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# Testing the Degradation Rates of Degradable, Non-degradable and Bio-degradable Plastics Within Simulated Marine Environments

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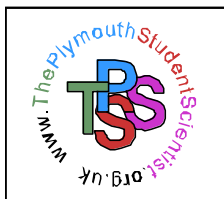
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# Testing the Degradation Rates of Degradable, Non-degradable and Bio-degradable Plastics Within Simulated Marine Environments

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2008

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## Abstract

Plastics are a serious problem in the environment today. They cause a number of difficulties for organisms in the water which often mistake them for food and suffocate, or they become entangled in them and drown. Plastics are highly versatile and hard wearing, they survive longer than their use requires and often end up in the environment. One of the largest forms of plastic pollution is plastic bags. Many plastics bags have been deemed 'degradable' and have been given a time frame in which they will break down, but this does not suggest the type of environments in which they break down. In order to assess this, six marine environments have been set up including mud, sand, saltwater, freshwater, buried in mud and saltwater in darkness to simulate deeper water. Three samples of plastic will be the focus of the project, a claimed degradable bag from Tesco, a non-degradable bag from Sainsbury's and a bio-degradable bag. They were all placed into the different environments and systematically tested for degradation every three months. The project ran for nine months. The samples were tested for degradation using several techniques. There were 'before and after' photographic records. The dry weight before and after was also taken. The samples capability to withstand load was tested using tensile strength testing and the chemical make up of the bonds contained within was found using a process called photo-acoustics. The result of the investigation showed that the Tesco, and Sainsbury's bags were practically identical chemically, they were both polyethylene based, and behaved similarly. The Bio-bag seemed to be starch based. The investigation found that all samples had succumbed to degradation in one form or another. The polyethylene samples deprived of light degraded very slowly and it was concluded that UV light was the trigger for causing degradation in these samples. The best environment for this was the freshwater simulation. Mud and sand caused least degradation. The Bio-bag degraded efficiently in all environments, but favoured environments with a more anoxic nature, such as being buried in mud. Here, there was a complete breakdown of the structure. The sample degraded even in the absence of light shown in the deep water simulation, where there was positive degradation. The conclusion of the investigation showed that polyethylene based plastics breakdown very poorly within the environment. Also that both samples degraded, but that the 'non-degradable sample' simply takes longer. The Bio-bag was very efficient at breaking down, but became very structurally weak after a very short period of time and is therefore not an adequate replacement for the polyethylene samples, further evidence that bio-degradable samples could be manipulated to eventually replace plastic as we know it.

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## **1. Introduction**

### **1.1 Plastics in the environment**

Plastics have been around for centuries, but the first synthetic polymer created occurred in the 19<sup>th</sup> century, by Leo Hendrik Baekeland in 1909 who created Bakelite. From this base polymer, many plastics used today have been created. Such polymers include polyvinyl chloride (PVC), polyester, polyamides and many more. The explosion of plastic use since the 19<sup>th</sup> century is incredible, from invention to becoming integral to every aspect of our lives is remarkable.

Plastics are polymers, long chains of molecules which contain repeat 'units' of monomers. Most plastics are atoms which contain bonds using carbon, hydrogen, oxygen, nitrogen and sulphide. These create the 'backbone' of the polymer, but may have additional branches of molecules protruding off. The variety of various 'backbones' leads to a variety of different plastics, each with variable chemical and physical properties. Due to the sheer quantity of molecules contained in plastics, they have a very high molecular weight. Some plastics are exceptionally hard wearing and therefore stay within the environment for a very long time.

Plastics are created from crude oil in a process known as fluid catalytic cracking, where the bonds and molecules within crude oil are 'sorted' or refined into groups of same molecular weight. This makes the process of removal of the desired molecules more efficient. Plastics and synthetic materials have found their way into every aspect of our lives. From plastic bags for shopping, to colouring in paint and are

“perfectly matched with modern day equipment such as mobile phone, bank cards and laptops” (Stevens, 2002). Therefore with such a reliance on this material, globally there will be a serious issue to address when the raw material (crude oil) begins to become far scarcer, and plastics are no longer the cheaper to other alternatives.

## **1.2 Manufacture of plastics and their uses**

Plastic is produced on a colossal scale, to the point where it is found in every corner of every home. Stevens (2002) suggests that 200 billion pounds of plastic is produced each year. More wealthy countries have a higher need for plastics. The United States is responsible for nearly a third of the overall production of plastics. So why are they so useful?

Plastics are highly versatile; they can be moulded and shaped into almost any design. Plastics are essentially very cheap to produce and due to their many uses, are highly desirable. Examples of how plastic usage can vary can include CDs and DVDs which have become important in creating a multi-billion dollar industry globally. However, plastics are also used in food preparation, furniture or even space exploration.

Due to the rapid expansion of the plastic industry over the last century, plastics and synthetic materials can be found everywhere. As a result of this, plastics have risen to become one of the most commercially used materials though-out the world and due to the high volume of production, these synthetics are often deemed a ‘one time use’ commodity. Therefore, overall waste plastic debris is becoming a series global problem, affecting wildlife, habitats and destroying the aesthetics of many areas around the world.

The plastic industry creates its product on a massive scale, with over fifty different types of plastics and an astronomical amount of uses for them. However, they can mostly fall into two categories, thermoplastics and thermosetting plastics.

Thermoplastics can be melted down and re-set making them far more re-usable, where as thermosetting plastics are ‘one time only’ use product.

### **1.3 Legislation**

One of the main causes for marine life entanglement within ocean ecosystems is due to discarded fishing equipment (mostly nets) which, once broken, is thrown overboard. This causes severe lacerations and drowning to organisms, such as seals. One case study involved recordings of the percentage of fur seal juveniles that were caught and entangled within marine debris. The results from two test sites in Alaska, St. Pauls Island and St. George Island, showed a definitive decrease in the percentage of entanglement from the mid-1970's to 2000. MARPOL 73/78 is a piece of international legislation implemented in 1972 (Bell & McGillivray, 2000). The most important aspect prevents the dumping of any material, except food, by ships at sea (Clark, 2003). From this time frame fur seals became less entangled, which further supports the cause for preventing entanglement at sea.

In order to ease the environmental issues being caused by plastics there have been a variety of laws to reduce plastic dumping in the environment. A levy system was imposed on customers in 2002; Ireland placed a charge on plastic bags to consumers (Department of the Environment and Local Government 4mar02). Could a similar project relieve stress in England? In October 2007 people living in London were called to vote on either a levy of 10p per bag used, or an outright ban on disposable plastic bags (<http://news.bbc.co.uk/1/hi/england/london/7084387.stm>). November 2007, the results were back, 58% in favour of a total ban. This may become a new amendment to the London Local Authorities Bill.

In February 2008, Marks & Spencer, a well known name in the high street, announced that they would now charge a fee of 5p per bag in their 600 UK stores, estimating a 70% reduction in bags leaving the stores. This type of solution has been trialled in many places in Europe and has proven to reduce free bag usage. In late February 2008, Gordon Brown declared that he intends all shops to implement a similar procedure.

### **1.4 Chemical make up**

In order to create a plastic, polymers are required. These are long chain molecules which contain repeating units. As polymers could theoretically continue on indefinitely, their size is characterized by their molecular weight. As mentioned before



plastics are either thermoplastic, or thermoset. The thermoplastic can have its physical state changed by the addition or removal of heat. In thermoplastics the structure is more linear with less branched chains. Roughly “90% of plastics today are thermoplastics” (Stevens, 2002)

Most plastics have additional additives to boost desired properties, such as performance additives like inert fillers to reduced production cost. These fillers could be utilised to help accelerate the chemical breakdown of a polymer.

Kiatkamjornwong *et al* (1999) suggested that research should be conducted into creating new plastics, such as photodegradable plastics, which contain substances sensitive to light. These include transition metals or a photosensitive group.

Examples of such photodegradable plastics are poly (L-lactide) (PLLA) and poly ( $\epsilon$ -caprolactone) (PLC). The chemical makeup of these structures allows UV light to penetrate with no reduction in its intensity, causing the overall breakdown of the material (Tsuji, 2005).

As well as additives most plastics also have plasticizers in them as well, this boosts physical properties such as durability or flexibility. Plasticizers make the plastic tougher. The higher the percentage of plasticizer included in plastic, the tougher it becomes.

## **1.5 Degradation of plastics**

“Commodity plastics are typically stable in almost all environments” (Stevens, 2002). This is generally because they are hard wearing, water resistant and are not readily broken down by biological organisms. Plastics are capable of degrading under both aerobic and anaerobic conditions. The ability for plastics to degrade with or without oxygen must be carefully considered if it is to be removed from the environment.

Plastic starts to degrade when radiation between 290nm to 315nm (UV-B radiation) hits it and weakens the bonds holding it together. Using this as a principle there have been many studies into a correlation between UV-B intensity and plastic breakdown (Mills, 2006). It is relative to the amount of light-stabilizer added to the plastic, this increases its' resistance to UV-B breakdown. The breaking of the chains in a polymer into smaller chains is known as chain scission. The continual breaking of the chains results in the polymer becomes unstable and brittle. Another aspect to

consider is that some of the polymers used in plastic production include a phenol group, or benzene ring. The benzene ring has a 'cloud' of de-localized electrons in it, and these have the ability to absorb energy from UV photons, therefore increasing the plastics resistance to photo-degradation. Zhao (2006) found that photocatalytic degradation processes of polyethylene were slow under normal UV-B and solar irradiation. However, with a TiO<sub>2</sub> catalyst in the air, the process was much faster. It is important to note the difference between degradation and fragmentation.

Degradation is the total breakdown of a substance, where fragmentation is due to breaking of the material. Often fragmented material will not continue to degrade after it has been damaged, the particles remain. However, this is where bio-degradable plastics are beginning to get attention. They break down to a point at which organisms such as bacteria and fungus are able to digest them (Kamiya, 2007; Volova, 2007).

Hydrolysis is the chemical breakdown of a substance due to water. There are few plastics currently in development which breakdown due to hydrolysis and more research into their development and uses is required (Andrady, 2000).

## **1.6 Biodegradable plastics**

Currently there are many alternatives to plastics polluting the environment. The most common is a bio-degradable plastic, which actively degrades rather than just breaking down after a certain length of time. There are many different types of compostable bio-degradable plastics currently in development. These range from oil-based plastics such as vegetable-oil (such as polyamide 11) and soya bean oil, to starch based compounds. Under the right circumstances such as light, moisture and temperature the plastics start to break down. This is why they are marketed as compostable bags, because compost heaps have the right elements to cause bio-plastic breakdown. One suggested disadvantages of using oil based biodegradable plastics are that they release additional CO<sub>2</sub> into the atmosphere, contributing to global warming, however this requires further research. Popular choices of bio-degradable plastics are starch based compounds. This is because they are formed from carbon within the environment via photosynthesis.

Materials such as polyhydroxyalkanoates claim to be 100% degradable; Volova (2007) found this to be apparent within eutrophic reservoirs. However, bio-degradable plastics are expensive to produce and cannot achieve the same 'economies of scale' which plastics like polyethylene can. Gerngross *et al.* (1999, 2000) indicated that the energy required to produce one kilo of polyhydroxyalkanoate (PHA) biopolymer (by fermentation) from plants was equivalent to the consumption of 2.65 kg of fossil fuel. While the production of one kilo of polypropylene required only 1.54 kg of fossil fuel. Bio-degradable plastics require oxygen to break down; they are likely to degrade very slowly within anaerobic conditions, such as a landfill site.

Inevitably different biodegradable plastics are linked to specific environments which trigger their degradation. As seen by Mohee (1998, 2007), in a compost environment bio-degradability can take as little as 1 to 6 months. So the operational conditions which trigger bio-degradation can be linked to type of environment and type of inoculum used (Nakassaki, 1997). This theory does not seem limited to bio-degradable plastics, as normal polymers tend to breakdown in relatively high temperatures (such as exposure to UV radiation). This is supported in Vikman *et al* (2002). Many plastic bags have fillers in them; inorganic inert substances like chalks which are added to the original polymer and can cause a variety of effects. Bio-degradable monomers include poly (vinyl alcohol), poly (glycolic acid), polycaprolactone, and poly (ethylene oxide) (Stevens, 2002).

### **1.7 Testing for degradation**

Zhao (2006) tested degradation using a technique called Fourier Transform Infra Red spectroscopy, or FT-IR (this technique was originally planned for this project). There have been many projects which have incorporated the FT-IR technique in the same way, including Kaczmarek *et al* (2004) and Signor *et al* (2003). However, there are many projects which prefer methods such as measuring CO<sub>2</sub> production in more 'real-life' simulations (Mohee, 2007). Although this is not useful in removing plastic from the environment, it may be used to assess the speed of plastic breakdown, instead of dumping it into a landfill site. This project will be looking at plastic bags primarily constructed from polyethylene; much of Mohees' research is highly relevant in this project.

Kudoh *et al* (1996) conducted a similar project. Several polyethylene samples were exposed to various levels of UV irradiation dosages and the tensile strength of the plastics were recorded. As expected the flexural strength of the samples decreased with higher doses.

Mohee (2006) conducted a project under real life conditions, in which he tested the degradation of two “normal” and a compostable plastic. After 55 days of testing it was seen that the “normal” plastics showed no degradation, however, the compostable bag degraded completely.

Various studies conducted use different methods for testing degradation. Nakassaki *et al* (2000) tested degradation through the measurement of CO<sub>2</sub> evolution by passing emitted gasses from a compost heap over sulphuric acid to absorb ammonia, then performing spectral analysis on it. Degli-Innocenti *et al* (2000) developed two methods for testing biodegradability. The first relied on the weight of a sample going into a compost heap in comparison to the weight of the sample after a period of time. This method has also been adopted for this investigation. The second was concerned with the ISO 14855 through the use of vermiculite, which is a clay mineral matrix. Mohee (1998) concluded a biodegradability coefficient by using a “real-life” approach. The study determined the reaction rates of constants by analysing oxygen uptake at different temperatures.

## **1.8 Problems within the marine environment**

Due to the longevity of plastics, and their resilience to degrade, they tend to stay within the environment long after their ‘use’ is over. Such as food wrappers, these will be around for many years after the food products have gone. As a result, plastics find their way into various eco-systems and habitats of both terrestrial and marine organisms. There has been extensive research in to the affect of plastics in the ecosystems of many organisms; bird life is a good example.

Types of human activity can greatly impact an ecosystem, such as cleaners or air blasting paint off a car can create small fragments of plastics no larger than 0.5mm known as “scrubbers”. Once discarded they find their way into the water column where they, not only further plastic pollution, but are also heavily laden with metals which can cause both toxic and non-toxic contamination (Gregory, 1996).

## 1.9 Impacts on wildlife

As mentioned before many types of wildlife are affected by plastic debris infiltrating the environment. Birdlife in particular is heavily affected by increasing plastic material located on shore. Hartwig (2007) found that synthetic material was becoming integrated in to Kittiwake nests in the Jammerbugt colony off Denmark. The study found the amount of litter in the nests had increased from 39.3% off 466 nests in 1992, to 57.2% of 311 nests in 2005. This growing level of plastic pollution causes serious harm to many species through ingestion and entanglement. The amount of marine animals which die each year as a result, is approaching 100,000 in the North Atlantic alone (Wallace, 1985). Small fragments of plastic are often mistaken for food, especially by sea birds. It is estimated that 44% of all sea birds ingest plastic while feeding (Rios, 2007).

Carr (1987) and Mascarenhas *et al* (2004) both contributed research on sea turtle populations, floating marine debris and its impact on the species. Mascarenhas *et al* (2004) researched *Lepidochelys olivacea* and *Chelonia mydas* located along the coast of Paralba. The paper found that in many necropsies, plastic was found in the sea turtles stomachs, not just disused fishing equipment but also anthropogenic debris including six pack rings, tar and plastic bags. The result of ingesting such material leads to intoxication, obstruction of the oesophagus or perforation of the bowels. These harmful effects are the fate of almost any species that mistakes synthetic material for food.

Ghost fishing is one of the main causes for entanglement related deaths in the marine environment. Ghost fishing is when broken, or old, fishing equipment is thrown overboard. Nets are often made of exceptionally hard wearing plastics and therefore stay within the marine environment for a very long time. These nets cause sever lacerations and often drowning of organisms which can range from fish and sea turtles to fishing sea birds and fur seals.

Although there is a multitude of data to suggest plastic fragmentation and its impacts on mammals and seabirds, there is less research into its affects on filter feeders, an area which requires more attention. The affect plastics may have on filter feeders has been assessed by Moore (2001). It was observed in this paper that the plastic

accumulation in the North Atlantic subtropical high pressure cell was up to six times that of the zooplankton recorded at each station. Zooplankton floating the water column and 'marine snow' are the main diet of most stationary filter feeders, such as barnacles and anemones, and mobile feeders such as basking sharks and herring. As a result, if there are more plastic fragments in the water column, then these organisms are at higher risk of ingesting plastics, which may lead to suffocation.

### **1.10 Invasion of species**

Plastics not only harm marine life via ingestions and entrapment but they can also act as carriers for invading species to enter new eco-systems. For example tar pellets being used as attachment surfaces for *Dosima fascicularis*, a stalked barnacle in the North Atlantic Ocean (Minchin, 1996). A species which was considered extremely rare before 1986, but now can be found stranded up and down Irish coasts. There are many other examples of such 'alien' species invading including bacteria, diatoms, algae and tunicates (Carpenter et al., 1972; Carpenter and Smith, 1972; Clark, 1997). There is a significant risk involved with 'alien' taxa being introduced to a vulnerable ecosystem, especially if the 'alien' species is highly competitive for resources. McKinney (1998), suggested that if this biotic mixing continued to occur then the overall biodiversity of the oceans may decrease as much as 58%.

### **1.11 Bio-fouling**

Katsanevakis (2007) found that in the ocean, sea-bottom marine debris can occur in high densities and have an impact on benthic communities by providing a refuge for mobile species. The mobile species in question mainly includes algae and bacteria. The unwanted accumulation of bacteria, microorganisms, algae or even animals on underwater structures is known as bio-fouling. Plastics have a very small surface area, so the most likely causes of bio-fouling are going to be bacteria and algae. Algae covers the whole of the surface area, this blocks the sunlight and therefore the UV-B radiation hitting the plastic (Andrady, 2000). This could be one of the reasons why plastic degrades slowly in the oceans. Anti-fouling is the removal of the substance marine life is clinging to. Andrady (2000) also discussed how bio-fouling causes the density of plastics to increase and therefore be submerged. This occurs to a point at which sunlight is unable to sustain the algae bio-fouler and it dies,

causing the plastic to float once more. This negative feedback system causes a continuous circulation of plastics through the water column.

## **1.12 Aims and Objectives**

One of the proposed methods of dealing with the currently growing plastic pollution is to create several plastic landfill sites and simply bury the problem. However, it has been found that paper, a very degradable material, does not break down in a land fill site, so what chance is there that this will solve the plastic problem? There has not been much research into how the natural environment impacts plastic degradation, for example will a plastic bag break down better in sand or in mud?

### **Aims**

The aim of this project is to see how the degradation rate of degradable, non-degradable and Bio bags alters in different simulated marine environments.

### **Objectives**

This project is going to investigate the degradation rates of two conventional plastics, one degradable the other non-degradable. Also in addition to this the degradation of a compostable Bio bag will also be investigated.

- Several samples of each type of plastic will be placed into a designated marine environment. There will be six environments including saltwater, freshwater, mud, sand and dark salt water (to simulated deeper ocean environment). To allow a broad scope of different environments.
- The samples will then be left to degrade for interval periods of three months. Where the samples tensile strength will be tested, and the chemical make up will be recorded via photo-acoustics.
- The samples will then be compared with one another to see how the environment affects degradation rates.
- The project will run for 9 months.

## **Hypothesis**

Certain environments which allow oxidation, hydrolysis and have an ample supply of UVB radiation hitting the sample, such as freshwater will show more degradation than other environments, such as being buried in sand or mud.

## **Hypothesis II**

That the Bio bag will degrade in environments which have compostable characteristics, such as anaerobic qualities, such as mud, much faster.

## **Null Hypothesis**

There is no difference in degradation rates across the various marine environments.

## **2. Methodology**

This project proposes to find out how environment affects degradation rates of three different plastics. In order to achieve this, the plastics must be left to degrade over a period of time, situated within various simulated environments.

This has been achieved by filling 5 clear Perspex boxes with the relevant materials to simulate a chosen environment, see fig 1.1.

The chosen environments are:

Sand – From Whitsand Bay

Mud – From the bank of the Tamar

Saltwater – From the chemistry lab

Tap water – Representing freshwater

Salt water in darkness – Simulating deep water





Fig 1.1 Picture showing the practical set up of the investigation



Fig 1.2 Ocean depth simulation environment

The amount of each sample being placed into its environment is spatially limited. Therefore, the maximum size of the sample is 200mm x 110mm, this was the maximum size the containers would account for.

The original project length was 12 months, but inevitably ran for 9. Enough samples were available to account for testing every 3 months for a year. 24 samples of Tesco bags were labelled A-Y, excluding a control sample. Sainsbury's bags were labelled 1-24 and Bio-bags labelled with numbers and letters. Four of each sample were placed into a box and left to degrade. Tests were carried out on non-degraded samples to use as a base for comparison of degradation.

## 2.1 Visual Record

In order to ascertain if there had been any fundamental changes in structure over time, such as fragmentation, a photo of each sample was taken before and after

exposure, see fig 1.3 and 1.4. This was done for comparison purposes and to support any observations upon removing the sample.



Fig 1.3, 1.4 Examples of photo records for Tesco and Sainsbury's samples

## 2.2 Dry Weights

As well as a visual record, the dry weight of each sample was taken using a Sartorius R200D fig 1.5. This was to see if the mass of the sample had altered during the degradation process. When a sample was removed from an environment, it was dried to remove moisture weight. Upon removal of some samples, especially those involving mud, the sample was rinsed in deionised water to remove any additional substrate. After being rinsed the sample was kept in an oven at 2°C to dry off any unwanted liquid, then the dry weight recorded.



Fig 1.5 Sartorius R200D scales for dry weight comparison

## 2.3 Tensile Strength

Samples needed to be prepared before tensile strength could be recorded.

Suggested in Stevens (2002) the sample was cut into a 'barbell' shape, fig 1.6.

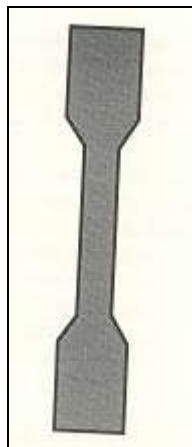


Fig 1.6 Barbell shape for tensile strength testing (Stevens, 2002)

The 'barbell' shape was cut using a scalpel and a ruler. The shape has two large squares which can be gripped by the Instron 3345 (Fig 1.7), which then slowly adds strain to the sample, recording the load applied and the resultant extension. This is a destructive process, once the sample has been tested, it had to be discarded.



Fig 1.7 Instron 3345 device used for tensile strength recording

For the first 3 month interval, there was only one recording of tensile strength. Subsequent testing periods revealed that carefully cut sample, could yield three repeats.

In addition ten repeats were performed on non-degraded samples. This was to gain a scope of the variability of this testing process, and give some insight into the errors which are associated with this technique.

## **2.4 FT-IR**

Fourier Transform Infrared Spectroscopy gives insight at the molecular level concerning the orientation and conformations of the polymer chains. This technique was employed to try and find out what the bond frequency was within the various samples and to see if there was change in frequency of certain bonds. A small plastic sample was placed into the device, IR radiation was passed through the sample, which absorbs certain frequencies of radiation depending on the bonds contained within it, the result being a spectrum containing various peaks. These peaks are likened to a finger print of the bonds and functional groups contained within. FT-IR can be used to identify unknown materials and determine the quality or consistency of a material.

Initially it was to be used on every sample in this project. However, though the control samples (un-degraded) created fine spectra, a problem arose when degraded samples, which had succumbed to bio-fouling, were tested. The samples could not be 'scrubbed' clean as this would taint the results. As a result, the thin layer of biological film created unreadable and useless spectrum, therefore this technique had to be modified.

## **2.5 Photo-acoustics**

The modification was a shift to photo-acoustics. A.G Bell in 1881 discovered as light hit the surface of a material an acoustic response was triggered, this is the result of thermal expansion of a material following an increase in its temperature due to the absorption of an external light energy is measured by specialised acoustic detection devices. With the input of light from a large range of wavelengths and the analysis of the resulting acoustics it is possible to identify both the chemical bond structure and

the chemical composition of a target sample.

The instrument in fig 1.8 is the Bruker IFS 66, used for photo-acoustics. Only a very small amount of sample is required for this technique. This is how repeat tests for tensile strength became possible, as not as much sample was required for photo-acoustics as was for FT-IR.



Fig 1.8 Bruker IFS 66 Photo-acoustic device

Before any testing could take place the instrument had to be calibrated using a completely black carbon background sample. In order to keep the instrument working correctly, this needed to be replenished regularly. In this project it was re-calibrated every five samples. The photo-acoustic sample was cut from the original sample using a cork borer, and placed within the instrument. CO<sub>2</sub> affects the spectra created in this technique heavily by creating large peaks. Before testing the sample chamber is purged with helium to clear any latent CO<sub>2</sub>.

To compare degradation a non-degraded sample is pivotal, it is from this that any shift in bonds can be seen and conclusions of degradation drawn. Repeats are easily done using the OPUS program. For this investigation the sample was scanned a recommended 32 times before being removed.

When analysing the spectrum the y scale has to be modified to show peaks in the spectra. However, it is not the frequency of the peaks, more the ratio of peak to peak

which is important. Therefore, the **y** scale in the result will alter to best express the peaks seen.

A standardized sample of polyethylene will be tested. A pure sample would not be plasticised in any way, and could therefore expose quantities and types of fillers which companies put into their bags. This could lead to alternatives suggested for fillers which facilitate degradation.

## **2.6 Light Experiment**

A method which was used was an experiment to test if there was any thinning of the sample by testing to see how much light passed through the plastic. A light reader was set up and the sample secured over the receiver. A lamp was shone at the sample and the resultant light detected was recorded. To make sure there were no additional light inputs, the test was conducted in a dark room, with the lamp being the only light source.

This method was only used once to test 3 month samples, because it was unbelievably difficult to set up, such as keeping the light source the same distance from the light detector. Ultimately the experiment was dropped due to logistics. The results of this preliminary study can be seen in the results section.

### 3. Results

#### 3.1 Dry Weights

Environment	Bag	Start weight	3 Months	Difference	Start weight	6 Months	Difference	Start weight	9 Months	Difference
<b>Sand</b>	Tesco (B,A,D)	0.4041	0.4024	-0.0017	0.4146	0.4152	0.0006	0.4184	0.3611	-0.0573
	Sainsburys (4,1,3)	0.3900	0.3905	0.0005	0.3785	0.3790	0.0005	0.3944	0.3957	0.0012
<b>Mud Buried</b>	Tesco (I,J,N)	0.3821	0.4164	0.0343	0.4291	0.4288	-0.0003	0.4061	0.4201	0.0140
	Sainsburys (11,16,9)	0.4020	0.4054	0.0034	0.3999	0.3772	-0.0227	0.3977	0.3967	-0.0011
<b>Mud Surface</b>	Tesco (Q,M,O)	0.3960	0.3700	-0.0260	0.3136	0.4733	0.1597	0.4335	0.4634	0.0299
	Sainsburys (15,13,12)	0.3739	0.5915	0.2176	0.3980	0.3964	-0.0016	0.3952	0.3950	-0.0002
<b>Freshwater</b>	Tesco (X,W,Y)	0.4158	0.4153	-0.0006	0.4019	0.3955	-0.0064	0.4093	0.4055	-0.0038
	Sainsburys (21,23,24)	0.3988	0.4115	0.0127	0.3906	0.4039	0.0133	0.3898	0.3920	0.0022
<b>Saltwater</b>	Tesco (H,G,F)	0.4004	0.3992	-0.0012	0.4373	0.4469	0.0095	0.3910	0.3891	-0.0019
	Sainsburys (5,6,7)	0.4005	0.3929	-0.0076	0.3901	0.4054	0.0153	0.3785	0.3785	-0.0001
<b>Saltwater Dark</b>	Tesco (U,R,T)	0.3846	0.4660	0.0814	0.4370	0.4660	0.0290	0.3940	0.3813	-0.0127
	Sainsburys (20,17,18)	0.4135	0.4371	0.0237	0.3973	0.4269	0.0296	0.3898	0.3889	-0.0009

Table 1 Dry weights before being placed into environment, and after designated time period

Table 1 shows the dry weights of the samples before being placed within their specific environment, and the resulting dry weight after removal at 3, 6 or 9 months. The third column gives the differences observed. Results were green if there was a weight decrease, and red if there was an increase. As seen in the table there is close distribution between samples which became lighter and those which became heavier.

### 3.2 Tensile Strength

Testing the variability of un-degraded samples:

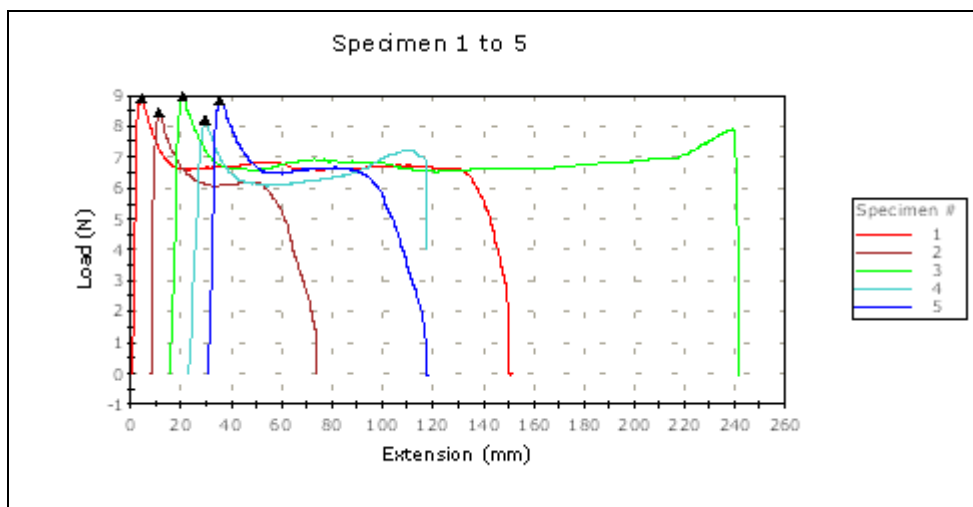


Fig 2.1 Variability testing of Tesco samples

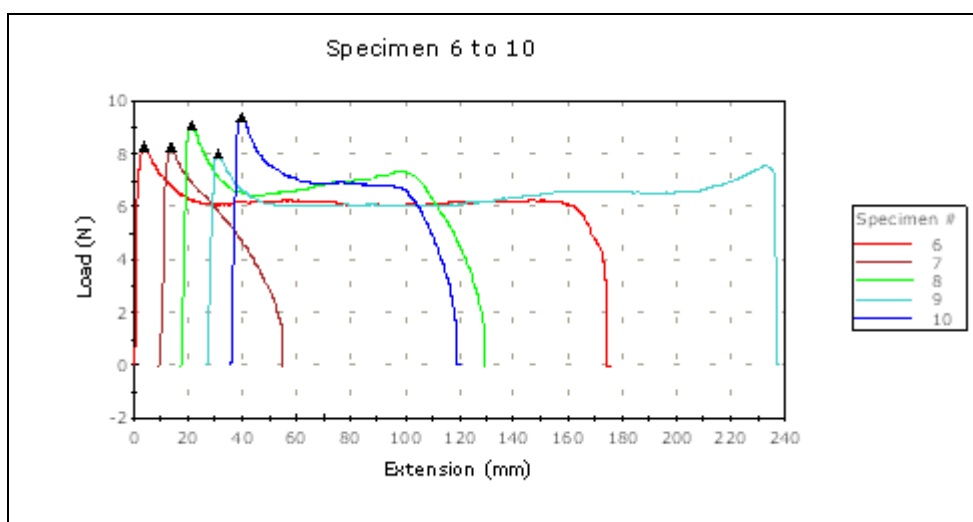


Fig 2.2 Further testing of Tesco sample variability



The graphs shown above demonstrate the variability testing performed on the Tesco samples. Ten repeat extensions were conducted on non-degraded samples to quantify the percentage variance associated with this method. Small triangles on the graphs indicate the point at which maximum load was achieved. Seen from the two graphs, extension of the samples varied greatly, from as little as ~70mm, to ~240mm. However, maximum load varied little, thus the reason it was the observed variable in this method.

Table 2 shows the results of the maximum loads achieved for the variability test for the three types of plastics used, additionally basic statistics are calculated also.

<b>Tensile Strength Variability</b>			
	<b>Plastic Sample</b>		
<b>Repeats</b>	<i>Tesco</i>	<i>Sainsbury</i>	<i>Bio Bag</i>
Test 1	8.90	10.65	8.60
Test 2	8.44	9.27	10.15
Test 3	8.95	10.72	10.46
Test 4	8.22	9.35	9.97
Test 5	8.85	10.60	10.35
Test 6	8.27	9.64	10.47
Test 7	8.25	9.61	12.35
Test 8	9.09	10.40	11.09
Test 9	7.99	9.49	9.16
Test 10	9.43	10.54	8.78
<b>Mean</b>	8.64	10.03	10.14
<b>S.Deviation</b>	0.47	0.60	1.12
<b>% Variance</b>	5.41	5.98	11.03
<b>Minimum</b>	7.99	9.27	8.60
<b>Maximum</b>	9.43	10.72	12.35
<b>Range</b>	1.44	1.45	3.75

Table 2 Max loads of un-degraded samples with basic statistics

The statistics show a small overall range in the Tesco (1.44N) and Sainsbury (1.45N) samples. In comparison, Bio-bags have a much higher range of 3.75N. The resultant standard deviations from the statistics allowed percentage variance to be calculated.

	<i>Tesco</i>	<i>Sainsbury</i>	<i>Bio Bag</i>
<b>% Variance</b>	5.41	5.98	11.03

Table 3 Percentage of variability of samples

The two super market values are low and only slightly higher for the Bio-bag, meaning the results can be assumed accurate.

From the tensile strength extensions, three different shapes were observed. Seen in fig 2.3, fig 2.4 and fig 2.1.

Fig 2.3 shows a sharp increase in strength, which levels off and then slowly increases to a maximum load, then breaches. This shape will now be referred to as *shape 1*.

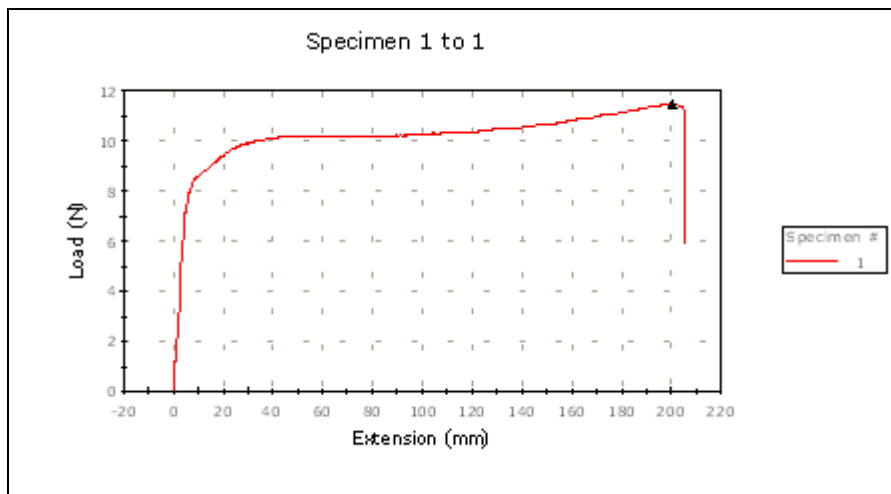


Fig 2.3 *Shape 1*

Fig 2.4 shows a sharp increase similar to *shape 1*. However, the maximum load is reached within the first half of the extension and then trails off slowly, referred to as *shape 2*.

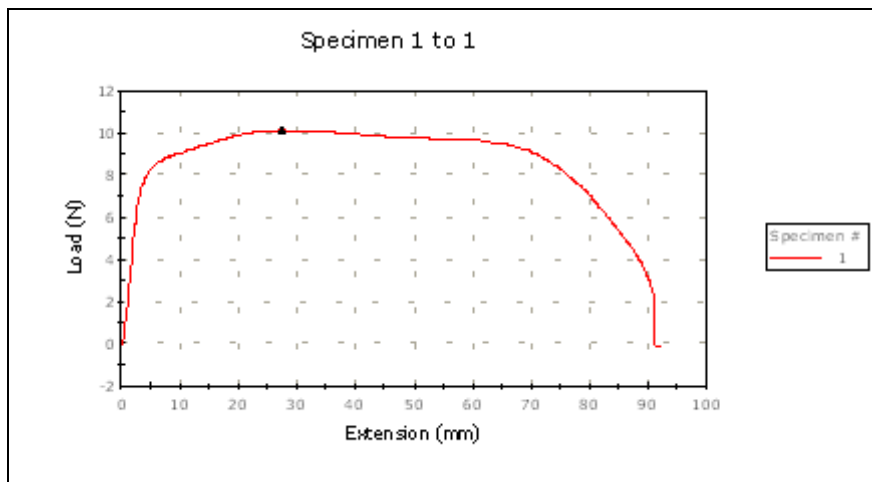


Fig 2.4 *Shape 2*

Shape 3 shows a rapid increase in load to a maximum and then a slow decline. Shape 3 is indicated in the previously shown figure, fig 2.1. The following tables' shows recorded maximum loads for the samples taken from each environment.

Environment	Tensile Strength			
	Time Period	Plastic Sample		
Mud Buried		Tesco	Sainsbury	Bio Bag
	3 Months	14.02	16.15	5.29 5.43 6.23
	Average	14.02	16.15	5.65
	Average Shape	1	1	3
	6 Months	16.04 13.90 14.69	11.24 10.76 15.79	2.45 3.65
	Average	14.88	12.59	3.05
	Average Shape	2	2	3
	9 Months	14.35 14.27 17.21	14.57 12.06 14.26	
	Average	15.28	13.63	
	Average Shape	1	1	

Table 3 Results of samples buried in mud

Environment	Tensile Strength			
	Time Period	Plastic Sample		
Mud Surface		Tesco	Sainsbury	Bio Bag
	3 Months	12.36	11.56	5.73 4.71 4.49
	Average	12.36	11.56	4.98
	Average Shape	1	1	3
	6 Months	14.30 11.66 11.75	11.53 15.67 15.93	4.08 4.77 3.89
	Average	12.57	14.38	4.25
	Average Shape	2	2	3
	9 Months	15.25 15.24 14.15	12.34 17.80 14.04	
	Average	14.88	14.73	
	Average Shape	1	1	

Table 4 Results of samples in mud surface

Environment	Tensile Strength			
	Time Period	Plastic Sample		
Salt Dark		Tesco	Sainsbury	Bio Bag
	3 Months	15.52	16.29	8.02 9.76 8.26
	Average	15.52	16.29	8.68
	Average Shape	1	1	2
	6 Months	14.82 14.92 15.94	15.91 12.71 13.29	6.57 5.62 2.40
	Average	15.22	13.97	4.86
	Average Shape	1	2	3
	9 Months	12.72 16.59 14.01	17.22 11.70 9.98	
	Average	14.44	12.96	
	Average Shape	1	1	

Table 5 Results of samples in dark sea water

Environment	Tensile Strength			
	Time Period	Plastic Sample		
Salt water		Tesco	Sainsbury	Bio Bag
	3 Months	10.15	12.63	9.06 11.03 11.21
	Average	10.15	12.63	10.43
	Average Shape	1	2	1
	6 Months	11.33 11.09 9.32	10.62 13.90 10.19	5.98 5.96 6.01
	Average	10.58	11.57	5.98
	Average Shape	2	2	3
	9 Months	9.08 8.69 9.74	12.14 12.46 8.24	
	Average	9.17	10.94	
	Average Shape	2	2	

Table 6 Results of samples in salt water

Environment	Tensile Strength			
	Time Period	Plastic Sample		
Sand		Tesco	Sainsbury	Bio Bag
	3 Months	15.17	11.49	
	Average	15.17	11.49	N/A
	Average Shape	1	1	
	6 Months	14.03 16.04 17.97	17.39 12.05 12.78	6.31
	Average	16.01	14.07	6.31
	Average Shape	1	1	2
	9 Months	13.26 13.99 12.21	14.79 15.25	
	Average	12.74	15.02	
	Average Shape	2	1	

Table 7 Results of samples in sand

Environment	Tensile Strength			
	Time Period	Plastic Sample		
Freshwater		Tesco	Sainsbury	Bio Bag
	3 Months	9.24	15.11	9.89 8.66 8.29
	Average	9.24	15.11	8.95
	Average Shape	2	1	1
	6 Months	10.97 13.40 13.32	8.73 11.58 13.43	6.03 5.68 5.81
	Average	12.56	11.25	5.84
	Average Shape	2	2	
	9 Months			
	Average			
	Average Shape			

Table 8 Results of samples in freshwater

It can be seen from these results, many of the samples experience a decrease in the maximum load capability, before becoming deformed and destroyed. Table 8, saltwater in darkness, showed a slight decrease in maximum load over all three samples. However, Table 3 and Table 4, environments involving mud showed a decrease in tensile strength for the Bio-bag, but an increase for both Tesco and Sainsbury's in mud environments.

It is important to note, the only samples which achieved *Shape 3* were Bio-bags. Tesco and Sainsbury's bags were classified as either *shape 1* or *2*, but were primarily *shape 1* in sand and dark saltwater. Many environments such as buried in mud and fresh water, Tesco and Sainsbury's samples changed from *shape 1* to *shape2* at 6 months and then back to *shape 1* at 9 months.

The graphs below are examples of extension data gathered, and comparisons between different plastic samples within same environments.

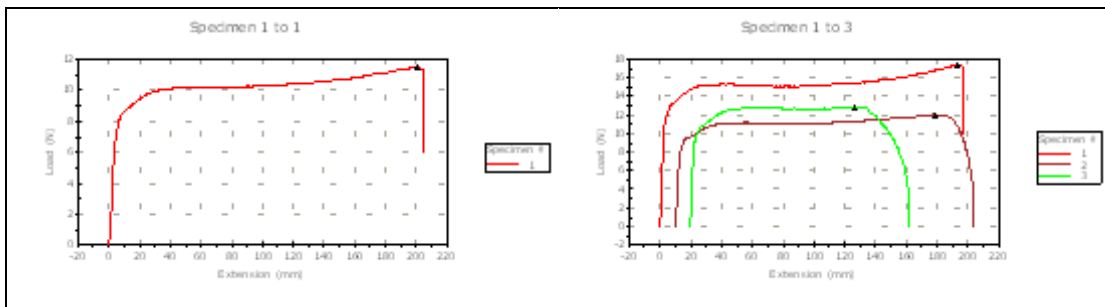


Fig 2.5 Sainsbury's comparison for 3 and 6 months in sand

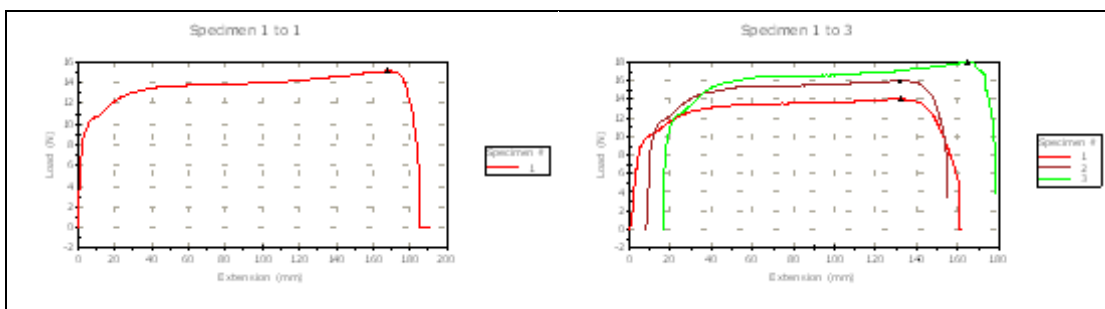


Fig 2.6 Tesco comparison for 3 and 6 months in sand

Fig 2.5 and 2.6 show extensions of Tesco and Sainsbury's samples kept in sand for 3 and 6 months. Great similarity between the two samples is common in numerous other environments.

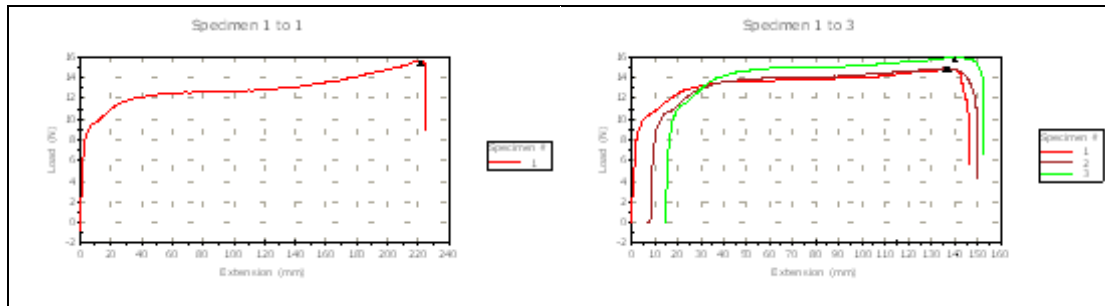


Fig 2.7 Tesco comparison for 3 and 6 months in dark salt water

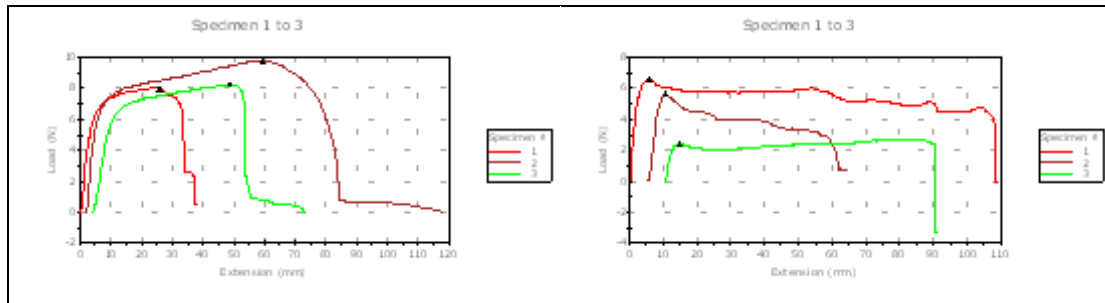


Fig 2.8 Bio bag comparison for 3 and 6 months in dark salt water

Fig 2.7 shows initial 3 months testing of Tesco samples kept in dark saltwater and testing again at 6 months. The sample is very strong, more so than the variability tests for Tesco plastic, and the strength does not alter over the 3 month period. Fig 2.8 shows the same time period and environment for the Bio-bag. Here it can be seen that the *shape* of the bag changes from *shape 1* to *shape 3* over the time period. In conjunction with this there is a definite fall in maximum load, decreasing from an average of 8.68N to 4.86N. A 44% decrease in maximum load, even in the absence of light.

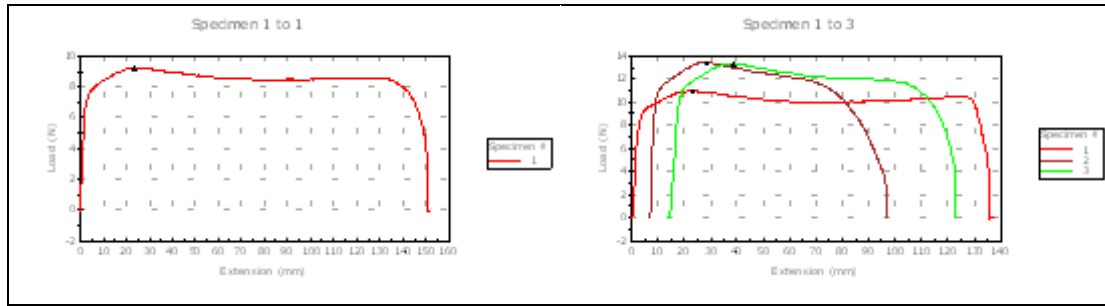


Fig 2.9 Tesco comparison for 3 and 6 months in freshwater

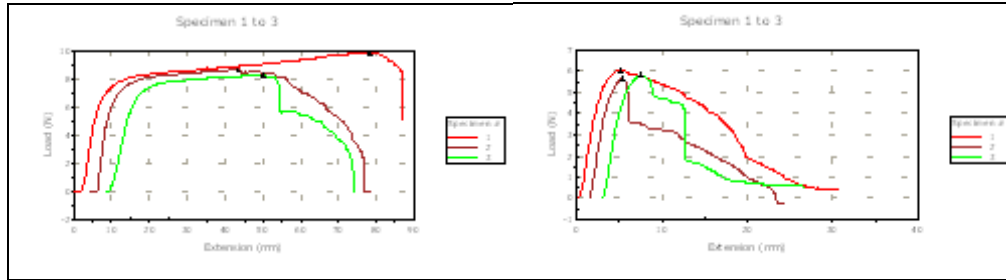


Fig 2.10 Bio bag comparison for 3 and 6 months in freshwater

Fig 2.9 and 2.10 shows the difference between Bio-bag and Tesco samples in fresh water. Notice that the Tesco sample increases in overall load. However, unlike the dark water sample, the fresh water sample has changed from *shape 1* to *shape 2*, meaning the sample reaches maximum load much faster in the 6 month than the 3 month samples. Fig 2.10 shows the Bio-bag changing to become weaker, and take on *shape 3* characteristics. There were ruptures very quickly in the freshwater Bio-bag sample.



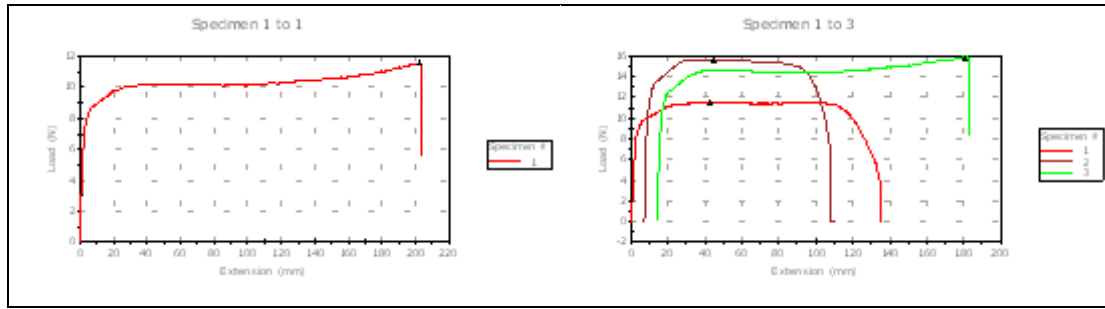


Fig 2.11 Sainsbury's comparison for 3 and 6 months in mud surface

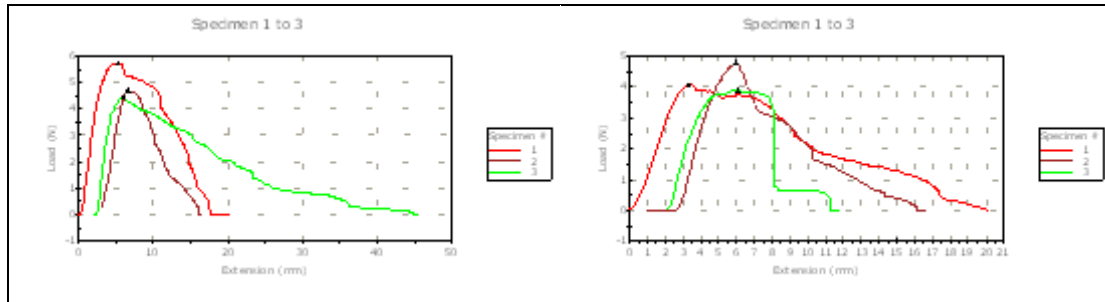


Fig 2.12 Bio-bag comparison for 3 and 6 months in mud surface

Fig 2.11 shows how the data from Sainsbury's samples which were left on the mud surface changed from 3 to 6 months. The sample at 3 months was strong and showed *shape 1* characteristics. At 6 months the sample strength had increased further, and two of the three readings had altered to show *shape 2* characteristics, reaching a maximum within the first half of the extension then declining. The Bio-bag samples showed completely different results to the Sainsbury's sample. Throughout the whole 6 month period, the sample shows predominantly *shape 3* properties. Reaching a maximum load quickly, then falling swiftly and slowly tearing. It can also be seen from fig 2.12 that the overall load of the 6 month sample fell, from that of the 3 month.

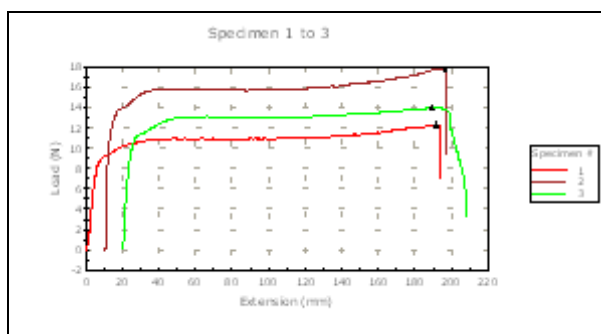


Fig 2.13 Sainsbury's comparison for 9 months in mud surface

For completeness fig 2.13 shows the 9 month Sainsbury's sample on mud surface, where all repeats show *shape 1* structure and again an increase in maximum load.

### 3.3 Photo-acoustics

There are several areas seen on fig 2.14 where the photo-acoustic data will alter when degradation occurs. These areas are associated with different bonds, which indicate what type of degradation is occurring within the sample.

Fig 2.14 is a typical spectrum attained from the photo-acoustic technique. Drawn on this figure there are several points of interest which, when altered can indicate degradation is occurring.

- A:** This area of the spectrum is where oxidation and hydrolysis occurs. Any increase in oxygen or –OH bonds, will cause an increase or hump in this area.
- B:** This large peak is simply due to the CH<sub>3</sub>-CH<sub>2</sub> bonds stretching.
- C:** This smaller peak is due to single CH, and CH<sub>3</sub> being close to a double bonded molecule.
- D:** This peak is CO<sub>2</sub>, mainly because the chamber was not purged correctly, in the analysis it is irrelevant.
- E:** This is the plasticiser, the higher this peak, the more plasticiser is present and the more durable the bag is. Plasticiser often has a phenol or benzene ring associated with it
- F:** This area is associated with C=O.
- G:** This singular peak is due to benzene, either alone or in a phenol group. The presence of benzene helps to reduce UV efficiency by absorbing energy.
- H:** This grouping at the end signifies how well structured the sample is. If it is relatively low, the structure has long chains, a more laminar shape. An increase indicates branching is occurring; the chains are breaking and becoming more complicated.

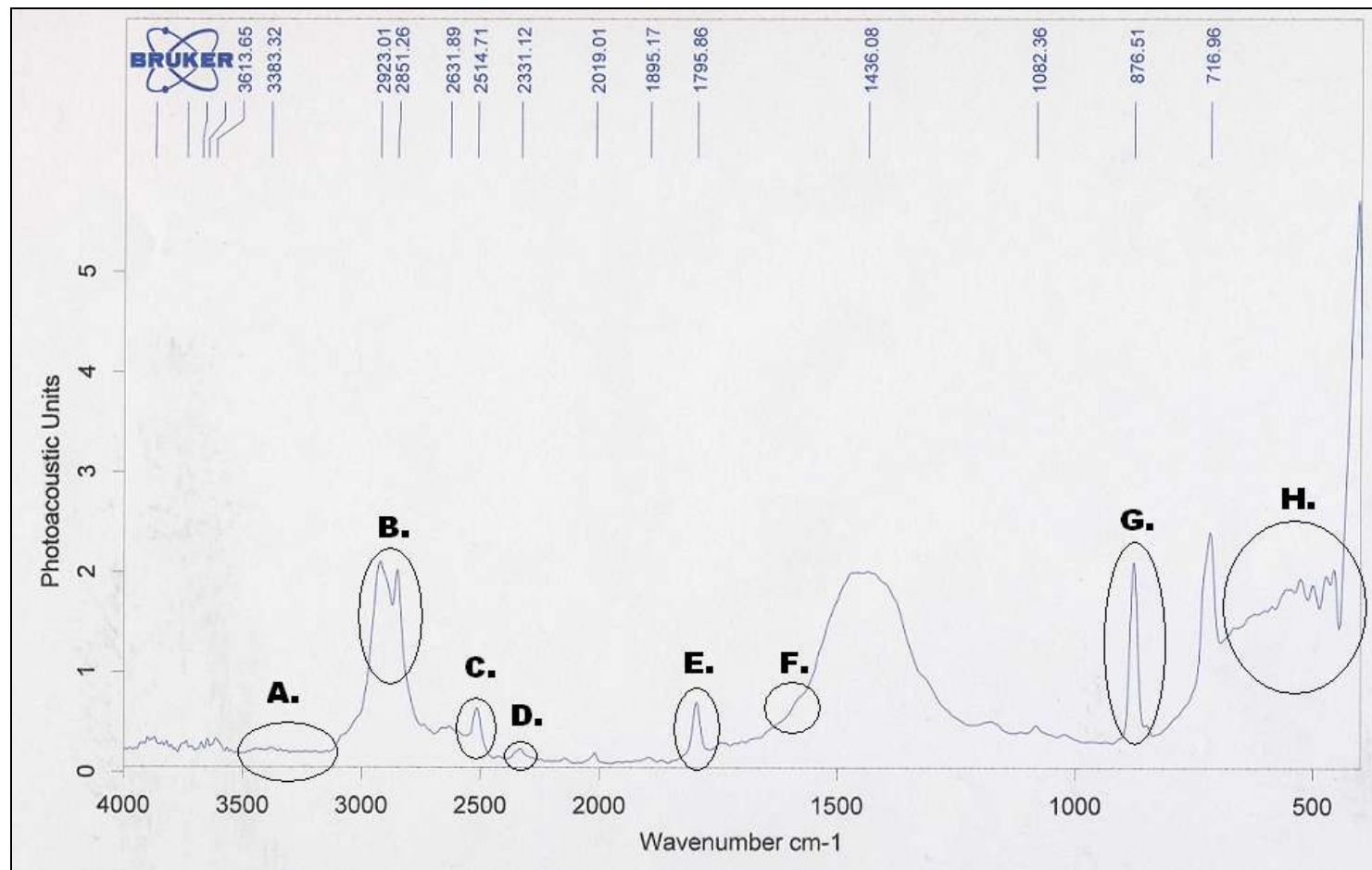
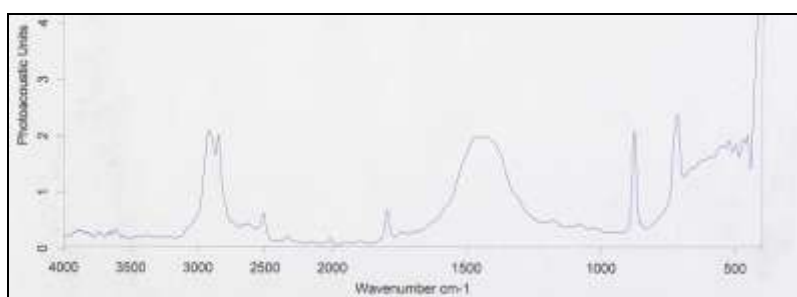


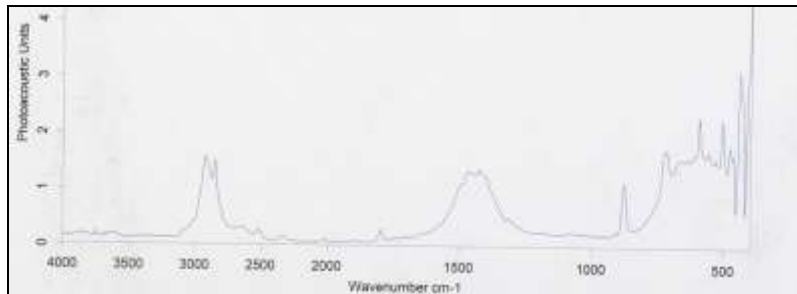
Fig 2.14 Areas and peaks which will alter due to degradation

If degradation is occurring then it is expected that there is an over complicating of the spectrum, the peaks will become more broad and shallow. There will also be additional peaks, such as oxygen. All indicating a breaking of the longer chains to smaller and smaller molecules until the structure is unstable and completely breaks down. Photo-acoustics is a comparative process; the ability to see differences lies with a contrast. Therefore, fig 2.15 shows the initial spectra for un-degraded samples of Tesco, Sainsbury's and Bio-bags.

#### Tesco Un-degraded



#### Sainsbury Un-degraded



#### Bio-bag Un-degraded

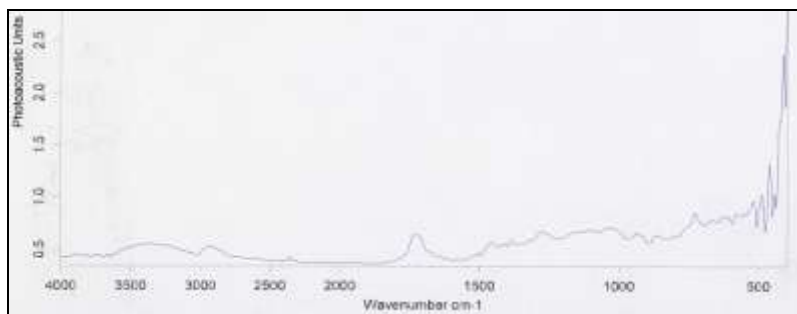


Fig 2.15 A base comparison for each of the three samples un-degraded

Fig 2.15 shows both Tesco and Sainsbury's have similar characteristics to polyethylene. They both contain large amounts of benzene at  $\sim 900\text{cm}^{-1}$  which resists photo degradation. They also contain clear peaks of plasticiser at  $1800\text{cm}^{-1}$  which resists degradation. The Bio-bag contains neither plasticiser nor benzene, but does contain large amounts of  $\text{O}_2$  and  $\text{H}_2\text{O}$ , with smaller peaks for CH bonds. There is also at the lower end of the scale, indicating that the Bio-bag is already highly branched.

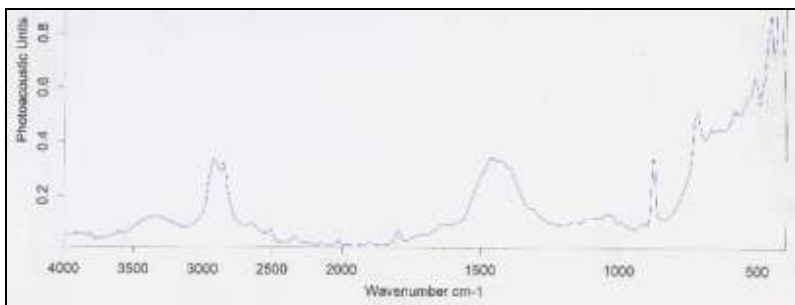
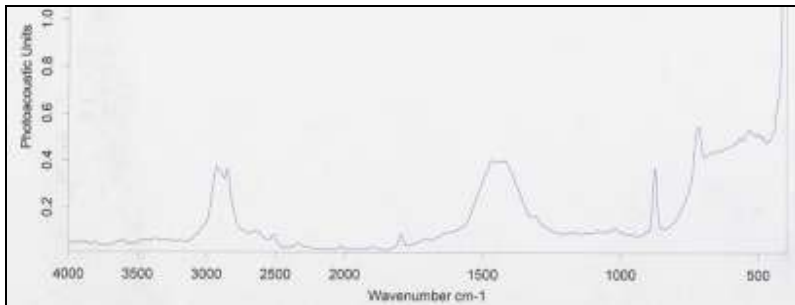
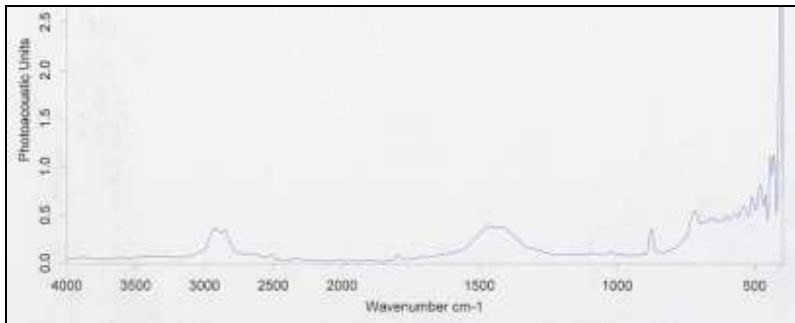
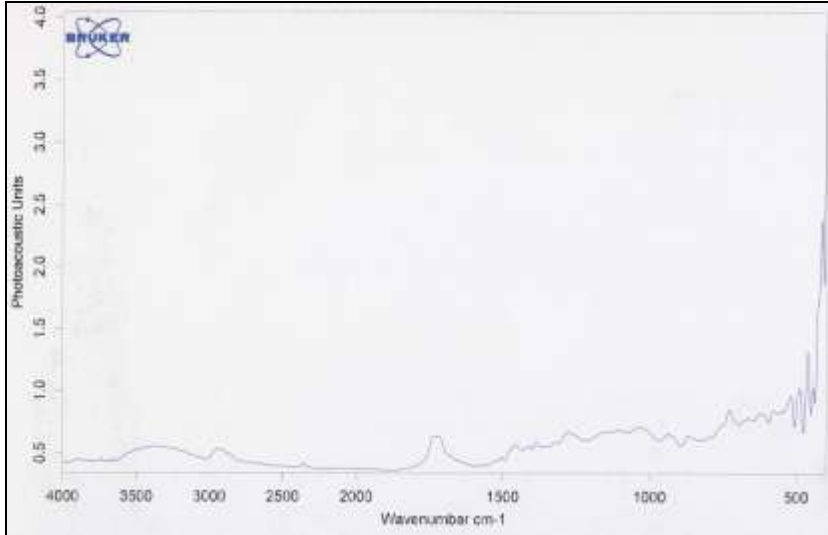


Fig 2.16 Photo-acoustic data: Tesco samples in saltwater over 9 months

Fig 2.16 shows the spectrum over 9 months for Tesco samples in saltwater. It can be seen in comparison over the time frame there is an addition of  $\text{O}_2$  and

-OH, in the higher end of the spectrum. Also a broadening of the main peak at  $1500\text{cm}^{-1}$ , and the appearance of a new peak at  $1050\text{cm}^{-1}$ . This along with a large increase in branched chains at the lower end of the spectrum indicates degradation is occurring. Fig 2.17 shows the same data for the Bio-bag.

### Bio-bag un-degraded



### Bio-Bag 6 months

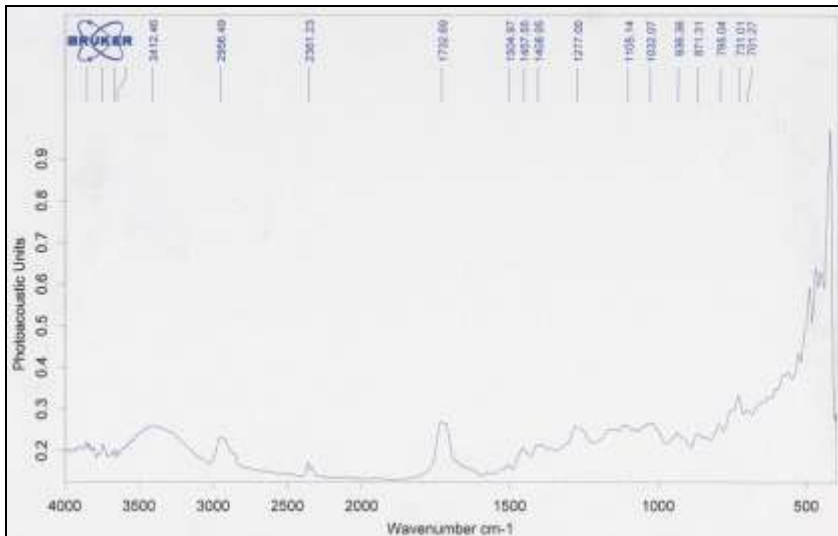


Fig 2.17 Photo-acoustic data: Bio-bag samples in saltwater over 6 months

Here there is an increase in oxidation and hydrolysis over the time period, with further complexing at the high end of the scale by six months. After six months there is no recognisable peaks below  $2361\text{cm}^{-1}$  ( $1732\text{cm}^{-1}$  is  $\text{CO}_2$ , due

to incomplete purging), thus showing positive degradation. In contrast to these results fig 2.18 and fig 2.19 show the same samples for saltwater in darkness.

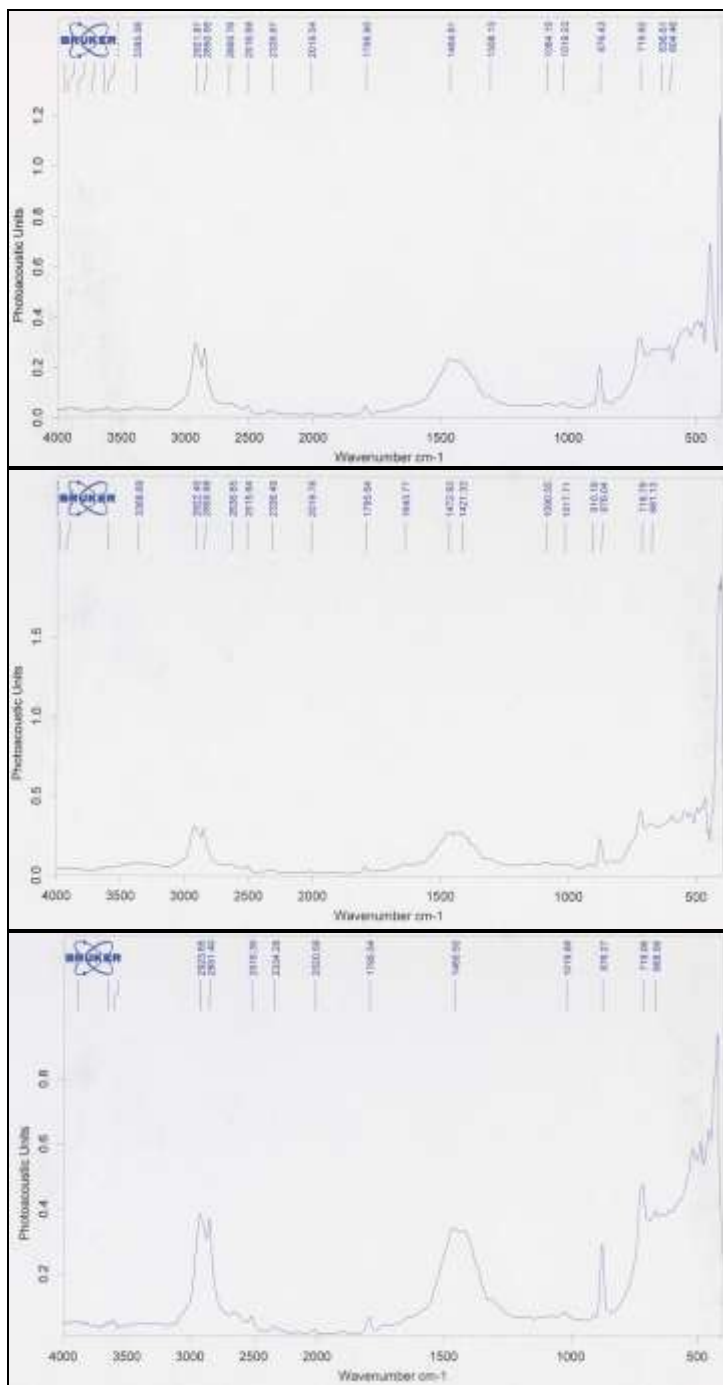


Fig 2.18 Photo-acoustic data: Tesco samples in dark saltwater over 9 months

Over the nine month period there is no outstanding changes in the structure of the Tesco sample. There is slight hydrolysis occurring, which is seen more clearly at 6 months. Overall the sample is relatively unaltered.

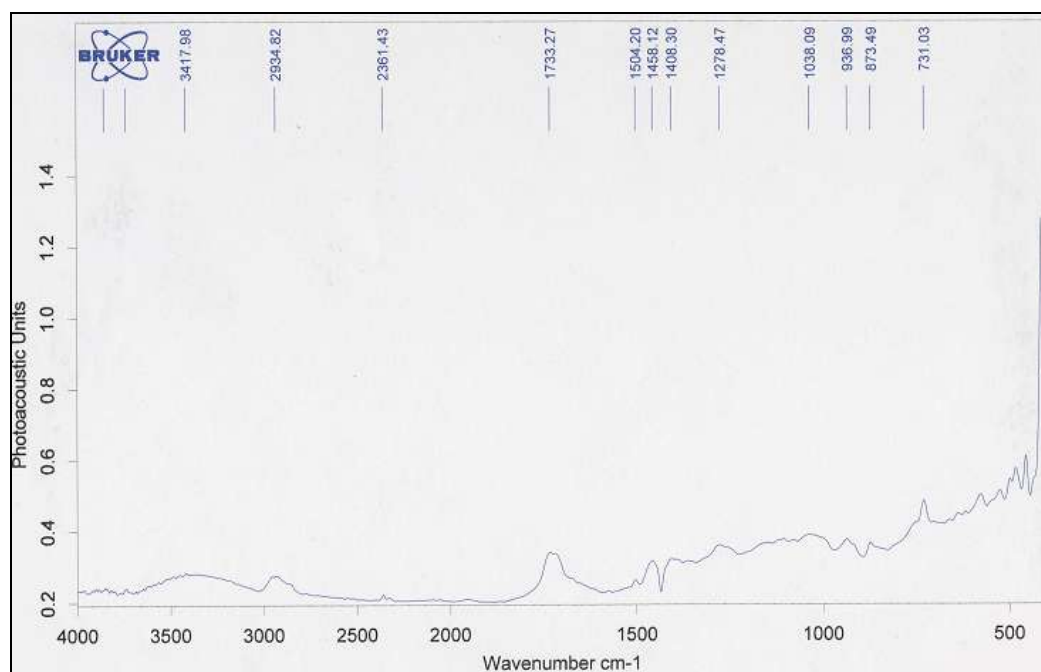
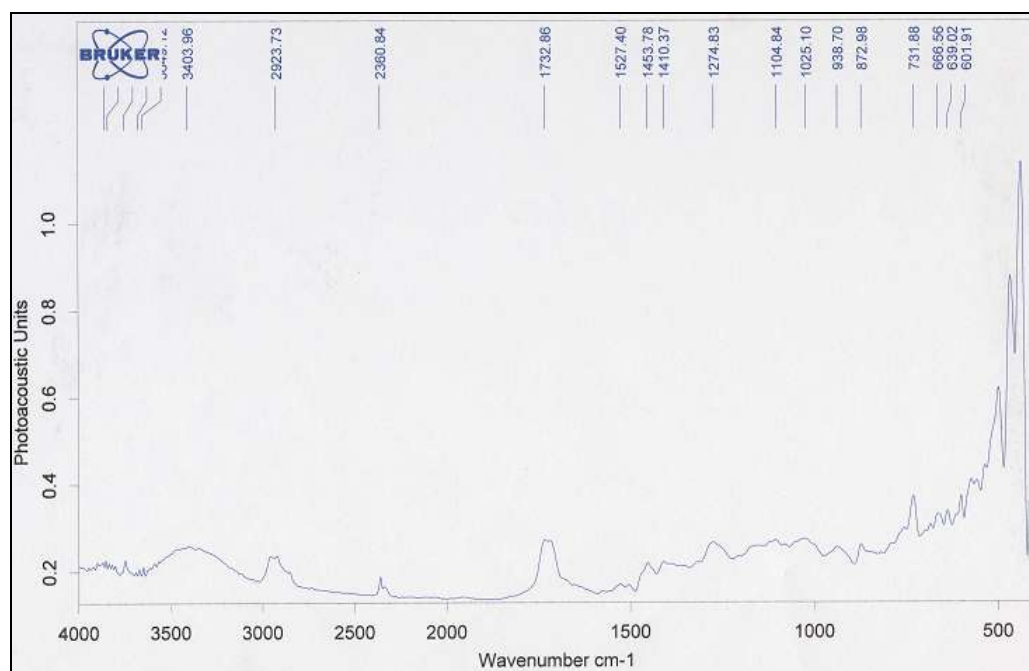


Fig 2.19 Photo-acoustic data: Bio-bag samples in dark saltwater over 6 months



However, the Bio-bag shows similar degradation in darkness as in light. There are large peaks of hydrolysis occurring after 3 months, and again no clear peaks below  $2900\text{cm}^{-1}$  disregarding  $\text{CO}_2$ . There is a decrease in the peak at  $2900\text{cm}^{-1}$ , which is the CH peak, this is expected as the sample is breaking down and branching.

### 3.4 Visual record

Before the samples were placed into their environments, they were also photographed. This was to document any change in physical appearance of the sample, along with any rips or physical changes. Many of the samples showed fading of the pigment, during the degradation process. Fig 2.20 shows this type of physical change, the Sainsbury's bag was vibrant orange before the degradation, and dull upon removal.



Fig 2.20 Sainsbury samples before and after degradation in salt water

Many of the samples showed similar deterioration, a fading of the colours when exposed to sunlight. However, samples which were kept in darkness showed no decrease in colour intensity, the sample pigment was still rich, as seen in fig 2.21.



Fig 2.21 Tesco samples before and after degradation in dark salt water

Seen in fig 2.22 the results are interesting, the Bio-bags showed definite rips and physical fragmentation after the degradation period. It is for this reason that some Bio-bag samples were difficult to test tensile strength, there simply was not enough sample left, as seen in fig 2.22.



Fig 2.22 Bio bag before and after degradation buried in mud

This is just a mere selection of the different types of visual physical changes which occurred. All Bio-bags became subject rips and tears although, not all were as extreme as the example in fig 2.22. All Tesco and Sainsbury's samples, except those kept in either darkness or sand, exhibited a de-colouration over the degradation period.

### 3.5 Light experiment

Light Experiment	
Sample	Light Detected (lux)
<i>Tesco</i>	
4	843
5	908
11	895
15	691
20	880
21	900
<i>Sainsbury's</i>	
B	508
H	565
I	250
Q	475
U	506
X	415

Table 9 Results gained from the pilot light experiment

Table 9 shows the results of the failed light experiment. Even though there is no subsequent data to compare, there is a definite difference in light detected. Tesco sample seemed to allow more light to pass through than the Sainsbury's samples, on average around twice as much.

## **4. Discussion**

### **4.1 Validity of Methods**

Environment Simulation:

The process of simulating the marine environments was difficult. The boxes were clear plastic material, which caused one problem. There was no way to ascertain how the UV radiation passing through the plastic may be attenuated. It was considered to try and quantify this attenuation, but there were inadequate resources available to do so. Therefore, it has been left in as a standard error, as all the samples will be hit by UV radiation of the same attenuation. Thus this error should not affect which samples degrade first, but may affect the rate of degradation. Each box also had a lid attached to it, see fig 3.1 this was to prevent rain water or other external factors tampering with the investigation.



Fig 3.1 Box environment for dark saltwater

The boxes were kept outside; this was to help simulate a more 'real' environment, by exposing them to a year's variation in temperatures.

A factor which was not considered when setting up the investigation is the types of flora and fauna in the substrate collected. The box which contained mud began to grow grass in it, due to available water and sunlight. While this helps to simulate a real-life situation in the environment, there was no real way of quantifying the growth of the grass.

Likewise, there was bio-fouling occurring on the saltwater samples. Again helps to see how plastics are utilized in a marine environment, but no real way of recording how much bio-fouling is occurring.

Ultimately the set up was adequate for this investigation although in furthering the project; some of these factors should be removed, for example, testing the saltwater for bacteria which may cause bio-fouling.

Weights:

The dry weights of all the samples were recorded using a Startorius R200D precision scale. The instrument can record weights up to 5d.p. For the purposes of this investigation, weights were recorded to 4d.p. although the accuracy of the device is recalibrated regularly, therefore it did not seem necessary.

The samples were removed from their environment, dried in an oven at 2°C for 60min, and then weighed. Samples in mud and those affected by bio-fouling were washed with distilled water, but not scrubbed so not to the taint results. Table 1 shows the mass of some samples increased over time, making this method redundant.

Tensile strength:

The template for the tensile strength test was cut using a scalpel and ruler. This may have caused some slight variation in the thickness of the sample. The main difficulty with this method is that more samples were needed in order to perform statistics on the significance of the data. The method was modified, from one test, to three when it was apparent there was enough sample to perform three repeats.

#### Photo-acoustics:

The photo-acoustic method was one of the most efficient used in the investigation. The instrument required little of the sample to analyse (allowing more tensile strength tests to take place). Once the sample was in the device, it ran a scan of the plastic 32 times, then averages out the differences to create the spectrum. More scans can be run, but 32 were recommended to be sufficient. An error associated the photo-acoustic data is if the chamber is not properly purged with helium. The result is a CO<sub>2</sub> peak on the spectrum. However, this is easy to identify and therefore ignored when analysing the spectra.

#### Photos/visual record:

There were no difficulties encountered with this method. The samples were simply photographed once they had been weighed. This was a comparative tool.

## **4.2 Discussion of results**

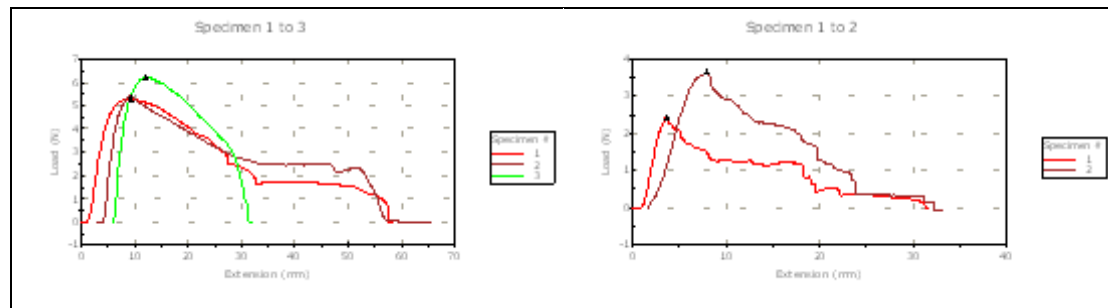
### Dry weights

As seen in the results the dry weights of the plastics altered over the degradation period. However, the results to try and quantify this were not successful. In more than one environment the sample gained weight, which seems unlikely. The cause was most likely bio-fouling which would increase the mass of the sample. This coupled with the sporadic difference in those which increased and those which decreased meant that these results are ultimately inconclusive. Bio-fouling is linked to benzene and phenol groups in polyethylene (Roberts, 2008)

### Tensile Strength

The tensile strength data showed that there was an overall increase in maximum load of the polyethylene based samples (Tesco and Sainsbury's). This was more apparent in the Tesco samples than the Sainsbury's,

throughout the period. The Bio-bag showed a decrease in tensile strength in every single environment although some were more prominent than others. Over the six month period, for the Bio-bag samples tensile strength values halved from their 3 month counterpart. Samples kept buried in mud, and sand became very brittle and damaged, as well as samples kept in salt water (both light and dark).

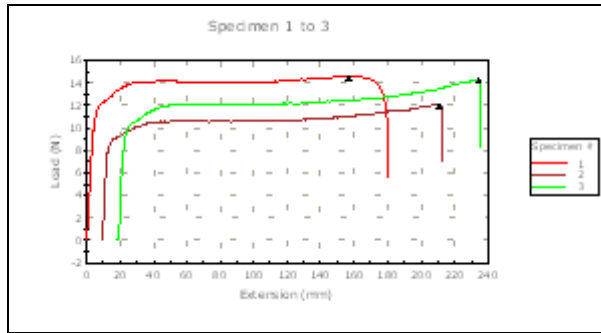


	First Peak (Load 10 % Change) (N)
1	5.287
2	5.427
3	6.230

	First Peak (Load 10 % Change) (N)
1	2.453
2	3.652

Fig 3.2 Comparison of Bio-bags for 3 and 6 months buried in mud

Looking at the Bio bags kept in mud in fig 3.2, these results show a significant fall in tensile strength over the time period. This is most likely due to the bags nature, it is designed to degrade in compost heaps. Being buried in mud, or sand, creates similar conditions, no light, and a more anoxic environment. There may also be bacteria, found in these environments which help facilitate the degradation process. In comparison to the Bio-bag, fig 3.3 shows a Sainsbury's bag after 9 month of degradation buried in mud.



	First Peak (Load 10 % Change) (N)
1	14.574
2	12.055
3	14.257

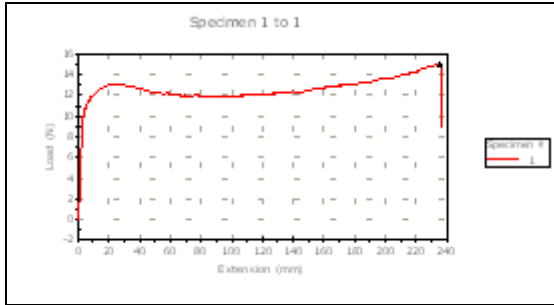
Fig 3.3 Sainsbury's sample buried in mud after 9 months

In contrast to the Bio-bag there was no reduction of tensile strength over the time period, interestingly there was an increase in maximum load taken by the material. Similar properties were found in any Sainsbury's or Tesco bags deprived of light. Suggesting that UV radiation is the key to triggering degradation within these samples, but not pivotal for Bio-bag breakdown.

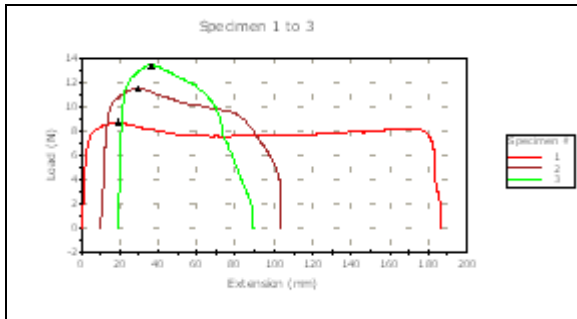
There is evidence to suggest there is more than just the one process underway. This is seen in the data for saltwater in the light and in darkness. Most of the samples in both environments showed a decrease in tensile strength, Tesco at 6 months in light showed only a slight increase. As the samples are kept within water, hydrolysis seems like the answer to how the bags are degrading in the darkness. However, this needs to be looked at in contrast to the photo-acoustics data.

The difference in *shape* of the tensile strength data also changed, this could be attributed to degradation occurring. Fig 3.4 shows data for Sainsbury's in freshwater. From the data the shape switches from *shape 1*, maximum strength achieved at the end of the extension, to *shape 2*, maximum strength

achieved much sooner. This could be due to a weakening of the bonds between molecules, and the sample deforms plastically much faster.



	First Peak (Load 10 % Change) (N)
1	15.109



	First Peak (Load 10 % Change) (N)
1	8.734
2	11.576
3	13.434

Fig 3.4 Sainsbury's sample in freshwater after 3 and 6 months

Even though the sample is degrading, the maximum load is increasing. This could be due to the intermolecular forces between the bonds of the plastic. The samples tested at 3 months were tested during summer weather, the samples would have been kept warmer and therefore be easier to pull apart. As the cold winter months arrived bonds vibrate less, the structure becomes more crystalline causing an increase in tensile strength. To ascertain if degradation is occurring more accurately the photo-acoustics data should be used in conjunction with this data.

### Photo-acoustics

The photo-acoustic data showed many different things in relation to degradation. The first being, concerning degradation the Tesco and the



Sainsbury's samples were effectively the same, as they both appear to be polyethylene based. The main feature of the photo-acoustics data which signalled degradation was an increase in complexity over the spectrum, coupled with an increase in branching chains found at the lower end of the spectrum. Any sample kept in water showed increasing oxidation and hydrolysis, this is to be expected as the samples are immersed in a replenished source of  $-OH$ , and  $O^{2-}$  ions. In saltwater, the polyethylene based samples began the process of degradation via hydrolysis. By 9 months they both had well developed hydroxide peaks, and were showing signs of increasing complexity at the lower end of the spectrum. However, even at 9 months there was little change in the quantity of broken chains, seen in fig 3.5.

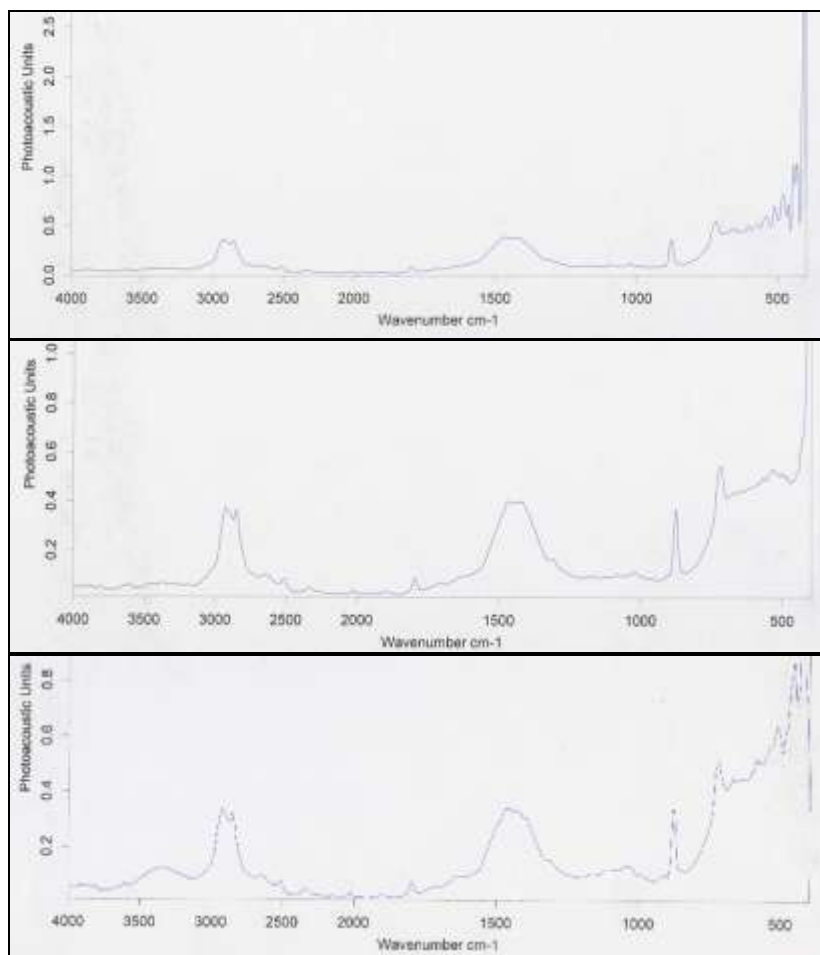


Fig 3.5 Photo-acoustic data: Tesco samples in saltwater

Perhaps if the samples had been left for longer the degradation would have become more apparent. As with many environments the Bio-bag began to degrade efficiently after 3 months. There was an increase in oxidation and branched chains, which continued to increased over the months. This increase in peak variability can be seen in fig 3.6

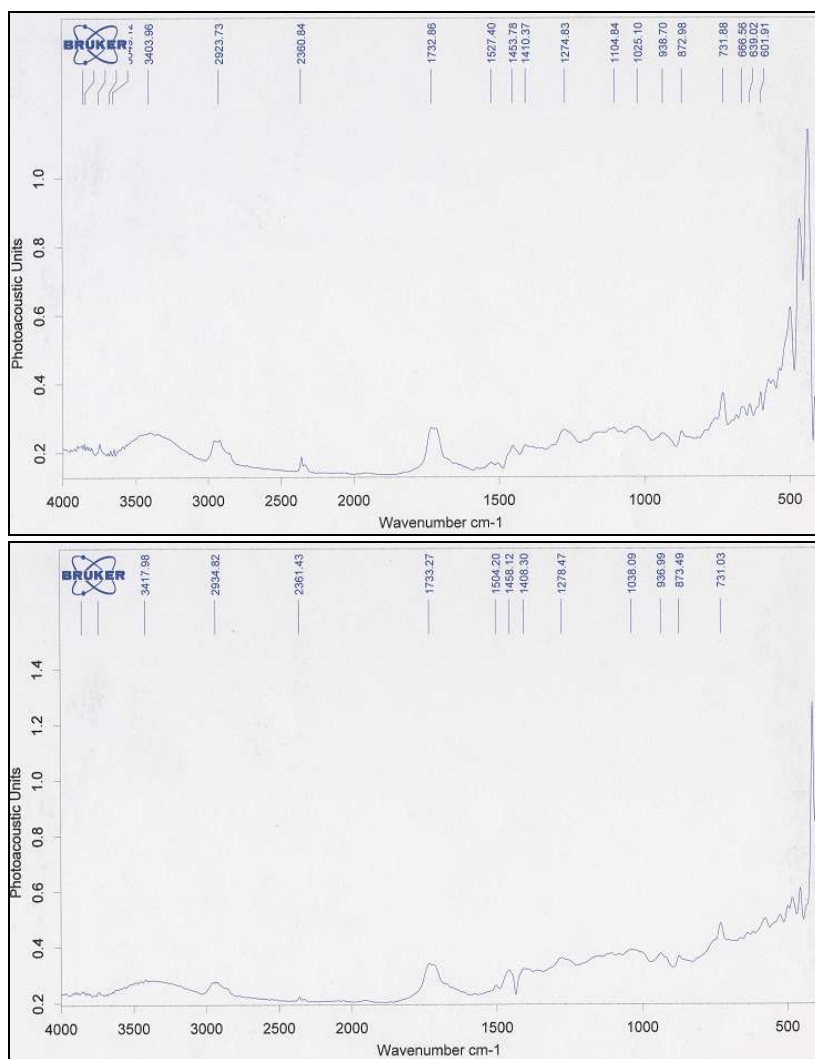


Fig 3.6 Bio-bag samples at 3 and 6 months in saltwater

In comparison to this, the polyethylene samples kept in darkness showed lower levels of hydrolysis and no branching or increased complication of the structure. This suggest the driving force for the addition of the -OH ion is UV radiation, which supplies energy for the process. Furthermore, the Bio-bag shows the same level of degradation in light as in darkness, indicating that UV radiation is not crucial for breakdown.

Looking at the samples involved in the mud based environments tells a different story. The polyethylene samples showed little change over the 9 month period. There was mild hydration, from the water in the mud. Other than that there was no real change in the photo-acoustic data, seen in fig 3.7.

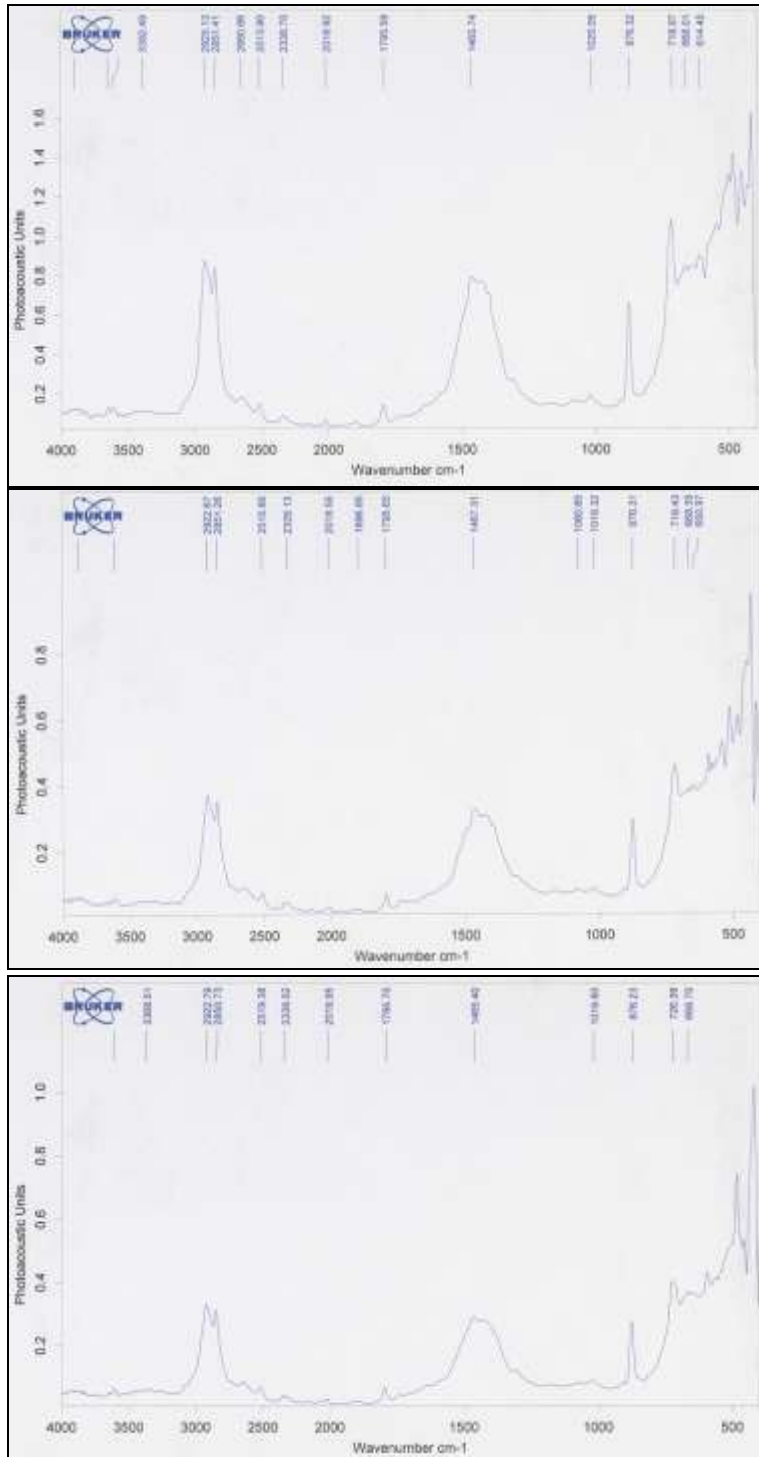


Fig 3.7 Photo-acoustic data: Tesco samples buried in mud over 9 months

Lack of degradation may be due to little UV light hitting the sample, also there is little oxygen available for oxidation. These types of conditions are more alike to those found in a compost heap. Not too surprisingly the Bio-bags degraded very well within these environments. There were some typical processes occurring at 3 months. However, by 6 months there was a complete breakdown of any recognisable peaks in the spectrum, shown in fig 3.8.

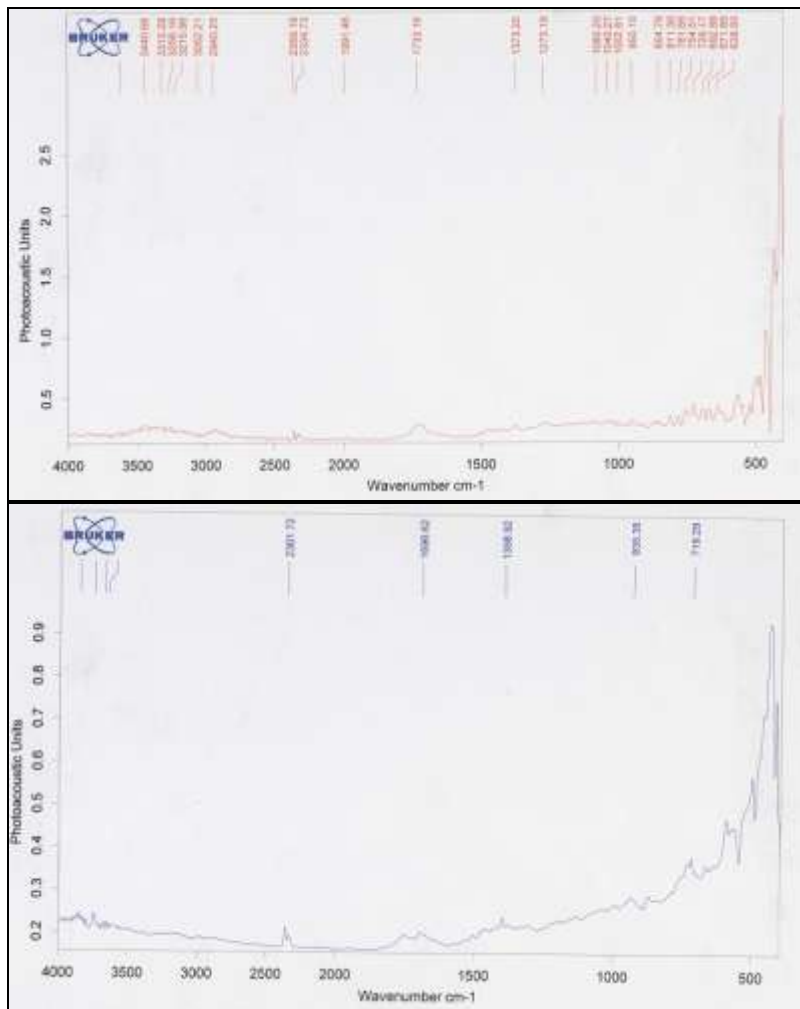


Fig 3.8 Photo-acoustic data: Bio-bag samples buried in mud for 6 months

This can be likened to the photographic evidence, showing rips and tears as the sample degraded. One important feature of the un-degraded Bio-bag is a peak of oxygen, and hydroxide bonds. These bonds are the samples structural 'Achilles heel'. Any bacterial breakdown will target these weaker

bonds, which give rise to easier breaks in the structural chain. The same pattern was apparent in the sand environment, very little breakdown in polyethylene samples, and almost complete breakdown in the Bio-bag. An interesting result was that of freshwater, mainly for the polyethylene samples. Fig 3.9 shows data for a Sainsbury's sample in freshwater.

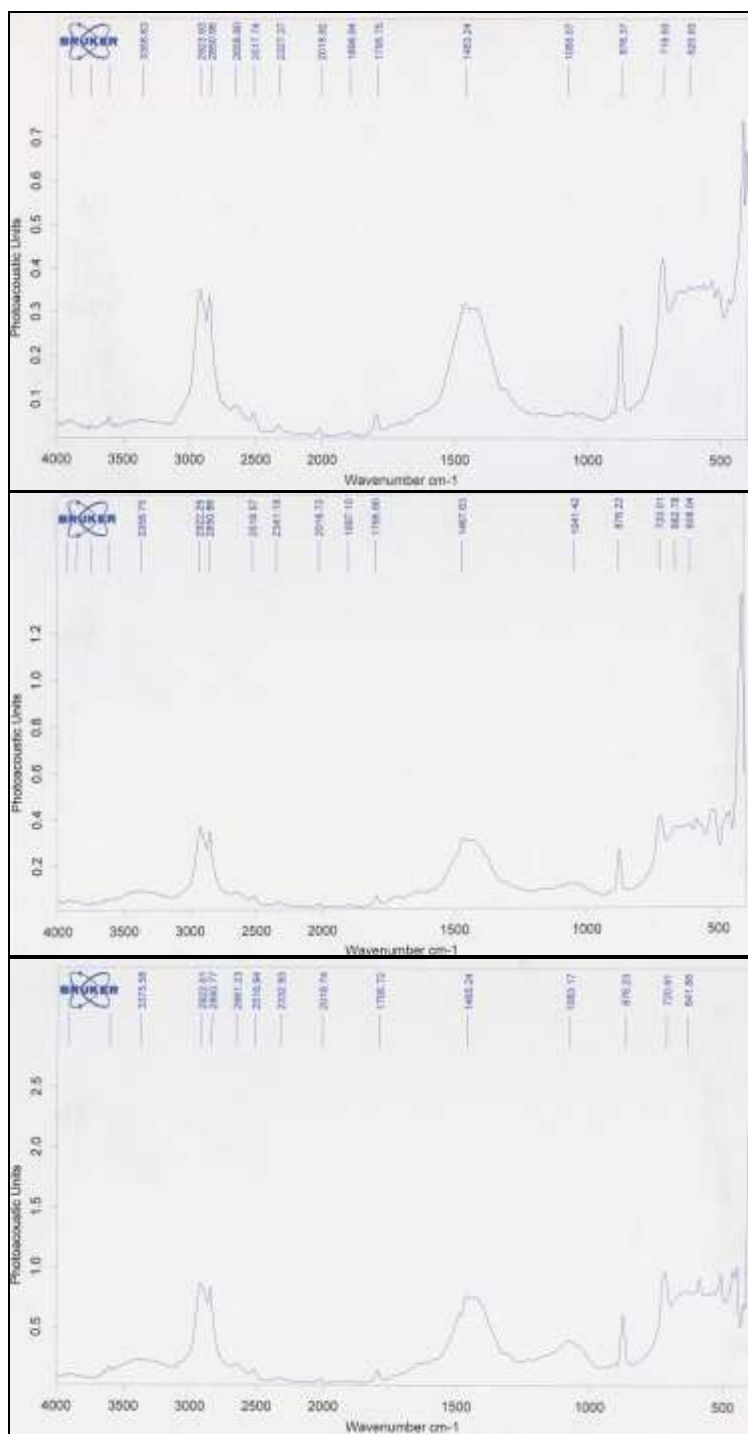


Fig 3.9 Photo-acoustic data: Sainsbury samples in freshwater over 9 months

In the first 3 months there is very little change. However, after six months there is a rise in oxidation/hydrolysis, a broadening of the main peaks with a new peak rising at  $1050\text{cm}^{-1}$ , followed by an increase in intensity of all these features, and the beginning of branching occurring thereafter. The oddity is that there is no change in the way the Bio-bag behaves in freshwater to saltwater though, as seen in fig 3.10.

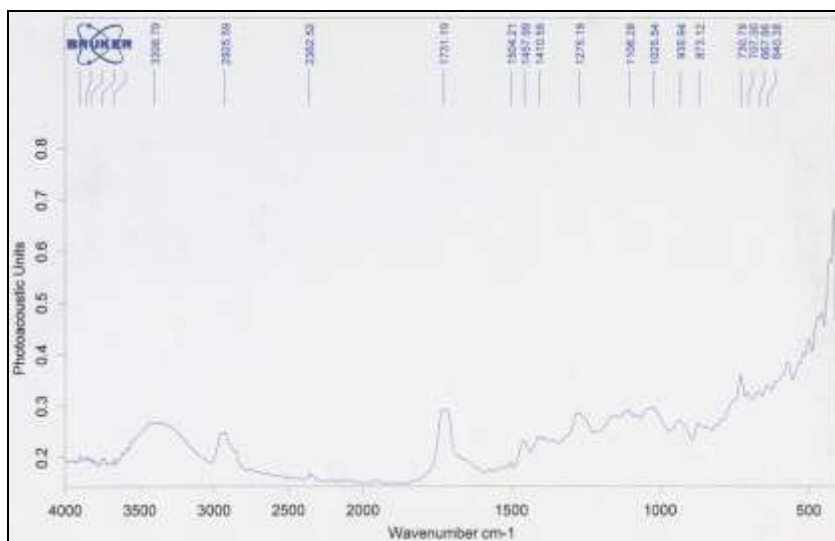
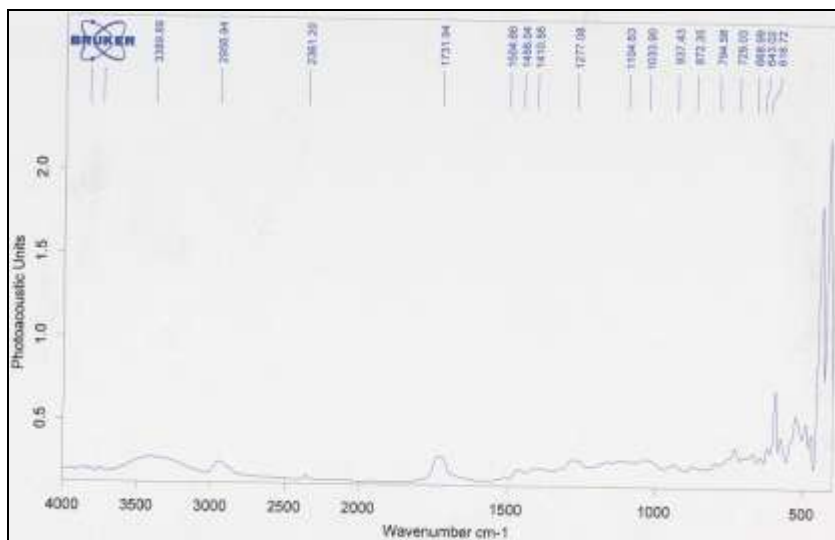


Fig 3.10 Photo-acoustic data: Bio bag samples in freshwater over 6 months

It has already been suggested that UV radiation is the trigger for polyethylene breakdown. As a result UV light must reach the sample easier in the freshwater environment, than saltwater. This has been attributed to bio-fouling. The saltwater sample is bound to have more types of microscopic algae which will take advantage of the surface area of the sample. There may be fewer organisms in the freshwater sample. Bio-fouling blocks UV light from hitting the sample surface and suppressing degradation, and is a real problem with plastic degradation in the open oceans (Roberts, 2008).

### **4.3 Future research**

Unfortunately this investigation only hinges on the tip of this subject. There has been a multitude of research into this area mostly because it is a very 'hot' topic at the moment. To further the work done in this investigation, the simulated marine environments need to be larger and more realistic. The main aspect of further work would be to produce enough samples to test (using statistics) the significance of the tensile strength method. Time is an important variable, it would be most interesting to keep the project running until the samples have completely degraded, testing every month. This would help to quantify the effect the weather has on the tensile strength of the samples. The effect of weather, or more specifically temperature, could be correlated with degradation rates by setting the environments up near a weather station. It may also prove relevant to expand the project into other types of plastic, such as butadiene, PVC or poly propylene.

## **5. Conclusion**

The results of the investigation showed all three different samples were capable of degradation, even the 'non-degradable' sample, suggesting the key factor between the two samples is merely time. There were certain environments which helped to facilitate breakdown of the samples and others which obstructed it.

It can be seen from the results that the polyethylene samples degraded very poorly in environments with no light, seen comparatively in the difference between saltwater and saltwater in darkness. The conclusion is that these samples require access to UVB radiation as an energy source to trigger chemical breakdown of the polymers and to help facilitate in the overall degradation of the plastic. Based on this analysis via several different methods, the original hypothesis can be supported and the null hypothesis rejected when concerning the Tesco and Sainsbury's plastics. However, due to the lack of significant statistical analysis the hypothesis cannot be proven, merely supported.

The Bio-bags degraded in all environments efficiently; UV radiation did not seem to affect the rate of degradation in any of the environments simulated. However, in environments which yielded more anoxic conditions, with possible source for bacterial breakdown such as mud, the degradation was far more advanced. Thus the original hypothesis is also supported for the Bio-bag, as some environments yielded superior conditions for biological breakdown.

The second hypothesis was that degradation in the Bio-bags would be more rapid than that in the other samples. In 6 months the Bio-bags were more broken down and weaker than polyethylene based samples were in 9 months. Therefore, the secondary hypothesis was also accepted.

Once degradation had started to occur, the polyethylene samples remained strong, and increased maximum load capability. Bio-bags became weak and structurally unstable. Therefore, this type of bio-degradable plastic is not a candidate to replace polyethylene plastics, but suggests that a more robust bio-polymer could replace plastics in the future.



## 6. References

- Andrady A.L., 2000. Plastic and their impacts in the marine environment. Proceedings of the international marine debris conference on derelict fishing gear and the ocean environment, August 6-11, Hawaii Convention Centre Honolulu Hawaii.
- Bell S. and McGillivray D., 2000. Environmental Law 5<sup>th</sup> Edition.
- Carpenter E.J., Anderson S.J., Harvey G.R., Miklas H.P. and Peck B.B., 1972. Polystyrene spherules in coastal waters. *Science* 178, pp. 749-750.
- Capenter E.J. and Smith K.L., 1972. Plastics on the Sargasso Sea surface. *Science* 175, pp. 1240-1241.
- Carr A., 1987. Impact of nondegradable marine debris on the ecology and survival outlook of sea turtles. *Marine Pollution Bulletin* 18, pp. 352-356.
- Clark R.B., 1997. Marine Pollution. Clarendon Press, Oxford.
- Degli-Innocenti F., Tosin M., Bellia G., 2000. The test method of composting in vermiculite is unaffected by the priming effect. *Polymer degradation and stability* 69 (1) pp. 113-120.
- Derraik J.G.B., 2002. The pollution of the marine environment by plastic debris: A review. *Marine pollution bulletin* 44 pp. 842-852.
- Gerngross T.U., Lynd L.R. and Wyman C.E., 1999. Biocommodity engineering. *Biotchnology progress* 15 (5) pp. 777-793.
- Gregory M.R., 1996. Plastic 'scrubbers' in hand cleansers: a further (and minor) source for marine pollution identified. *Marine pollution bulletin* 32 (12) pp. 867-871.
- Gregory M.R., 1999. Plastics and south pacific island shores: environmental implications. *Ocean & coastal management* 42 (6-7) pp. 603-615.
- Hartwig E., Clemens T. and Heckroth M., 2007. Plastic debris as nesting material in a Kittiwake-(*Rissa tridactyla*)-colony at the Jammerbugt, Northwest Denmark. *Marine pollution bulletin* 54 (5) pp. 595-597.
- Jiang Z., Yang H., Sun L. and Shi S., 2002. Integrated assessment for aerobic biodegradability of organic substances. *Chemosphere* 48 pp. 133-138.

- Kaczmarek H., Gorzata Swietek M. and Kaminska A., 2004. Modification of polystyrene and poly vinyl chloride for the purpose of obtaining packaging materials degradable in the natural environment. *Polymer and degradation and stability* 83 (1) pp. 35-45.
- Kamiya M., Asakawa S., Kimura M., 2007. Molecular analysis of fungal communities of biodegradable plastics in two Japanese soils. *Soil science and plant nutrition* 53 (5) pp. 568-574.
- Katsanevakis S., Virriopoulos G., Nicolaidou A., and Thessalou-Legaki M., 2007. Effect of marine littler on the benthic megafauna of coastal soft bottoms: a manipulative field experiment. *Marine pollution bulletin* 54 (6) pp. 771-778.
- Kiatkamjornwong S., Sonsuk M., Wittayapichet S., Prasassarakich P. and Venjanukroh P-C., 1999. Degradation of styrene-g-cassava starch filled polystyrene plastics. *Polymer degradation and stability* 66 pp. 323-335.
- Kudoh H., Sasuga T., Seguchi T., 1996. High energy ion irradiation on mechanical properties of polymeric materials. *Radiation physics and chemistry* 48 pp. 545-548.
- Mascarenhas R., Santos R. and Zeppelini D., 2004. Plastic debris ingestion by sea turtle in Paraiba, Brazil. *Marine pollution bulletin* 49 (4) pp. 354-355.
- McKinny R.L., 1998. On predicting biotic homogenization – species-area patterns in marine biota. *Global ecology and biogeography letters* 7 pp. 297-301.
- Micales J.A., Skog K.E., 1996. The decomposition of forest products in landfills. *International biodeterioration & biodegradation* 39 (2-3) pp. 145-158.
- Mills W., 2006. Quantifying the degradation rates of two plastic polymers; degradable and conventional non-degradable plastic bags under simulated marine conditions in the laboratory. Masters thesis.
- Minchin D., 1996. Tar pellets and plastics as attachment surfaces for lepadid cirripedes in the North Atlantic Ocean. *Marine pollution bulletin* 32 (12) pp. 855-859.
- Mohee R., 1998. Composting potential of bagasse and broiler litter and process simulation using a dynamic model. Ph.D Thesis, University of Mauritius.
- Mohee R. and Unmar G., 2007. Determining biodegradability of plastic materials under controlled and natural composting environments. *Waste management* 27 (11) pp. 1286-1493.

Moore C.J., Moore S.L., Leecaster M.K. and Weisberg S.B., 2001. A comparison of plastic and plankton in the North Pacific Central Gyre. *Marine pollution bulletin* 42 (12) pp. 1297-1300.

Nakasaki K., Ohtaki A. and Takano H., Biodegradable plastic reduces ammonia emission during composting. *Polymer degradation and stability* 70 pp.185-188.

Rios L., Moore C., Jones P.R., 2007. Persistent organic pollutants carried by synthetic polymers in the ocean environment. *Marine pollution bulletin* 54 (8) pp. 1230-1237.

Roberts T.A., 2008. The effects of bio-fouling on various plastic bag densities in the marine environment. University of Plymouth (submitted).

Signor A.W., Vanlandingham M.R. and Chin J.W., 2003. Effects of ultraviolet radiation exposure on vinyl ester resins: characterization of chemical, physical and mechanical damage. *Polymer degradation and stability* 79 (2) pp. 349-368.

Stevens E.S., 2002. Green plastics: An introduction to the new science of biodegradable plastics. Princeton University Press.

Tsuji H., Echizen Y., Nishimura Y., 2005. Photodegradation of biodegradable polyesters: A comprehensive study on poly(L-lactide) and poly( $\epsilon$ -caprolactone). *Polymer degradation and stability* 91 (5) pp. 1128-1137.

Vikman M., Karjomaa S., Kapanen A., Wallenius K. and Itavaara M., 2002. The influence of lignin content and temperature on the biodegradation of lignocellulose in composting conditions. *Applied microbiology biotechnology* 59 pp. 591-598.

Volova T.G., Gladyshev M.I., Trusova M.Y. and Zhila N.O., 2007. Degradation of polyhydroxyalkanoates in eutrophic reservoir. *Polymer degradation and stability* 92 (4) pp. 580-586.

Wallace N., 1985. Debris entanglement in the marine environment: a review. In *Proceedings of the workshop on the fate and impact of marine debris*. Eds pp. 259-277.

Zhao X.U., Li Z., Chen Y., Shi L. and Zhu Y., 2007. Solid-phase photocatalytic degradation of polyethylene under UV and solar irradiation. *Molecular Catalysis A: Chemical* 268, pp. 101-106.

**Websites:**

[www.wateronline.org](http://www.wateronline.org), accessed on 15/10/2007

[www.wikipedia.com](http://www.wikipedia.com), accessed on 17/11/2007

[www.afsc.noaa.gov](http://www.afsc.noaa.gov), accessed on 30/11/2007

[www.news.bbc.co.uk/1/hi/england/london/6994751.stm](http://www.news.bbc.co.uk/1/hi/england/london/6994751.stm), accessed on 28/02/2008

[www.brukeroptics.com](http://www.brukeroptics.com), accessed on 27/02/2008