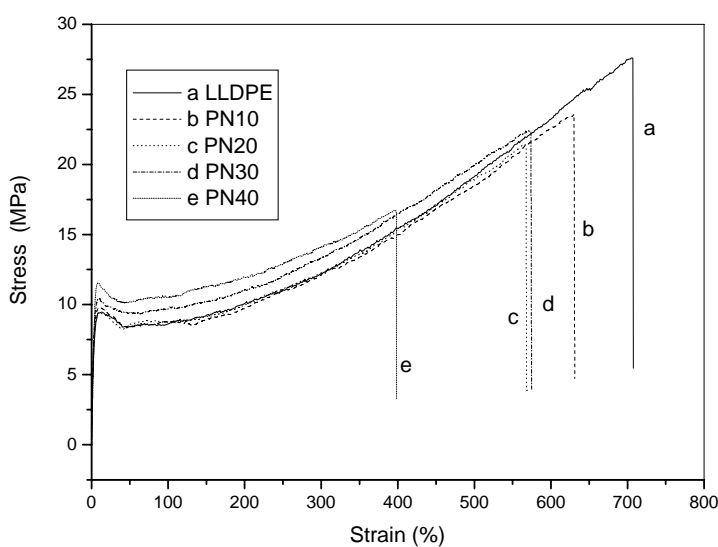
Figure 22: Stress strain curves for the LLDPE-Polystarch N blends

Here it can be seen that incorporation of polystarch N to the matrix generally decreases the percentage of elongation. The maximum decrease is for the blend having 40% w/w polystarch N. This indicates that addition of polystarch N to matrix decreases its ductile nature. Tensile, Young's modulus and percentage of elongation for the various compositions is given in Table 5.

Table 5: Mechanical properties of LLDPE-Polystarch N blends

Materials	Tensile Strength (MPa)	Young's modulus (MPa)	Elongation (%)
LLDPE	27.0	143	693
PN10	22.3	167	594
PN20	22.3	165	593
PN30	23.0	161	587
PN40	17.0	187	405

Here as the amount of polystarch N increases the tensile strength of the blend decreases from 27 MPa to 17 MPa. More significant variation was observed for the blends having 40%w/w polystarch N. This is because the additives used during the formulation, Polystarch N contains 25% w/w of corn starch and tensile properties of starch are less when compared to LLDPE. Similar trend was observed for the LDPE/cassava starch blend by Nakamura et al. [Nakamura, 2005]. However it's notable that the Young's modulus increases as a function of the amount of polystarch N, i.e. for blend having 40% w/w (PN40) polystarch N, 30.7% increase was observed when compared to matrix alone. This can be explained by the crystallinity, hydrogen bonding and stiffening effect of the starch present in polystarch N [Chandra, Rustgi 1997]. Young modulus values also show that the matrix became more rigid by the addition of polystarch N.

6.2 Biodegradation Results

Investigation of biodegradation of polymers is a critical functionality for their application. Currently, no official standard method was established in determining biodegradability of polymers. The enzyme method [Tomasi et al 1996], the microbiological method [Benedict et al. 1983] and the soil burial method [Mergaert et al. 1993] have been used by different researchers. The biodegradation method is not suitable for Saudi Arabian sandy desert due to the climatic condition, because throughout the whole year the weather remain dry with very low humidity. Microorganism can not survive long due to extreme hot and harsh weather and give discontinuous and erratic biodegradation results which can not be interpreted with support to other researchers' evidence and that is why we rejected the biodegradation results. Here in this study we performed the natural ageing studies for LLDPE blends which is very suitable for Saudi Arabian harsh climatic condition and also scientific evidences are available to interpret the experimental results.

6.3 SEM analysis

The SEM images for the LLDPE-Polystarch N blend (PN20) taken at different exposure time (0, 50, 95 and 120 days) is presented in figures 23 (a-d). Initially it's clear that there is no crack on the surface of the blend. When the time of exposure increases, degradation of the material starts and gradually the affected area increases. For the material after 50 days of exposure, initiation of cracks and degradation occurs; after 95 days of exposure, degradation propagates rapidly, bigger cracks are shown as white area while some parts

are still unaffected shown as black area and after 120 days of exposure, very big cracks and degradation took place for almost all parts of the blend. This degradation is due to the degradation for the starch as well as for the oxidized the LDPE amorphous regions. Thereby, the surface area of polymer blends increases and this improves oxygen-based reactions that enhances and increases LDPE chain oxidation reaction.
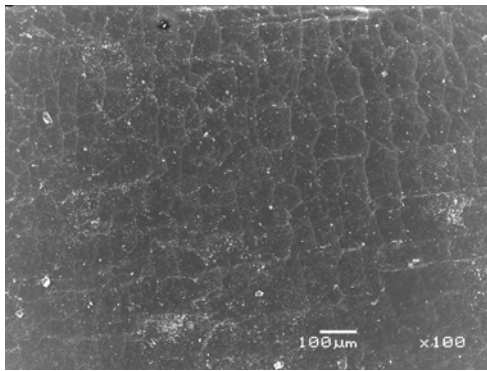
a
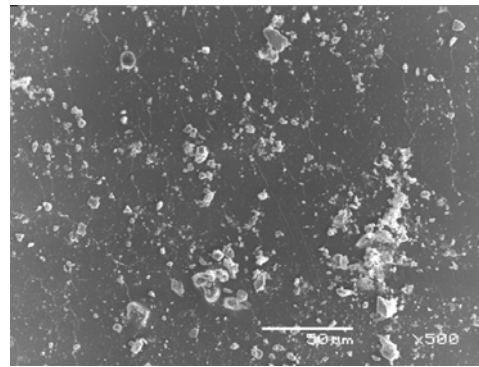
b
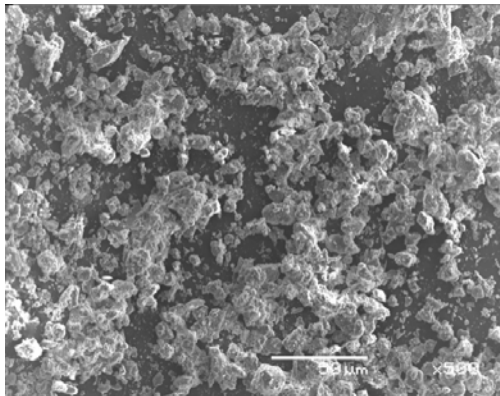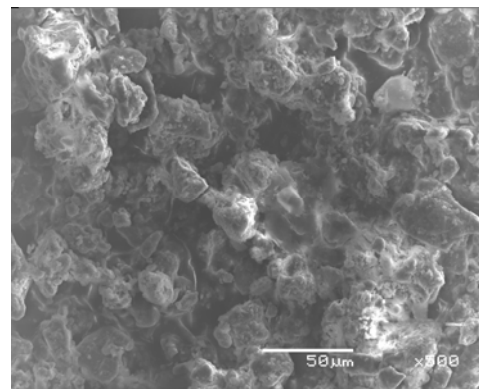
c   d

Figures 23 (a-d): SEM images of PN20 at various interval of time (0, 50, 95 and 120 days)
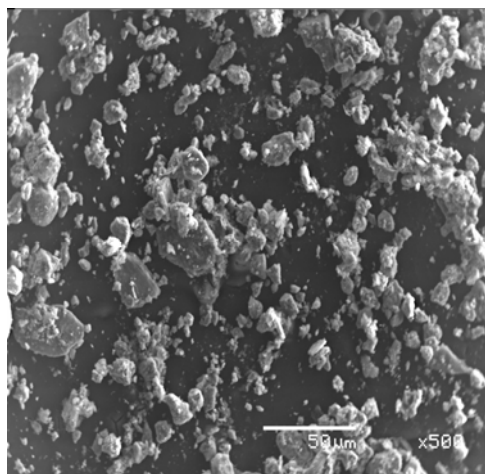
a. PN30
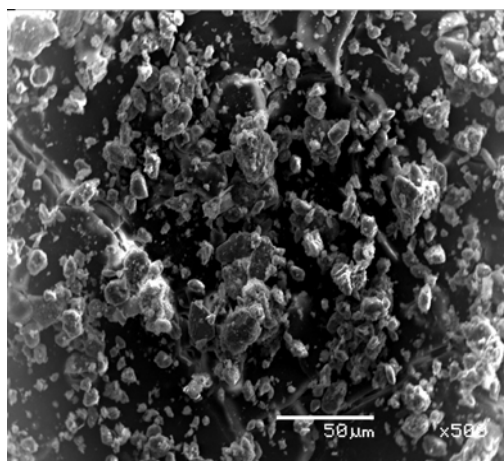
b. PH30
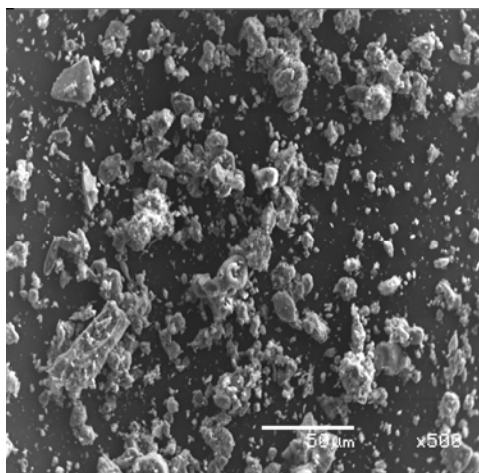
c. PQ30

Figures 24 (a-c) Comparison of the SEM images of degraded LLPDE blends

after 50 days

Figures 24 (a-c) shows the SEM images of the LLDPE blends (PH30, PN30, PQ30) which were taken after 50 days. From this it's clear that when compared to PN30 and PH30, the degradation is higher for the blends containing PDQ-H. This is due to the

variation in the nature of the additives used for this study. Here the polystarch N contains only polyethylene and corn starch, while polystarch H consists of some UV and oxidative prodegradants which increases the degradation rate. However the PDQ-H is a non-starch based additive. This additive enhances more the degradation via photo (UV) and oxidative methods there by a drastic decrease in the molecular weight of the blends.

6.4 GPC analysis

GPC is recognized as a useful aid in the study of polymer degradation of polymer blend or composites. It can provide useful information regarding the mass average molecular weight (M_w), number average molecular weight (M_n) and poly dispersity index (PDI) of the material. If degradation is to take place, then M_w will either increase (chain buildup) or decrease (chain breakdown) and the polydispersity (PDI) will be broadened [Hinsken, Moss 1991] Table 6 gives the variation in the M_n, M_w and PDI of the LLDPE/Polystarch N blend as a function of the ageing time.

Table 6: Variation in the M_n, M_w and PDI of the LLDPE blends as a function of the ageing time

Materials	50 days			150 days			235 days		
	M_n	M_w	PDI	M_n	M_w	PDI	M_n	M_w	PDI
PN20	301	2674	8.88	670	3445	5.14	778	3110	4
PN30	415	3116	7.50	603	2982	4.95	705	3024	4.29
PN40	508	3871	7.64	746	3838	5.14	692	2955	4.27
PH30	166	842	5.08	228	962	4.22	540	1794	3.32
PQ30	434	1703	3.93	220	779	3.55	401	1256	3.13

Here as the time increases the value of M_n and M_w for the LLDPE-blends increases as a function of time, while PDI value decreases irrespective of the additives used. When the amount of polystarch N in LLDPE increases, the M_n and M_w value increases and the PDI value decreases. The lower value for PDI is observed for the blend having 30% w/w of PDQ-H. The degradation of polymers may proceed by one or more mechanisms, including biodegradation, chemical degradation, photo and thermal oxidation depending on the polymer environment and desired application. The combination of different environmental factors such as sunlight, heat, oxygen, humidity and microorganisms has synergistic effects on the degradation rate of starch or photodegradable additives filled LDPE. These factors can trigger autoxidation of chemically unstable pro-oxidants, generating free radicals which attack the molecular structure of the polyethylene. The molecular weight of the polymer chain is reduced until ultimately a level is reached at which consumption by microorganisms can take place at a significant rate.

6.5 Differential Scanning Calorimeter (DSC)

The capability of UV-sunlight irradiation on the plastic to cause changes in some of its measurable physical and chemical properties can be detected by thermal analysis. To determine the morphological and structural changes in the polymers, the change in thermal parameters such as the melting temperature (T_m) and heat of fusion (ΔH_m) of LLDPE and its blends exposed to natural ageing were investigated by DSC. Here the LLDPE which is used as matrix is a semi crystalline polymer with a high degree of crystallinity. By DSC, during heating, this crystallinity is revealed by an endothermic peak of melting at a temperature close to 100°C. The calorimetric cooling and heating curves obtained for four samples (LLDPE, PN20, PN30 and PN40) after ageing of 95 days is given in the figures 25 a and b.

a.
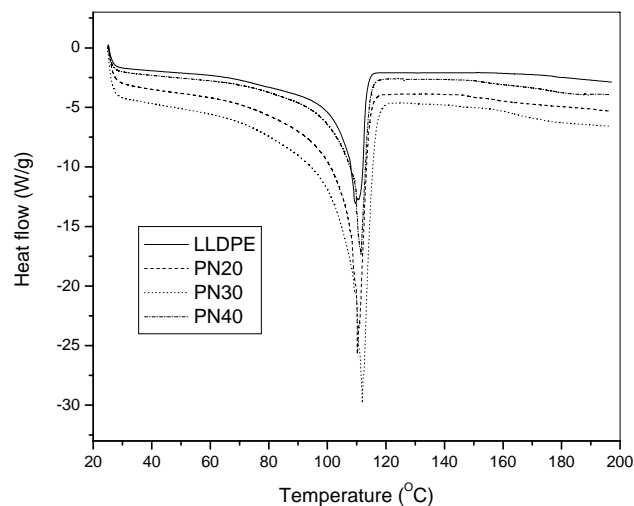
b.
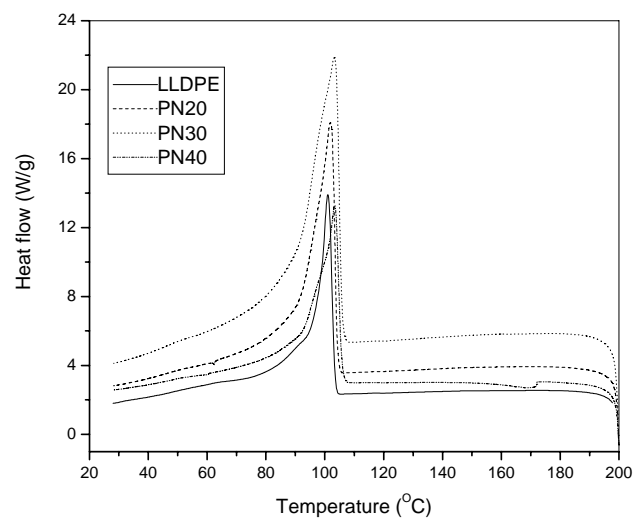
Figures 25 (a, b): DSC heating and cooling curves for the LLDPE-Polystarch N blends

after ageing of 95 days

From the heating and cooling curves of the DSC, one can observe that the T_g and T_m value does not vary too much as a function of the amount of polystarch N. However the ΔH_{fus} value increases (Table 7). This increase is attributed to the increase in the

crystalline level of LLDPE by UV radiation from the sunlight and consequently, the heat of fusion increases [Abd El-Rehim, Sayed 2004]. Long term run can cause chain scission there by a reduction in the molecular weight.

Materials	T_g (°C)	ΔH_{Cry} (J/g)	T_m (°C)	ΔH_{fus} (J/g)
LLPDE	101	123	110	140
PN20	101	123	110	152
PN30	103	127	112	156
PN40	103	130	112	159

Table 7: DSC Parameters for the LLDPE-Polystarch N blends

A comparison of the heating and cooling curves for the blends PN30, PH30 and PQ30 is given in the figures 26 a and b. Here it can be seen that there is not very much variation in the T_g and T_m values of the blends.

a.
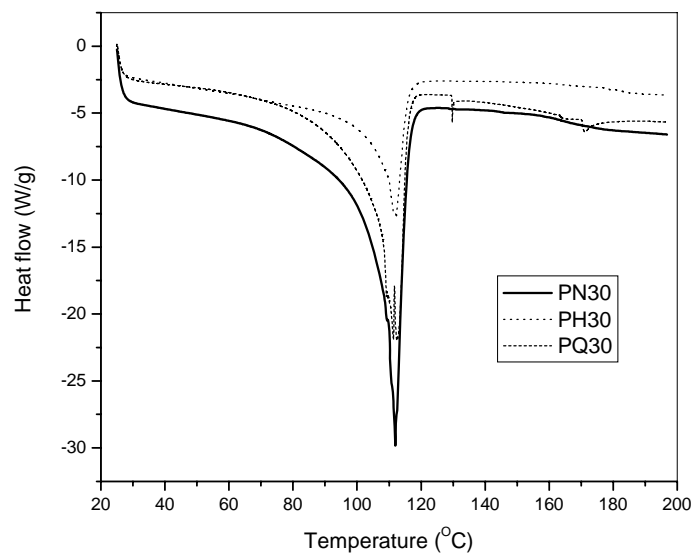
b.
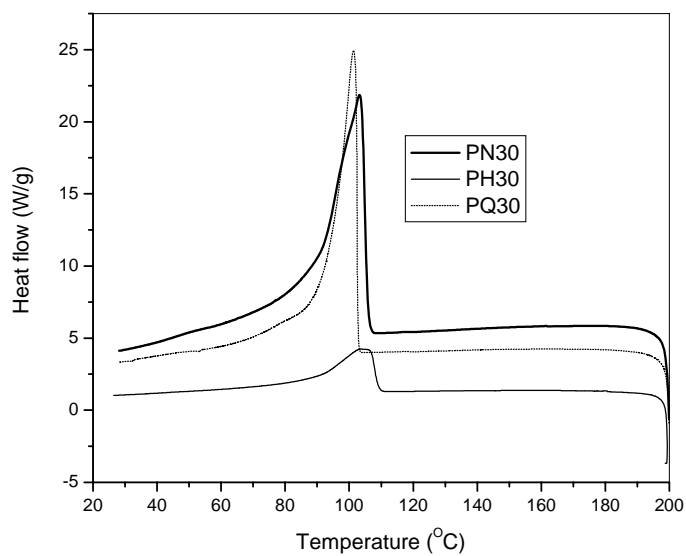
Figures 26 a and b: Comparison of the heating and cooling curves for the blends

with different additives (30%w/w)

6.6 FTIR analysis

Structural changes such as an oxidation level of LDPE due to the UV-sunlight can be accurately detected by FTIR. Spectra FTIR, according to the time of ageing for the LLDPE and PN30 after 95 days and 235 days is given in the figure 28.
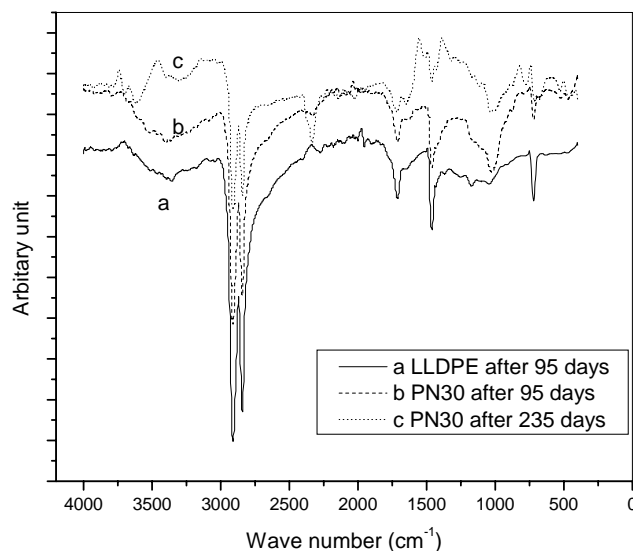
Figure 27: FTIR spectra for the aged LLDPE (after 95 days) and

PN30 blends (after 95 and 235 days)

For LLDPE peaks were observed at 2917, 2843 cm^{-1} corresponds to the vibration mode of $-CH_2$ group. The peaks at 1715 cm^{-1} shows the band vibration of the C=O group which appears due to the photo-oxidation of the LLDPE. This band increases more considerably with the time. The peak at 1463 cm^{-1} corresponds to the deformation and elongation mode of CH_2 group [Gisjsman, 1997 and Allen 2000]. Several peaks at 900–1040 cm^{-1} appears because of the vibration of CH_2–O groups or double bonds C=C [Tidjani 2000 and Gulmine 2003]. On comparison of the LLDPE (after 95 days) with the PN30 (after 235 days) it can be seen that the peak intensity for the peak appearing at 1031cm^{-1} becomes more and more broader and stronger due to rupture of double bonds as a result

of severe degradation. The strong peak at 1715 cm^{-1} increases more considerably with the exposure time. This is because different types of radicals form on the film surface under the action of the light and/or heat can lead to reactions of reticulation of chains, reactions with oxygen in air and reactions of scission of chains [Abdelkader 2010]. The mechanism of degradation greatly depends on the nature and stability of the radical formed in the course of the reaction of photo-oxidation [Hanafi 1999]. For LLDPE, stable radicals are formed due to tertiary carbons and these radicals propagate to react with other radicals causing reticulations of the chains. Very reactive radicals are formed due to the secondary carbons of LDPE which cause reactions of chains scission [Briassoulis 2006]. In the case of PN30 before and after 95 and 235 days, peaks were observed between 3100 to 3400cm^{-1} is due to –OH stretching vibrations. A comparison of FTIR of PN30, PH30 and PQ30 taken after 95 days of degradation is given in the figure 28.
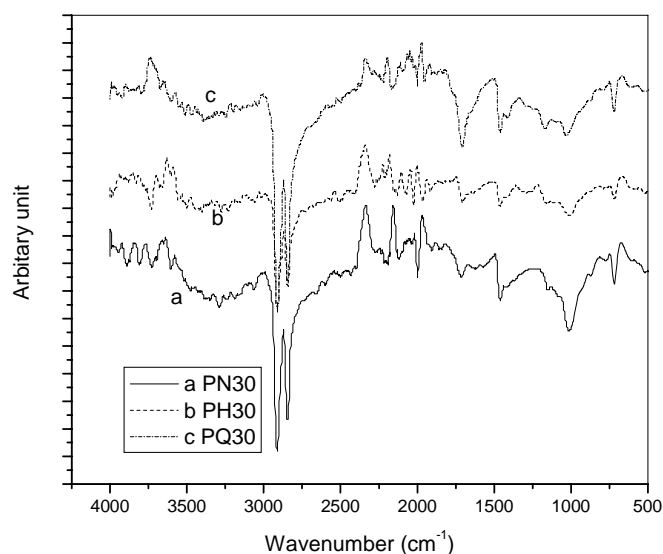
Figure 28: FTIR spectra of PN30, PH30 and PQ30 after 95 days of degradation

It's clear that the addition of PDQ-H increases the biodegradation of the LLDPE when compared to PN30 and PH30. Here for the blend PQ30 the intensity of the peaks at 713 cm^{-1} and 1031 cm^{-1} and the peak at 1177 cm^{-1} becomes more prominent. Also the intensity of the peaks at 1463 cm^{-1} corresponds to the deformation and elongation mode of CH_2 group decreases. Moreover the intensity of the peak at 1715 cm^{-1} for PQ30 increases and is broader than that of PH30 and PN0. This shows that addition of PDQ-H to LLDPE produces more carbonyl groups which are a direct indication of enhanced biodegradable nature when compared to PN30 and PH30.

CHAPTER SEVEN

7 ECONOMIC ANALYSIS

Cost of Polyethylene=1200 Dollar per ton

Cost of Cornstarch   =   400 Dollar per ton

In our experiment, we found that with the increase of starch addition degradation increases rapidly but mechanical strength decreases very sharply after addition of 40% starch, so starch can be added up to 20 to 25 percent for safety use of plastic bags with sufficient strength.

Total use of Plastic material in Saudi Arabia=1200,000 tons/year

Plastic packaging is 30% of total plastic consumption

Total Plastic bags consumption=360,000 tons per year

Total cost without starch=1200*360000

$\qquad$ =432,000,000

Total cost with starch   =(1200*.8+400*.2)*360000

$\qquad$ =374,000,000

Total Savings for using biodegradable plastic bags

$\qquad$ =217 million Saudi Riyal per year

CHAPTER EIGHT

CONCLUSION AND RECOMMENDATION

1. All the samples showed the degradation behavior, specially samples blended with PDQH additive showed severe degradation.

2. Samples becomes very brittle and lost its strength within one month of exposure.

3. Samples become porous and start taken away by the flowing air after two months.

4. The samples exposed for 4 months showed cracked, fractured big pits which indicate severe photo-degradation and will be converted to powder soon as compared to the samples exposed for 30 days only.

5. The photographs taken after 9 months shows that all the exposed parts are severely degraded and are taken away by air. Only the portions which are attached by the tapes are left.

6. The additive PDQ-H shows the highest degradation rate compared to other additives. Polystarch –H is the second and the Polystarch-N shows the lowest degradation behavior.

7. The investigation found that addition of polystarch additives to the LLDPE decreases its tensile strength while an increase in tensile modulus. SEM analysis showed that addition of more polystarch to the LLDPE enhances the biodegradable nature. The value of M_n and M_w for the LLDPE-blends increases as a function of time, while PDI value decreases. After the degradation T_g and T_m of the blends does not show drastic variation when compared to matrix alone.

8. It can be concluded that within 8 to 9 months, all the samples were completely degraded and converted into powder remnants.

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APPENDIX

A SEM Elemental Analysis Results and Images

Table A.1 Elemental Analysis of 30% Polystarch N30 after 30days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	82.03	88.65
Na K	ED	3.29	2.48
Mg K	ED	1.60	1.14
Al K	ED	3.03	1.94
Si K	ED	7.18	4.42
S K	ED	1.03	0.55
Cl K	ED	0.39*	0.19*
Ca K	ED	1.45	0.62
Total		100.00	100.00
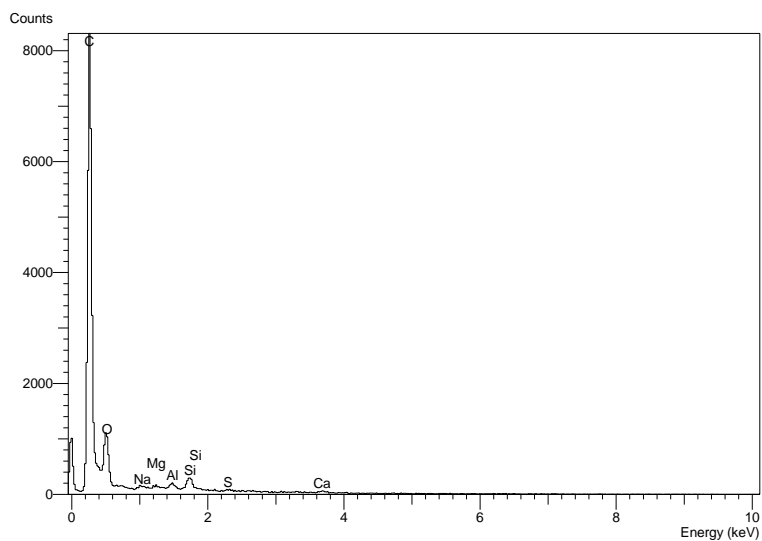
Figure A.1 Spectrum of 30% Polystarch N30 after 30days

Table A.2 Elemental Analysis of 10% PDQ-H after 30days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	93.81	96.57
Al K	ED	1.49	0.91
Si K	ED	3.44	2.02
S K	ED	0.01*	0.01*
Cl K	ED	0.11*	0.05*
K K	ED	0.05*	0.02*
Ca K	ED	0.92	0.38
Fe K	ED	0.17*	0.05*
Total		100.00	100.00
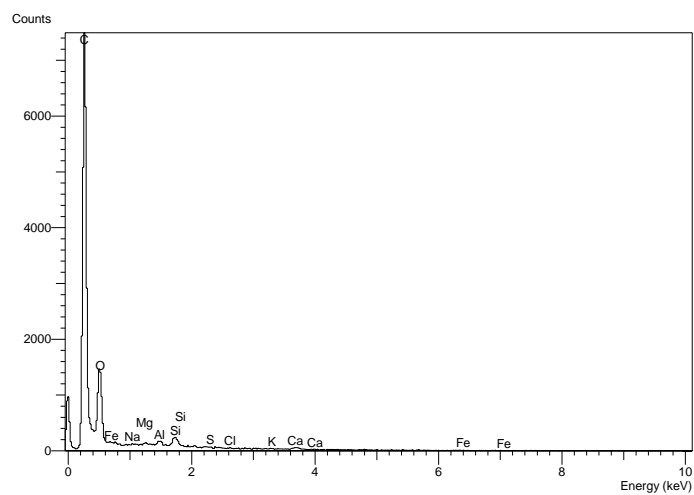
Figure A.2 Spectrum of 10% PDQ-H after 30days

Table A.3 Elemental Analysis of 20% Polystarch plus H after 30days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	82.44	89.19
Mg K	ED	1.90	1.35
Al K	ED	4.39	2.82
Si K	ED	9.84	6.06
K K	ED	0.61	0.27
Ca K	ED	0.39*	0.17*
Fe K	ED	0.43*	0.13*
Total		100.00	100.00
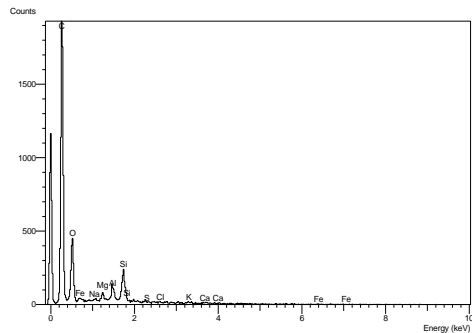
Figure A.3 Spectrum of 20% Polystarch plus H after 30days

Table A.4 Elemental Analysis of 20% PDQH after 30days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	91.57	95.10
Mg K	ED	0.81	0.55
Al K	ED	1.92	1.18
Si K	ED	4.41	2.61
S K	ED	0.68	0.35
Ca K	ED	0.33*	0.14*
Fe K	ED	0.37*	0.11*
Total		100.00	100.00
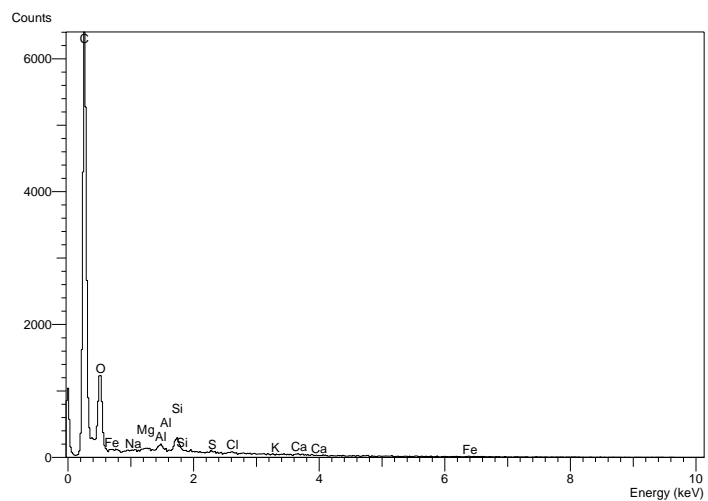
Figure A.4 Spectrum of 20% PDQH after 30days

Table A.5 Elemental Analysis of 20% Polystarch N after 30days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	82.81	89.61
Mg K	ED	1.68	1.19
Al K	ED	4.07	2.61
Si K	ED	8.99	5.54
S K	ED	0.38	0.21
K K	ED	0.52	0.23
Ca K	ED	1.01	0.44
Fe K	ED	0.54	0.17
Total		100.00	100.00
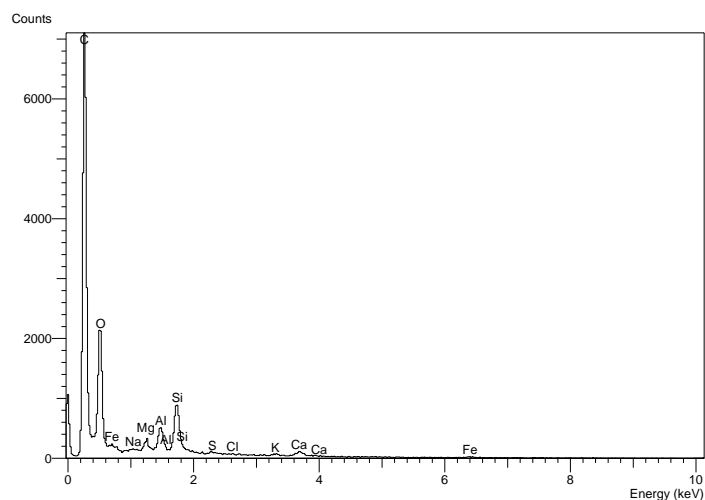
Figure A.5 Spectrum of 20% Polystarch N after 30days

Table A.6 Elemental Analysis of 3% PDQH after 120days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	75.38	85.19
Mg K	ED	2.75	2.04
Al K	ED	3.16	2.12
Si K	ED	11.10	7.15
S K	ED	1.47	0.83
Cl K	ED	0.48	0.25
K K	ED	0.75	0.35
Ca K	ED	4.03	1.82
Fe K	ED	0.37	0.12
Zn L	ED	0.52*	0.14*
Total		100.00	100.00
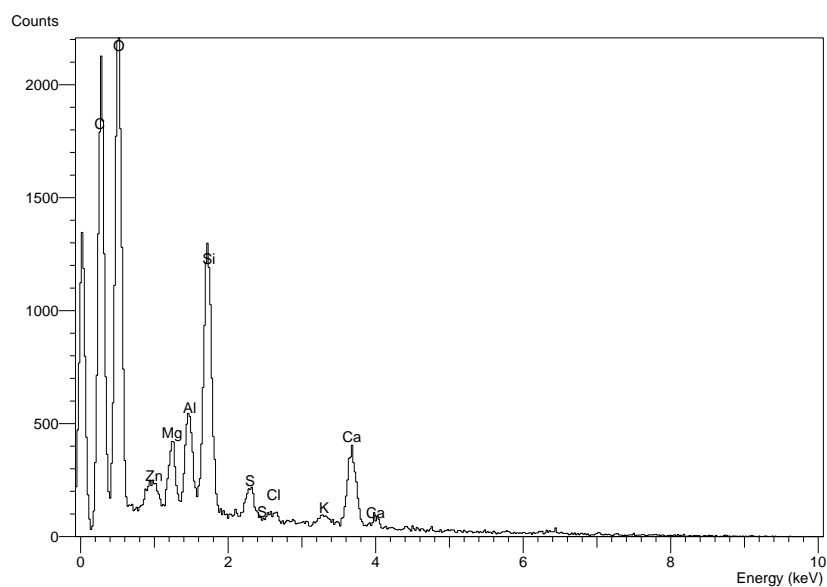
Figure A.6 Spectrum of 3% PDQH after 120days

Table A.7 Elemental Analysis of 10% PDQH after 120days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	85.03	91.36
Mg K	ED	1.67	1.18
Al K	ED	2.72	1.73
Si K	ED	6.02	3.68
S K	ED	1.01	0.54
Cl K	ED	0.11*	0.05*
K K	ED	0.59	0.26
Ca K	ED	2.53	1.08
Fe K	ED	0.32*	0.10*
Total		100.00	100.00
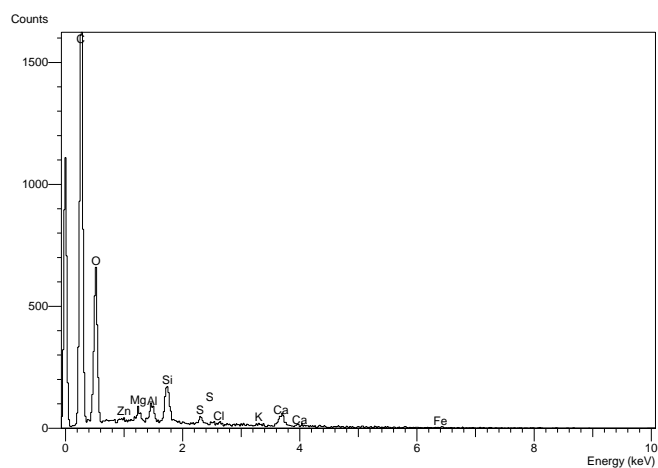
Figure A.7 Spectrum of 3% PDQH after 120days

Table A.8 Elemental Analysis of 20% Polystarch H after 120days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	75.35	85.04
Mg K	ED	2.92	2.17
Al K	ED	3.92	2.62
Si K	ED	10.84	6.97
S K	ED	1.17	0.66
Cl K	ED	0.26	0.13
K K	ED	0.81	0.37
Ca K	ED	4.09	1.84
Fe K	ED	0.34	0.11
Zn L	ED	0.30*	0.08*
Total		100.00	100.00
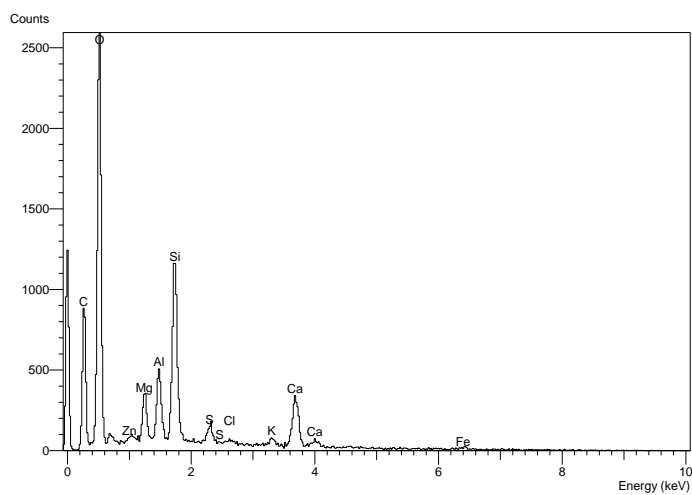
Figure A.8 Spectrum of 20% Polystarch H after 120days

Table A.9 Elemental Analysis of 30% Polystarch H after 120days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	73.87	83.98
Mg K	ED	3.09	2.31
Al K	ED	4.01	2.70
Si K	ED	11.81	7.65
S K	ED	1.20	0.68
Cl K	ED	0.07*	0.04*
K K	ED	1.01	0.47
Ca K	ED	4.44	2.01
Fe K	ED	0.51	0.17
Total		100.00	100.00
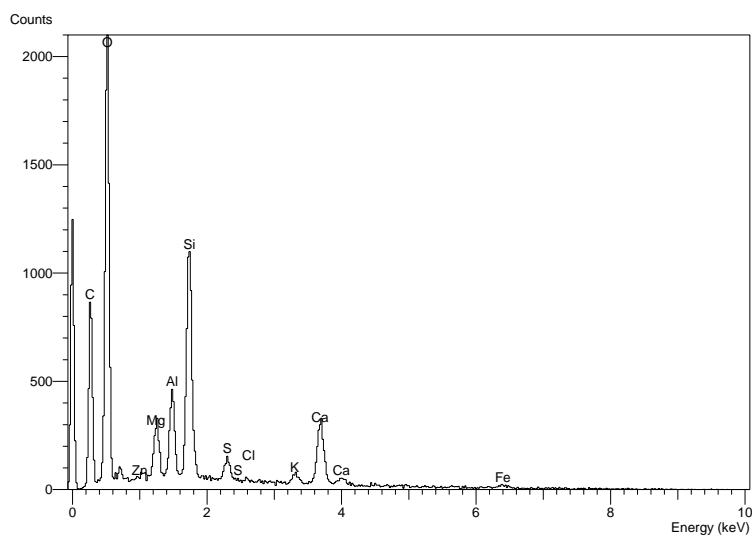
Figure A.9 Spectrum of 30% Polystarch H after 120days

Table A.10 Elemental Analysis of 20% Polystarch N after 120days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	75.62	85.47
Mg K	ED	3.19	2.37
Al K	ED	3.41	2.29
Si K	ED	9.85	6.34
S K	ED	1.25	0.71
Cl K	ED	0.48	0.24
K K	ED	0.84	0.39
Ca K	ED	4.05	1.83
Fe K	ED	0.08*	0.03*
Zn L	ED	1.22	0.34
Total		100.00	100.00
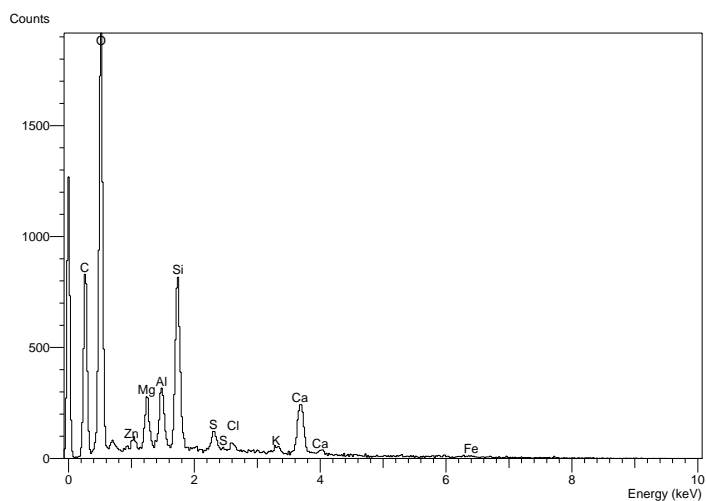
Figure A.10 Spectrum of 20% Polystarch N after 120days

Table A.11 Elemental Analysis of 30% Polystarch N after 120days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	78.29	86.93
Mg K	ED	2.82	2.06
Al K	ED	3.63	2.39
Si K	ED	9.17	5.80
S K	ED	0.98	0.55
Cl K	ED	0.29	0.14
K K	ED	0.62	0.28
Ca K	ED	4.09	1.81
Fe K	ED	0.11*	0.03*
Total		100.00	100.00
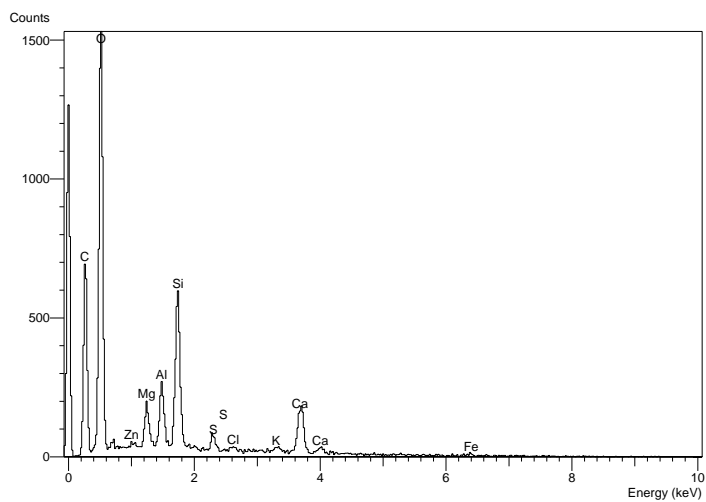
Figure A.11 Spectrum of 30% Polystarch N after 120days

Table A.12 Elemental Analysis of 10% PDQH after 180days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	86.55	94.17
Mg K	ED	0.06*	0.04*
Si K	ED	0.16*	0.10*
S K	ED	0.68*	0.37*
K K	ED	0.21*	0.09*
Ca K	ED	10.87	4.72
Ti K	ED	0.94*	0.34*
Fe K	ED	0.54*	0.17*
Total		100.00	100.00
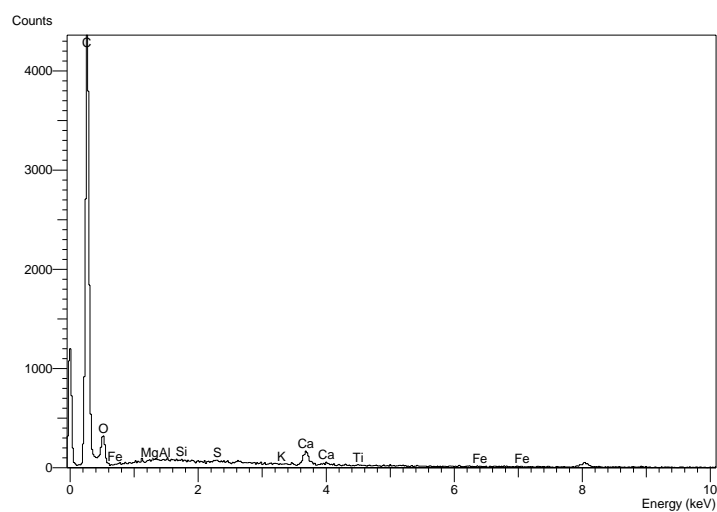
Figure A.12 Spectrum of 10% PDQH after 180days

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Table A.13 Elemental Analysis of 20% Polystarch H after 180days

Elmt	Spect. Type	Element %	Atomic %
O K	ED	70.17	82.41
Mg K	ED	1.58	1.22
Al K	ED	4.19	2.92
Si K	ED	12.09	8.08
S K	ED	1.61	0.95
K K	ED	1.53	0.73
Ca K	ED	5.37	2.52
Ti K	ED	0.07*	0.03*
Fe K	ED	3.38	1.14
Total		100.00	100.00
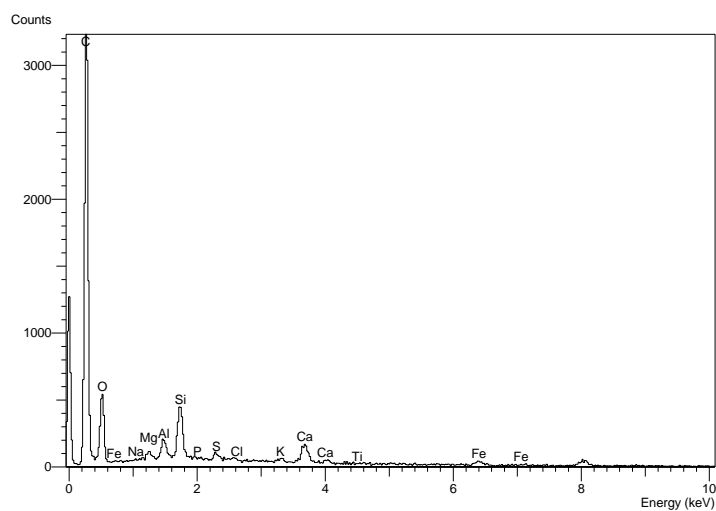
Figure A.13 Spectrum of 20% Polystarch H after 180days

B Surface Images Obtained by SEM
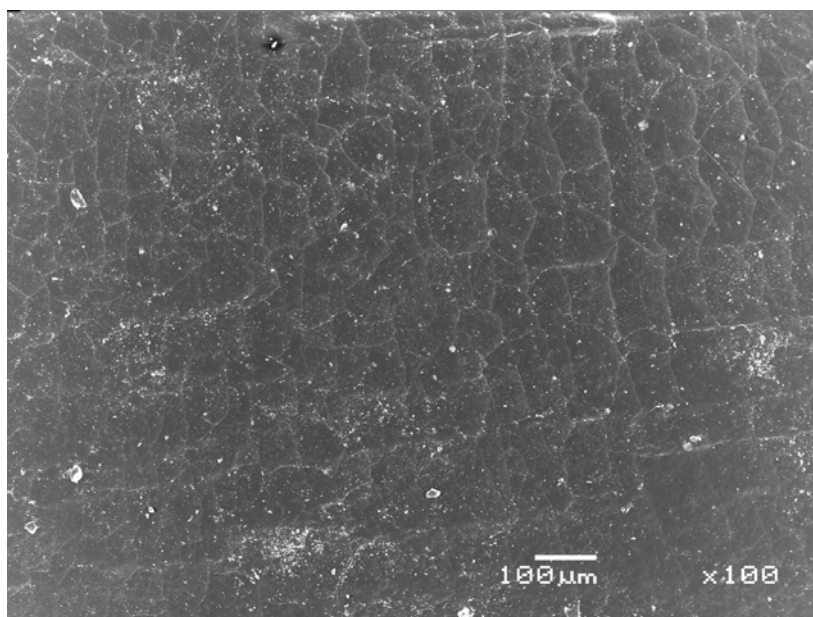
Figure B.1 Fresh sample without additive
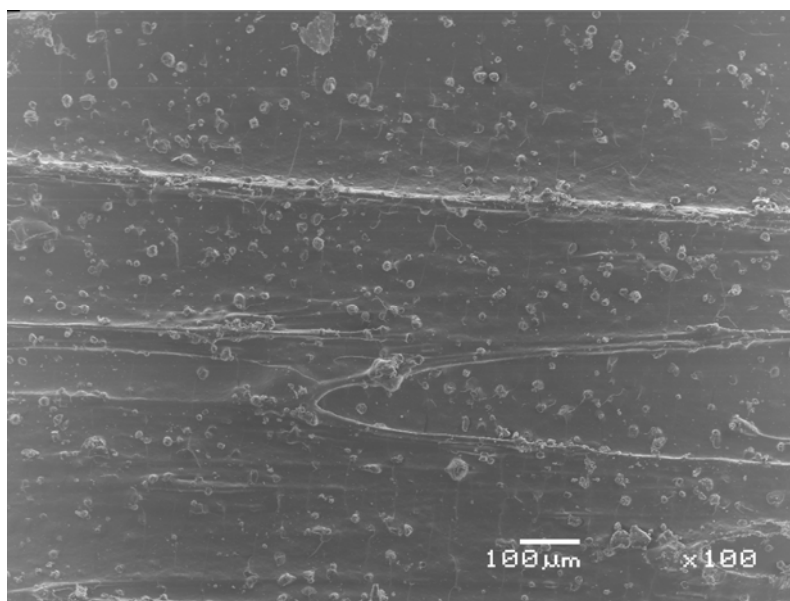
Figure B.2 SEM image of 10%Polystarch H after 30 days
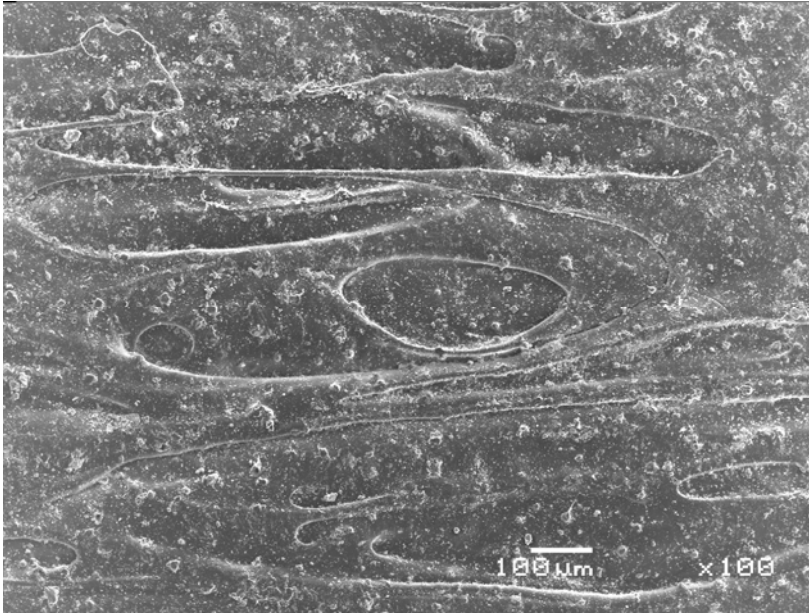
Figure B.3 SEM image of 20%Polystarch H after 30 days
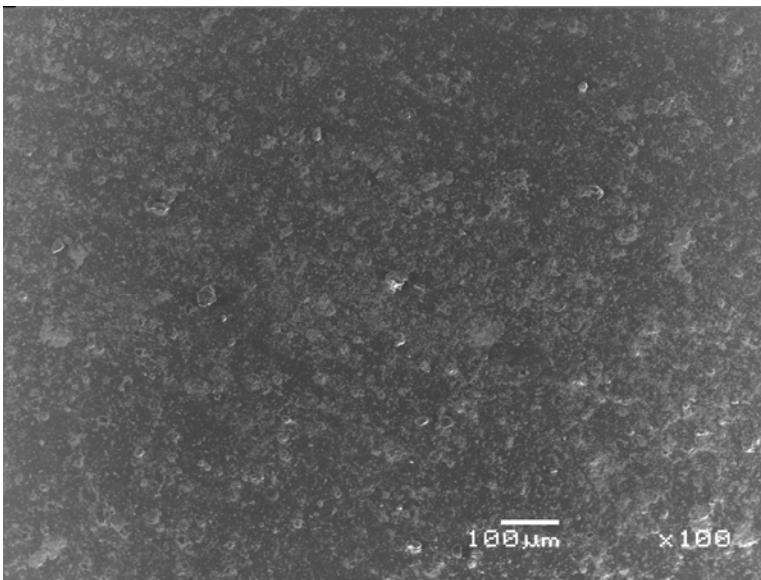
Figure B.4 SEM image of 30%Polystarch H after 30 days
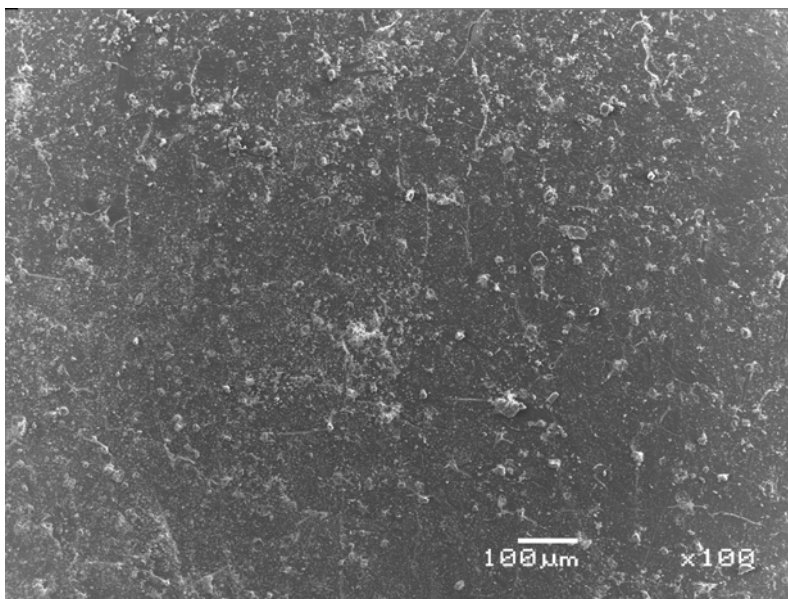
Figure B.5 SEM image of 10%Polystarch H after 30 days
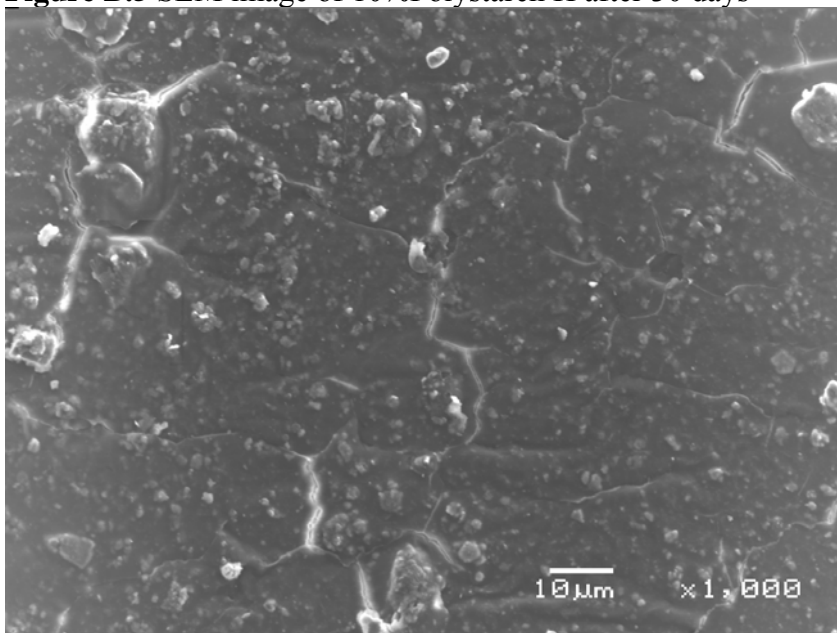
Figure B.6 SEM image of 20%Polystarch N after 30 days
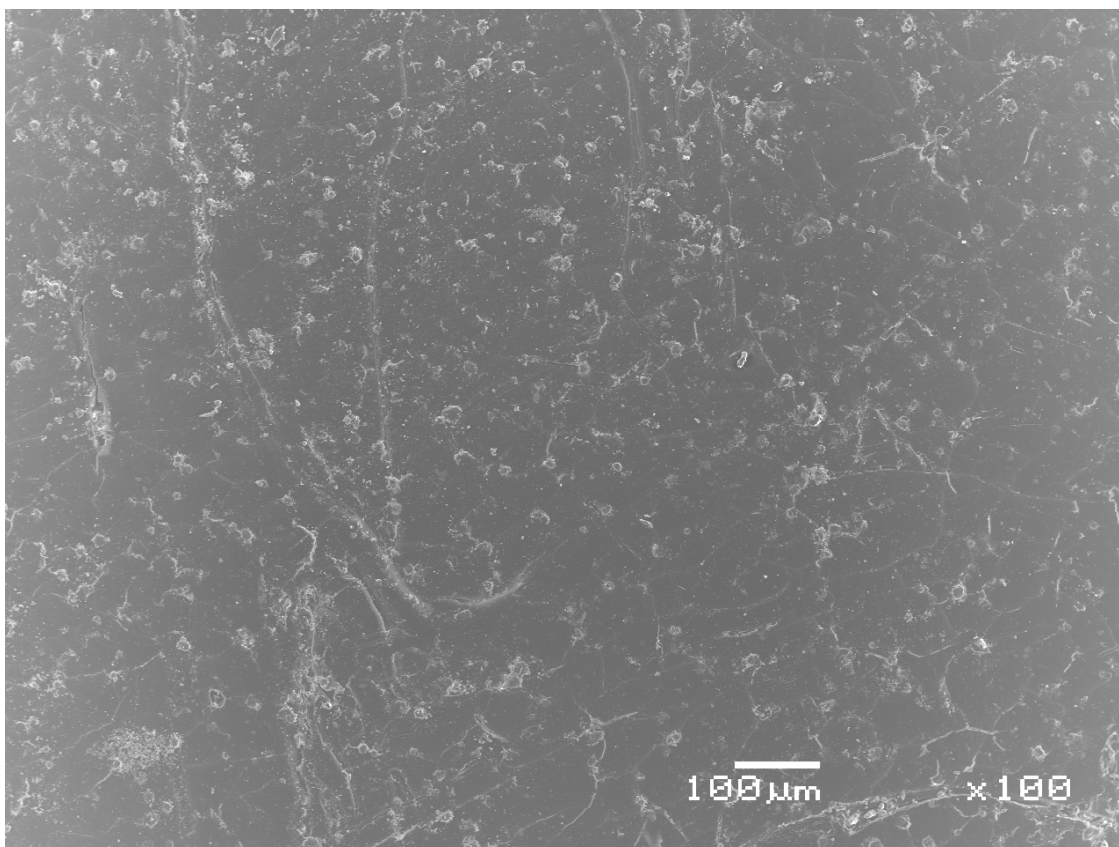
Figure B.7 SEM image of 30%Polystarch N after 30 days
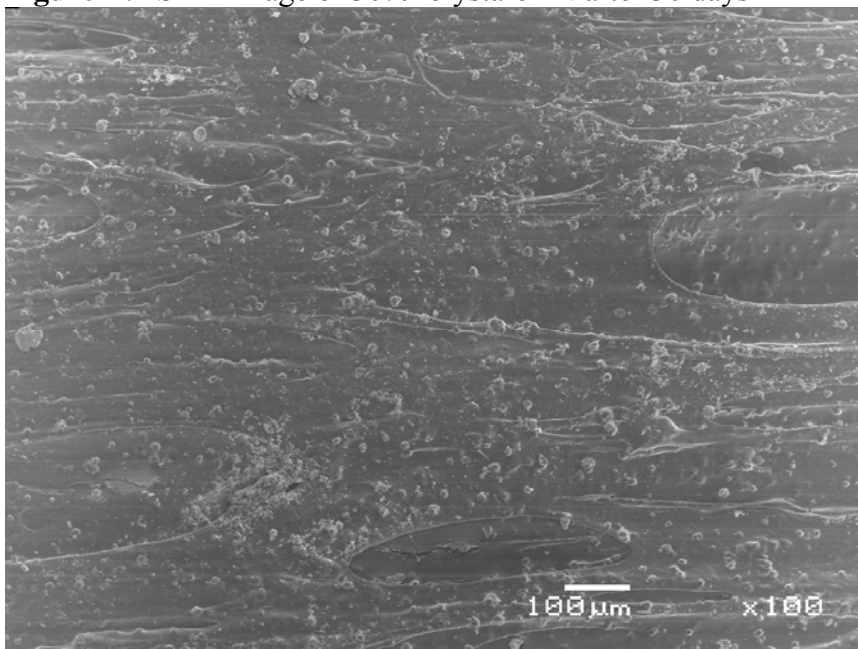
Figure B.8 SEM image of 40%Polystarch N after 30 days
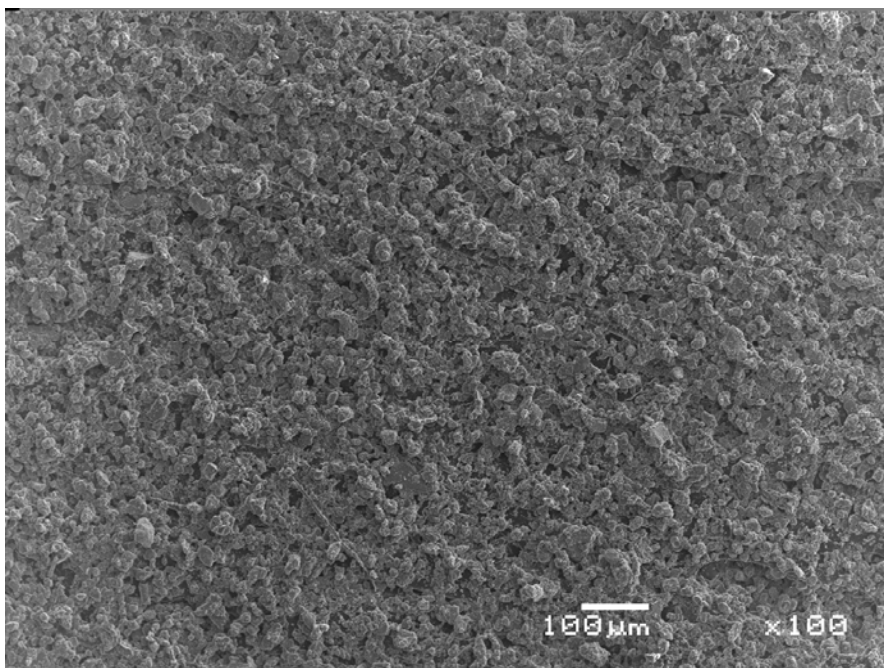
Figure B.9 SEM image of 20%Polystarch H after 120 days
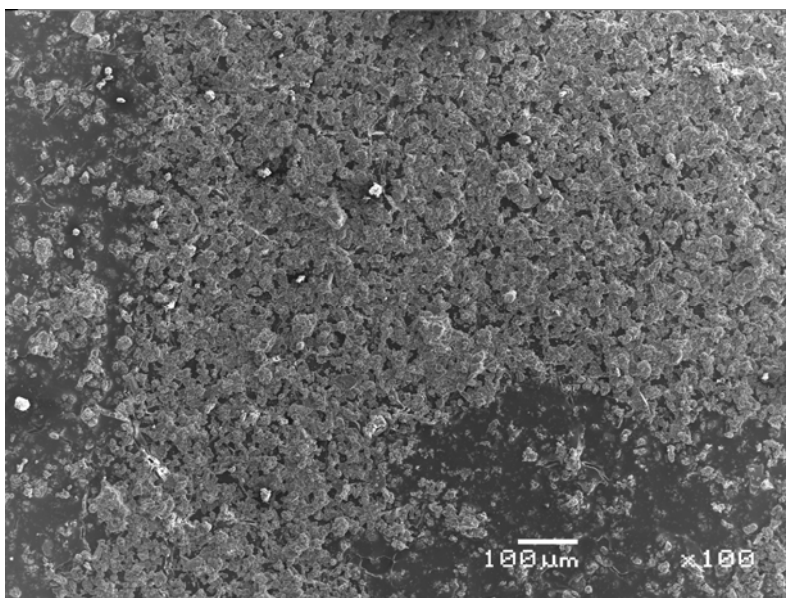
Figure B.10 SEM image of 30%Polystarch H after 120 days
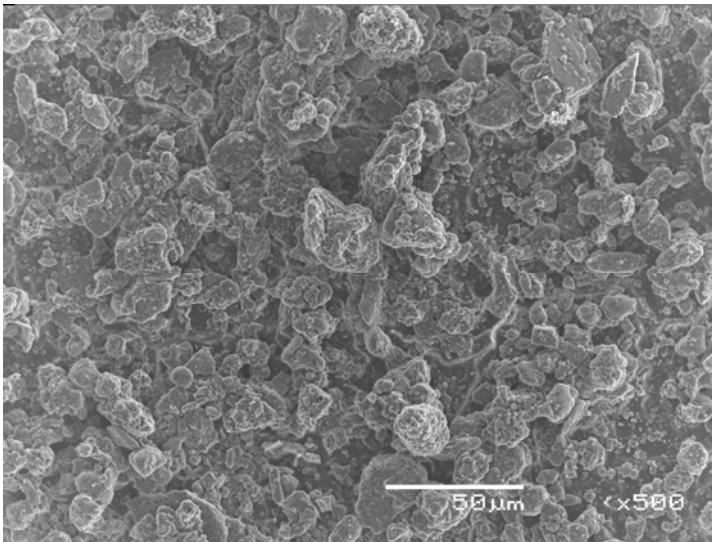
Figure B.11 SEM image of 20%Polystarch N after 120 days
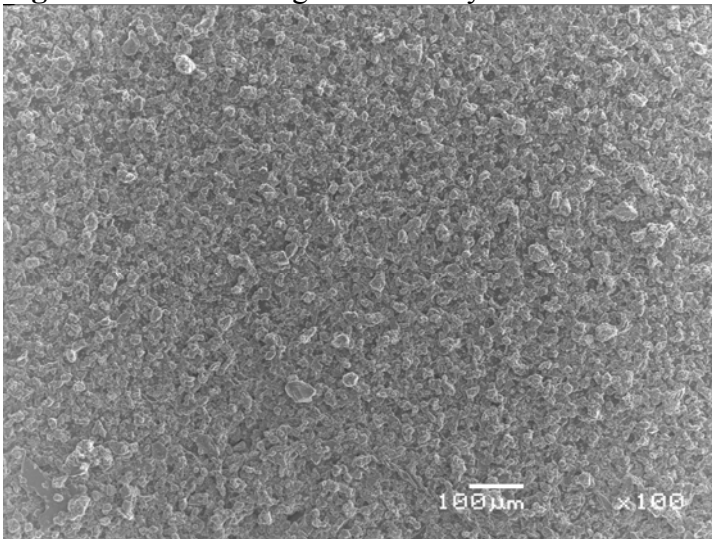
Figure B.12 SEM image of 30%Polystarch N after 120 days
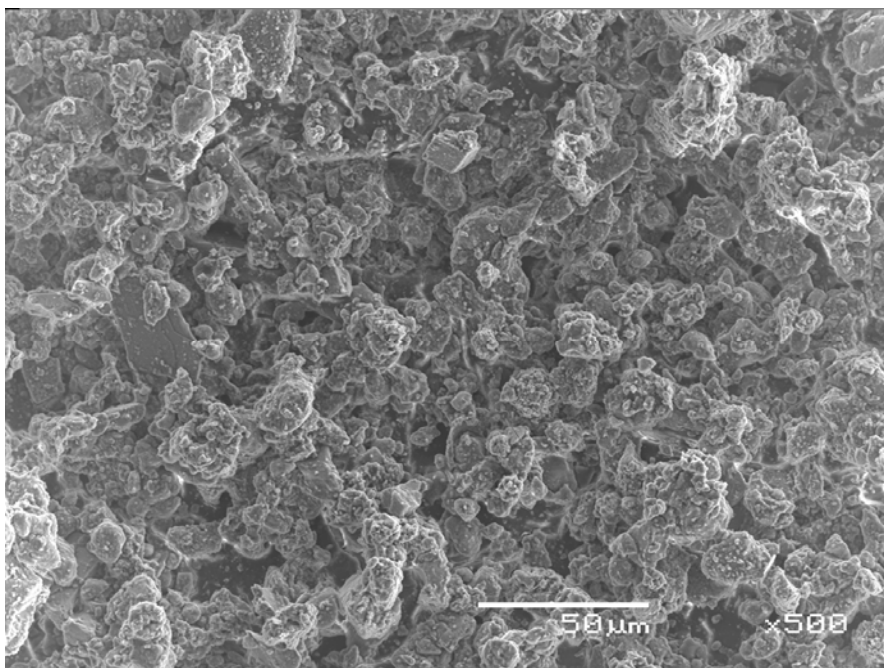
Figure B.13 SEM image of 40%Polystarch N after 120 days
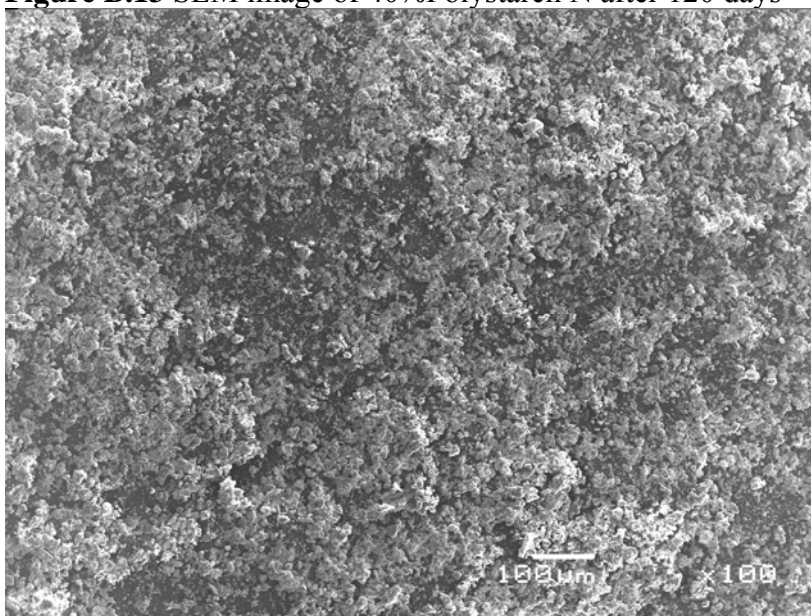
Figure B.14 SEM image of 10%PDQH 120 days
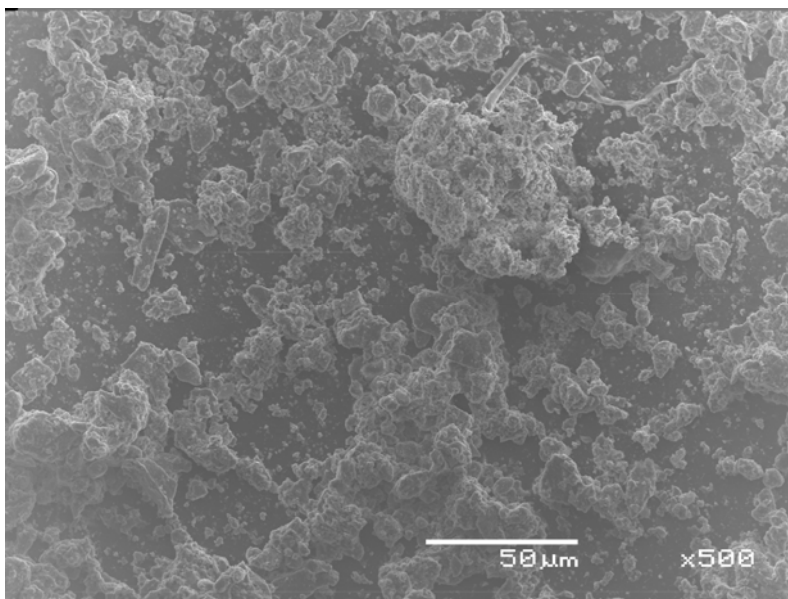
Figure B.15 SEM image of 20%PDQH after 120 days
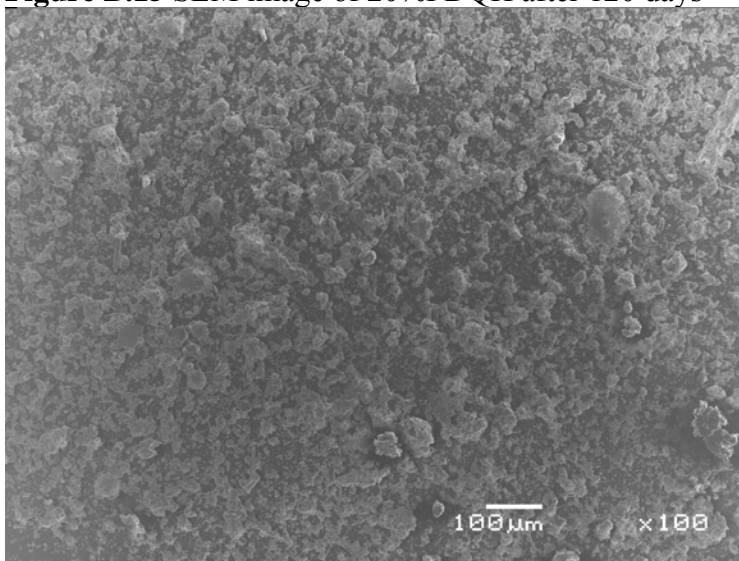
Figure B.16 SEM image of 30%PDQH after 120 days
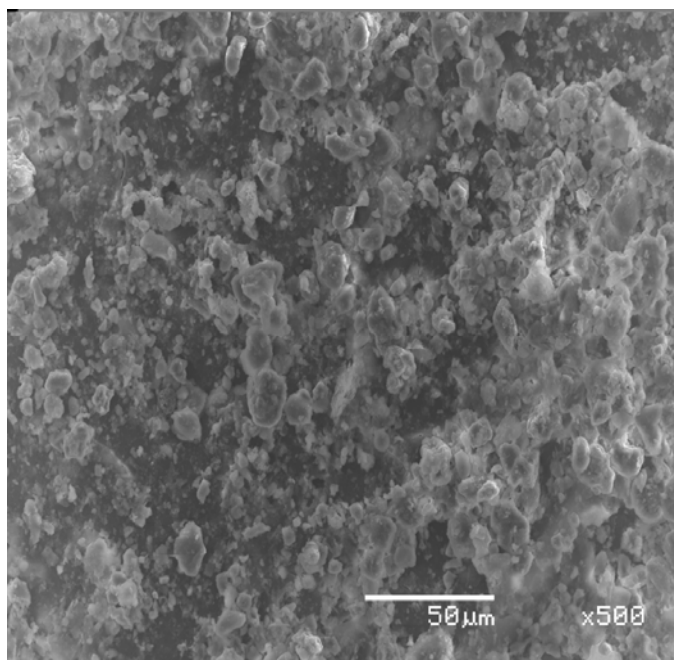
Figure B.17 SEM image of 20%Polystarch N after 180 days
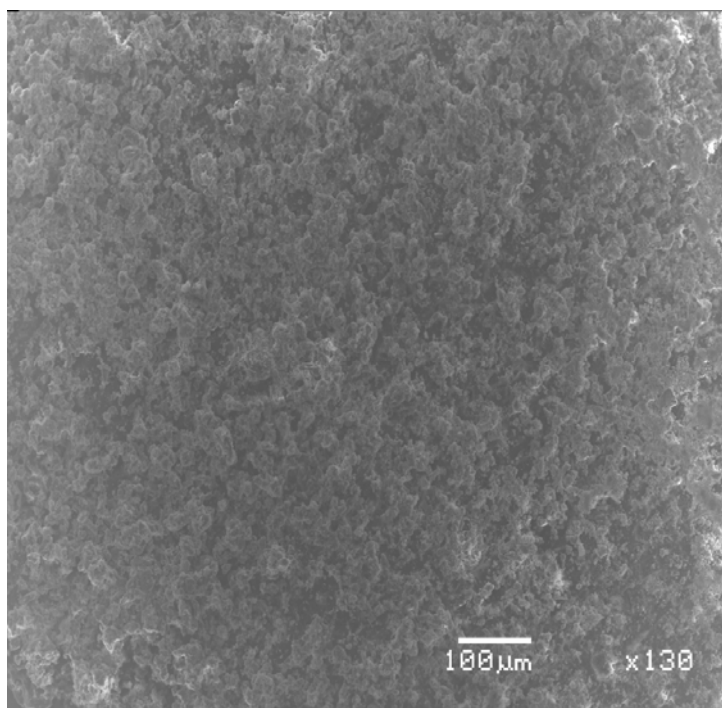
Figure B.18 SEM image of 40%Polystarch N after 180 days
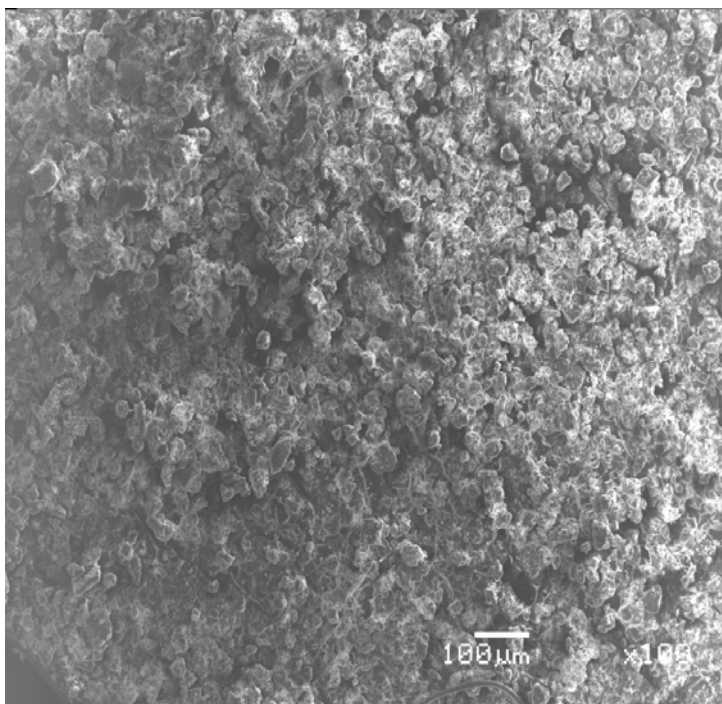
Figure B.19 SEM image of 10% PDQH after 180 days
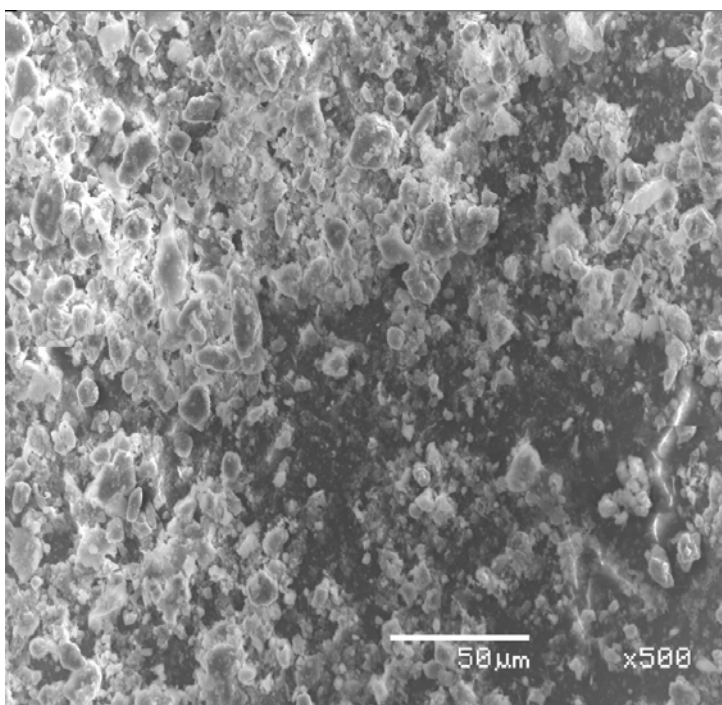
Figure B.20 SEM image of 20%PDQH after 180 days
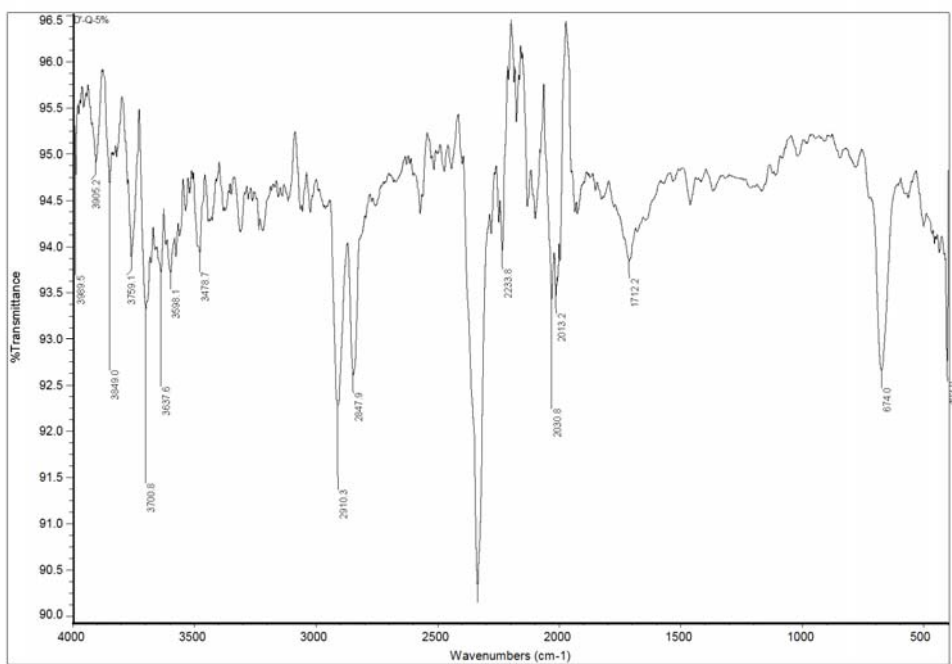
C FTIR Analysis Results
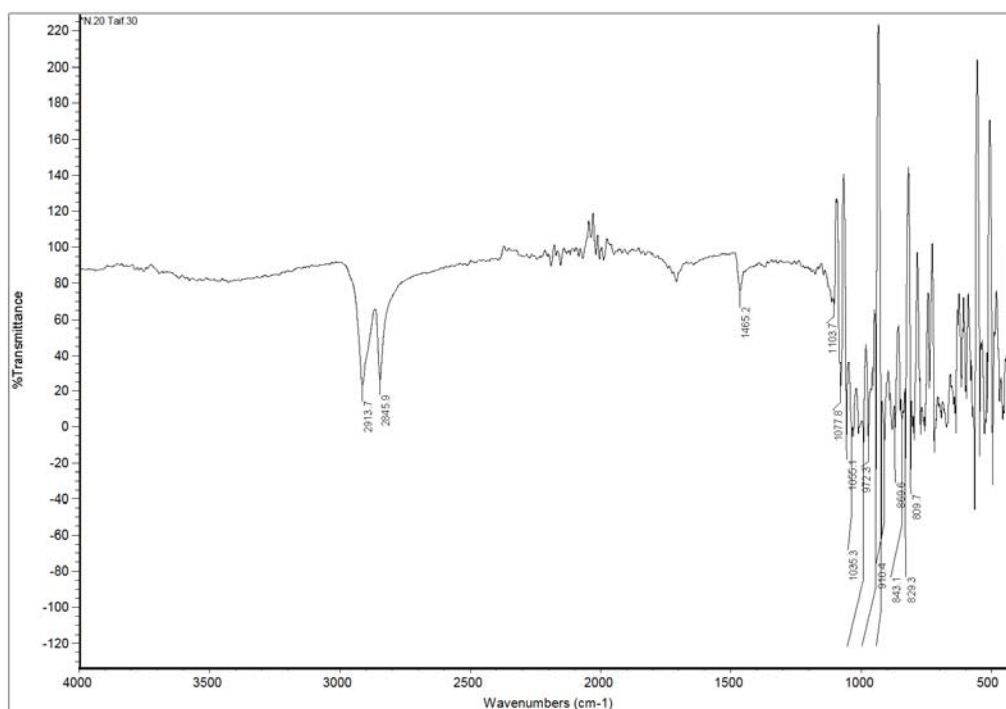
Figure C.1 FTIR spectrum of 20% Polystarch N after 30 days
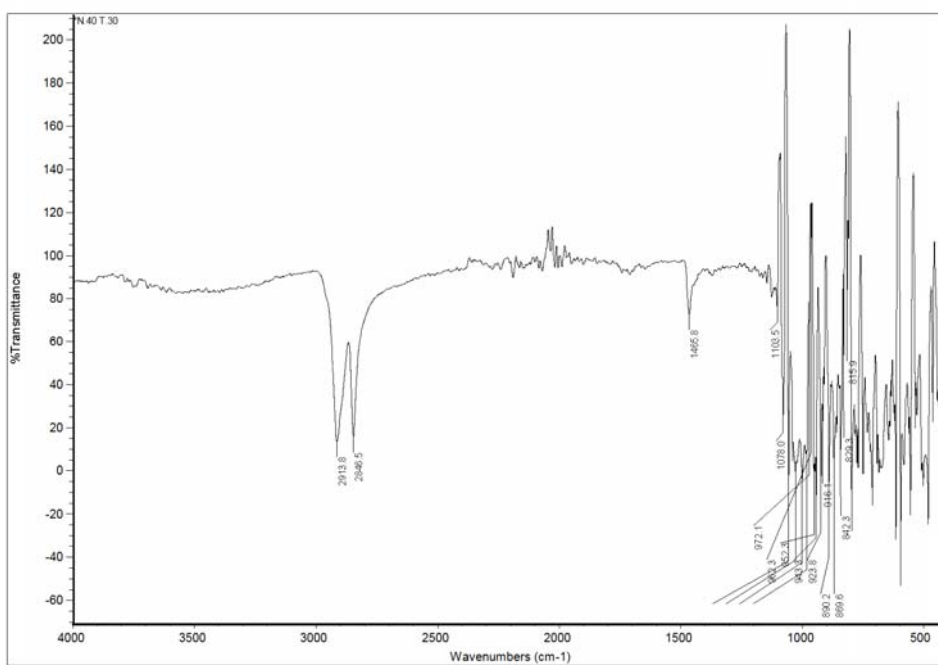
Figure C.2 FTIR spectrum of 40% Polystarch N after 30 days
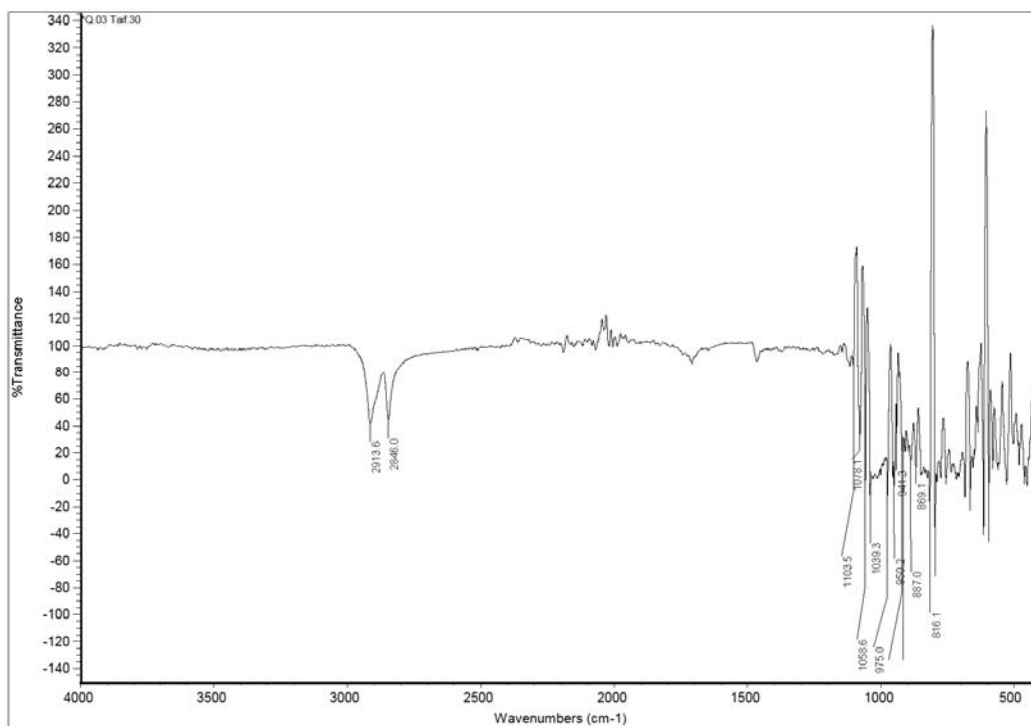
Figure C.3 FTIR spectrum of 3% PDQH after 30 days
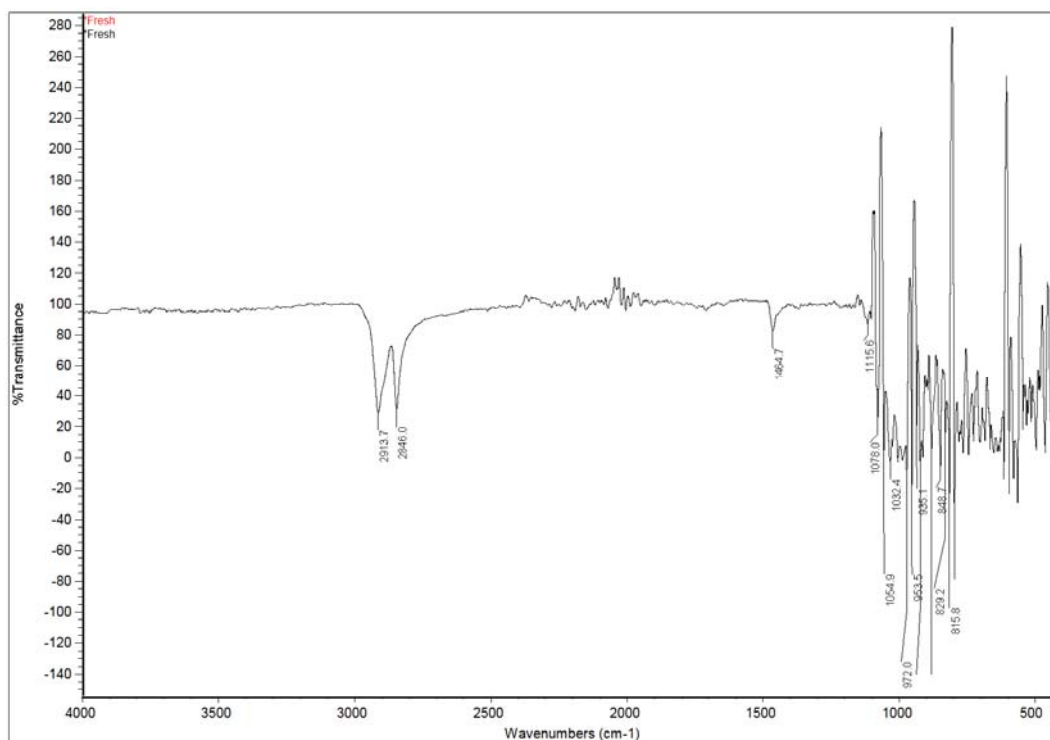

Figure C.4 FTIR spectrum of Fresh sample
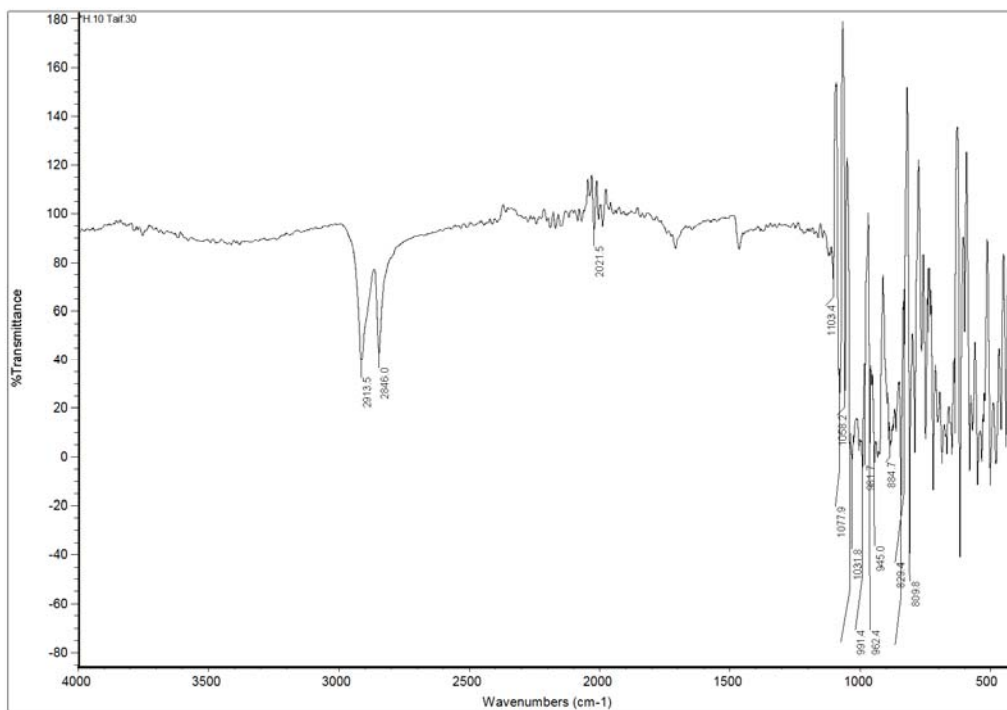
Figure C.5 FTIR spectrum of 10% Polystarch H after 30 days
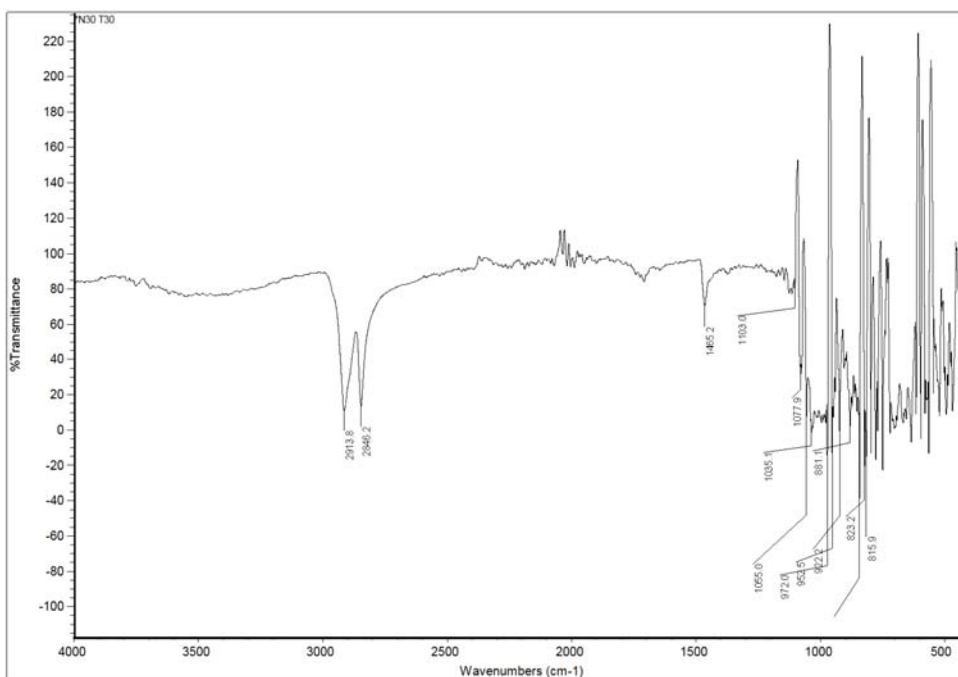
Figure C.6 FTIR spectrum of 30% Polystarch N after 30 days
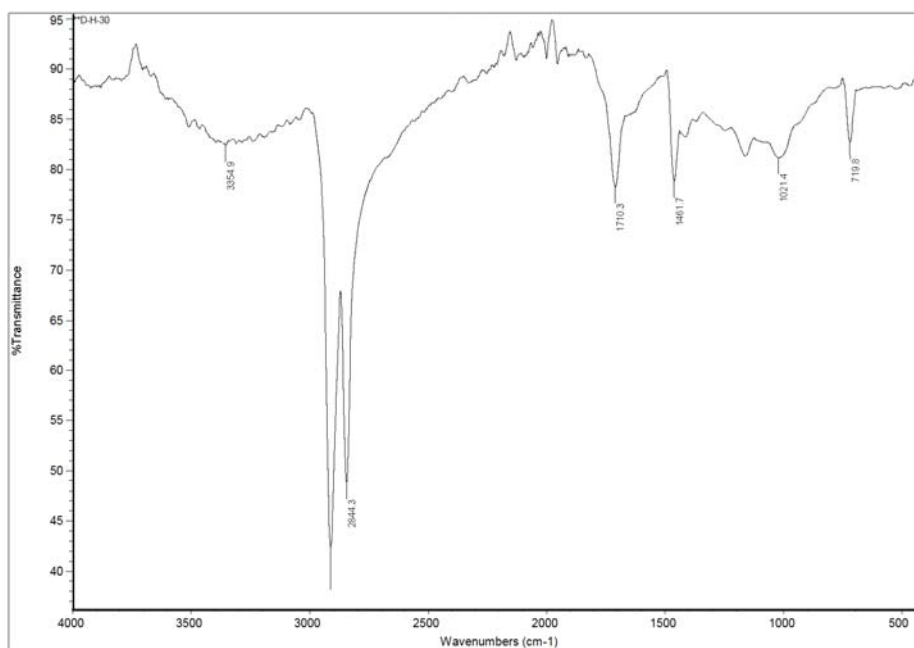
Figure C.7 FTIR spectrum of Polyethylene
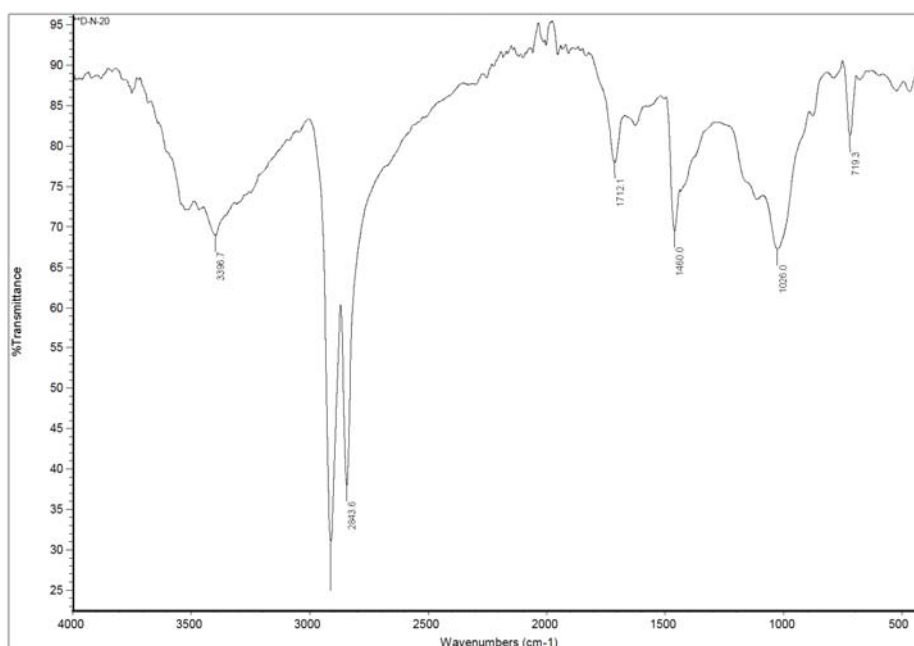
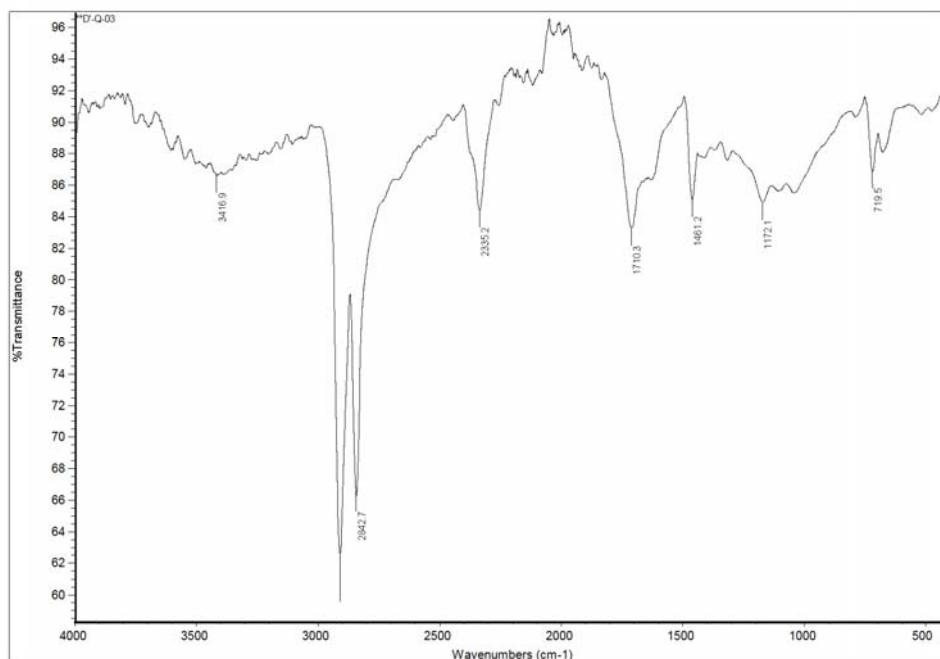**Figure C.8** FTIR spectrum of 20% Polystarch N after 80 days
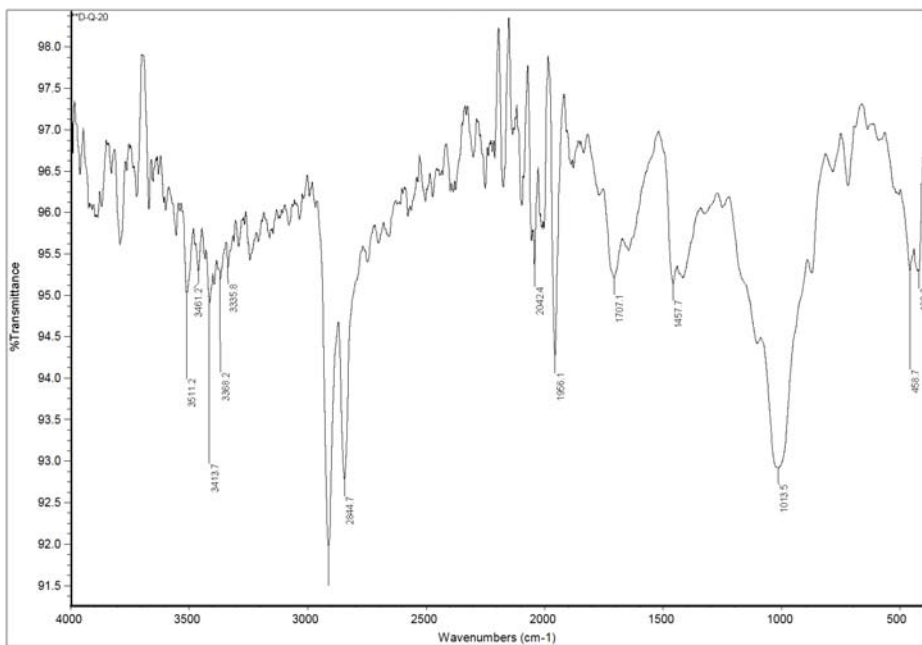
Figure C.9 FTIR spectrum of 20% PDQH after 80 days
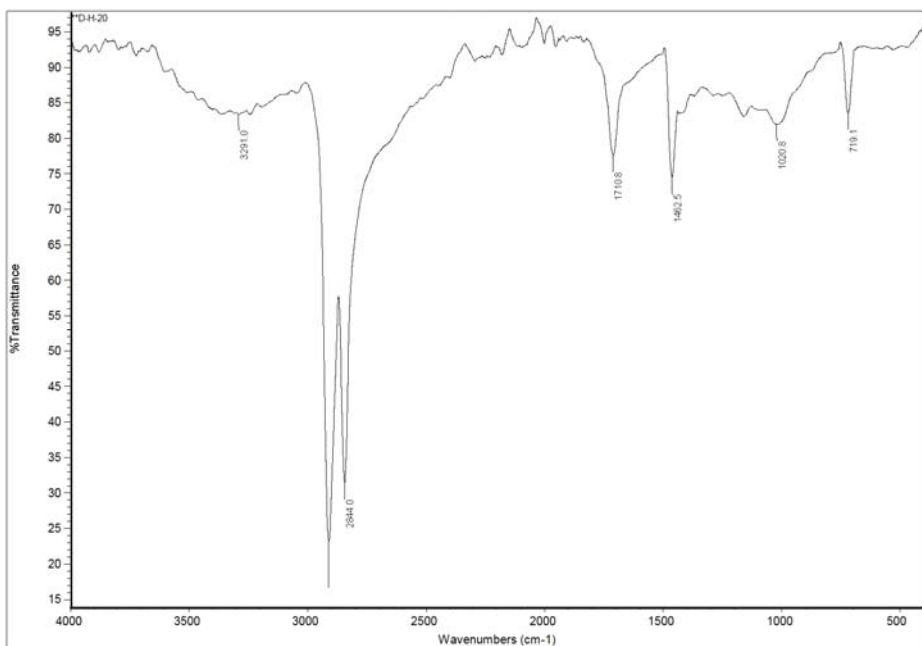
Figure C.10 FTIR spectrum of 20% Polystarch H after 80 days
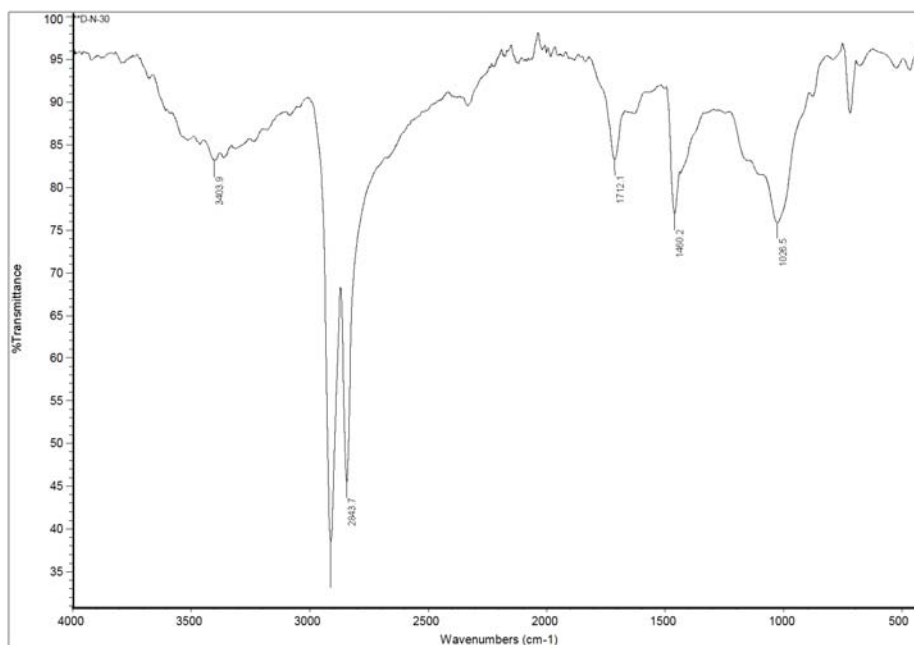
Figure C.11 FTIR spectrum of 30% Polystarch N after 80 days
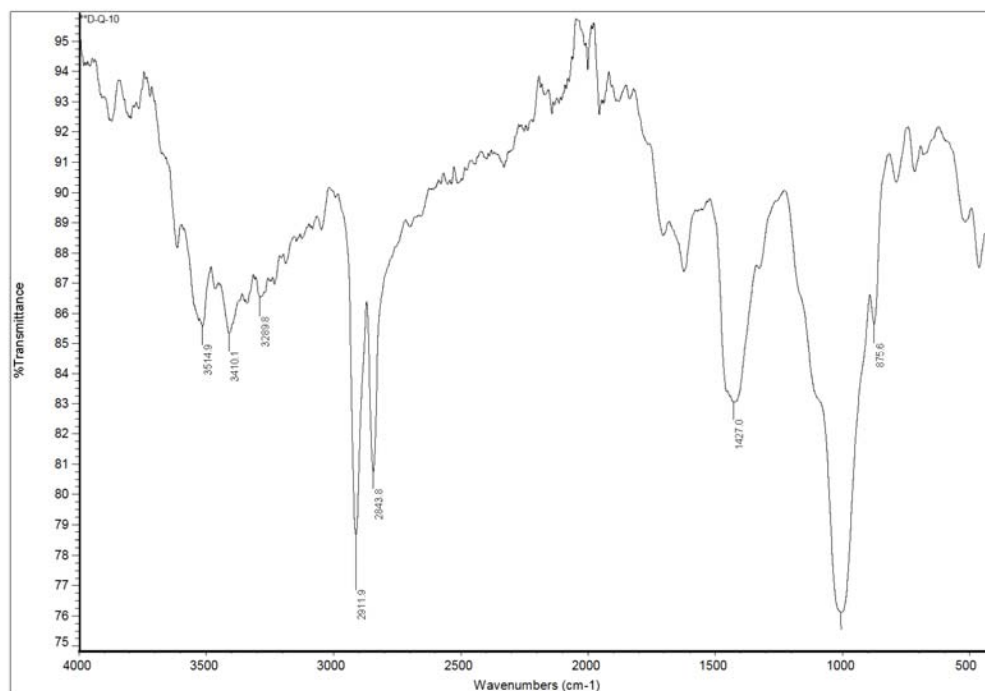
Figure C.12 FTIR spectrum of 10% PDQH after 80 days
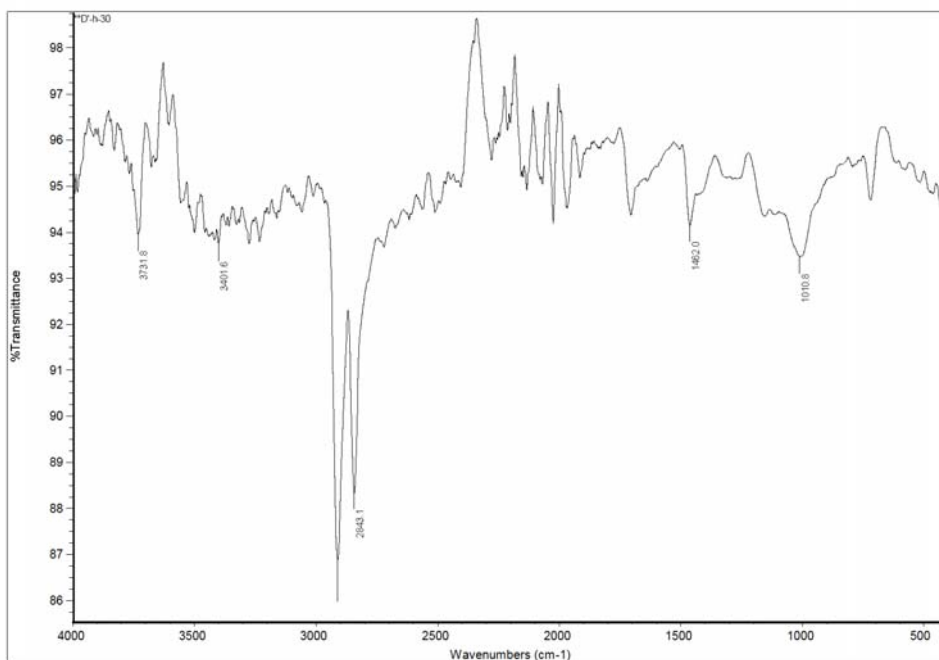
Figure C.13 FTIR spectrum of 30% Polystarch H after 95 days
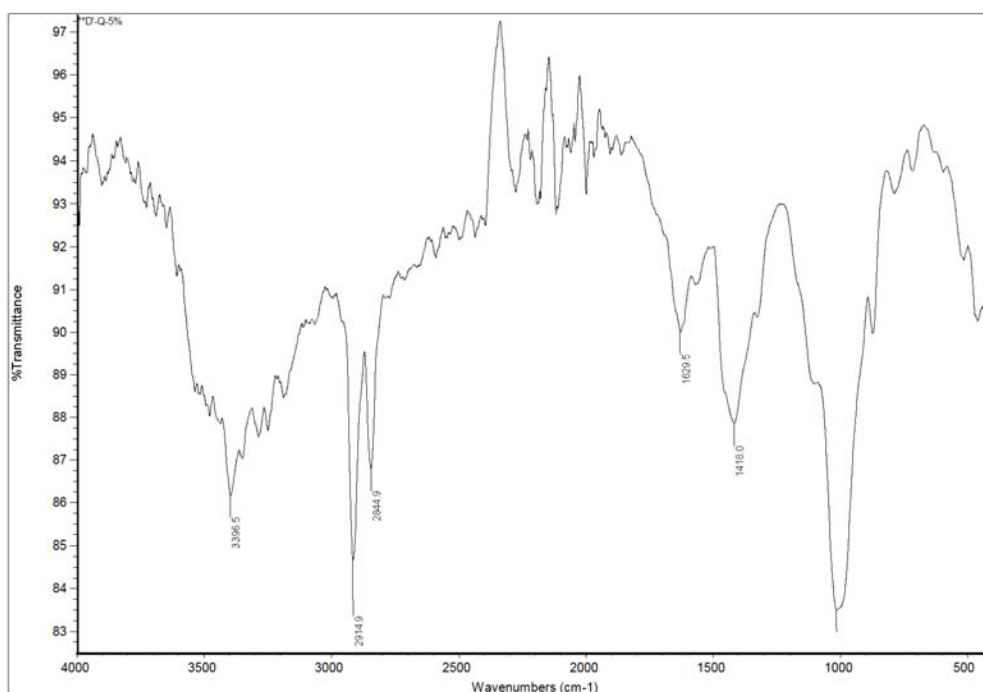
Figure C.14 FTIR spectrum of 5% PDQH H after 95 days
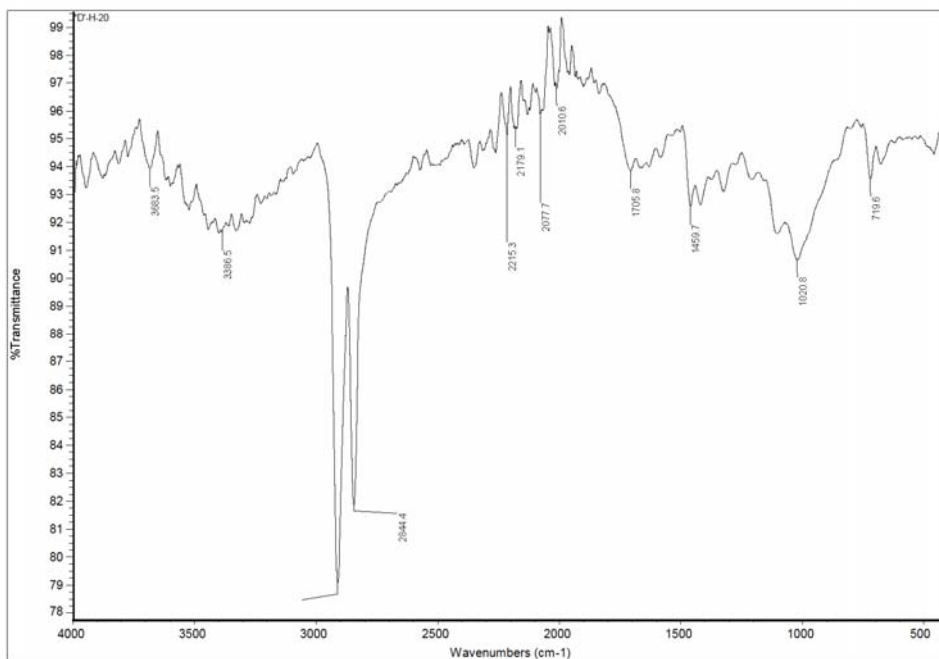
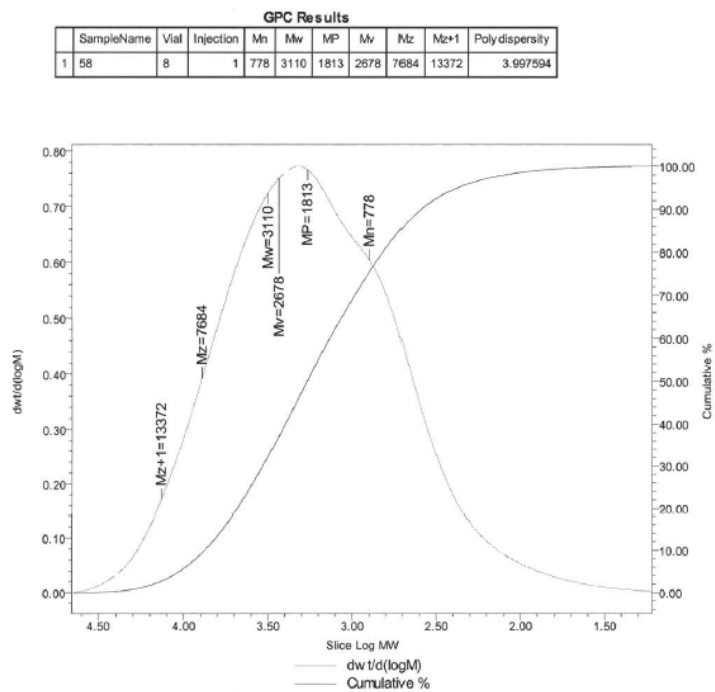**Figure C.15** FTIR spectrum of 20% Polystarch H after 150 days
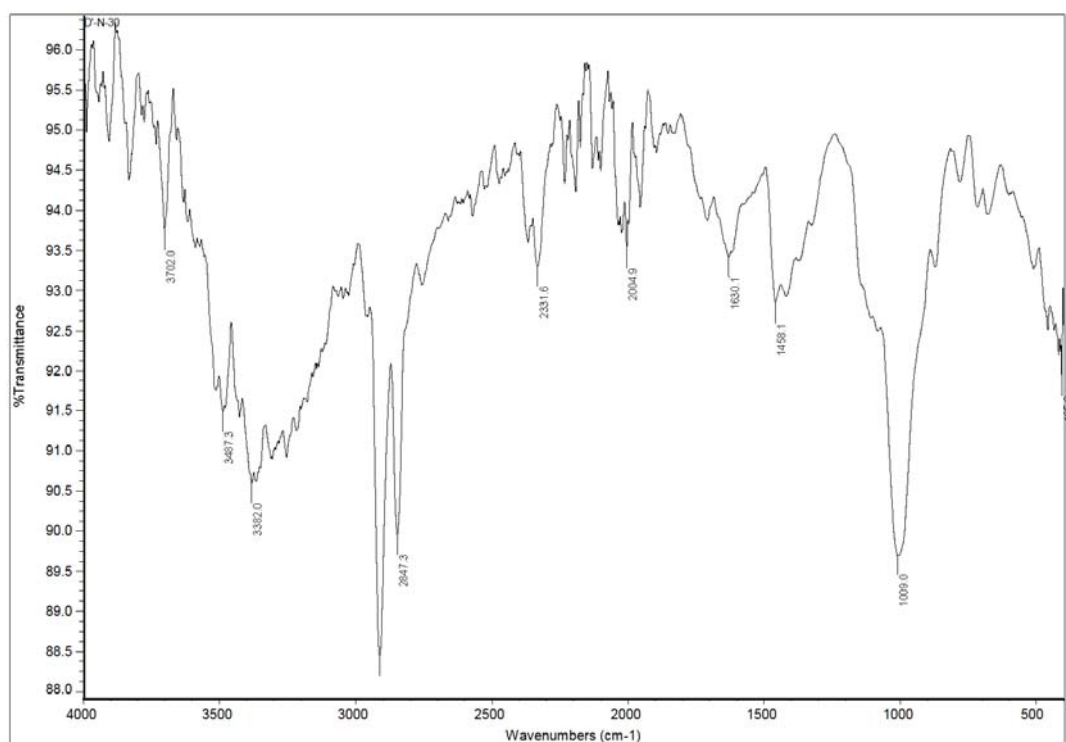
Figure C.16 FTIR spectrum of 30% Polystarch N after 150 days

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Figure C.17 FTIR spectrum of 5% PDQH after 150 days
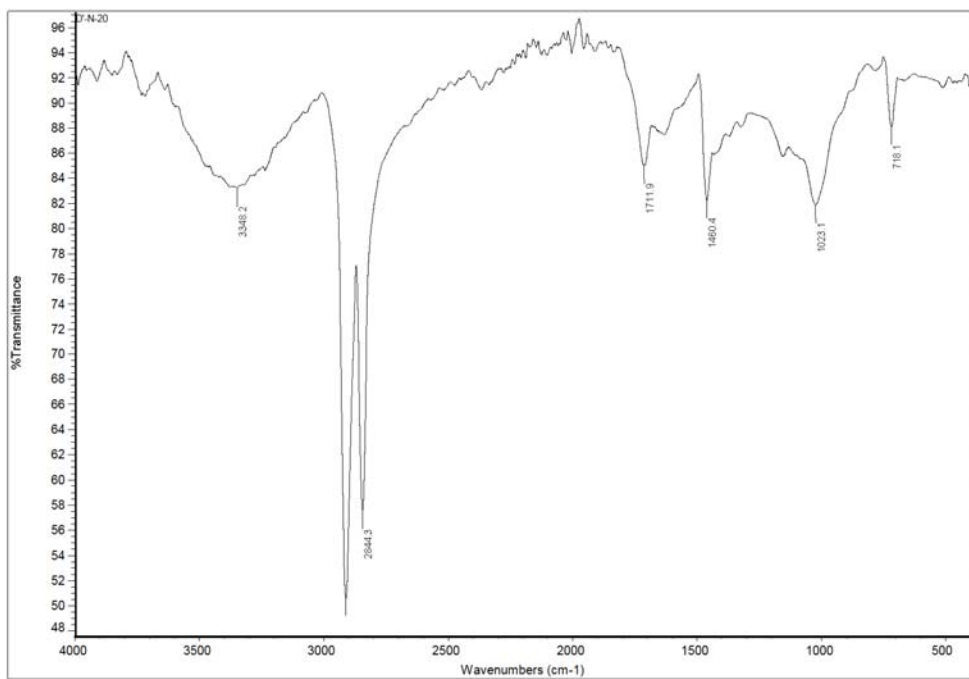
Figure C.18 FTIR spectrum of 20% Polystarch N after 150 days
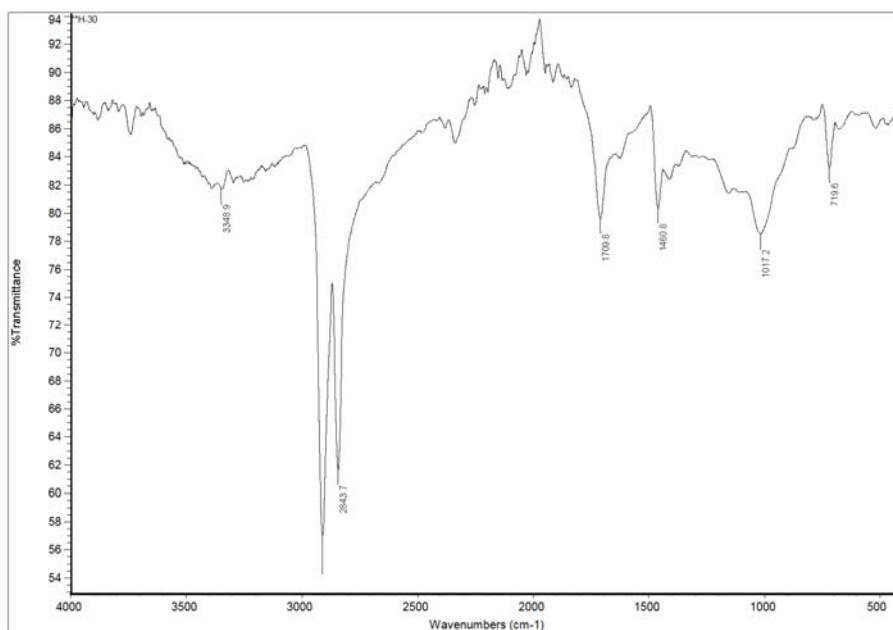
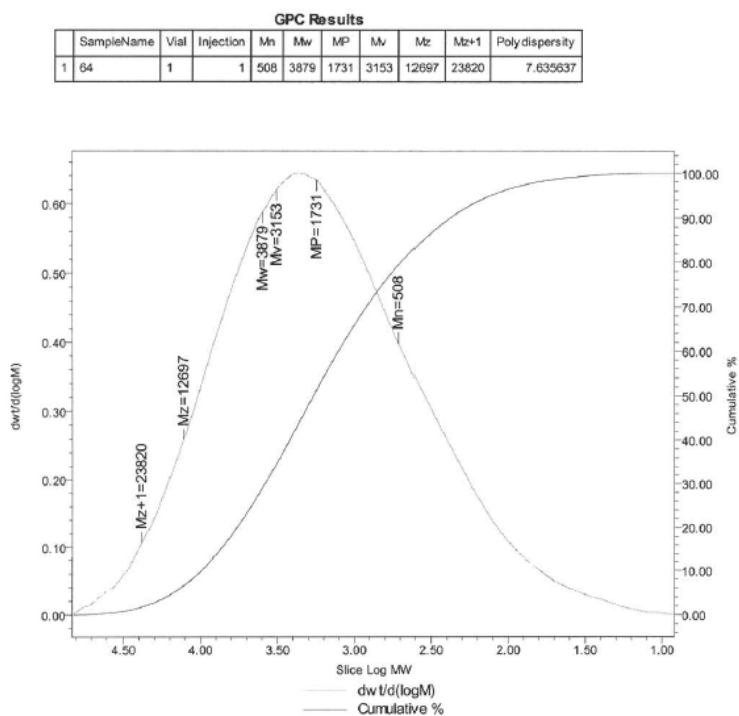**Figure C.19** FTIR spectrum of 30% Polystarch H after 150 days

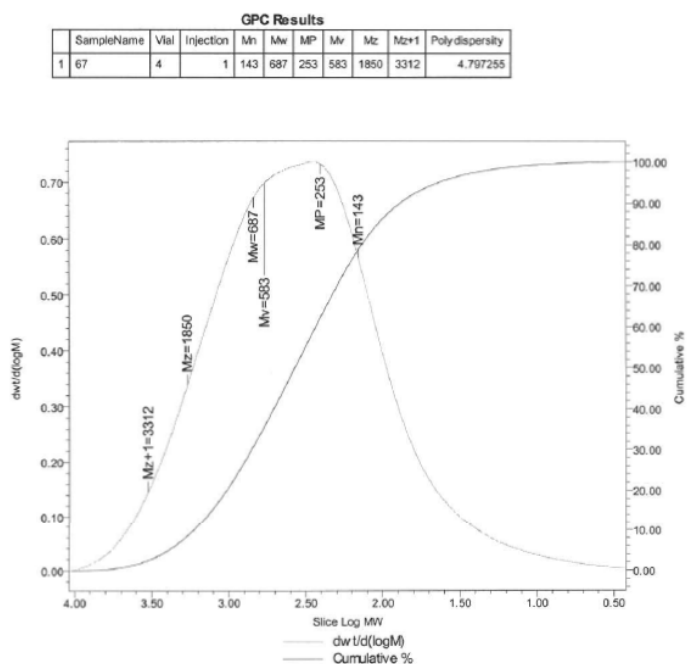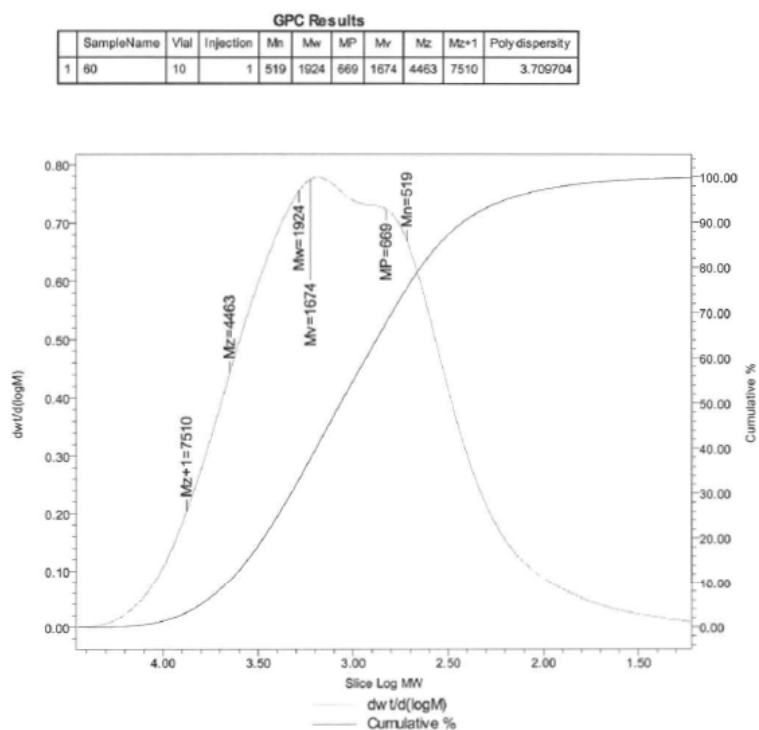**Figure C.20** FTIR spectrum of 3% PDQH after 150 days

D GPC Results

GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	58	8	1	778	3110	1813	2678	7684	13372	3.997594

Figure D.1 Molecular distribution of 20%Polystarch N after 235 days

GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	64	1	1	508	3879	1731	3153	12697	23820	7.635637

Figure D.2 Molecular distribution of 20%PDQH after 120 days

GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	67	4	1	143	687	253	583	1850	3312	4.797255

Figure D.3 Molecular distribution of 20%PDQH after 235 days

GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	60	10	1	519	1924	669	1674	4463	7510	3.709704

Figure D.4 Molecular distribution of 20%PDQH after 150 days

GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	46	1	1	495	2291	1489	1970	5415	8669	4.632552
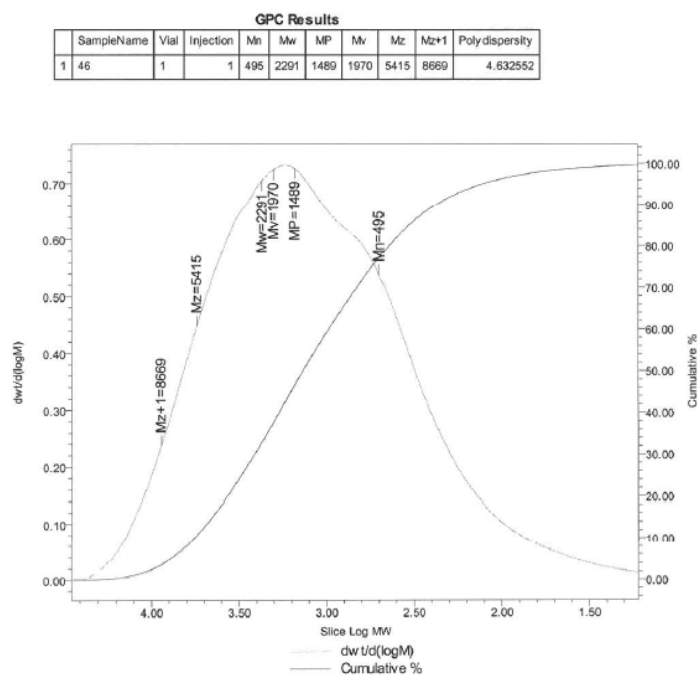
Figure D.5 Molecular distribution of 20%PDQH after 130 days

GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	29	1	1	308	1597	493	1331	4534	7762	5.193352
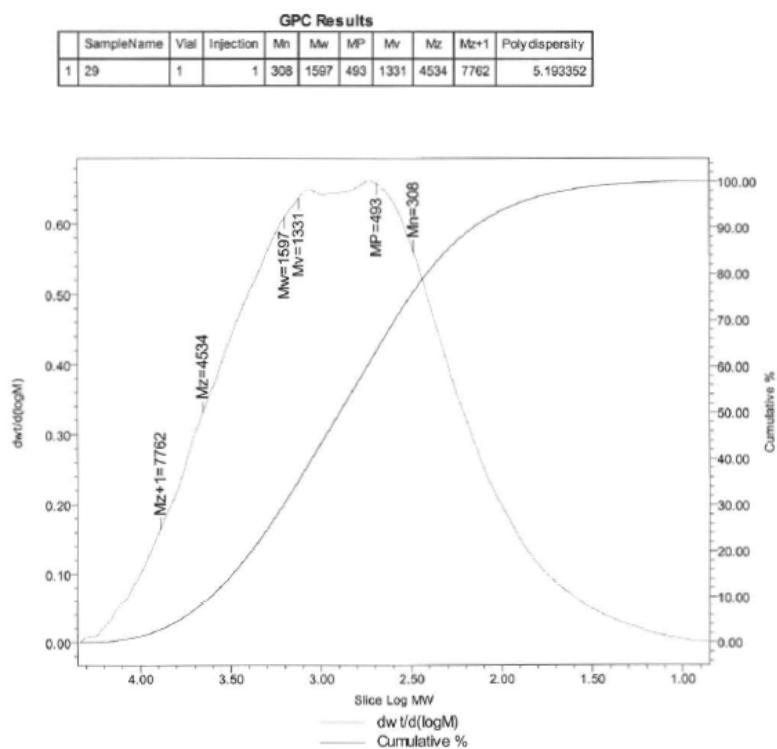
Figure D.6 Molecular distribution of 20%PDQH after 180 days

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GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	36	8	1	557	3208	1600	2676	9439	17941	5.760483
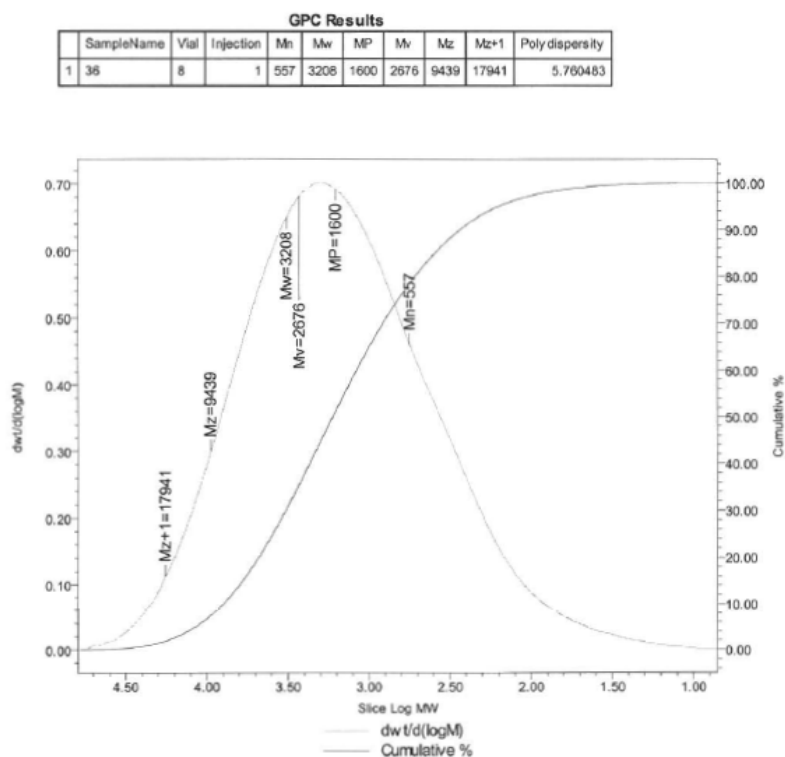
Figure D.7 Molecular distribution of 20%Polystarch H after 180 days

GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	3N30	6	1	603	2982	1656	2544	7852	14536	4.945693
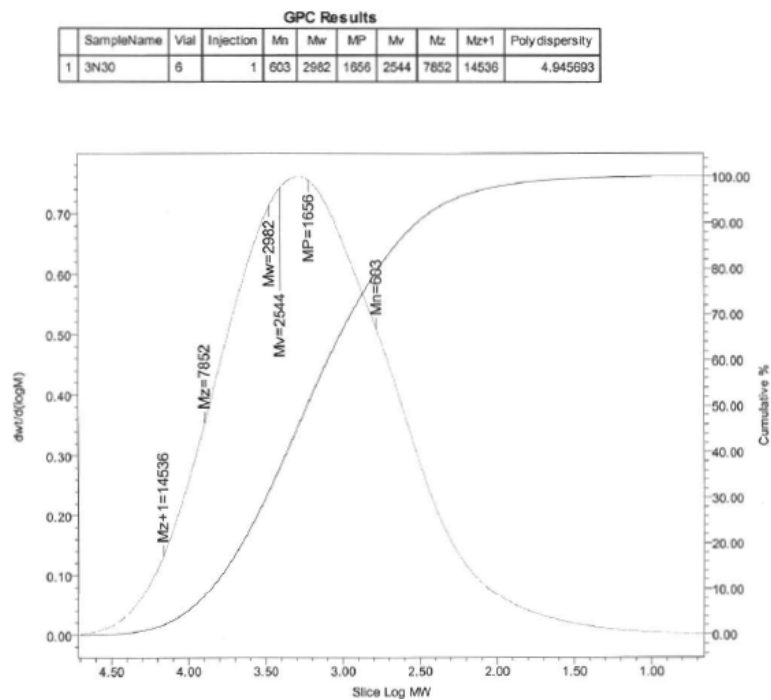
Figure D.8 Molecular distribution of 30%PDQH after 180 days

GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	3PE	8	1	893	4990	2541	4199	13961	25495	5.588932
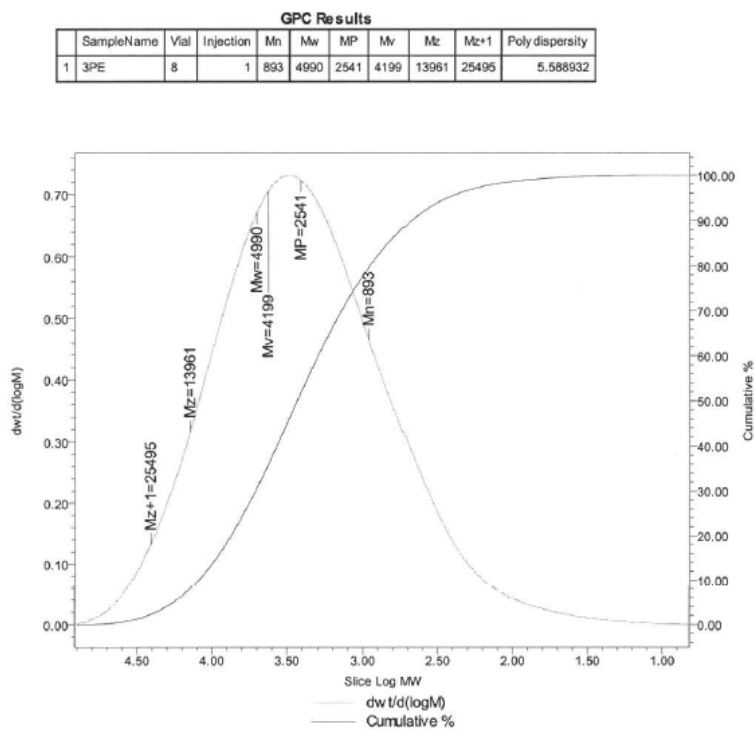
F

igure D.9 Molecular distribution of 30%Polystarch N after 100 days

GPC Results

	SampleName	Vial	Injection	Mn	Mw	MP	Mv	Mz	Mz+1	Poly dispersity
1	PE_DH20	3	1	1171	4141	2719	3644	8857	14103	3.534678
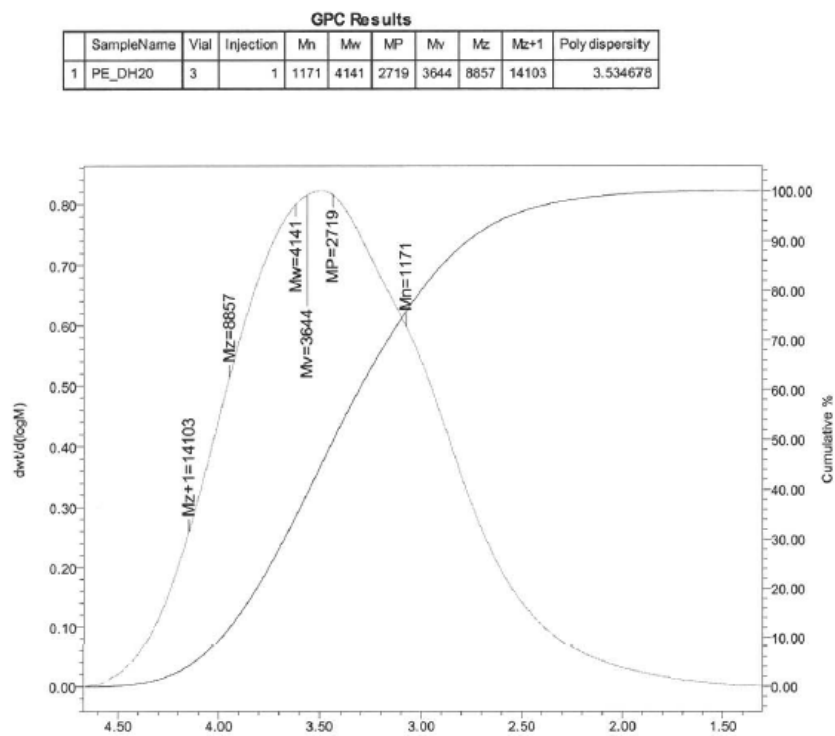
Figure D.10 Molecular distribution of 30%Polystarch H after 100 days

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E DSC Results

Sample: N-40
Size: 5.0000 mg
Method: Heat/Cool
Comment: D-30

DSC

File: C:...\Desktop\Ruhul\Dharan.002
Operator: Anwar Parvez
Run Date: 14-Oct-2008 14:52
Instrument: DSC Q1000 V9.4 Build 287

Exo Up   Universal V4.2E TA Instruments
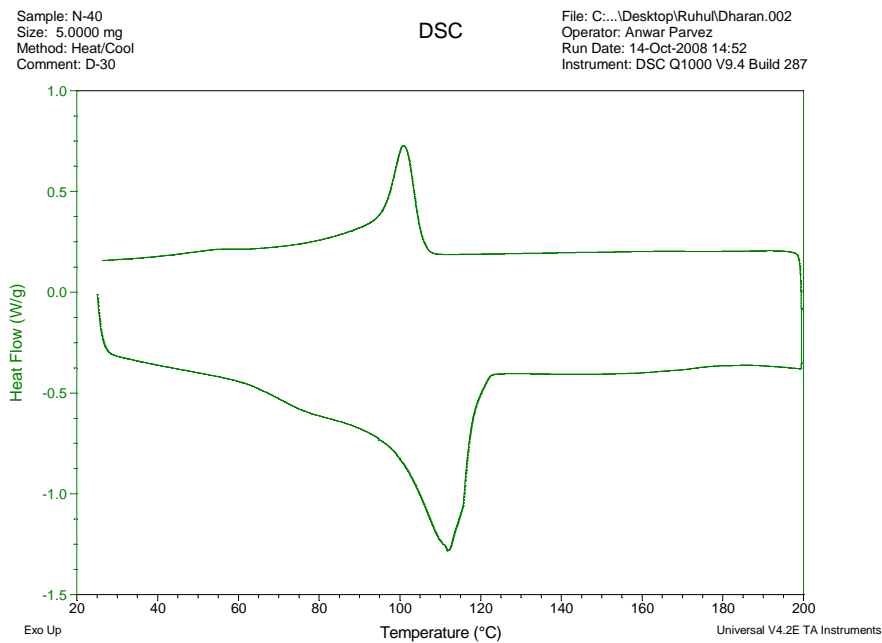
Figure E.1 DSC results of 40% Polystarch N

Sample: Q-05
Size: 6.3000 mg
Method: Heat/Cool
Comment: D-30

DSC

File: C:...\Desktop\Ruhul\Dharan.005
Operator: Anwar Parvez
Run Date: 14-Oct-2008 17:37
Instrument: DSC Q1000 V9.4 Build 287

Exo Up   Universal V4.2E TA Instruments
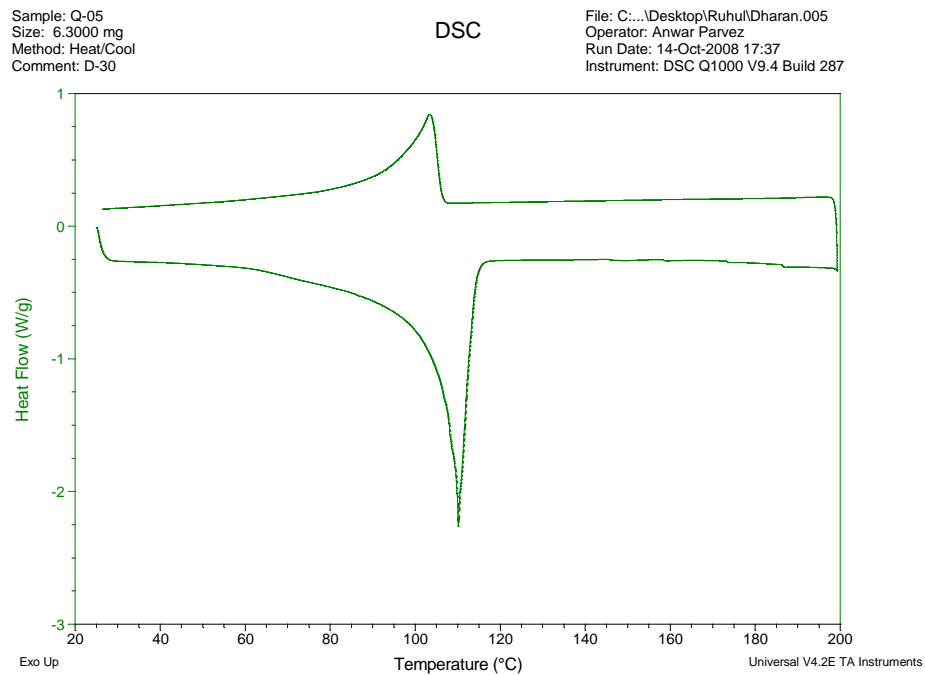
Figure E.2 DSC results of 5% PDQH
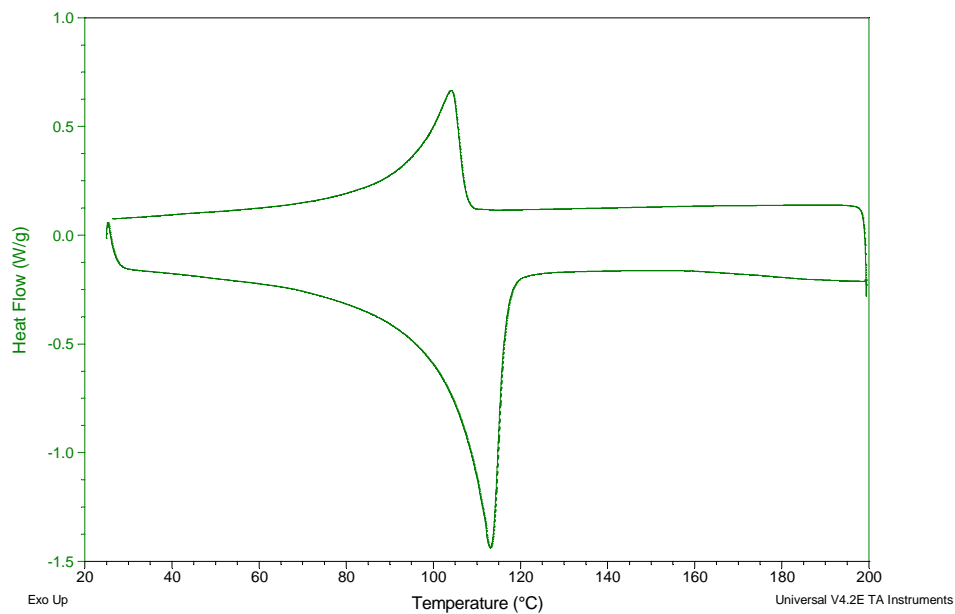
Figure E.3 DSC results of 20% PDQH

Figure E.4 DSC results of 20% Polystarch N

Sample: N-30
Size: 12.2970 mg
Method: Rubber
Comment: 29/12/2008

DSC

File: C:...\Desktop\Ruhul\N-30.001
Operator: Anwar Parvez
Run Date: 30-Dec-2008 16:23
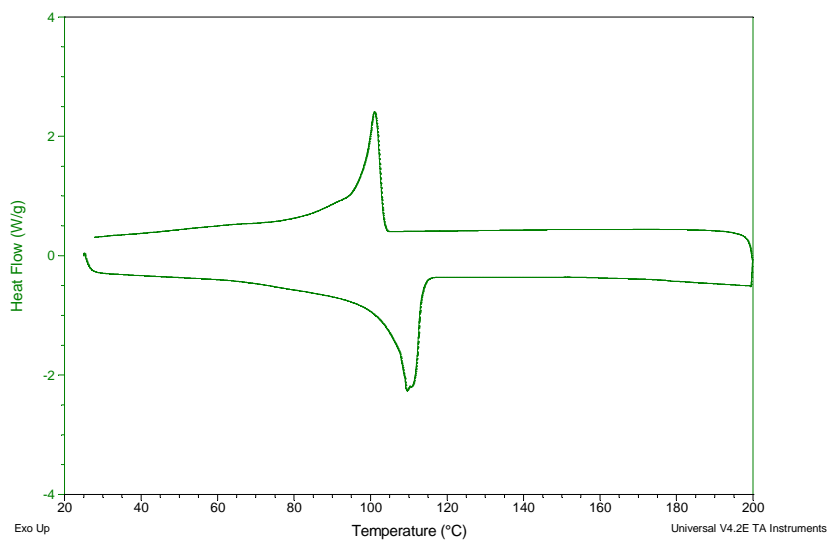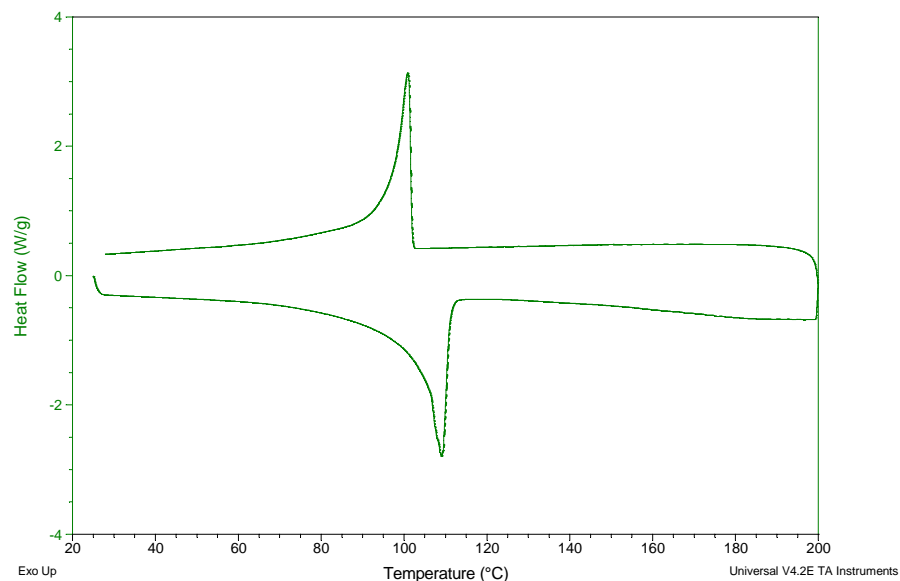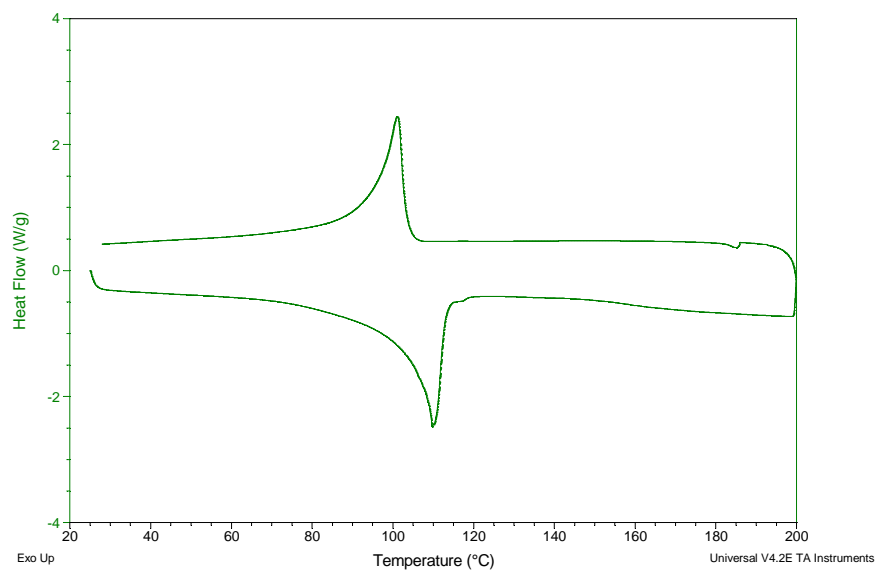Instrument: DSC Q1000 V9.4 Build 287
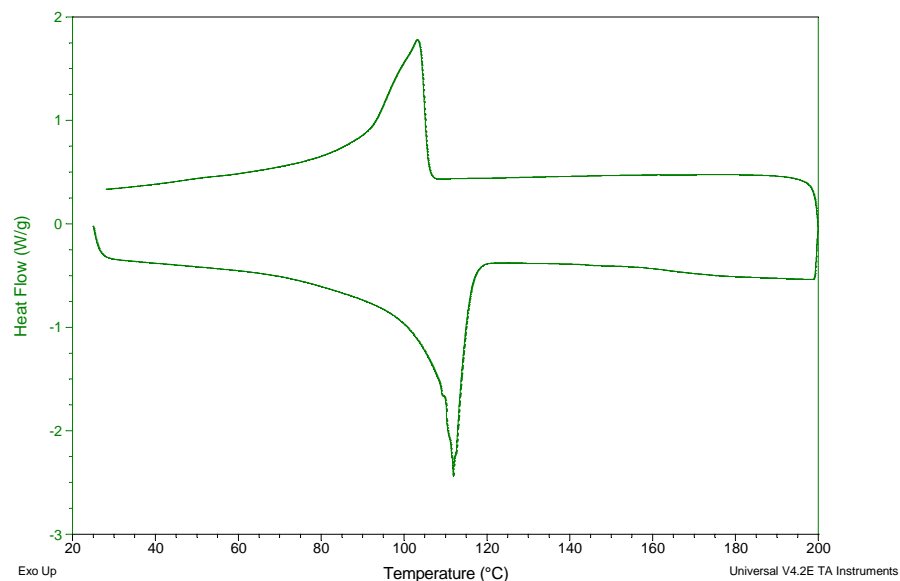
Figure E.5 DSC results of 30% Polystarch N

Sample: O-70
Size: 5.7770 mg
Method: Rubber
Comment: 29/12/2008

DSC

File: C:...\Desktop\Ruhul\O-70.001
Operator: Anwar Parvez
Run Date: 31-Dec-2008 12:21
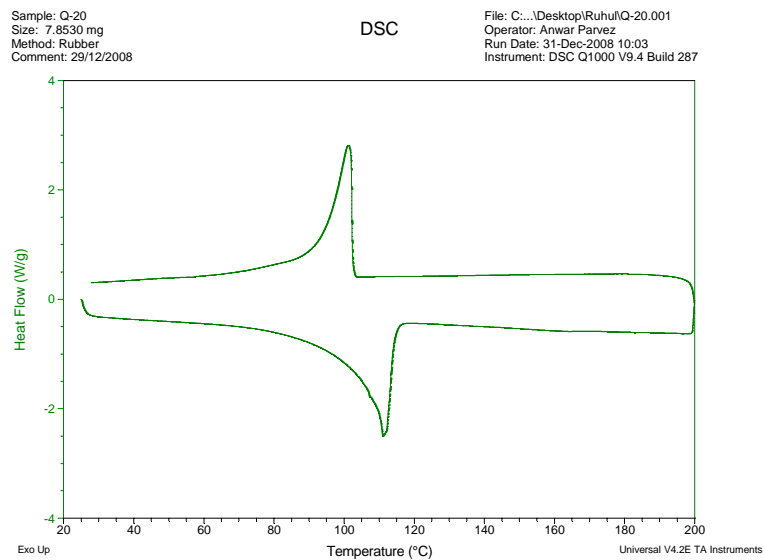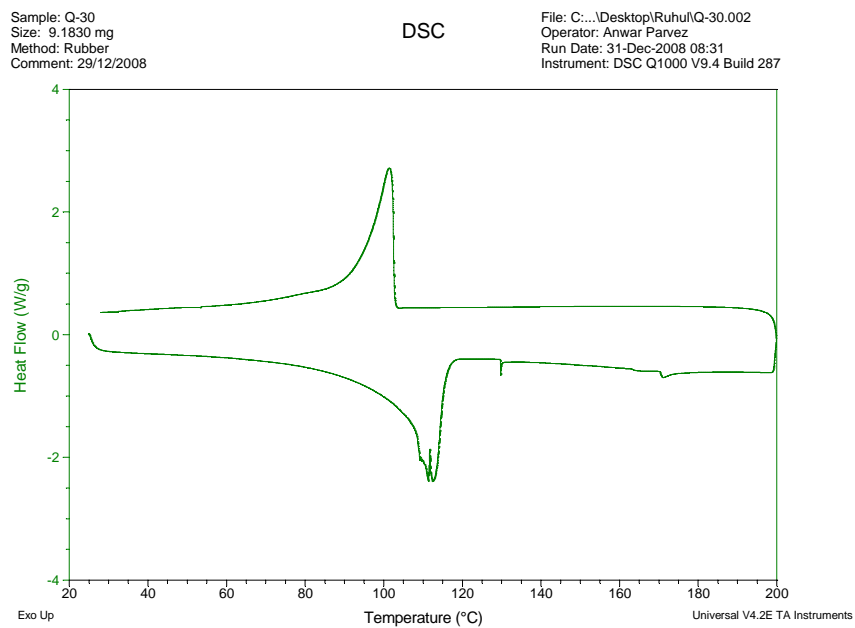Instrument: DSC Q1000 V9.4 Build 287

Figure E.6 DSC results of Polyethylene

Figure E.7 DSC results of 3% PDQH

Figure E.8 DSC results of 10% PDQH

Figure E.9 DSC results of 20% PDQH

Figure E.10 DSC results of 30% PDQH

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