Tossed at Sea: Plastic Degradation in Aquatic Environments

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To my family and friends for their consistent support and encouragement throughout the years.

Abstract

Aside from the aesthetic problem plastics in the ocean present, there is also great concern for the environmental impacts as well. Prior to 2009, the primary environmental concern regarding plastic hinged on the idea that plastic does not readily degrade and may take hundreds to thousands of years to do so. The reasoning behind this is that plastics are predominantly composed of hydrocarbons. Hydrocarbons, by their chemical nature, tend to be highly unreactive, especially the alkanes.

The idea of hydrocarbon stability in natural environments was challenged when Saido (2009) reported detectable amounts of styrene monomers, dimers, and trimers in ocean water and sand from beaches along the Japanese coastline. These molecules are not synthesized in nature but are the result of manmade products.

Reported here is the first evidence of a novel abiotic degradation process which has been observed between ocean water, UV light, and plastic polymers in controlled laboratory experiments. The production of small micro-particulates from parent plastic samples can be seen suspended in water by the un-aided eye in just days to weeks. All plastics studied (HDPE, PETE, and PC) display similar particulate production. After 18 months, the largest populations of micro particulates with a range of 5-60 microns have been found to exist between 5-10 microns.

Fourier Transform Infrared (FTIR) analysis of the initial and residual material over time shows oxidation of the polymers in laboratory studies with the formation of O-H, C=O, and C-O bonds. FTIR of plastics in field experiments exhibit similar patterns as well. Field samples appear to oxidize more readily as salinity increases. Given that the FTIR spectra are similar to what we see in the laboratory experiments, it is likely that small micron and sub-micron plastic particulates are entering the marine water column faster (days to weeks) than previously expected (decades to centuries). Small micro-plastics can cause entanglement and ingestion problems of microorganisms including planktonic species as are similarly observed in larger biota.

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CHAPTER 1

Plastic Debris in Aquatic Environments

This dissertation work presents an investigation of physical and chemical changes associated with the entry of plastic materials into aquatic systems. A review of the impact from global plastic production and various degradation mechanisms are provided in this first chapter to rationalize the persistence of plastics in natural environments. In addition, this chapter explains that poor waste management contributes a major source of plastic debris entering into aquatic systems, and describes potential problems posed by these synthetic polymers. These factors are the motivation for this study. Subsequent chapters are organized in a traditional thesis layout consisting of a literature review, methodology, data analysis, and finally a discussion of those results, conclusions.

Plastic has been an obliging product to our ever innovative ideas during the last half century. Once taking advantage of natural products (rubber, shellac, etc.), humans have minimized flaws, such as decreasing brittle tendencies at low temperatures or reducing tacky characteristics at higher temperatures, to create a more versatile and useful polymer. However, these manipulations have come at a price as these compounds cannot be easily recycled. As such, accounts of plastic debris accumulating in the environment have continued to grow over the last several decades. To fully understand how these products enter into our environments, the magnitude of the current problem, and estimate potential impacts, their production and disposal rates along with some of the characteristics of our more popular polymers must first be examined.

"Reduce. Re-use. Recycle"

1.1 Production, Consumption, and Disposal of Synthetic Polymers

Plastic production has been steadily increasing for the last 60 years and shows no signs of diminishing (Figure 1.1). In 2013, the total global production was up 4% from the previous year to nearly 300 million tonnes (MT)[1]. According to the Plastics Europe Market Research Group, global plastic production is estimated to reach upward of 400 MT by the year 2050[1]. Despite recycling campaigns, the percentage of plastic waste recycled has not improved significantly over the years. Nearly one-third of the plastic resin manufactured is transformed into consumer packaging including disposable single-use items[2]. In the U.S. alone, the total plastic resin production for 2012 reached 106 billion pounds[3,4]. However, less than 6 billion pounds of the 64 billion pounds plastic received from municipal solid waste (MSW) was recovered for recycling in 2012 (Figure 1.2)[4].

The consistent, increasing trend of plastic production can be attributed to several characteristics of the synthetic polymers. Due to their light weight, strength, moisture and air barrier properties, plastics are more cost effective storage and shipping products over conventional materials like wood, glass, and metal. These polymers are highly versatile making them suitable for a variety of applications from medical devices, including synthetic organs[5], to common disposable cutlery.

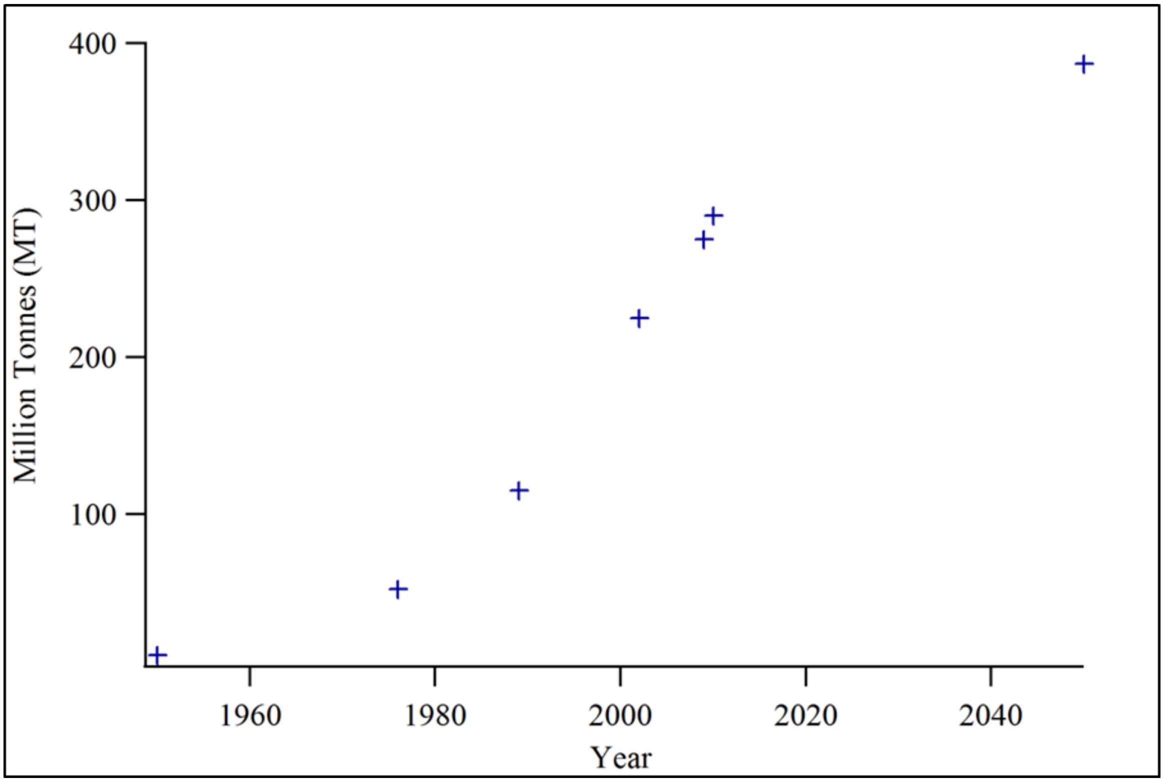


Figure 1.1 Global Plastic Production Per Year. *Created using data obtained from the Plastics Europe Research Group (1).* Plastic production has been rapidly increasing since the 1970s. The Plastics Europe Research Group estimate that global production can reach 400 MT which is a modest prediction using an equal per capita production as 2010.

Plastics can be placed into one of two categories, thermosets or thermoplastics. Thermosets can be defined as those synthetic polymers which remain liquid at low temperatures but become irreversibly rigid when exposed to high temperatures (above 200 ºC) or through a chemical reaction. Epoxy is a common type of chemical thermoset. The malleable nature of thermosets allows them to be molded into their final form or used as adhesives. In contrast, thermoplastics are polymers which are usually produced in solid pellets referred to as “nurdles” in industry. These pellets are shaped into their respective products by first melting until malleable or liquefied, and then pressing the molten material into a mold. Another and more increasingly common method uses a process known as injection molding. In this process, the molten material is injected into a ready-made mold then allowed to cool to its final form.

Thermoplastics are more prevalent in mass production. These include well-known types of plastic such as high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), polycarbonate (PC), polypropylene (PP), polyethylene terephthalate (PETE), polystyrene (PS), expanded polystyrene (EPS), and polyvinyl chloride (PVC) to name a few. A list of these plastics’ structures, production percentages, examples of final products, and identification codes can be found in Table 1.1.

Although HDPE, LDPE, and LLDPE are comprised of the same type of polymer, polyethylene (PE), differences between the various plastics are attributed to the amount and type of branching units in their respective structures. High density polyethylene is a polymer with a low degree of branching in its structure. As a result HDPE possesses stronger intermolecular forces and tensile strength compared to the other types of polyethylene described here. Low density polyethylene polymers have a considerable amount of short and long chain branching and so are less capable of organizing into a compact crystalline structure. This reduces their intermolecular forces greatly. However, this structure also provides them with unique flow properties. This allows their use in producing both rigid and film wrap products easily. Linear low density polyethylene

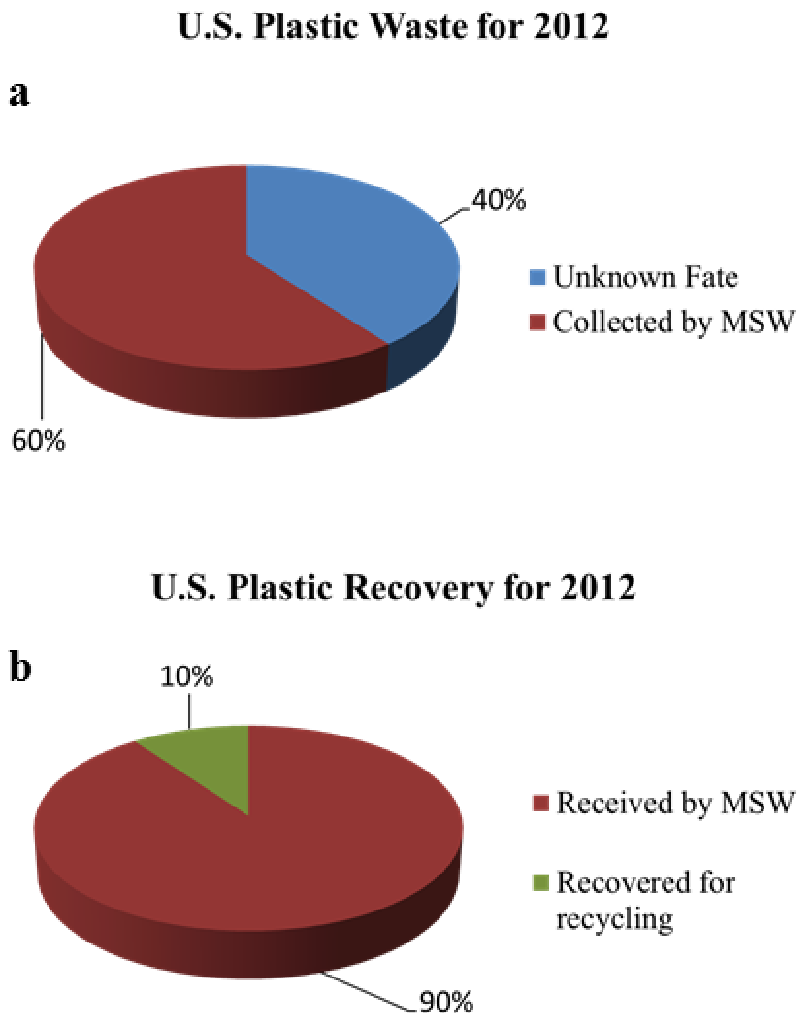


Figure 1.2 U.S. Plastic Waste and Recovery for 2012. Charts were created using data obtained from the American Chemistry Council (ACC) and the Environmental Protection Agency (EPA) for the year 2012. **a.** Municipal Solid Waste received 64 billion pounds of plastic in 2012 which represents roughly 60 % of the total plastic produced (106 billion pounds) in 2012 according to the ACC. **b.** Of the 64 billion pounds of plastic waste received by the MSW, less than 6 billion pounds were recovered for recycling.

polymers contain a number of short chain branches which allows for a predominately linear polymer. As such, its intermolecular forces are greater than LDPE which also gives this polymer a higher tensile strength and puncture resistance (Fig. 1.3).

Similarly to the PE family, the PS group can be found in various forms. The production of expanded polystyrene (EPS) involves blowing agents which form bubbles and cause an expansion in the foam. The results are lightweight, white foam commonly used in packaging and coolers. Polystyrene commonly describes the more rigid products of injection molding such as smoke detector housings, compact disc cases, etc.

Of all the thermoplastics available in the United States, high density polyethylene leads in production followed by PP, PVC, and LLDPE. High density polyethylene bottles are also one of the most recycled plastic items yet only 6 % of the total volume produced annually is recovered for recycling. Bottles produced using polyethylene terephthalate are recycled at higher rates within the last few years but these rates are low in comparison to rates of their production and consumption[4,6].

Plastic waste which is not salvaged, those collected by MSW but not recycled and that of unknown fate (Figure 1.2), will either end up in a landfill and/or due to poor waste management and natural disasters end up littering terrestrial and aquatic environments. The remainder of this chapter addresses the plastic debris that enters into inland water and marine environments. We investigate the origins and pathways of theses synthetic polymers as they move from one environment to another, and bring to light the environmental concerns that exist with these contaminants. Along with identifying possible sources of their origins, the many different ways which plastic is problematic for our planet is discussed. Potential pathways of degradation and those more likely to occur in natural environments are also examined analyzed. Finally we will explore the term "microplastics," which has been incorrectly defined in some literature reports, causing ambiguous complications with new literature reporting "true" microplastics in the environment.

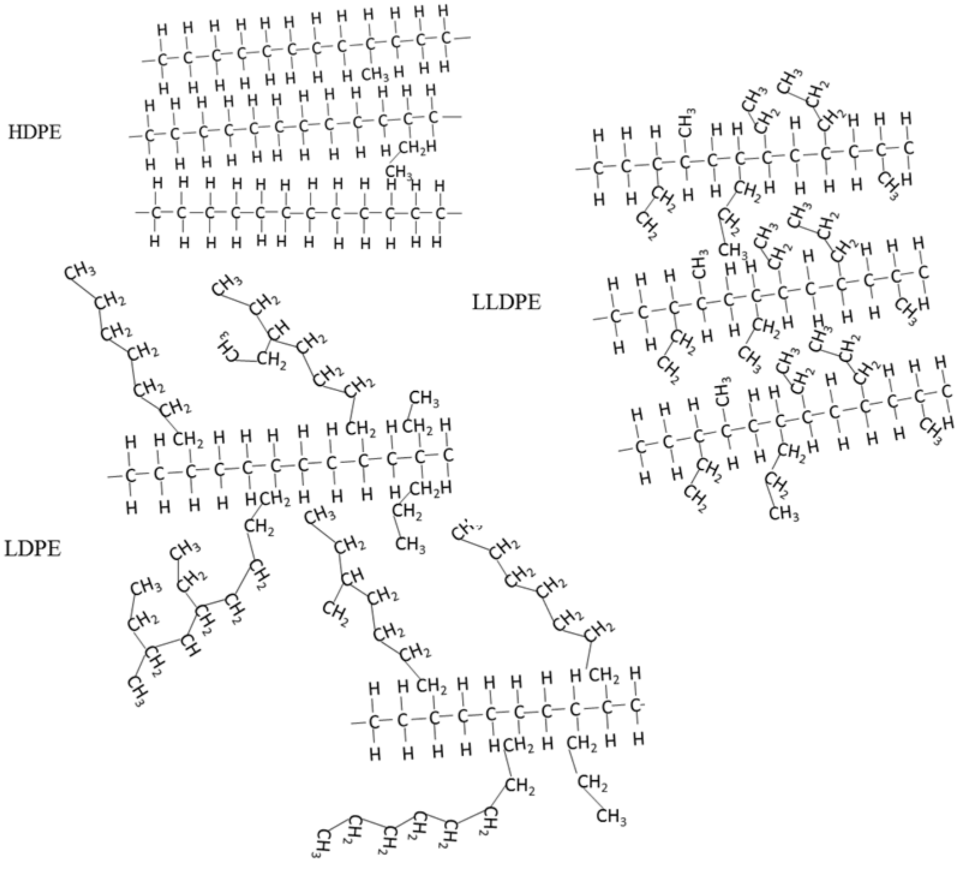


Figure 1.3 Polyethylene Structures. A schematic of HDPE, LDPE, and LLDPE. HDPE has considerably less branching and so can pack tighter during crystallization giving it the greatest amount of intermolecular forces and tensile strength of all of the polyethylene family. LDPE has extensive branching of long and short chains which prevent packing, resulting in a less dense material as well as weaker intermolecular forces. LLDPE has short chain branches throughout which are small enough to allow for moderate packing and a linear structure overall, similar to HDPE but less dense.

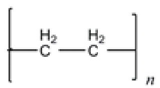
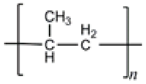
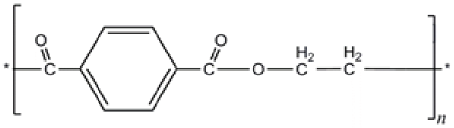
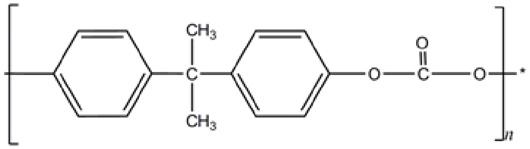
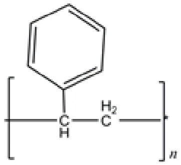
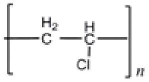
Classification	Code	Structure	Production†	Final Product Examples
Polyethylene High Density Polyethylene (HDPE) Low Density Polyethylene (LDPE) Linear Low Density Polyethylene (LLDPE)	 2 4 4		 19% 7% 15%	- Beverage containers Bags, six-pack rings, bottles Cling wrap, bags
Polypropylene (PP)	5		18%	Storage containers, bottles, rope
Polyethylene Terephthalate (PETE/PET)	1		‡	Packaging, bottles, containers
Polycarbonate (PC)	7*		‡	Greenhouse walls, Nalgene bottles
Polystyrene (PS) Expanded Polystyrene (EPS)	6		5% 1%	Packaging, utensils styrofoam cups, coolers
Polyvinyl Chloride (PVC)	3		17%	Tubing, pipes, keychains

Table 1.1 Commonly Manufactured Synthetic Polymers. Listed are the more common types of plastics produced annually in the U.S. Percentages were calculated using data provided by the American Chemistry Council for the year 2013.

†Based on data obtained from the American Chemistry Council (March 2014).[3]

* Code 7 does not solely refer to polycarbonate but mixed plastic types and "other" types which do not have their own codes.

‡ Data was not available for the individual polymer type but combined with other forms and constitute just over 16% of the total thermoplastics produced.

1.1.1 Freshwater Systems

There are only a few studies of plastic debris for inland waters compared to those in marine environments. However, the concern and public attention of marine plastic debris, which originated mostly from activists and scientists, are changing that as literature for limnetic systems is on the rise as of 2013 since rivers and streams are conduits for much of marine debris[9]. Aside from a few differences origins and types of debris, much of the litter found in both aquatic systems begins with poor waste management. The transfer of plastic litter from one locale to another may arise from natural or anthropogenic means. One obvious anthropogenic method would be littering, either intentionally or unintentionally. Another anthropogenic issue arises from some drainage networks. Some municipalities combine sewer systems with stormwater systems which can bring a large amount of debris into fluvial networks. This waste continues onward to coastal and marine waters during flooding events[7]. A “water wheel,” which takes advantage of natural river currents to help remove debris from the river where it is then placed into dumpsters and later taken to landfills, was built along the Jones Falls River in Baltimore, MD. The largest amounts of debris collected are cigarette butts followed by polystyrene containers and other types of plastic bottles[8].

Some of the natural factors which are responsible for bringing plastic into aquatic systems include storms producing floods and strong winds (Figure 1.2). The types of debris carried are dependent upon the mass and/or density of the material being transported. Plastic bags and bottles are lightweight items which are easily transported from one site to the next. Once a piece of debris has entered into an aquatic environment, they may continue downstream with the assistance of currents and winds until eventually ending up in marine waters. Larger items introduced by floods may remain in a single area for some amount of time once flooding recedes. Others may become entangled with fauna along riparian zones, those areas which interface between the land and water of a river or stream. In a 2014 study of the Chicago River, Hoellein found that the riparian zone collected the most plastic compared to riverine beaches and benthic sites, the lowest level of an aquatic zone often including the sediment surface and home to a community of organisms[9]. They also found that most of the debris observed in the benthic zones was heavier items[9].

Other anthropogenic sources of plastic found in freshwater are small beads like those found in exfoliating facial cleansers, body scrubs, and some popular toothpastes. Aside from the possible dental hygiene problems these beads may contribute to, they are also problematic for many of the mollusk and fish communities as discussed below in section 1.2[10]. A study published in 2013 found a staggering amount (greater than 450,000 beads per km^2) of plastic beads in the Laurentian Great Lake surface waters[11].. The greatest populations were located near two major cities and where lake currents converged with 20 % of the particles measuring less than 1 mm in size based on SEM analysis[11].

As mentioned earlier, there are some differences in the types of plastic debris in freshwater systems compared to those observed in more marine environments. For example, aside from fishing line there is overall less fishing gear debris observed in freshwater systems compared to marine environments[9].

Figure 1.4 Synthetic Materials Meet Nature. Picture taken around the Charlottesville and Shenandoah National Park area displaying plastic debris entangled in the riparian zone after a flooding event.

1.1.2 Marine Water Systems

Fluvial networks and other terrestrial sources contribute to marine debris but it is difficult to calculate exactly how much. Rough estimations have been suggested however that nearly 80 % of marine debris arises from land-based sources[2]. The main issue is that the amount of plastic entering the ocean is dependent upon many variable factors (such as disposal methods, waste management, storms, natural disasters, etc.). However, a report in *Science* looking into coastal countries' inputs of plastic estimate that roughly 1.6-4.7 percent of the plastic waste generated terminates in the ocean, based upon worldwide data on solid waste, population density, and economic status[11]. These numbers could increase during major natural events similar to what occurred in the Sabine National Wildlife Refuge in Louisiana during the 2005 hurricane season or the Fukushima earthquake of 2011. In Louisiana, millions of cubic yards of debris ranging from plastic straws to roofs were introduced to marshes and coastal areas[7]. The Fukushima event included an even larger debris field and items such as houses along with all of their contents to be transported by the ocean.

In addition to the land-based sources discussed, there are a number of ocean-based origins for marine debris as well. Again, much of the discarded items can be attributed to poor waste management (accidental or deliberate) and failure to secure items properly while at sea. Barges, cargo ships, oil platforms, oil rigs, all boats big and small are potential sources of marine debris[2,7]. Everything from plastic lids and bags to fishing gear and cargo may wind up as marine debris. Most of the world's fishing fleet uses plastic fishing gear including nets, ropes, and lighting equipment[2]. Nearly 18 % of marine debris is estimated to derive from the fishing industry[7].

Although it is illegal for commercial vessels to dispose of their waste while at sea, it does not seem to apply to many military vessels. In1993 Betsy Bayha, of radio station KQED, reported on the debate of Navy trash dumping. She recounted how a sailor who went AWOL after refusing to follow orders to dump trash including plastic and other toxic materials overboard brought attention to this problem[12]. Eventually the U.S.

Congress demanded that the Navy comply with an international maritime treaty which banned the disposal of plastic while at sea by the end of that year. However, the Navy was unable to fulfill that mission stating that they would need another five years to accomplish this goal. The main reason for the extension request was because many naval vessels are quite large and can be akin to small ocean cities, and more time was needed to install compactors and other waste management equipment[12]. It was reported that as much as 28 thousand tons of waste, including plastics, were thrown overboard naval ships annually during the 1990's[12]. Although stipulations were placed by Congress, from recent anecdotal stories however, it has been suggested that many if not all military ships still toss their waste at sea and often use it for target practice until it sinks beneath the waters. It is also quite likely that other commercial and private boaters illegally dump waste while at sea. It is clearly difficult to enforce such laws in such vast open ocean waters.

Although trying to discern whether waste is the result of terrestrial or marine inputs can be challenging, it is possible to speculate on the sources of some plastic marine debris based on type and location. For example, the discovery of thousands of shoes, rubber ducks, or plastic nurdles found adrift in the Pacific Ocean can be attributed to cargo accidents, due primarily to storms while at sea, and not from riverine sources[13, 14]. Over 195 shipping incidents occurred annually from 1971 to 1990 resulting in 13 million tonnes of debris to be lost at sea[15]. In 2014 the largest recorded loss of shipping containers occurred when the Svendborg encountered hurricane-force winds and waves of 30 feet off the Atlantic coast near northern France[35]. On any day, millions of containers are in oceanic transport carrying all types of products. With ships making thousands of journeys each year it should not be too surprising that millions of tonnes of debris eventually end up polluting our oceans. Figure 1.5 illustrates popular cargo routes.. Another example of easily discernable sources of debris would be the increased observance of heavy items such as crab pots and nets seen along the benthic zones of open oceans which are also not likely from riverine or terrestrial sources but marine fishing industries[9]. However, the presence of bags, bottles, films, and other light-weight plastics make it difficult to determine the origin as terrestrial, fluvial, or from marine sources as all are possible.

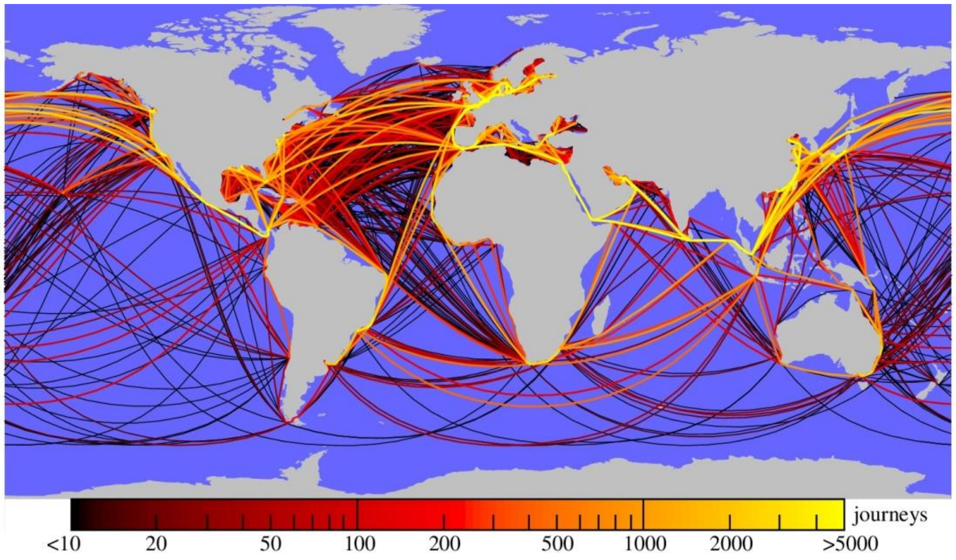


Figure 1.5 Shipping Routes of Cargo Ships Greater than 10,000 GT During 2007[16]. Color scale is dependent on the number of voyages along each route and assuming ships travelled using the shortest paths on water possible. Image used with permission and obtained from B. Blasius.

1.2 Inherent Dangers of Plastics

Regardless of origin, plastic debris entering the ocean has an impact on marine biota. Some organisms have adapted and use the material as a replacement for everyday shells, like fiddler crabs. However, most interactions between the synthetic materials and marine organisms are not as benign and include entanglement, ingestion, and the absorption of other toxic compounds which concentrate in plastic at sea. A number of reviews describe these impacts at length and the focus of this section will be to briefly summarize general findings and include recent findings.

1.2.1 Entanglement

Derelict fishing gear; either discarded nets or tangled fishing line can result in "ghost fishing[18]." Ghost fishing is a term that describes the result of abandoned fishing gear which ensnarls and captures fish and other organisms.

Six-pack rings and even small milk rings entangle many organisms from birds, to fish, to turtles, and sea lions. Often, the trapped organism cannot freely move or grow properly, resulting in starvation, drowning, slower movements making them easier prey, and deformations which may contribute to other health issues[17, 18]. Many of the organisms which become entangled are initially curious about the foreign items and begin innocently playing with the debris.[17] Fur seals for example, are often seen approaching plastic waste, poking their heads into holes or loops which slip over with great ease[17]. Removing their heads from the loops is difficult or impossible due to long guard hairs which prevent the material from slipping off. As a seal grows, the material begins tightening around the necks and may sever arteries in the process of strangulation[17]. The plastic material remains after the seal decomposes to become a further threat to others[17]. Many types of marine species become entangled in various plastic materials at many locations[19]. A variety of each type of each species is included: seabirds; turtles; whales; seals; fish and crustaceans[18].

Not all organisms that become ensnarled in plastic waste are mobile. Coral reefs, despite their static nature, are also in danger of becoming entangled. These already threatened ecosystems are often damaged by discarded fishing nets. These nets tumble along until they reach shallow seas, snagging on a reef. They can either rip off coral branches or wrap around a collection of reefs, devastating many clusters at a time[20].

1.2.2 Ingestion

Many animals, terrestrial and aquatic, mistake discarded plastic as potential food. A comprehensive list for entanglement[19] could also serve as a list of species that are commonly observed to ingest these polymers. Of course, not having the capability to digest these synthetic materials, the end result is usually dire. Larger pieces remain in the stomach or digestive tract causing blockage ultimately causing the animal to die of starvation[17,18]. Small items may pass through only to cause perforation[18] of the intestine lining, known as peritonitis, a life threatening condition which could lead to sepsis. For smaller organisms like copepods however, tiny pieces (1.7−30.6μm) of plastic may eventually pass through their digestive systems only to accumulate along their carapace or become entangled in their appendages[21]. Pieces of plastic small enough to ingest but too large to pass quickly through a copepod can stay in the system for over a week causing similar ailments seen in macro-organisms. Research to date concludes that microplastics pose an apparent threat in the potential detrimental decline of zooplankton[21], an important group residing along the bottom tier of the food chain, and may potentially result in trophic cascades or regime shifts in our oceans.

Many freshwater organisms also ingest plastic. In addition to small fragments, other threats are small polyethylene beads found in a variety of cosmetic goods and toothpaste items[10]. These beads enter fluvial systems from municipal drainage and sewage inputs as well as from industrial facilities[11]. As mentioned in section 1.1.1, these beads are threatening to freshwater mollusk and fish populations and some of this material is ultimately transported to the ocean.

Figure 1.6 Contents of a Dead Albatross Chick. Each bag (a and b) represents the contents of one albatross chick's stomach. Much of the debris are unidentifiable pieces of plastic however, some of the materials are quite distinguishable and include items such as: lighters, glow sticks, golf balls, printer ink cartridges, bottle caps, and et cetera. Pictures were taken by H. Sullivan at the 2014 International Ocean Research Conference in Barcelona, Spain.

1.2.3 POP Transportation

Due to their chemical make-up, plastic polymers have hydrophobic characteristics and absorb other less hydrophilic compounds present in waters. Many of these compounds are quite toxic and have been globally banned for years but are still present in oceans. These compounds are referred to as persistent organic pollutants (POP) and include dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCB), and other polycyclic hydrocarbons (PAH)[22, 23]. Even at low concentrations, POP can have adverse effects on marine organisms including compromised immune systems resulting in an increased risk of disease, retarded or stunted growth, and death[24]. Many POP disrupt the normal hormone regulation of an animal and are classified as endocrine disrupting compounds (EDCs). These compounds cause reproductive disorders including sterility and intersexing of some fish[25].

Oceanic plastic may concentrate toxic or lethal levels of POP so if the initial ingestion of plastic does not kill an organism, toxic POP will[22]. The bioaccumulation of POP from plastic debris first became evident in studies performed on seabirds and turtles later but can likely be found in all aquatic life[24, 26]. The bioaccumulation of POP introduces the compounds into the food chain where they can continue to biomagnify from one trophic level to the next.

1.3 Plastic Degradation

The degradation of polymeric materials can be caused by a number of chemical reactions. It is typically initiated by the absorption of ultra violet (UV) light which leads to the deterioration of such physical properties as tensile strength and reduced molecular weight of the material[27]. In natural environments, this process is more colloquially referred to as "weathering." The degree of sensitivity with which a polymer may degrade is dependent upon the chemical composition that in turn affects its ability to absorb tropospheric UV radiation which includes both UV-B (280 nm - 315 nm) and UV-A (315 - 400 nm)[27,28].

Synthetic polymers can be placed into one of two degradation categories based on their interactions with UV light. In one category, which includes polymers like polyacrylnitrile (PAN) and polyvinyl chloride (PVC), the physical properties are more resilient to extended UV exposure. The radiation does cause chromophoric groups to undergo a chemical change leading to discoloration of the material, but the backbone chain remains relatively intact[27]. In the next category, polymers like polyethylene (PE), polypropylene (PP), and polystyrene (PS), become embrittled upon UV exposure. Embrittlement can occur by either one or some combination of the following effect: scission of the backbone, photoinduced crystallization, and/or crosslinking[27]. Crystallization and crosslinking can initially improve the properties of the synthetic polymer but extended UV exposure does ultimately lead to deleterious effects. We will describe the various types of degradation in the following sections that occur in a natural environment.

1.3.1 Photo-degradation

Probably the most important and the initial type of deleterious process a polymeric compound undergoes in the environment is solar degradation. As stated previously the UV-A and UV-B region are primarily responsible for the initial degradation of polymeric materials[27-29]. The sun provides a near Boltzmann distribution of energies with a maximum near 500 nm[27]. Since shorter and more energetic wavelengths interact and are absorbed by the ozone layer, typically only those having energies greater than 300 nm make it to the earth's surface[27]. This is important as the energy a quantum has is dependent on wavelength, λ, as is shown by equation 1.1 where h is Plank's constant, c is the velocity of light, λ is the wavelength of the photon and N is Avogadro's number. The energy of one mole or 6.022 x 10^{23} photons is known as an Einstein.

$$E = Nhc/\lambda \qquad \text{Eq 1.1}$$

The energy required to break the carbon backbone (C-C) found in typical plastic resin materials is approximately 83 kcal/mol, or 347 kJ/mol. This energy translates to a wavelength of 345 nm which falls into the UV-A region. So energies associated with wavelengths of 345 nm and shorter (300 nm) have the capacity to rupture the C-C backbones of polymers. Again, only a small fraction of the light received at the Earth's surface meet that requirement which may explain why photo-degradation appears somewhat of a retarded process in the environment.

In a natural environment, the ambient temperatures, and amount and type of UV exposure varies based on geographical location and time of year (and day). Therefore, the rate of degradation a piece of discarded plastic experiences is affected by its global position. Furthermore, as UV light enters a body of water, it attenuates by either absorption and/or scattering, resulting in even fewer photons being available to rupture C-C bonds. Therefore, photo-degradation is expected to be greater within tropical latitudes and terrestrial locations, and much less prevalent in aquatic environments.

1.3.2 Hydrolysis

Hydrolysis is a reaction in which bonds are cleaved by the addition of water. This type of degradation occurs as water spontaneously ionizes into its hydronium cation (H_3O^+) and hydroxide anion (OH^-). Polyethylene terephthalate and amides (nylon) which have C-O and C-N bonds, respectively, and are weaker than C-C bonds can undergo hydrolysis relatively faster than polyethylene. The presence of salts helps facilitate this separation but the overall reaction usually requires the presence of a strong base or acid to act as a catalyst[30]. The hydrophobicity of the polymer can also affect the rate of hydrolysis[31]. As such, this type of degradation is an extremely slow process in natural settings and much less effective than photo-degradation. The half-life of hydrolysable bonds in poly(amides) is roughly 83 thousand years[31].

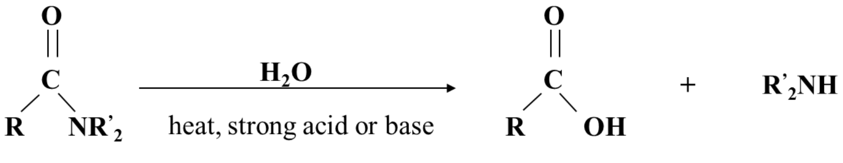


Figure 1.7 Hydrolysis of an Amide. Amides, in the presence of water and either a strong acid or base (heat preferred) will hydrolyze to produce a carboxylic ester and the appropriate amine.

1.3.3 Thermal-degradation

Heating a polymer to temperatures greater than 160 ºC can cause the backbone to undergo molecular scission. The polymer bonds may also react with another part of the polymer (crosslinking) altering physical properties. Crosslinking may temporarily make the product stronger and more resistant, but reduction in molecular weight can occur[28]. Due to the extreme temperatures necessary, thermal-degradation is not considered an environmental degradation process[29].

1.3.4 Thermo-oxidative degradation

Thermo-oxidative degradation is a slow oxidative process that can occur at "moderate" temperatures[29]. In the presence of oxygen, the thermal stability of a polymer drastically reduces[32]. For example, at low pressures polyethylene begins to lose its mechanical strength upon exposure to air with 100 ºC (212 ºF) temperatures for less than 48 hours.[32] Like thermal-degradation, thermos-oxidative degradation is an extremely slow process in natural environments.

1.3.5 Biodegradation

Microbes capable of metabolizing high molecular weight synthetic polymers like those found in solid plastic goods are extremely rare[29,33], and when/if they are capable of biodegradation, only a small fraction of the material is incorporated and utilized as biomass[28]. The remainder of the material can remain undisturbed for some time. Prior to any biodegradation, polymers need to be initially degraded by some other abiotic process such as photo-oxidation[28]. In their solid crystalline state, plastics are too large to pass through the cell membrane and so must first be depolymerized into monomers, dimers, or trimers before absorption[28,33]. Once the synthetic material has passed through the membrane it can be further degraded via enzymes (extracellular and intracellular)[28]. Complete mineralization occurs once a carbon in a polymer has been converted to CO_2 and/or incorporated[29]. In aerobic conditions, the products are often just CO_2 and water whereas in anaerobic conditions (landfills and other anoxic environments) methane is also produced[28,34]. Ultimately, the biodegradation of plastics in aquatic environments is minimal due to the lack of specialized microbes. Further, degradation may require a consortium of microbes to break a polymer down into subunits. In addition to bacterial biodegradation, there have also been reports of possible fungi biodegradation of polyurethane but again this may only apply to lower molecular weight or previously abiotically degraded polyurethane[34].

1.4 Microplastics

The term “microplastics” has been used in literature to describe plastic debris that can range anywhere from 5 mm to true micron scale pieces[29]. This may cause some ambiguity as more micron sized particulates are being found in both fresh and marine environments. “True” microplastics, unseen by the human eye, can be problematic for planktonic species and likely cause similar health hazards observed in larger organisms[21]. Microplastics may originate from a variety of sources like cosmetics and industrial processing, or they may have derived from chemical and/or mechanical breakdown of larger plastic debris.

1.5 Dissertation Overview

As plastic materials enter a natural setting, interactions between the two may occur. These interactions may be benign or they may cause the release of harmful contaminates which can impact ecosystems. To date there have not been sufficient studies looking into the interactions between water and plastic, specifically the chemistry of polymers. The purpose of this study is to address a series of questions that have evolved from literature research. Hypotheses for these queries are presented in Chapter 2, providing current supportive literature.

Research Questions

1. Is degradation of aquatic plastic primarily due to abiotic or biotic processes?
2. Do salts, like those common in seawater, help facilitate degradation despite attenuated UV light and reduced temperatures?
3. If particulates are formed from degradation processes, what sizes are typically produced or released in aquatic environments?
4. Does oxidation occur more readily in polymers with oxygen included in their backbone structures?
5. Does the isotope composition of plastic change as it undergoes natural or simulated degradation? If so, can these changes be used as a type of geochronometer to predict the residence time of detrital material at sea?

1.6 Summary

The mass production of plastic polymers is expected to continue on an exponential path. Currently, plastic waste is not completely recovered or destroyed hence much of the plastic debris enters into aquatic environments. Much is known in regards to ingestion and entanglement of these polymers with marine and terrestrial wildlife. Less is known about the chemistry of the polymers as they are exposed to natural water environments. The purpose of this work is to investigate how plastic polymers react in various aquatic environments.

The following chapter will address my hypotheses as well as provide a review of current knowledge. Chapter 3 lays out the methodologies that will be employed to test these hypotheses. Chapters 4 and 5 provide the data obtained from these experiments and conclusions that can be inferred. Supplemental information and additional data is provided in Appendix I.

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CHAPTER 2

Review of Related Literature

The amount of plastic debris found in our oceans has not increased to the extent expected since the 1980's despite the increased production and waste generated[11]. This begs the question: "where is all of the plastic?" According to a 2014 report published in the *Proceedings of the National Academy of Sciences,* approximately 99% of oceanic plastic could not be accounted for[11]. The fate of this unaccounted plastic might be ingestion by marine organisms, deposition to sediments due to sinking from surface waters due to increased weight from biofouling, or washed up on shorelines[12]. Clearly a better understanding of the ocean-plastic cycle is needed.

The remainder of this chapter introduces the research questions investigated as a part of my doctoral research/studies. In order to better guide the reader, each research subject is organized with a subheading and corresponding thesis that this work aims to address along with current theories.

2.1 Plastic Degradation in Aquatic Environments

Question 1: Does oxidation of plastic decrease in seawater due to attenuation of UV light and lower ambient temperatures, or does the presence of salts help facilitate degradation?

Working thesis: The presence of strong oxidizing compounds (eg. sulfates and chloride ions) in seawater facilitate the oxidative degradation of plastic polymers despite lower temperatures and attenuated UV light.

In section 1.3.1 I described photo-oxidation as probably the most important deleterious process synthetic plastics may undergo in the environment. Also, recall that light reaching the earth's surface has wavelengths in the UV-A and UV-B regions, and are energetic enough to rupture the carbon-carbon backbones common among polymeric compounds.

It has been previously demonstrated that degradation of plastics (polypropylene[13] and LDPE[13, 14]) occurs more readily with exposure to air, or lying on a beach surface, in the case of pure polymers. The same material floating in seawater and exposed to sunlight exhibits severely diminished degradation rates.[6] Reduced degradation experienced in floating samples was attributed to lower oxygen content and relatively lowered temperatures present in the water environments, in addition to UV attenuation from the surrounding seawater[6]. Although these results support the idea that light attenuation limits plastic degradation, the study was flawed in two regards. The first involves the metric by which degradation was measured. The only metric recorded was tensile strength which showed that the air-exposed samples had a greater reduction in tensile strength compared to those floating in seawater. As discussed earlier, many degradation processes can occur making plastic stronger via photo-induced crystallization and/or crosslinking[4]. The process of crosslinking results in some bonds being ruptured while other bonds are formed, and can potentially release material into the surrounding environment following bond breaking. Despite appearing strong, these materials likely experienced some form of deleterious process, and thus tensile strength alone is not a good indicator for degradation.

The second concern is not accounting for the very different chemical environments to which the samples were exposed. Oxygen and UV light are important factors in the degradation of polymers exposed to air, but likely not the only contributors in marine waters. As mentioned in chapter 1, hydrolysis often occurs in the presence of water. Although not as dominant of a deleterious process compared to photo-oxidation, hydrolysis occurs fairly readily, especially for more hydrophilic polymers[15]. This process is supported by the observation of increased degradation rates in polymers exposed to air with increasing relative humidity[16].

Salinity may also be important in plastic degradation. The average salinity of oceanic water is approximately 35 parts per thousand (or g/L). Chloride is the largest component, accounting for roughly 55 % by mass of the salt content. Figure 2.1 illustrates the composition and relative abundance of salts found in most ocean waters. Arguably the most important components of oceanic water – besides water and oxygen – are the chloride and sulfate anions, as these ions are electrophilic and thus strong oxidizing species.

In addition to the photo-degradation effect of UV light on polymeric compounds, light can also interact with other molecules such as water. UV light that possesses the energy necessary to rupture a molecule of water can have one of two results. The first is a

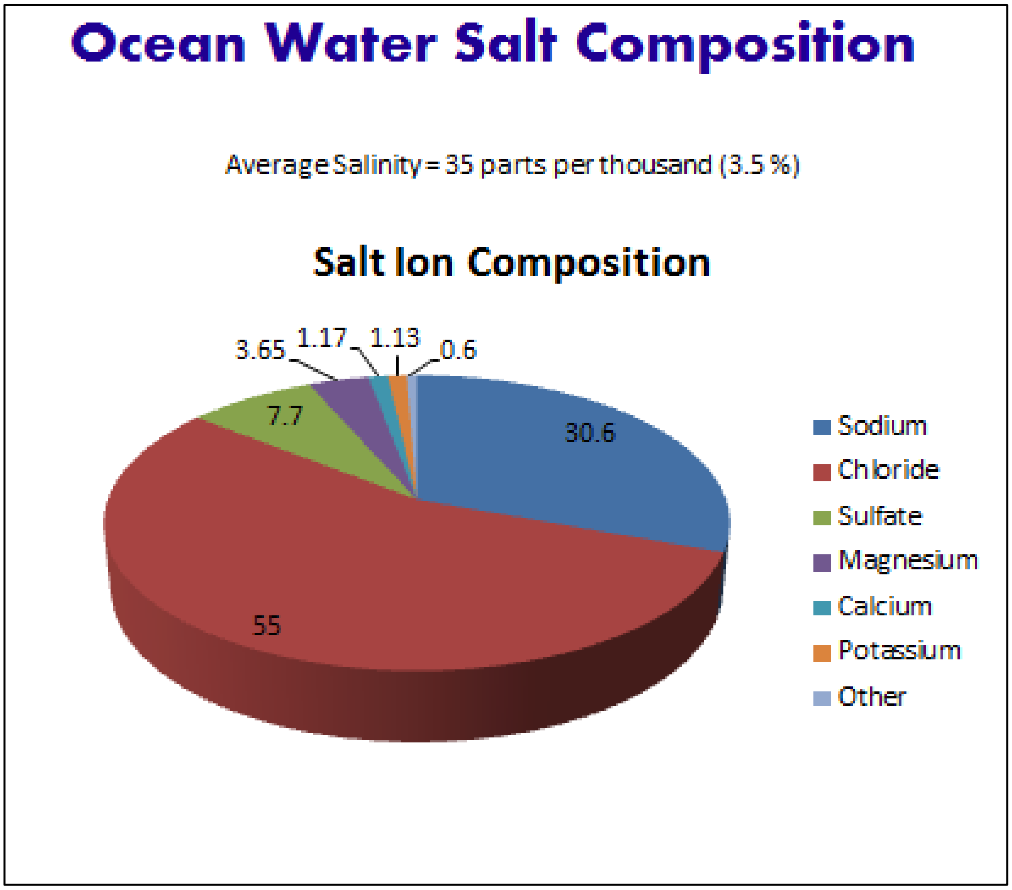

Figure 2.1 Ocean Water Salt Composition. Ocean water is comprised of an average of 3.5% of various salts. Chloride and sulfate ions are extremely electrophilic and thus prove to be great oxidizers.

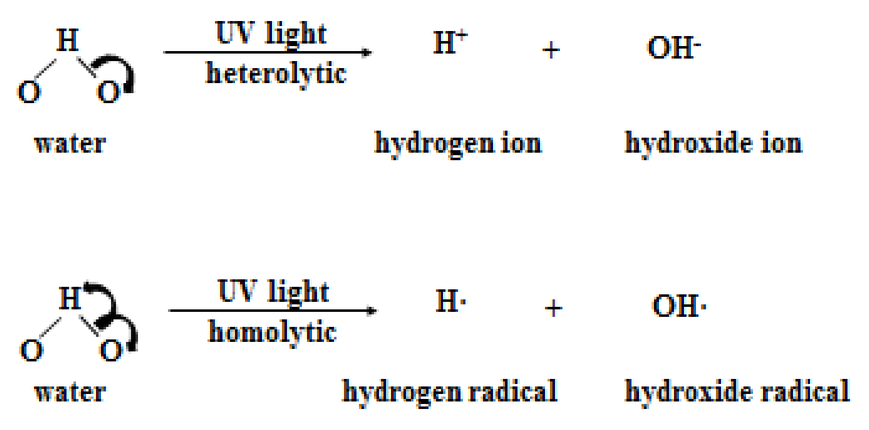

Figure 2.2 Fission of Water Molecules via UV Radiation. When the covalent bond of a water molecule interacts with UV light it may either do so as a heterolytic or hemolytic cleavage. Heterolytic cleavage results in two charged species, a negatively charged hydroxide ion and a positively charged hydrogen ion. A homolytic cleavage divides the electrons evenly between the two pairs in a covalent bond resulting in the formation of two radicals, a hydrogen radical and a hydroxide radical. Radicals are highly energetic, short-lived species that are extremely reactive.

heterolytic cleavage resulting in a hydroxide ion (OH^-) and a proton (H^+), more frequently represented as a hydronium ion (H_3O^+). The second result arises from a symmetric cleave (homolytic) of the H_2O bond which yields the radical equivalents (Figure 2.2). Radicals are highly unstable species due to unpaired electrons and therefore quite reactive.

It has been demonstrated that sulfate radicals help facilitate hydroxyl radical formation in the presence of chloride at pHs reflective of marine environments (pH 8.1)[17]. The sulfate radical based oxidation of organic matter discussed in this paper is proposed as a possible water treatment process, and is reportedly already used in ground water remediation[17]. The series begins with the production of sulfate radicals ($SO_4\bullet^-$) via UV light exposure. The unstable sulfate radical rapidly strips an electron from a Cl^- ion producing a chloride radical ($Cl\bullet$) that continues the product pattern with the products produced being highly pH dependent. At low pH (<5), the chlorine derived oxidation products (ex. chlorate, ClO_3^-) are favored however, at higher pH (>5) the $Cl\bullet$ reacts primarily with water yielding hydroxyl radicals ($OH\bullet$). Based on the sulfate and chloride content of ocean water and the pH found in marine environments; the production of hydroxyl radicals is highly probable. These hydroxyl radicals may then be able to interact with marine plastic polymers causing degradation by oxidative processes. A proposed mechanism of this reaction is shown by Figure 2.3. Increasing the concentrations of chloride and sulfate ions, or increasing the salinity of the water, is expected to increase hydroxyl radical formations and the severity of oxidation on marine detritus plastic. It is proposed that areas with greater salinity are likely to result in plastic that is oxidized more readily.

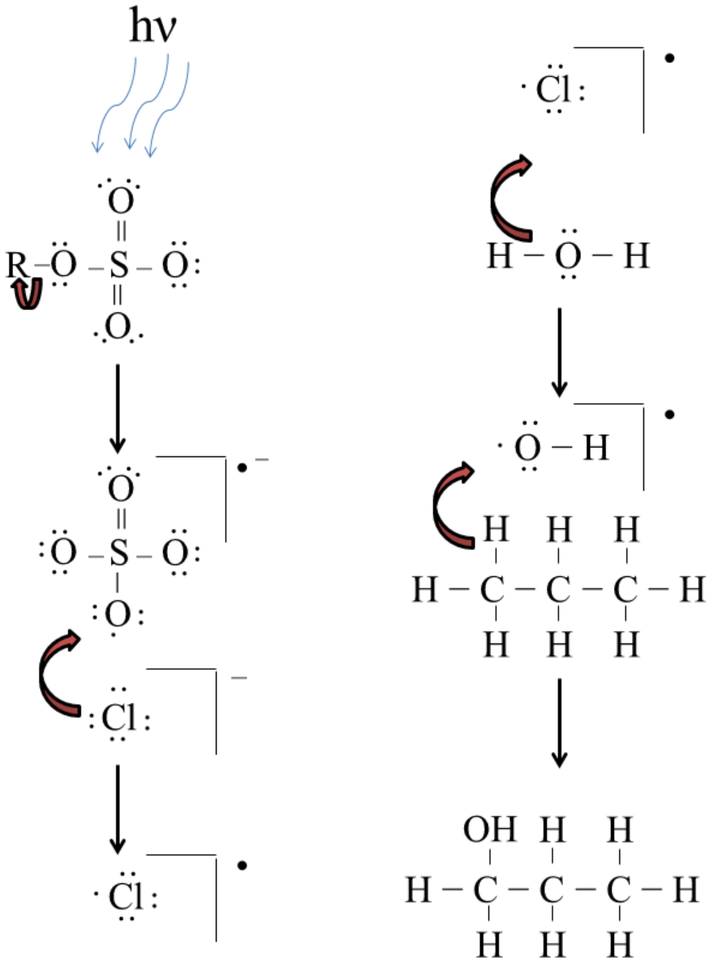

Figure 2.3 Hydroxyl Radical Formation Facilitated by Sulfate and Chloride. This mechanism is based on the model from Lutze et al. and shows the cascading effect of systematic electron stripping from one species to another, ultimately producing the hydroxyl radical[17]. Once formed, a hydroxyl radical can then oxidize an organic compound like the alkane displayed here.

2.2 Degradation: Abiotic vs. Microbial

Question: Is degradation of aquatic plastic due primarily to either abiotic or microbial processes?

Working theory: Due to the extremely slow bio-mechanisms described in literature, abiotic processes are likely the major contributor to plastic degradation in marine environments.

One explanation for the “missing” ocean plastic is microbial degradation[18]. Two key observations support the hypothesis of microbial degradation. The first is an increased population (25 %) of *Vibrio Cholera* bacteria present on marine detritus plastic compared to surrounding seawater and seaweed[18]. The second observation came from Scanning Electron Microscopy (SEM) images which revealed that the surface of the plastic appeared pitted. In the pits of the plastic, “bacterial-like” cells were observed, suggesting perhaps the microorganisms were degrading the surface away[18]. Although microbial degradation may be occurring, it is not likely to account for the apparent ”missing” marine plastic.

Biodegradation is any process in which some organic substance is broken down by a living organism. For micro-organisms, this process is extremely slow for the degradation of polyethylene [-21]. Hydrocarbons, in their solid crystalline form, are typically too high in molecular weight to readily pass through the microbial membranes. Generally speaking, an increase in molecular weight results in a decrease in the ability for microbial biodegradation. In order for a microbe to degrade a polymer, it must first be depolymerized by some other process (abiotic) into its monomeric subunits. Once depolymerized, the molecule can then be absorbed and mineralized by microbial organisms[22].

The natural biodegradation of plastic, once depolymerized by any of the previously mentioned abiotic processes, can proceed either aerobically or anaerobically.Both pathways result in end products of carbon dioxide and water, with the additional production of methane from anaerobic processes. The biodegradation rates are dependent upon many factors including type of organism and environmental conditions[22].

Bioplastics were first introduced as a means to break down polymers into smaller fragments to reduce overall visibility. However, it was subsequently discovered that the small fragments were still too large to be utilized by bacteria and that the term bioplastic was a misnomer[22]. There were also concerns about the potential release of persistent organic pollutants (POPs) into the environment as they began to fragment and degrade[22]. Even today, many of the plastics produced are made of potentially harmful monomers like bisphenol-A (BPA), found in polycarbonates, which has endocrine disrupting characteristics. As polycarbonate begins to degrade into its monomeric subunits, it is possible that bio-activated BPA is released into the environment.

Since the 1970's, many other alternative "bioplastics" began to appear in the market including plastics doped with starch and plant-based plastics. Plant-based plastics merely describe the source of the starting material, i.e. ethylene for polyethylene plastics. Once polymerized however, there is little difference between the plastics made from plants and those from petroleum-based sources, aside from ^{13}C isotope ratios. Those plastics doped with starch do biodegrade, however this degradation is only observed at starch specific sites and then only the starch is degraded[23]. Once the starch has been degraded no other biodegradation appears to occur, leaving the remainder of the plastic in the environment untouched until some form of abiotic degradation proceeds.

To date, no true biodegradable plastic exists and all plastic degradation must begin with some form of abiotic process. Therefore, it is not likely that micro-organisms are the main cause for a decline in plastic accumulation as postulated[18], but more likely the result of abiotic processes. In fact, any degradation is more than likely due to many different abiotic processes including oxidative and mechanical breakdown.

2.3 Particulate Sizes Produced in Aquatic Environments

Question: What size particulates are produced and released upon oxidation of plastic in aquatic environments?

Working thesis: As plastic degrades, the backbone of the polymer begins to break away into pieces that can eventually flake off and continue to undergo degradation likely producing micro and even nano-plastics.

Very recently the number of reports involving microplastics in aquatic environments has spiked. Among numerous articles, some ambiguity exists as to what classifies as microplastic. Some have broadly defined microplastics as those pieces of plastic material which are < 5 mm[25-27]. For clarification, microplastics will be defined here as those pieces of plastics which are less than 1 mm (1000 microns) in size. This distinction is important as many “true” microplastics are too small to be detected by the human eye and so not easily capable of being studied, alsoposing additional threats aside from those pieces of plastics that are larger than a millimeter and easily identifiable.

Microplastics are further characterized in literature as either primary or secondary microplastics – primary microplastics describe plastics manufactured at the micron scale, typically for an intended product such as toothpastes, ‘microscrubbing’ facial and hand cleansers[28-30], etc., while secondary microplastics refer to the liberated fragmented material from a “parent” plastic after degradation[31-33]. Secondary microplastics in the ocean are primarily the result of decades of UV exposure on beaches and shoreline which breaks down the plastic into tiny fragments where it is then washed or blown into the sea[6,25,34-36].

There are a plethora of images which can be found with a simple internet search of animals, both marine and terrestrial, consuming synthetic polymers, mistaking it for a viable food source. Most of these images depict larger animals eating meso or macro-sized plastic particles. However, micro and nano-sized plastic particles are similar in size to the diet of many zooplankton. Along with the increasing reports of microplastics in the environment, it is of great concern that new studies reveal that zooplankton may be affected like larger animals when they digest plastic fragments, and ingested microparticles can transfer in the food web[37,38]. The ingestion, egestion, and adherence of plastic beads for a majority of the zooplankton has been observed[38]. Ingestion of microplastics varies among life stages and taxa as well as the size of the microplastic[38]. Micro-beads ranging in size from 1.7 – 30.6 µm were ingested[38]. They also noted that beads > 7.3 µm limited algal consumption as well which may reduce the nutritious benefit zooplankton predators receive, possibly impacting their health as well[38]. The microplastic beads were observed to remain in the zooplanktons’ bodies from hours up to a week[38]. In a natural setting, this would put other animals at risk that eat zooplankton, and could transfer microplastics further up the food chain.

In addition to ingestion, researchers noted that upon egestion, the microplastic beads (polystyrene) were surrounded by a viscous material which caused the excreted material to adhere to the organism[38]. This proved problematic as the microplastics can concentrate between external appendages of copepods. The swimming legs, feeding apparati, antennae, and furca were all covered extensively which limited swimming and feeding[38]. A question that still needs to be addressed regarding microplastics and primary producers is the potential health effects, if any, EDCs may pose on primary producers and consumers.

More studies are needed to understand how secondary microplastics are produced and introduced into aquatic systems. These small polymers can threaten species and possibly disrupt food chains.

2.4 Summary

There have been very few if any investigatons of the potential chemical effects aquatic environments have on plastic detrtitus material. This work aims to address several questions. Does the chemical make-up of an aquatic environment effect the degradation of plastic? As already discussed, the presence of strong oxidizing agents found in marine systems may contribute to the oxidation of organic polymers which may not occur in limnetic systems. Is biotic degradation a key factor for removing plastic from aquatic environments? By investigating possible abiotic processes, we may be able to align with prior studies that document low rates of biological degradation dependent on abiotic processes prior to microbial breakdown. Another presumption found in literature assumes that secondary microplastics take decades to form. However, if there are chemical reactions in marine environments that start the degradative process due to the presence of oxidizers and UV light, production of microplastics may occur at a faster rate.

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CHAPTER 3

Research Design and Methodology

3.1 Introduction

In this work, we attempt to test the hypotheses described in Chapter 2 by taking advantage of both laboratory-based and field-based experiments. While the importance of field-based experiments cannot be disputed as they represent a variety of factors that may impact plastic polymers and their degradation in the environment, laboratory-based experiments are equally important. By taking a sample of the ocean water and bringing it into the laboratory, we can not only control the temperature and light the samples are exposed to, but we can also inactivate microorganism contributions by autoclaving water samples prior to exposure so that only abiotic processes are observed in these experiments. In addition, any plastic particulates that may flake off of the parent material are “captured” by keeping them enclosed and separated from other samples.

3.2 Materials and Methods

All plastic materials were purchased from United States Plastic Corporation, a major distributor of industrial and commercial plastic products. We chose to focus on the three most popularly used and discarded plastic: HDPE, PETE, and PC[1,2]. PC and HDPE samples were purchased in bottle form and were products of Themo Scientific. PET bottles were manufactured by Silgan Plastics. All samples chosen were clear plastics to eliminate any contributions from dye materials. All samples were described to contain pure polymers with no other additives which may also impact the chemistry.

Samples were washed, rinsed with deionized (D.I.) water, and dried before use in experiments. All samples were cut into 1” squares with the exception of those used in one of the two field experiments, which were left intact.

Lab based environment

For laboratory experiments, a modification of the method ASTM D4329-05 “Standard Practice for Fluorescent UV Exposure of Plastics”[10] was used, a protocol originally designed to simulate effects of sunlight, moisture, and heat exposure. The modification was to include exposure at 0 ‰ salinity and 25 ‰ salinity. The UV light source was a 26 W (UV output 315-390 nm) Solar Bulb on a timer providing 8 hours of exposure per day. This bulb, in keeping with the ASTM method was kept 12” from our sample beakers. Beakers containing each sample were housed in a water bath shaker kept at 22 °C. The samples were placed in beakers either filled with water (0 or 25 ‰ salinity) or as “dry” samples. Samples were arranged and their positions systematically rotated weekly to minimize any effects from temperature or UV light variations (Fig. 3.1). The shaker was set to 65 RPM which gently swayed the water in order to mimic subtle wave action.

Prior to beginning the degradation study, the water bath temperature was monitored over a period of eight hours with the UV lamp on to determine the extent of temperature control possible. At the start of the day, a calibrated thermometer and digital display of the water bath shaker both read 22 °C. After the 8 hour UV exposure cycle, the thermometer and digital display again read 22 °C. Therefore, any concern of additional heat received from the lamp was not warranted and a consistent temperature was maintained by the water bath and monitored throughout the study. Thus, one may conclude that any degradation processes that occur will be directly dependent on UV exposure and the contents of the water.

Seawater was collected just offshore of the First Landing State Park located on the southern coast of Virginia (coordinates 36.9199, -76.0548). Seawater was autoclaved to inactivate any microorganisms that may be present. The pH of the water at time of collection was 8.1, and remained unchanged after autoclaving. The salinity measured at collection was 25 ‰, and also did not change after autoclaving.

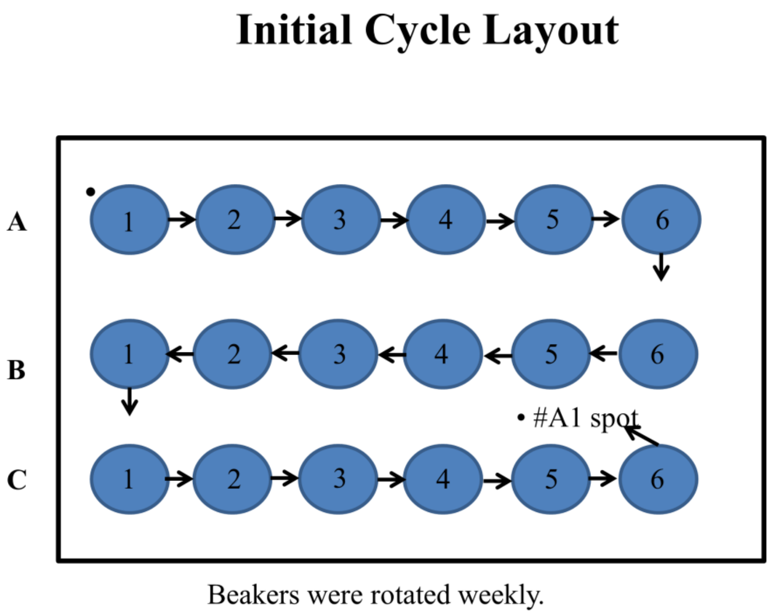


Figure 3.1 Laboratory Degradation Experiment Layout. Each row (A, B, or C) represented a polymer type and intial beaker position for each polymer is given a numerical value. Beakers were rotated to ensure all samples received similar UV conditions.

Field based environments

Two sites were chosen for their differing salinities and ease of access while still remaining mostly undisturbed. The first location was along the Wicomico River, a river with tidal flow from the Chesapeake Bay (coordinates 37.9032, -76.2931). The average surface salinity measured at this location was 7 ‰. This site will be referred to as the "Lynton" location, named for the property owner. Samples were suspended using fishing line to float at or near the surface, and also at least 8 inches below the surface. The line was weighted with a concrete block and tied to a floating buoy, then anchored to a dock.

The second location was along the Cobb Mill Creek which mixes with the Mockhorn Bay along the Eastern Shore of Virginia and home of the Long Term Ecological Research (LTER) center of UVA (coordinates 37.2873, -75.9253). The salinity of this site varied greatly with the tide and weather, but the average salinity for this location was recorded to be around 26 ‰. Squares of each sample type were suspended with fishing line. Unlike the first location, we were not permitted to string them vertically as the samples needed to be confined to a basket (Fig. 3.2).

Figure 3.2 LTER Field Degradation Experiment. Located on the Eastern Shore of Virginia.

3.2.1 Samples and Population

Field samples mimicked those employed in the laboratory setting (HDPE, PC, and PETE). Due to the difficulty in accessing samples in the field (travel time and cost), any sample removed was not re-introduced into the experiment. Therefore, a larger sample population was required. For lab studies, three samples of each plastic for each condition were employed. For field studies, the sample quantity was increased to twelve samples of each type of plastic.

Each plastic is made up of repeating units, called monomers. These polymers therefore contain numerous bonds to be investigated and monitored for changes.

3.2.2 Sample Preparation

All samples were gently washed and thoroughly rinsed with deionized water after removal from an experiment and before analysis. Specific sample preparation for each analytical technique can be found in respective subsection in 3.3. Most techniques required minimal processing aside from elemental analysis isotope ratio mass spectrometry (EA-IRMS). All samples were immediately returned to the experiment after analysis where possible.

3.2.3 Sample Collection

The laboratory experiment continued for 18 months and samples were periodically analyzed to monitor any potential changes in surface or chemistry.

Field experiments continued for a year and samples were retrieved for analysis but were not returned to the field due to budget and time constraints.

3.3 Instrumentation

This section provides a brief description of the analytical tools used, and rationale for selecting each method. Instrument descriptions are given under their respective sub-headings.

To monitor the potential chemical changes in samples during degradation experiments, a non-destructive analytical method referred to as infrared spectroscopy was pursued. This method uses absorption energies in the infrared (IR) region to help quantify and identify the types of bonds present initially, bonds that may be breaking over time, as well as additional bonds that may be forming (see section 3.3.1).

Visual observations were recorded over time and any surface alterations were monitored using a high power magnification microscope such as a scanning electron microscope (see section 3.3.2).

Particulate matter that flaked off of the “parent” material during the laboratory degradation experiments was retrieved and analyzed using a particle counter. This instrument not only provided quantification but also the size of particulates present as well (see section 3.3.3).

Elemental Analysis – Isotope Ratio Mass Spectrometry (EA-IRMS) is the only instrument used which is destructive to our samples and thus was used only after previous analytical methods were performed. This method provided information used to determine if, over time, the isotope ratios of samples changed throughout degradation.

3.3.1 Fourier Transform Infrared (FTIR) Spectroscopy

Energy in the infrared (IR range is absorbed and converted by organic molecules into molecular vibrational energy. This energy is quantized but does not appear as sharp lines in spectra due to the rotational energies that accompany vibrational energies, and so appear as broader bands. The overall frequency of absorption is dependent upon the mass of the atoms that make up the molecule, the geometry of the atoms and their bonds, as well as the force constants of the bonds[1]. Band positions described throughout this document are presented as wavenumbers ($\bar{\upsilon}$) with units in reciprocal centimeters (cm^{-1}). Older IR methods and literature used wavelengths (λ) in the units of micrometers (microns). The mathematical relationship between wavenumbers and wavelength is reciprocal.

$$cm^{-1} = {10^4}/{\mu m} \qquad \text{Eq. 3.1}$$

Two classifications of vibrational energies exist which describe stretching and bending. A schematic depicting these types of energies is shown in Figure 3.3. Despite the various types of vibrational energies that may exist, only those that contribute to a dipole shift of the molecule are observed in IR[1]. For example, in the molecule carbon dioxide (CO_2), which is linear by nature, only the asymmetrical stretching is observed in addition to the bending energies (Fig. 3.4).

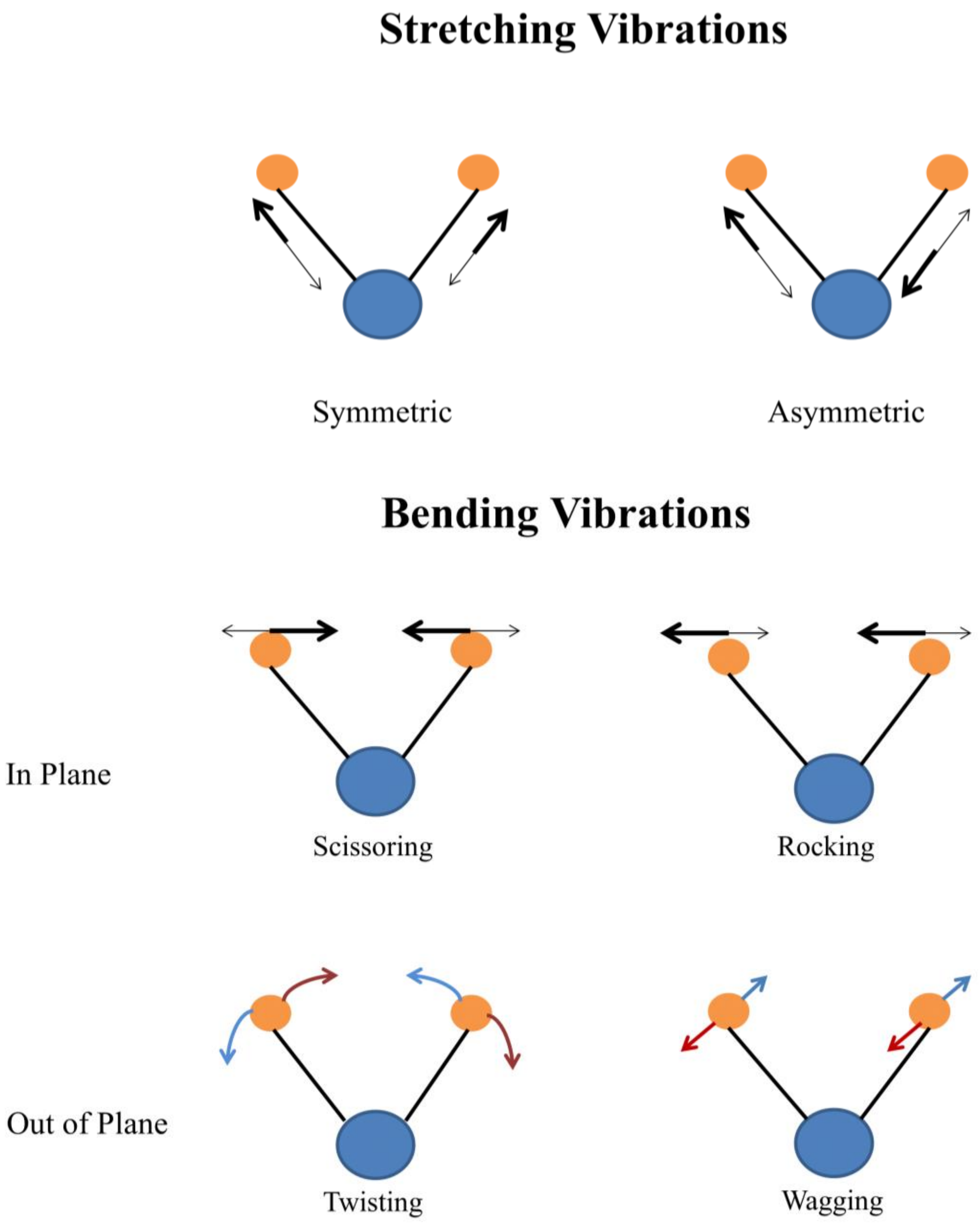
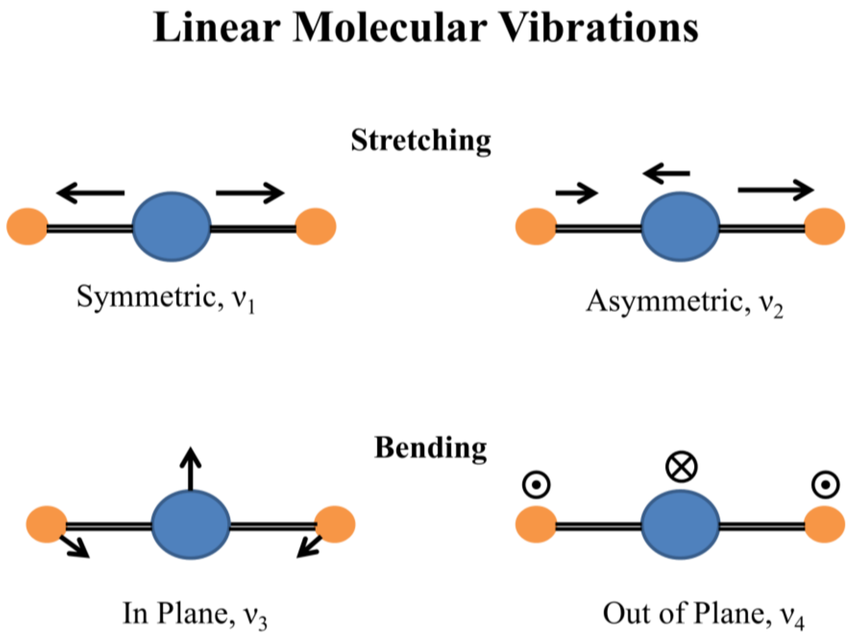


Figure 3.3 Prevalent Stretching and Bending Modes in FTIR. This schematic depicts the simplified types of atomic vibrations that occur upon IR light absorption. Black arrows represent the weighted dipoles. If the dipoles are equal (see Figure 3.2), the resulting dipole moment cancels out. Red and blue arrows show respective movement out of their planes.



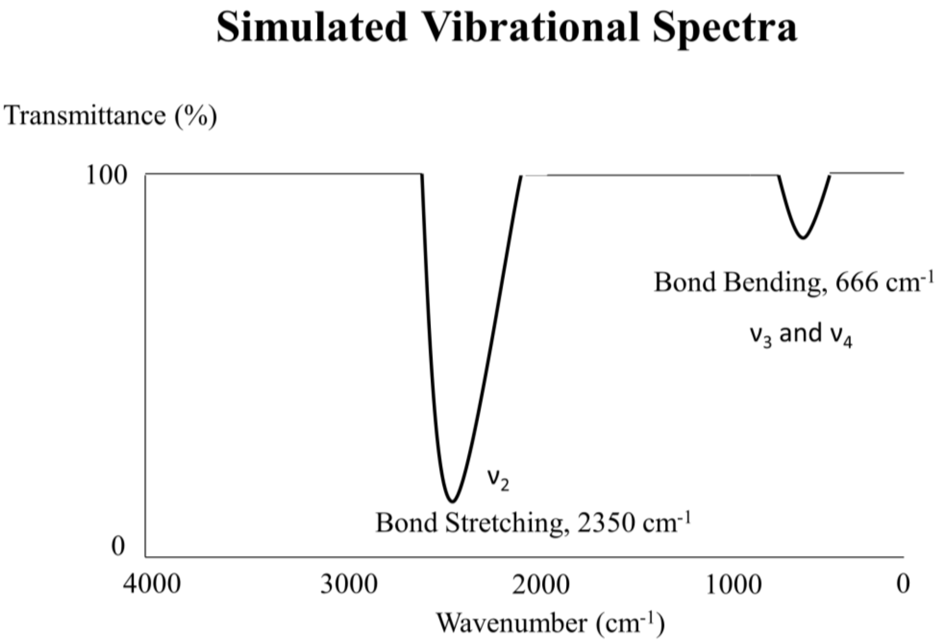
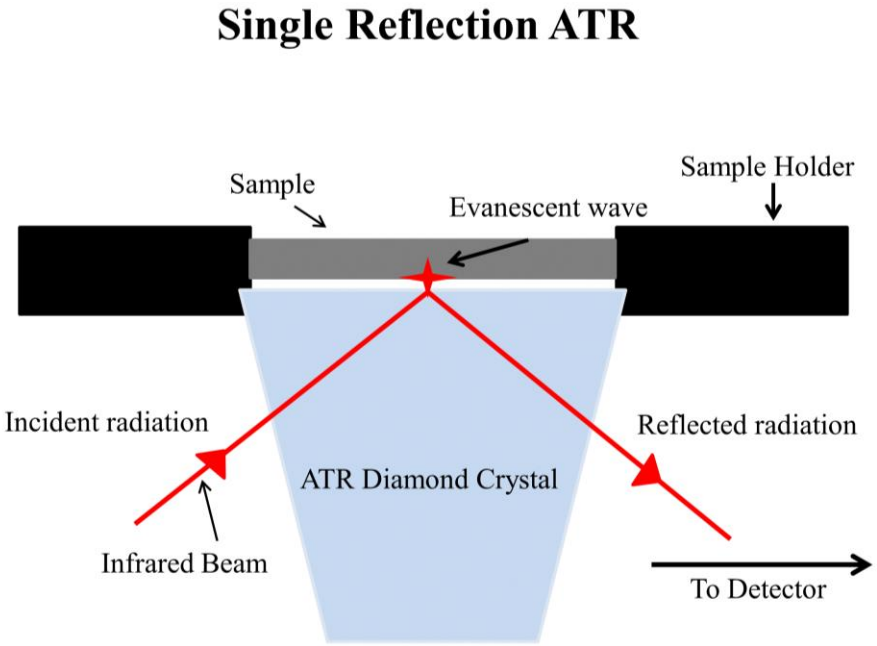


Figure 3.4 Carbon Dioxide Molecular Vibrations in IR. Carbon dioxide (CO_2) is a linear molecule containing three atoms with a total of four possible fundamental vibration energies. Black arrows represent the direction and magnitude of the dipole. In ν4, the symbols reflect arrows either going into or out of the page. The first vibrational mode, ν_1, is symmetrical in nature and thus produces no change in the dipole moment of the molecule, and so is considered inactive in IR. The other vibrational energies do create a dipole moment and can be analyzed in an IR spectrum however, 3 and 4 are energetically equivalent and so are considered doubly regenerative (same peak).

Many FTIR instruments can be outfitted with attenuated total reflection (ATR) accessories. These operate by measuring the changes observed in a reflected infrared beam as it comes into contact with the sample. This is usually done with an optically dense crystal having a high refractive index (at a certain angle)[2]. The internal reflectance generates what is known as an evanescent wave which extends from the surface of the crystal and into the sample held in contact (Fig. 3.3). The protrusion of IR energy from the crystal to and into the sample surface typically only reaches a few microns (≤ 5 μ). This is useful to follow any chemical changes that may occur along the surface of our polymeric samples upon degradation.

The instrument used throughout our degradation experiments was a Thermo Fisher Nicolet 6700 FTIR that was fitted with a diamond ATR (Thermo Fisher Smart iTR^{TM}). This model was equipped with a deuterated triglycine sulfate (DTGS) detector, using a potassium bromide (KBr) beam splitter, and a HeNe laser. The spot size for sample analysis was 2.5 millimeters across. It was programmed to measure 30 scans per sample with a resolution of 4 cm^{-1} with a scan range of 4500 – 500 cm^{-1}. In addition, a background scan was taken every 15 minutes. The spectra were then ATR corrected (to remove any response from the diamond) and the baseline corrected before exporting the data from the processing software for analysis. The data from each sample was then normalized by standard deviation, resulting in the spectra which are displayed here. Measurements were performed in triplicate for each polymer type, and nine different spots along the surface of a polymer were analyzed



for consistency and found to differ less than 0.002 Absorbance Units suggesting no statistically-significant difference between sample runs or surface areas measured.

Figure 3.5 Single Reflection ATR. The internal reflection of IR energy along the interface of two mediums (crystal and sample) with different refractive indices creates an evanescent wave that penetrates into the medium with the lowest refractive index (sample).

3.3.2 Scanning Electron Microscopy (SEM)

Optical microscopes use photons (visible light) for visualization of samples, but are limited by the wavelength of visible light and so cannot often exceed magnification over 2000 times before the human eye can no longer distinguish the image being observed[3]. This restriction is a result of what is referred to as the Rayleigh criterion (Eq. 3.2) which describes the minimum criteria needed for resolvable detail where θ (radians) represents the angle of resolution, λ is the wavelength (m) used, and d is the diameter (m) of the circular aperture (or human eye). A visual representation of the Rayleigh criterion is demonstrated in Figure 3.6.

$$\theta_{min} = 1.22\frac{\lambda}{d} \qquad \text{Eq. 3.2}$$

Electron microscopes produce images of a sample by scanning the surface using a focused beam of electrons which can achieve higher resolution and much higher magnification (up to 2 million times) due to the extremely small wavelengths involved. In De Broglie’s equation describing the wavelength of electrons (Eq. 3.3), where *h* is Plank’s constant, *m* is mass, and *v* is velocity, the equation can be written to include wavelengths achieved at various voltages (Eq. 3.4)[4]. If using a voltage of 10keV for example, an electron would have an associated wavelength of 0.012 nm. As voltage increases so does the resolution.

$$\lambda = h/mv \qquad \text{Eq. 3.3}$$

$$\lambda = 1.23/(V)^{1/2} \qquad \text{Eq. 3.4}$$

Electron microscopes also have a greater depth field which ables the viewer to discern peaks or valleys, offering topographical features present on a samples’ surface..

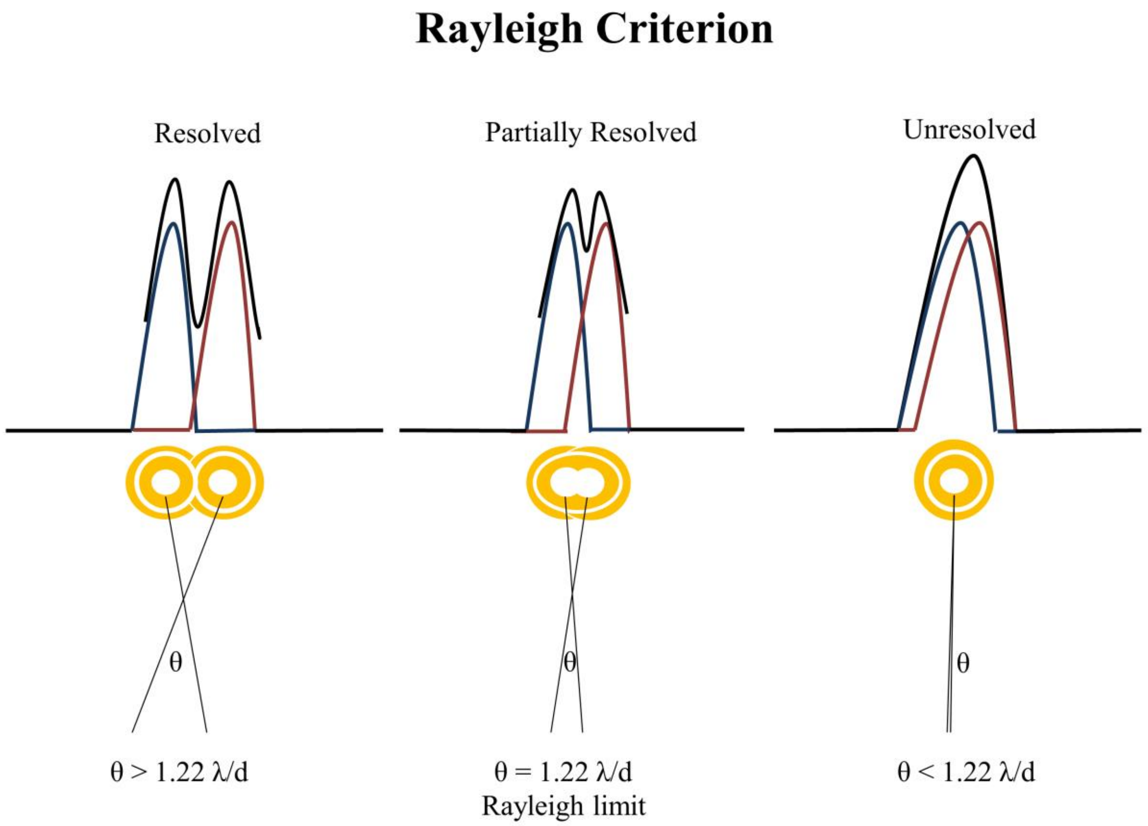


Figure 3.6 The Rayleigh Criterion. If the central maximum (θ) of one diffraction pattern coincides with first minima of the other diffraction pattern then the two sources will be resolvable. The minimum value of θ must be greater or equal to 1.22 λ/d in order to be resolved. The blue and red lines represent two distinct sources of diffraction. The black trace above each series represents the likely combined result that may be visually observed. The yellow circles display any overlapping between the two diffraction sources and are referred to as “Airy disk” in literature.

Electron microscopy is typically performed under a vacuum (10^{-4} – 10^{-7} mbar) that makes it possible for electron emission as well as the acceleration needed. For polymer analysis, it is best to use low-vacuum mode when possible. Polymers are non-conductive samples being comprised of primarily hydrocarbons. As the focused electron beam hits a polymer, the localized electrons cannot be easily conducted away which can cause what are known as "charging effects.[5]" The effects can present as abnormal contrast, a distortion in the image itself, or a shift in the image. In "normal" vacuum mode, one can go through the extra steps and coat the specimen in a thin metal coating to help reduce charging effects. However, the coating itself may mask some of the finer details in the sample's surface. Low vacuum (LV) mode helps reduce the charging effects by the addition of a gas in the specimen chamber which can absorb some of the excess electrons[5]. Because LV mode does not require additional and often complex sample preparations, imaging can be performed without any further modification. This not only saves time but helps to maintain the integrity of the sample itself allowing the investigator to examine the surface changes after experimentation.

By using SEM in LV mode, it is possible to discern changes in the surface of plastic throughout the degradation process. We suspect these changes will be quite small and not readily visible via optical microscopy requiring the resolution afforded in SEM. This will help us to determine if any visual cracking or separation of the polymer is present. Additionally we may be able to determine the scale of particulates that may present themselves along the surface. The instrument we will employ is located in the Nanoscale Materials Characterization Facility here at UVA. It is an FEI Quanta 650 Scanning

Electron Microscope that is currently operated by Richard White who is the facility's laboratory Manager.

Field samples were cleaned of any physical debris, gently washed, and rinsed thoroughly with DI water prior to imaging. In some instances (LTER site) organism attachment was too great and could not be completely removed without causing further damage to the surface.

Images from laboratory experiments were obtained using the standard high vacuum mode as low vacuum was unavailable at the time. As a result the images are not as detailed[1] as those from the field samples, which occurred much later after additional funding became available. Fortunately, the images were able to be captured before any possible charging effects occurred. Due to time and financial constraints, only samples in the brined water were examined as these appeared to have changed the most visually and chemically based on FTIR data that was obtained at the time.

3.3.3 Particle Size Coulter Counter

A particle size coulter counter was utilized in order to determine the size of particulates that flakedoff of the "parent" specimen over time. This choice of instrument was chosen over other applications such as multi-angle laser spectroscopy (MALS) or dynamic light scattering (DLS) which required either known concentrations of the samples being analyzed or monodispersed samples. Since we will not know the concentration of particulates present and the particulates present will likely not be uniform in size, we needed an analytical method that could count how many particles were present and also afford some information as to the general size(s) of the particulates.

Coulter counters, named after the developer Walter H. Coulter, were primarily developed to efficiently count blood cells by measuring changes in electrical conductivity as blood cells suspended in a fluid medium and passed through a small orifice[6]. In the past seven decades, Coulter counters have been utilized to characterize all kinds of industrial particulate materials as well (explosives, minerals, pigments, metals, clay, etc.)[6].

A small tube affixed with a small aperture (size can vary dependent on sample needs) is immersed in a small beaker containing the particulate matter which is suspended in an electrolyte (dependent on sample material investigated). An electrode is placed in the sample beaker and another is located in the aperture tube. When an electric field is applied to the electrodes the effective resistance between the electrodes is measured. The aperture creates what they call a "sensing zone[6]." As the suspended particles pass through this zone, they cause a brief change in the impedance across the aperture, measured as a voltage or current pulse[6]. The amplitude or pulse height is proportional to the volume or size of the particle[6].

Analysis by Coulter counters can be achieved in about a minute per sample with counting rates ranging up to 10,000 particles per second, and with accuracy better than 1%[6]. Using different sized apertures (20 – 2000 μm) allows particle size ranges between 0.4 – 1600 μm. This technique is only limited in the samples that can be analyzed by their ability to be suspended in an electrolyte solution. Size distribution is not a real issue as it is in MALS or DLS. Each size of particulates is assigned a "bin" which represents a size range. These bins can be adjusted to be more inclusive or exclusive as needed. As data points come in they "fall" into their respective bin sizes.

We were given access to the Beckman Coulter Particle Counter Z1 located in the Biology department here at UVA in the Genomics Core Facility (GCF). This instrument is outfitted with a 100 µm aperture and is the only aperture size currently available for this particular instrument. An aperture that size can count particles that falls between 2 – 80 microns. The electrolyte for plastic polymers requires the standard suspension medium (Isotone II Diluent) which the lab has readily available. The sample size requirement is small (0.5 mL) and the sample can be retrieved after analysis. Pictures of the instrument can be found in Figures 3.7 and 3.8.

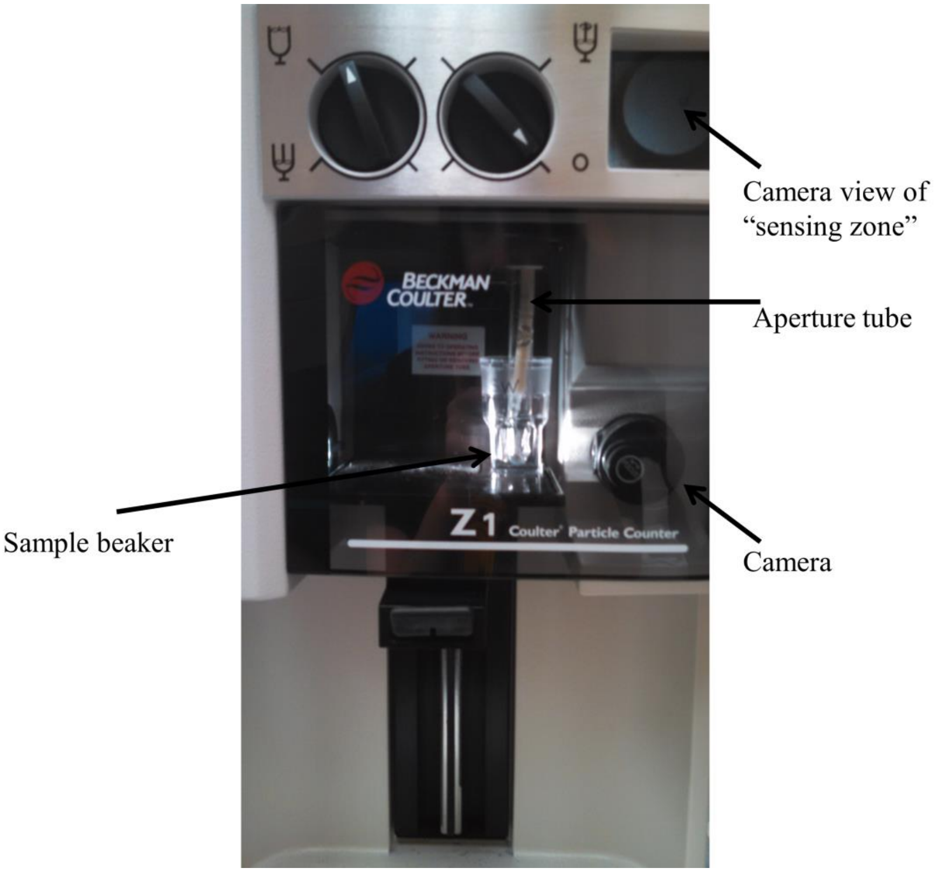


Figure 3.7 Beckman Coulter Counter Z1. In this image, you can see all of the main features of the Coulter counter. Note that it includes a camera feature with a viewing screen to ensure particles are flowing through the aperture cleanly and no clogs due to oversized particles are occurring.

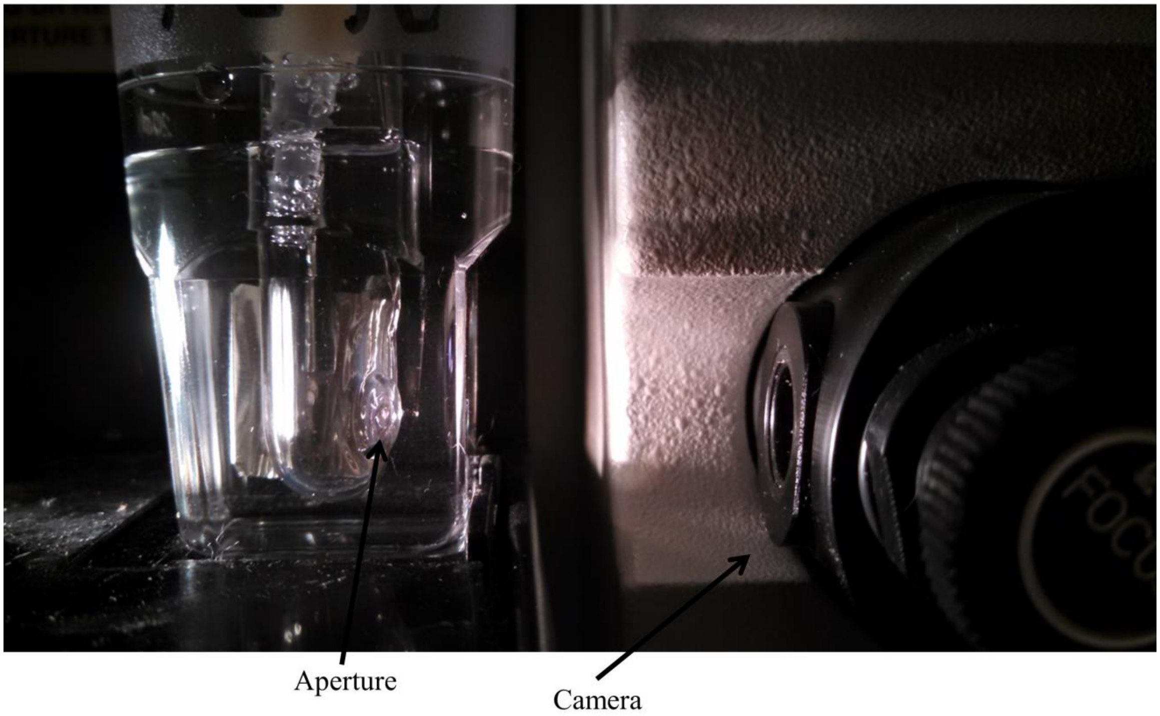


Figure 3.8 Coulter Counter Camera and Aperture. This picture was taken with the door open to fully show the features of the aperture tube that is immersed in the sample beaker solution and the camera.

3.3.4 Elemental Analysis – Isotope Ratio Mass Spectrometry (EA-IRMS)

The last analytical technique we subjected our samples to was an isotope ratio mass spectrometer (IRMS) that was interfaced with an elemental analyzer (EA). This is a destructive technique in nature that relies on combusting organic samples into their respective gaseous forms to be introduced to the mass spectrometer (MS).

Each sample is delivered via a carousel that drops one sample at a time into the combustion furnace (Fig. 3.9). The combustion furnace (1200 °C) consists or granulated chromium III oxide which acts as a combustion catalyst. Along with each sample, O_2 is pulsed into the furnace. All combustible material is then converted into combustion products (CO_2, NO_x, and SO_2 for sulfur containing materials) and flow out of the furnace due to a steady flow of helium (He) carrier gas, and into another furnace. The reduction furnace (650 °C), containing copper granules, converts the various NO_x gases into the more inert N_2 for analysis. In order to remove water, a byproduct in any combustion process and detrimental for mass spectrometers, the sample gases migrate through a trap filled with anhydrous magnesium perchlorate. The remaining gases are then introduced into a gas chromatograph (GC) column that separates the gases so each species is introduced to the mass spectrometer at different times. The first gas to elute from the GC column is N_2, followed by CO_2, and then SO_2.

As the gas samples are introduced into the MS via a small capillary, they become ionized by a bombardment of electrons that is generated from a filament in the ion source. This is necessary as only charged particles are able to be analyzed by this technique which separates based on a mass-to-charge ratio (m/z). These ions are focused into a beam that is accelerated. The ions fly uninterrupted until they reach a magnetic field created by an electromagnet. Once they enter this field, they bend in their projection relative to their size (Fig. 3.10). In other words, the larger molecules will have a broader angle of deflection while smaller molecules will have the greatest curvature in theirs. These differences in flight deflections result in separation of the gases based on their charge to size. Since most of the charges are -1, the separation is mostly due to mass separation. The separated ions are then "collected" in Faraday cups and each ion impact is recorded and translated into a signal that is stored for processing and analysis.

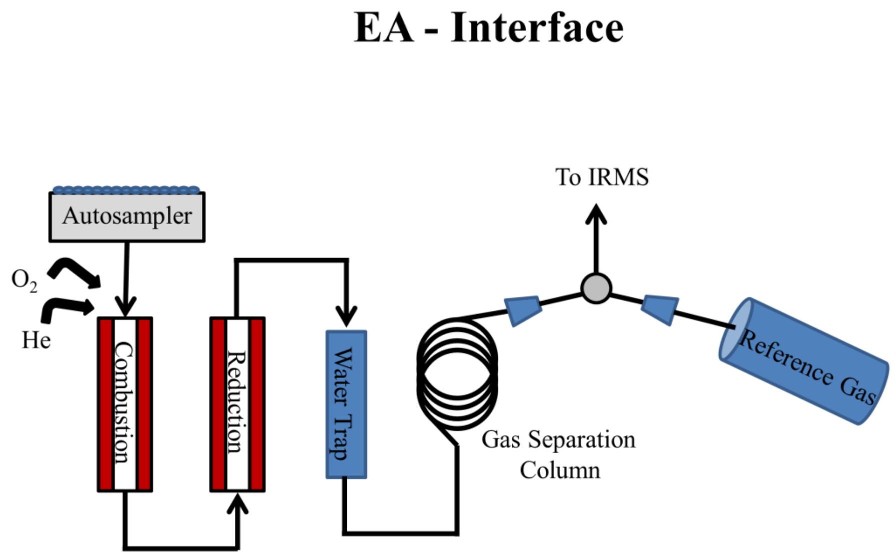


Figure 3.9 Elemental Analyzer (EA) Interface. Samples are introduced into the combustion furnace along with a pulse of O_2, and a steady stream of He. Materials are combusted into gaseous products then introduced to the "Reduction" column which converts any NO_X gases into the more inert N_2. Water is trapped to prevent it from entering the GC column and ultimately the MS. All other gaseous samples are separated into their respective species and then introduced to the IRMS.

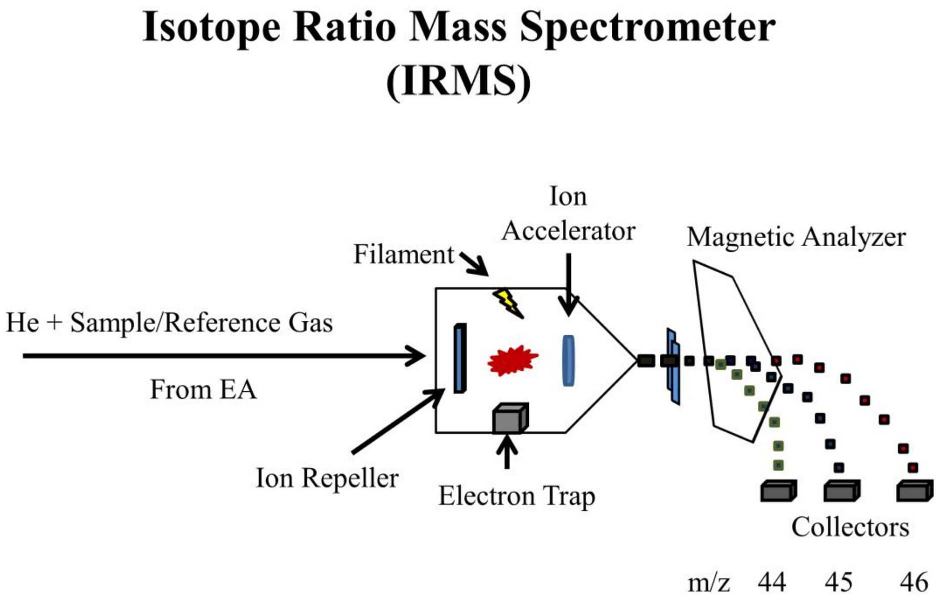


Figure 3.10 Isotope Ration Mass Spectrometry. In this schematic of an isotope ratio mass spectrometer for measuring CO_2, multiple collectors allow for simultaneous detection of various isotopes.

Results from IRMS are reported as per mil (‰) based on the following equation:

$$\delta\,^{X}E = \left[\frac{R_{sample} - R_{std}}{R_{std}}\right] * 1000\ \text{‰} \qquad \text{Eq.3.5}$$

where *X* is the heavy isotope for element *E* and *R* is the ratio of heavy to light isotopes for a given sample or standard (std.) of that element *E*. For carbon isotope analysis, the ratio is $^{13}C/^{12}C$. There are multiple internal laboratory standards for carbon analysis in addition to the reference CO_2 gas used. These internal standards were combusted, like samples, from a solid organic material. We used orchard leaves for standards in our plastic analysis. All standards are relative to an international standard for carbon isotope analysis which was Peedee Belemnite (PDB), a type of limestone ($CaCO_3$), but has since been exhausted and replaced with Vienna PDB. Standards result in, by definition, a delta ($\delta^{13}C$) value of 0.0 ‰.

Thin shavings (~0.2 mg) from the surface of plastic samples were placed into tin capules and converted to CO_2 and analyzed, using Carlo Erba elemental analyzer (EA) that is interfaced with an Optima stable isotope ratio mass spectrometer (Micromass). Carbon isotope compositions were determined by gases from a single combustion. Three different trials were performed for each sample, taking care to only use the near surface material.

3.4 Data Analysis

All data collected from the various operating software for each respective instrument described previously, was further evaluated using Igor Pro, a scientific data analysis software, widely used for its technical graphing and data analysis abilities. Computational analysis will also be supplemented with Microsoft Excel.

3.5 Summary

Samples of a variety of plastic polymers used by consumers regularly were subjected to degradation experiments either in the lab or in field studies. Changes to the surface features or chemical make-up were monitored throughout both experiments periodically. Laboratory samples were analyzed and quickly returned while field samples will be collected and not returned after analysis. The data obtained from these experiments can be found in Chapter 4.

3.6 References

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CHAPTER 4

Results

3.1 Introduction

The broad purpose of this study and central problem addressed by these experiments is to determine how plastic polymers degrade in aquatic environments. Using dual field and laboratory experiments, this project aims to address whether varying conditions such as salinity have an impact on polymer degradation. Also of interest is what physical changes occur, or if chemical changes alter the surface chemistry of these polymers. Additionally, are secondary microplastics produced as a result of abiotic degradation in aquatic environments? Finally, we will determine if isotopes should play a role as geochronometers in determining residence times at sea for detritus plastic materials.

Data reported in this chapter is organized in two regards. The bulk of data displayed in this chapter has been categorized based on the type of analysis (observational, surface, or chemical); this was achieved primarily by the analytical instrument utilized. Under each major heading, data are displayed based on polymer type. Some analysis is discussed but the majority is reserved for Chapter 5.

3.2 Observational

3.2.1 Lab Experiments

This degradation experiment lasted 18 months, but it was apparent within a few weeks that changes occurred in the ocean water samples that were not observed in any of our freshwater samples. Small white particulates were noted along the bottom or floating in the beakers after gentle swirling of our marine samples. These particulates were not present in the freshwater samples. A select set of samples were covered with aluminum foil, blocking exposure to UV, to determine if the observed particulate was the result of mechanical action alone. Alternatively, trace amounts of sand and minerals present in the ocean water might have been scraping the plastic and removing small pieces. After many more months it became evident by the lack of particulates observed in our “dark” marine samples that UV light was required to produce the observed particulates. Surprisingly, the most inert of the polymers, HDPE, produced the most particulates by visual inspection. A time series of particulate formation is shown by Figure 4.1.

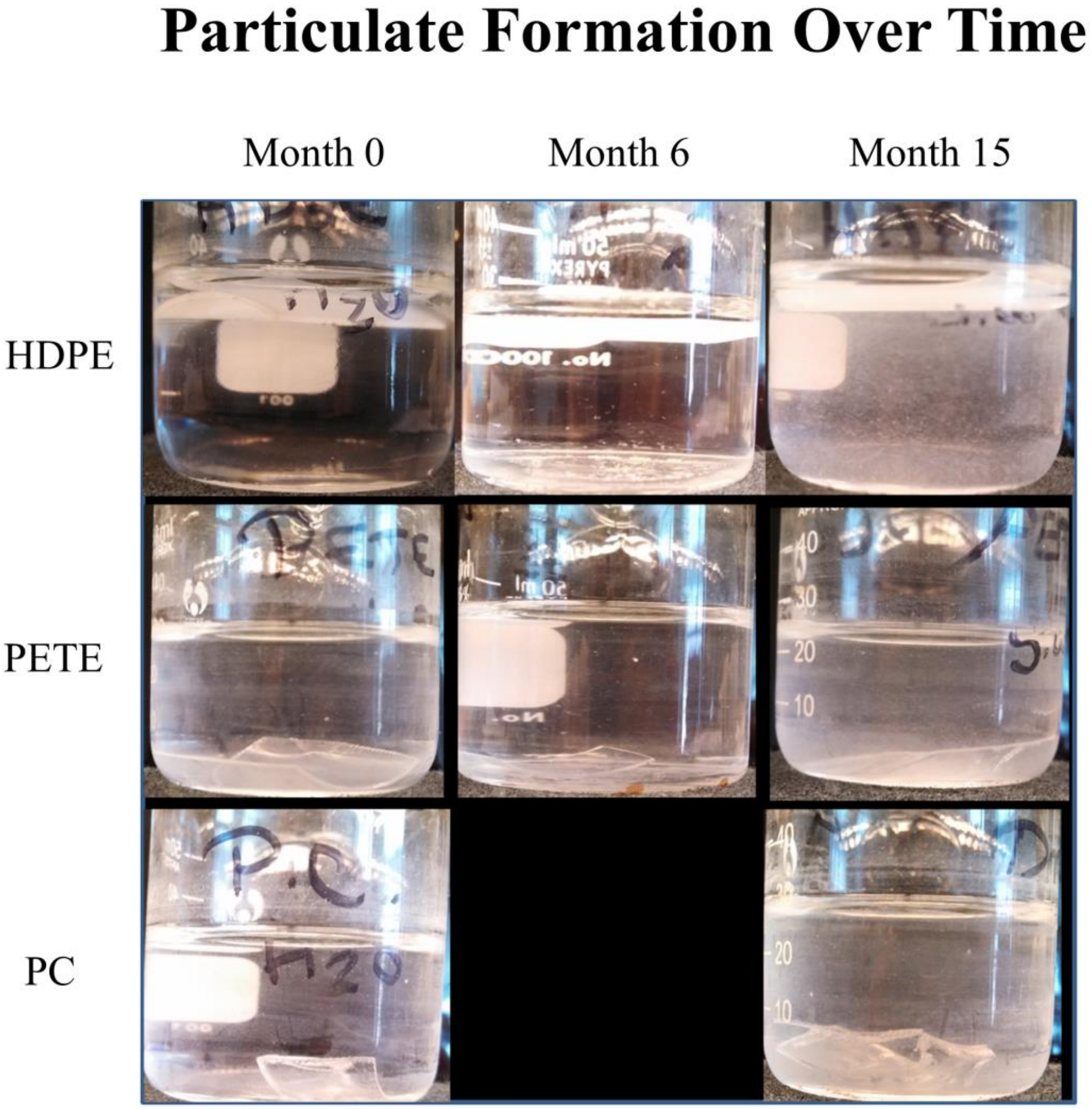


Figure 4.1 Particulate Formations Over Time. Each row represents a single sample of a respective polymer over time. All samples in ocean water had similar effects for our laboratory study. Note that due to its density properties that HDPE floats in our water samples while PETE and PC do not.

The HDPE plastic squares in the top row of Figure 4.1 are less dense than the marine water and float. The particulates however appear to be denser and sink toward the bottom of the beaker. The images were captured after a quick swirl to suspend particles for better visibility. This change in density suggests that the overall chemistry of the plastic is being affected. Since both PETE and PC are denser than the water sample and lie on the bottom of the beaker, changes in the chemical or physical properties are not as easily notable other than the presence of particulates. To determine if any chemical changes did occur, FTIR (section 4.4) was used to investigate if any additional chemical bonds were formed or impact of functional groups on the overall chemistry of the particulates.

3.2.2 Field Experiments

Since field samples were placed in open water areas, no particulates were observed, likely swept away via tidal currents. Observations of the conditions and any physical changes apparent in the plastic samples were noted for each field experiment, and are outlined into two separate headings. The field experiments not only varied in salinity, but also how the plastics were oriented in their respective aquatic environments.

3.2.2.1 Lynton Dock (7 ‰ salinity)

The plastic bottles floating along the surface did not biofoul as might be expected for a natural aquatic environment. Neither algal growth nor mollusk attachments were evident at the surface. The bottles strung 8 inches below the surface showed slight signs of algal growth as some had a minimal slimy feel, but this material easily washed away. The surface bottles did not appear to alter in appearance much even after 9 months into the experiment. Those bottles below the surface did change somewhat, not only in appearance but also in texture, which became less rigid.

3.2.2.2 LTER Dock (26 ‰ salinity)

Samples located at the LTER site had substantial biofouling. Not only was the basket which held our samples filled with seaweed at first sampling (5 months), but a fish, lots of small shrimp, and tiny crabs were also present. Seaweed clogged the cage, reducing the flow of water and producing an environment in which aquatic organisms were able to thrive. Initially, the plastic samples were not fouled significantly, simply covered in the sea plants. The plants and other organisms were removed and the basket reset after each sampling visit.

Upon a second sampling visit in January of 2015 (8.5 months), the measured salinity at high tide was a surprisingly low 12 ‰. Strong storms in the area may have caused this reduction in surface salinity.

Notable physical changes were observed in the plastics at the LTER; overall appearing less transparent and becoming more opaque, and rougher in texture. These physical changes were further assessed by more quantitative methods such as scanning electron microscopy (SEM) and Fourier-transform Infrared spectroscopy (FTIR).

3.3 Scanning Electron Microscopy (SEM)

Aside from the images displayed in this chapter, additional SEM images are provided in Appendix I.

3.3.1 Lab Experiments

Freshwater samples showed no changes in physical appearance, no production of plastic particulates were observed in any of the beakers, and no chemical changes were observed in FTIR data (section 4.4). All SEM images displayed have a magnification of 500X unless otherwise noted.

HDPE – New

A sample of “new” HDPE plastic, or a sample prior to being employed in our degradation experiments, displayed minimal flaws aside from those likely due to the extrusion process used to form the bottle. The surface was relatively smooth with some areas of scarring. There was some minimal debris scattered about the surface (Figure 4.2).

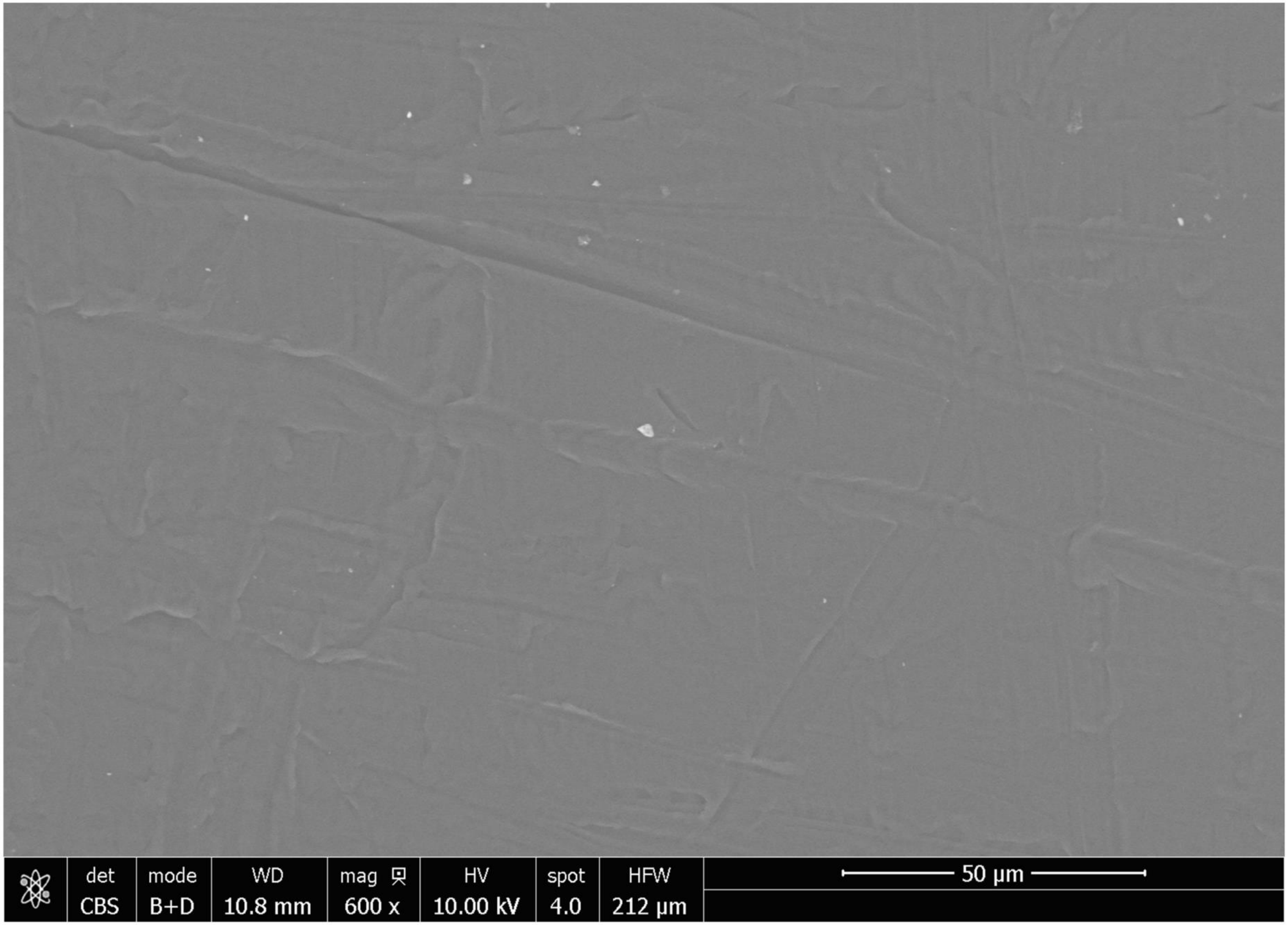
HDPE – 6 Months

After six months in the laboratory degradation apparatus, the surface of HDPE seemed to vary from what was initially observed. The once smooth surface topography changed to one of ripples and grooves. There was a larger amount of debris present as well, presumably plastic particulates. Plastic particulates were observed in the beakers upon extraction of the samples.

HDPE – 15 Months

Samples observed via SEM after 15 months of degradation displayed the greatest surface changes. The entire surface appeared extremely textured from what is likely oxidized plastic. Plastic particulates found on the surface measure in the 10’s of microns and possibly in the nano range, and reflect what is likely present in the beaker water column, which became increasingly opaque and milky overtime. The sample displayed in figure 4.4 is the same sample featured in figures 4.3 and 4.2.

In the bottom portion of the image, one region appears to have larger pieces flaked off, leaving the next layer of polymer exposed and accessible for degradation. The differences between the oxidized and virgin polymer layers are possibly easier to discern in Figure 4.4. The main subject of this image was a particle measuring less than 3 microns, but the boundary between modified and virgin polymer can also be seen.



New HDPE

Figure 4.2 SEM Image of New HDPE. General surface is smooth aside from some scarring from the extruding process.

Lab HDPE – 6 Months

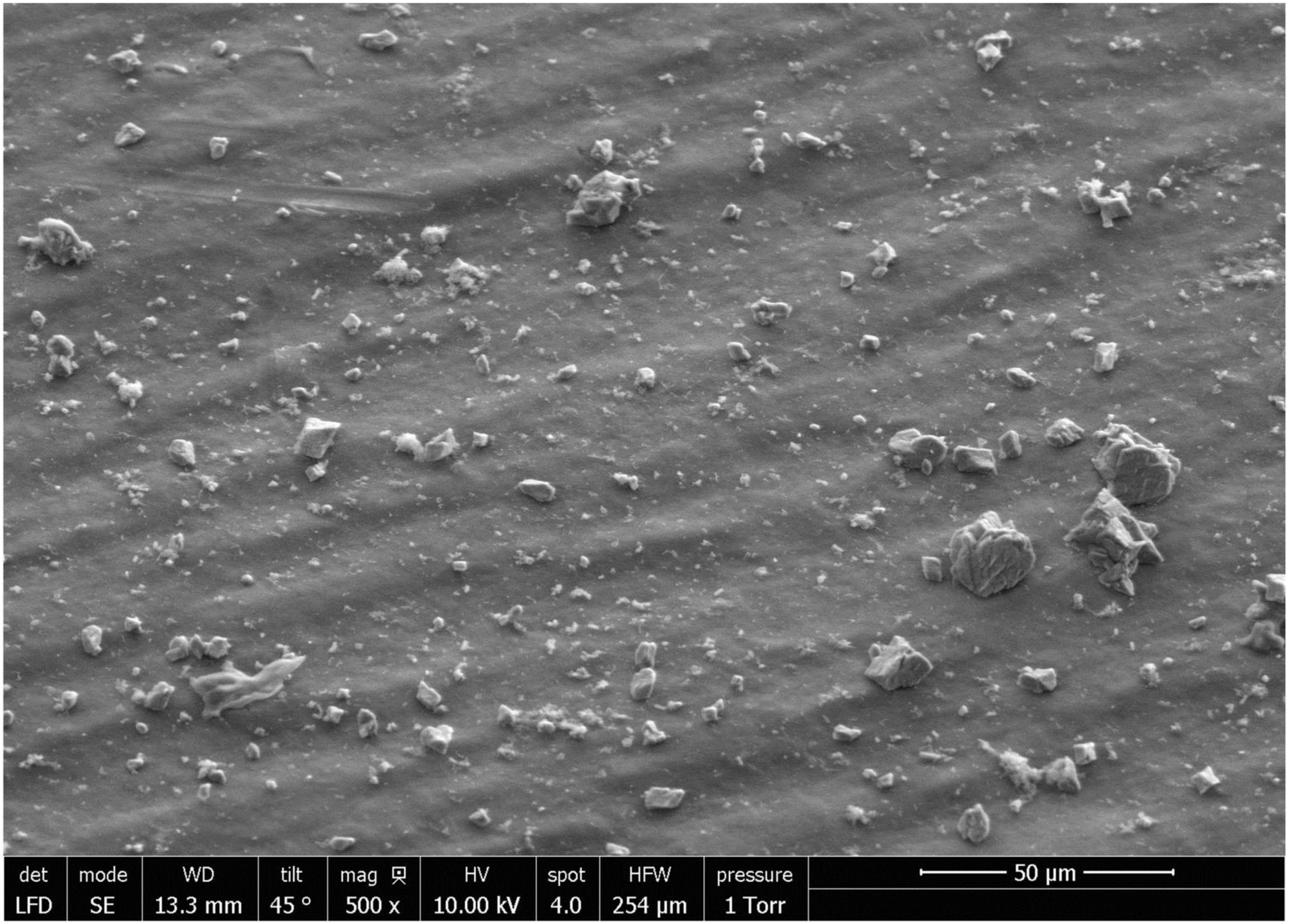


Figure 4.3 SEM Image of HDPE After 6 Months of Lab Degradation. Some of the scars from the extrusion process remains but the overall topography of the surface has become rippled and a lot of debris is present. In the top left, the surface appears to peel away, exposing the next layer.

Lab HDPE – 15 Months

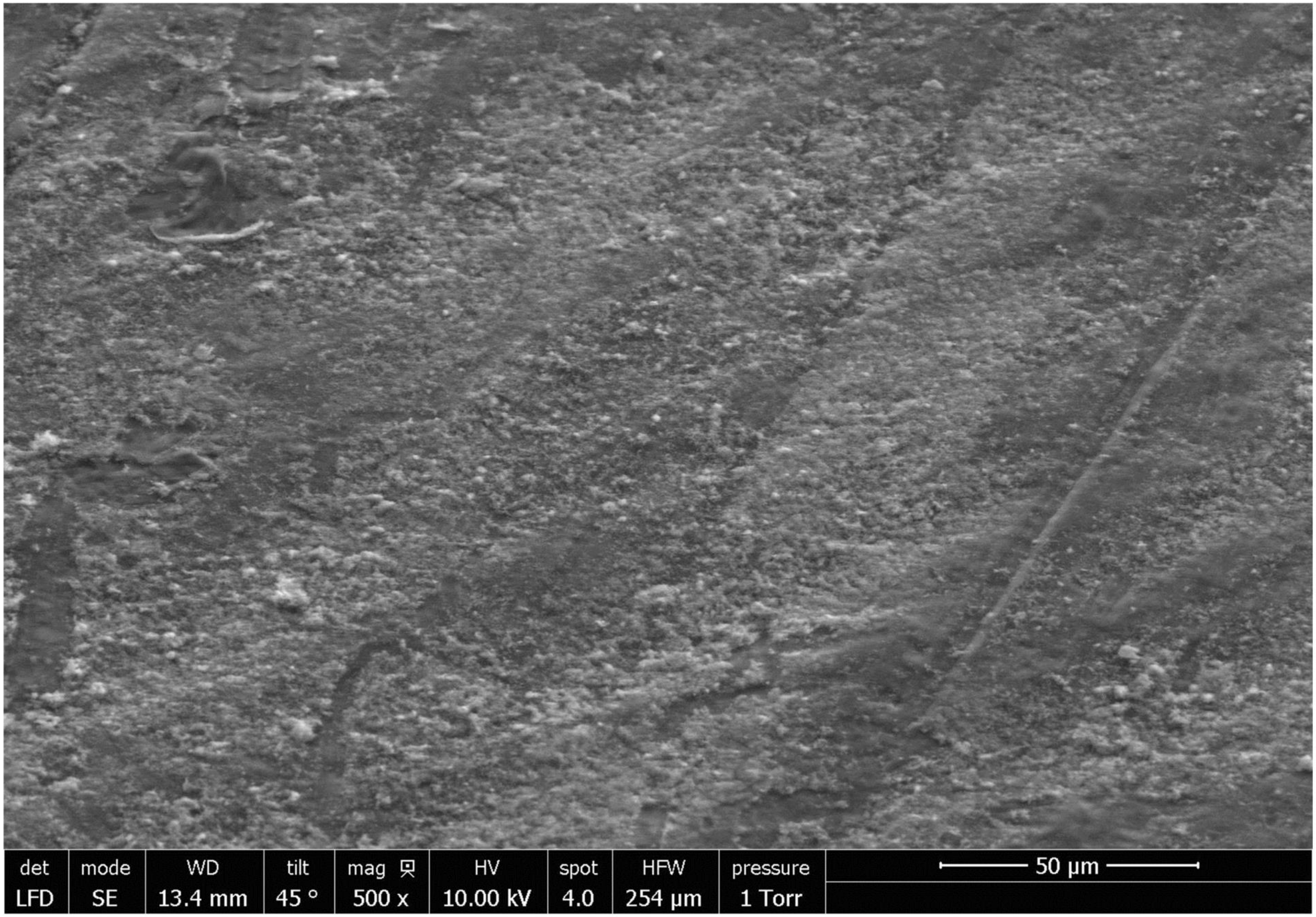


Figure 4.4 SEM Image of HDPE After 15 Months of Lab Degradation. Much of the surface appears textured and riddled with microplastics. In some areas it is apparent that chunks of material have calved off from the surface, exposing the next layer of polymer below.

Lab HDPE – 15 Months (10,000x)

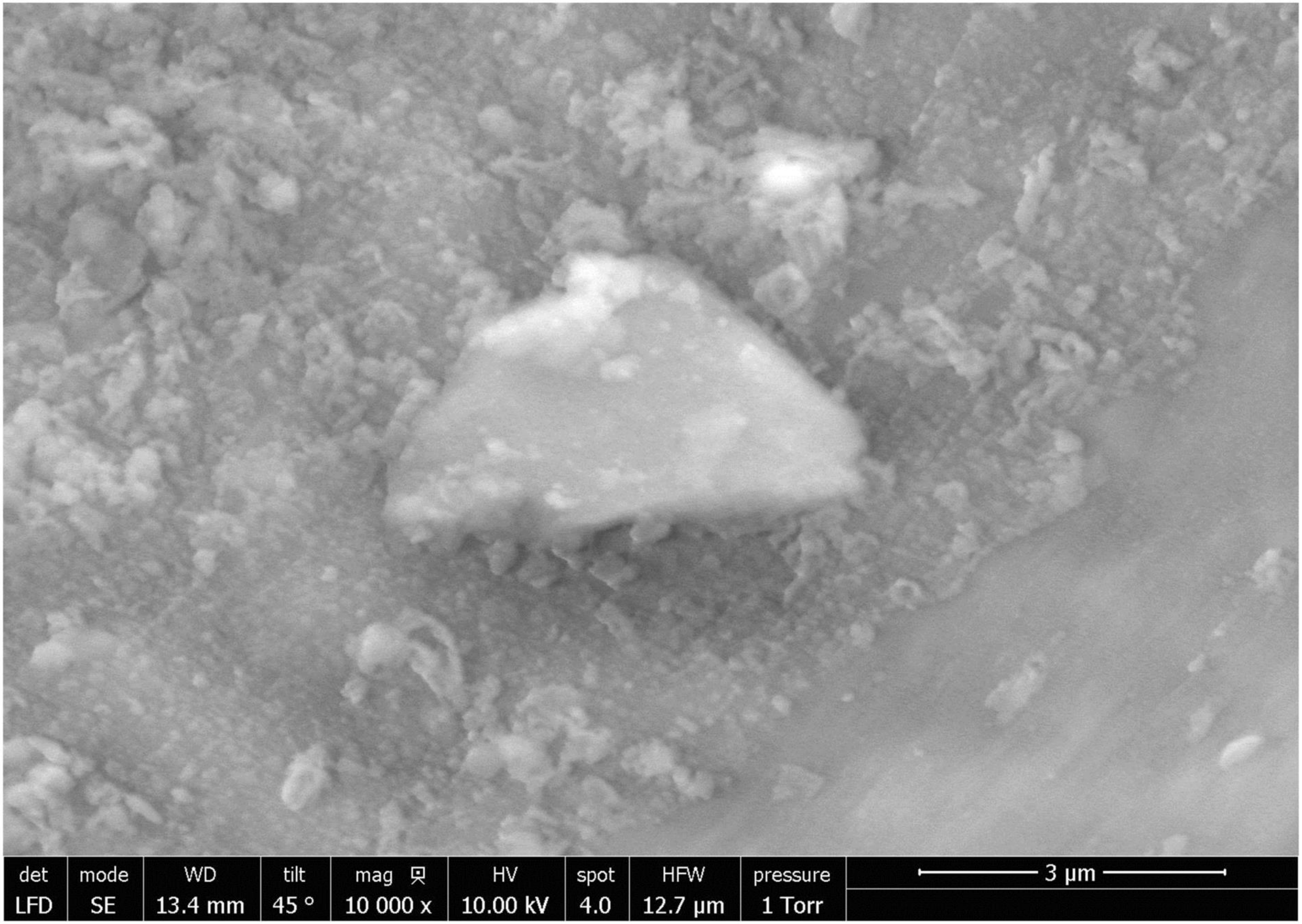


Figure 4.5 Close Up SEM Image of HDPE Surface After 15 Months. The largest particle visible in this image measures around 3 microns. Most of the particulates seen are estimated to be only hundreds of nanometers in diameter. Also, note the clearly visible boundary between oxidized surface and the virgin polymer layer below.

PETE – New

Virgin PETE plastic was imaged to determine initial surface features and characteristics prior to degradation experiments. The surface (Figure 4.6) showed a relatively smoother texture than the "new" HDPE sample. Again, only a few pieces of debris were on the surface offered minimal contrasting features even at 1000X.

PETE – 6 Months

Once the experiment had progressed for 6 months, samples were removed from the experiment temporarily to image via SEM. Significant changes were noted to the surface topography, most notably, the heavy presence of surface debris. Again, the debris was presumably the plastic particulates found contaminating the marine water beakers. In addition, areas along the surface appear to have flaked away, exposing the underlying polymer layer. Particulates coating the surface of PETE appear to be much smaller than those found on the HDPE samples for the same time frame. The largest appear to be in the 10 micron scale, while the majority of particles were in the nanoscale region (Fig. 4.7). Similar to the HDPE surface after 15 months of exposure, the PETE surface shows signs that the surface polymer has been removed in some areas, exposing the next layer of PETE polymer.

PETE – 15 Months

The greatest observed surface change occurred in the PETE samples after 15 months of exposure. An increased population of particulates and an increase in exposed lower layers of polymers were observed (4.8). The exposure of lower layers was enhanced by sharp, breaking fissures as opposed to the “peeling” nature of the HDPE samples. The sharp fissures are highlighted at 5000X magnification in Figure 4.9.

Another noticeable difference amongst the particulates found on the surfaces of HDPE and PETE is that PETE particulates appear to be less dense or “fluffier” in texture as compared to the more solid and “chunky” appearance of those seen in HDPE (especially those found after 6 months of exposure).

New PETE

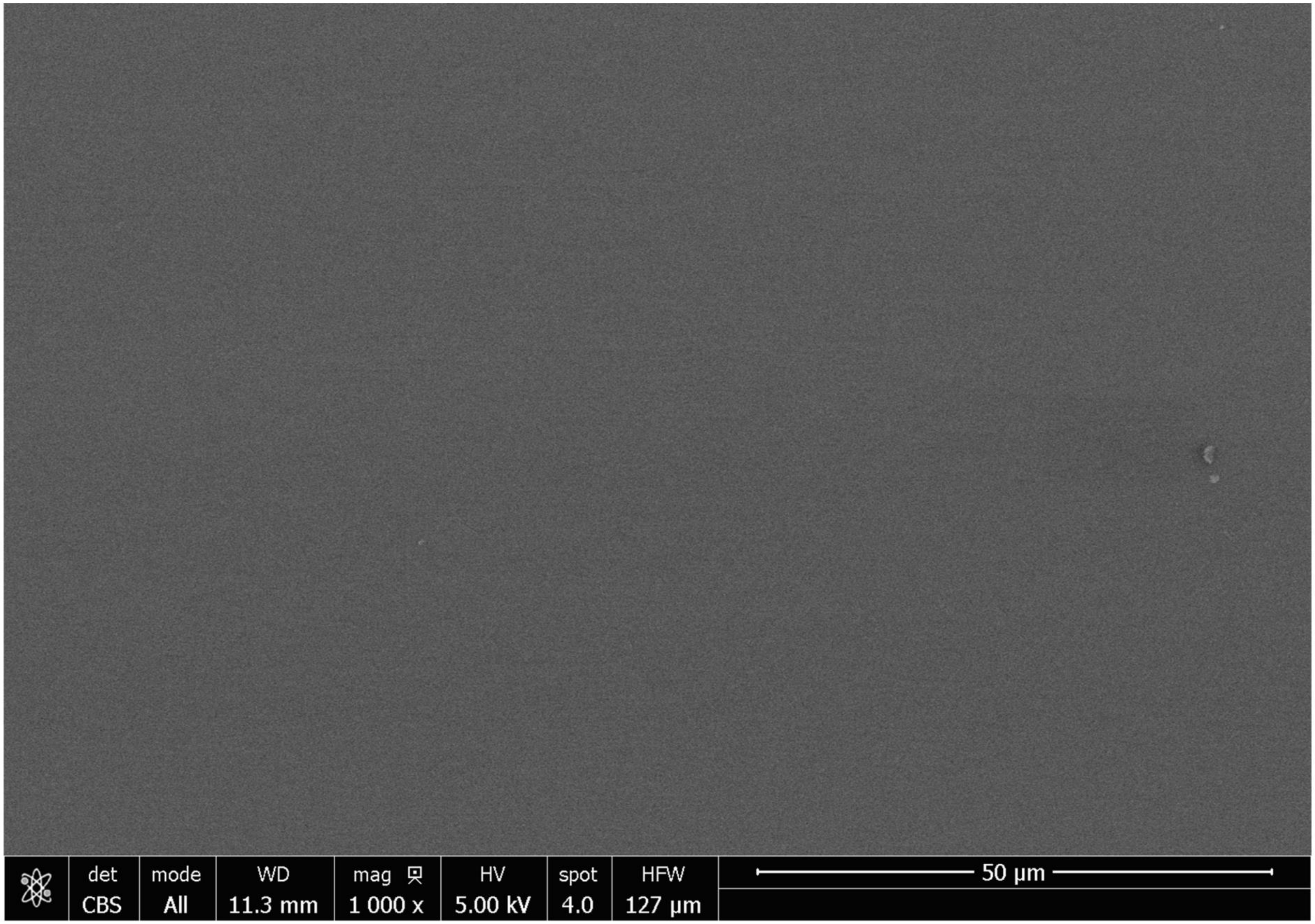


Figure 4.6 SEM Image of the Surface of Virgin PETE Polymer. Unlike the new HDPE sample, PETE appears to have a much smoother surface topography.

Lab PETE – 6 Months

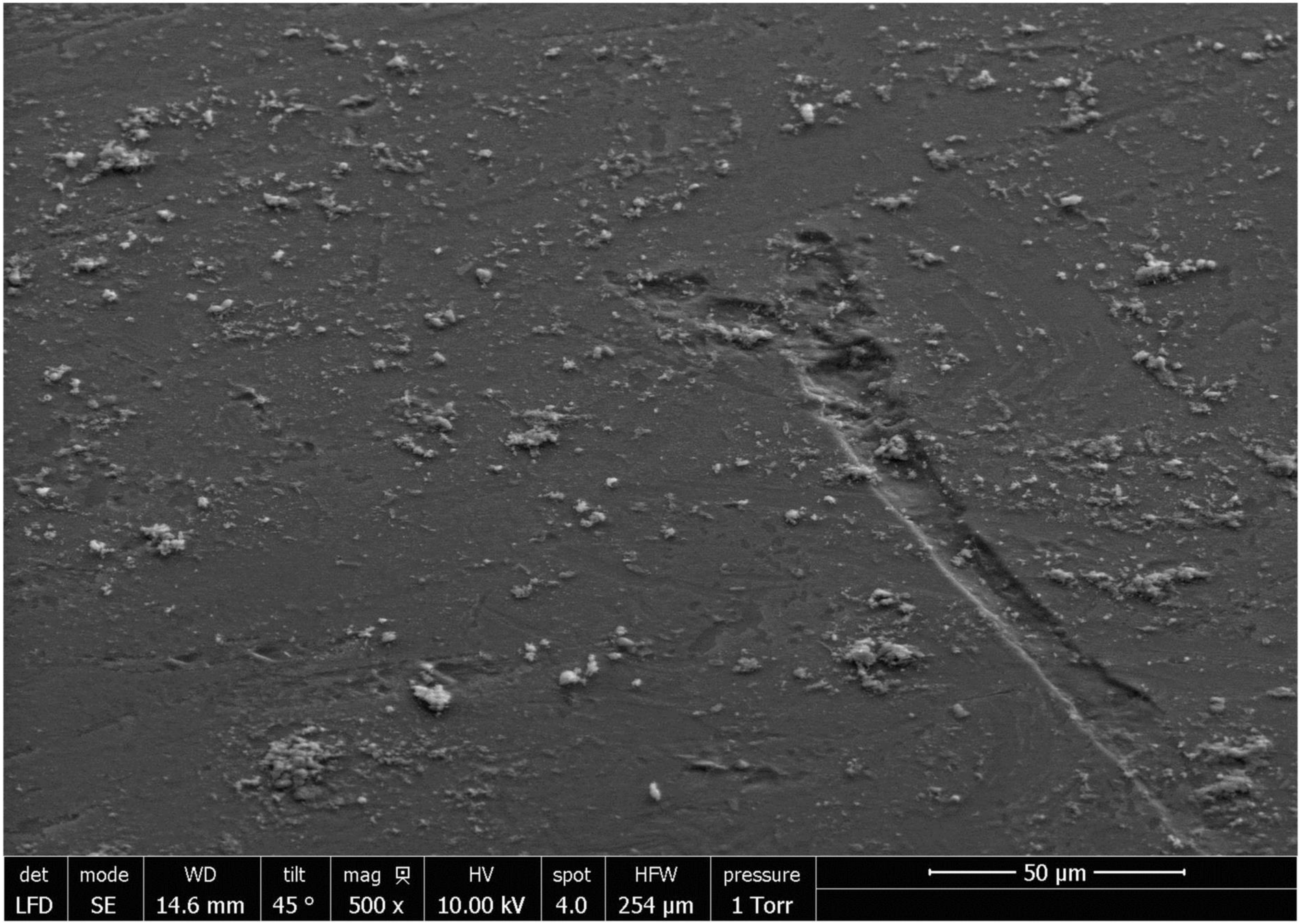


Figure 4.7 PETE After 6 Months of Degradation. A noticeable production of micro-particulates similar to HDPE samples can be seen on the surface in addition to pockets of exposed underlying polymer layers.

Lab PETE – 15 Months (500x)

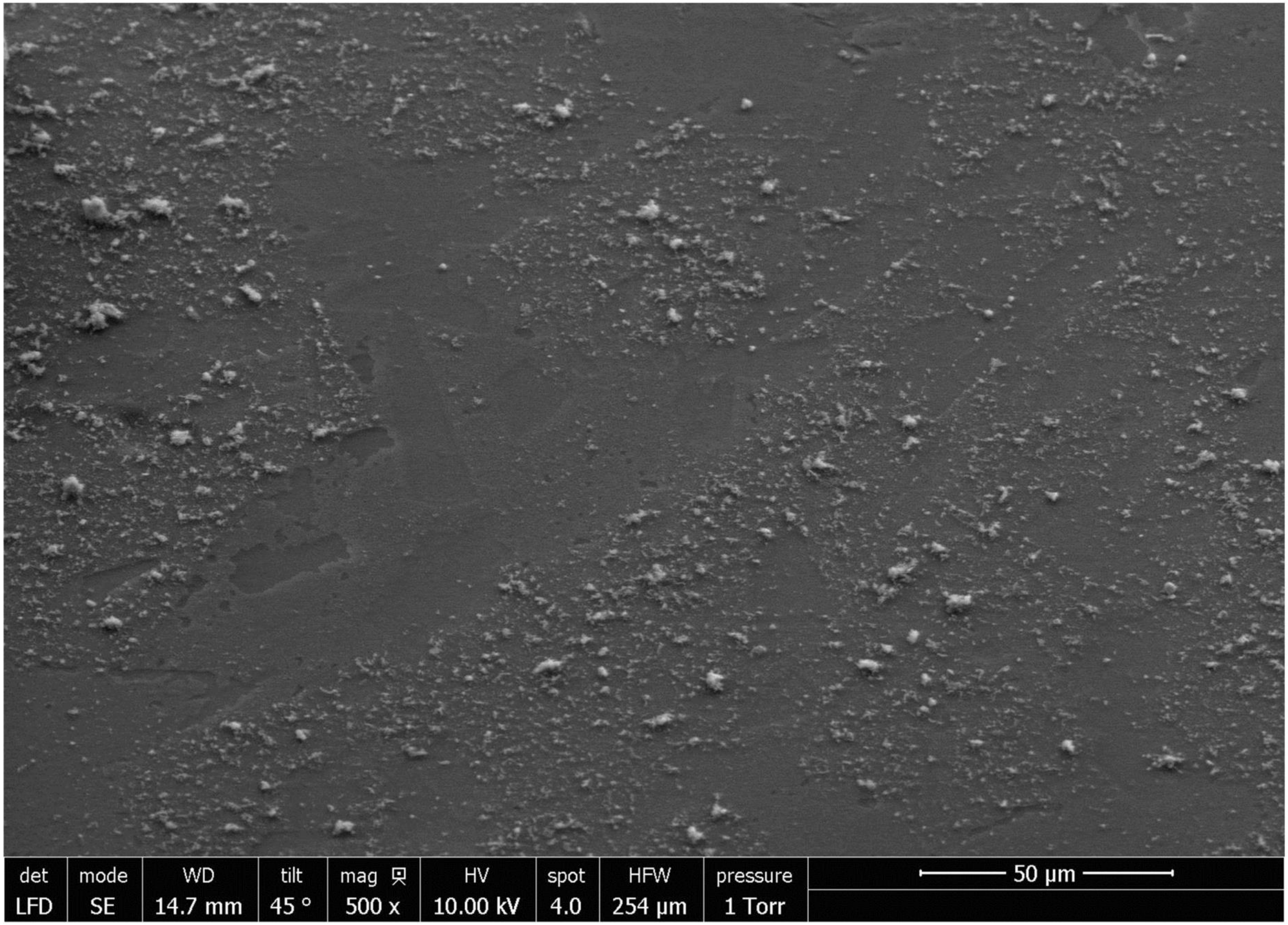


Figure 4.8 SEM Image of Surface Topography of PETE After 15 Months. The particulate sizes do not appear to differ greatly from those seen after 6 months but there is more evidence of surface layer removal.

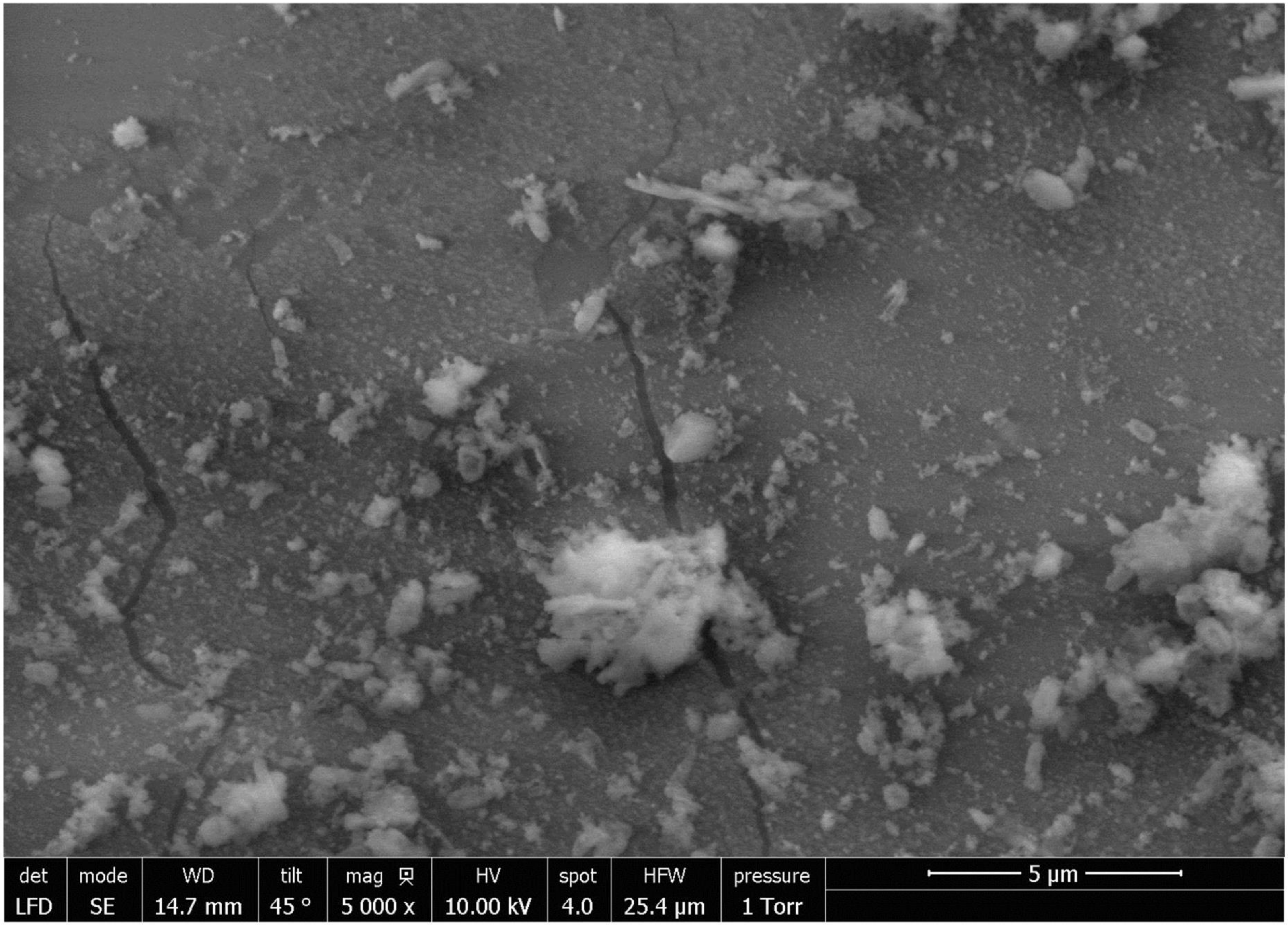

Lab PETE – 15 Months (5000x)

Figure 4.9 The Various Surface Characteristics Observed on the Surface of PETE After 15 Months. This one image captures the three dominant patterns of particulate formation, flaking off, and cracking observed after 15 months.

4.3.2 Field Experiments

The purpose of this section is to compare the surface of polymers exposed to different salinities to determine if any notable changes occur. SEM images were obtained using low vacuum mode for the samples presented here as it was made available during this time. Additional SEM images are located in Appendix I.

Lynton Dock (7 ‰)

Recall that the samples for this location were bottles and strung to fishing line either along the surface or 20.5 cm below. Samples were cut from bottles for analysis, leaving the rest to continue with the experiment.

HDPE – 9 Months

After 9 months of exposure to direct sunlight and water with low salinity, HDPE samples showed some signs of oxidation along the surface of the polymer. Physical scarring from production, like those in the "new" sample were visible, but areas were observed where the overall texture of the surface had changed (Fig. 4.10).

The HDPE sample retrieved from below the water's surface appeared to have the greatest change in surface topography (Fig. 4.11). A counterintuitive result considering UV light is quickly attenuated in aquatic environments. One reason supporting the increased change is an increase in surface oxidation below the surface where salinity is likely greater than that found at the surface, where rainwater (less dense than seawater) may concentrate after rain storms. Although the salinity was not measured at this depth, rain water or river inputs are known contributors to lower salinity, less-dense water nearer to the surface.

PETE – 9 Months

The sample of PETE obtained from surface of this site looks considerably more oxidized (Fig. 4.12) than the HDPE sample. In laboratory experiments, which used a bulb that produced 100X less photons in the UV region than the Sun, there did not appear to be much difference in the degree to which PETE degraded compared to HDPE. However, in the field under the power of the Sun, PETE appears to oxidize more readily. In fact, the surface appears more oxidized than the HDPE sample below as well. This could be due to the different chemical structures. Remember that this polymer has, in addition to C-C bonds, C-O bonds that are not as stable and allow for faster degradation when greater energy is available.

Lynton HDPE Sfc. Sample (7 ‰)

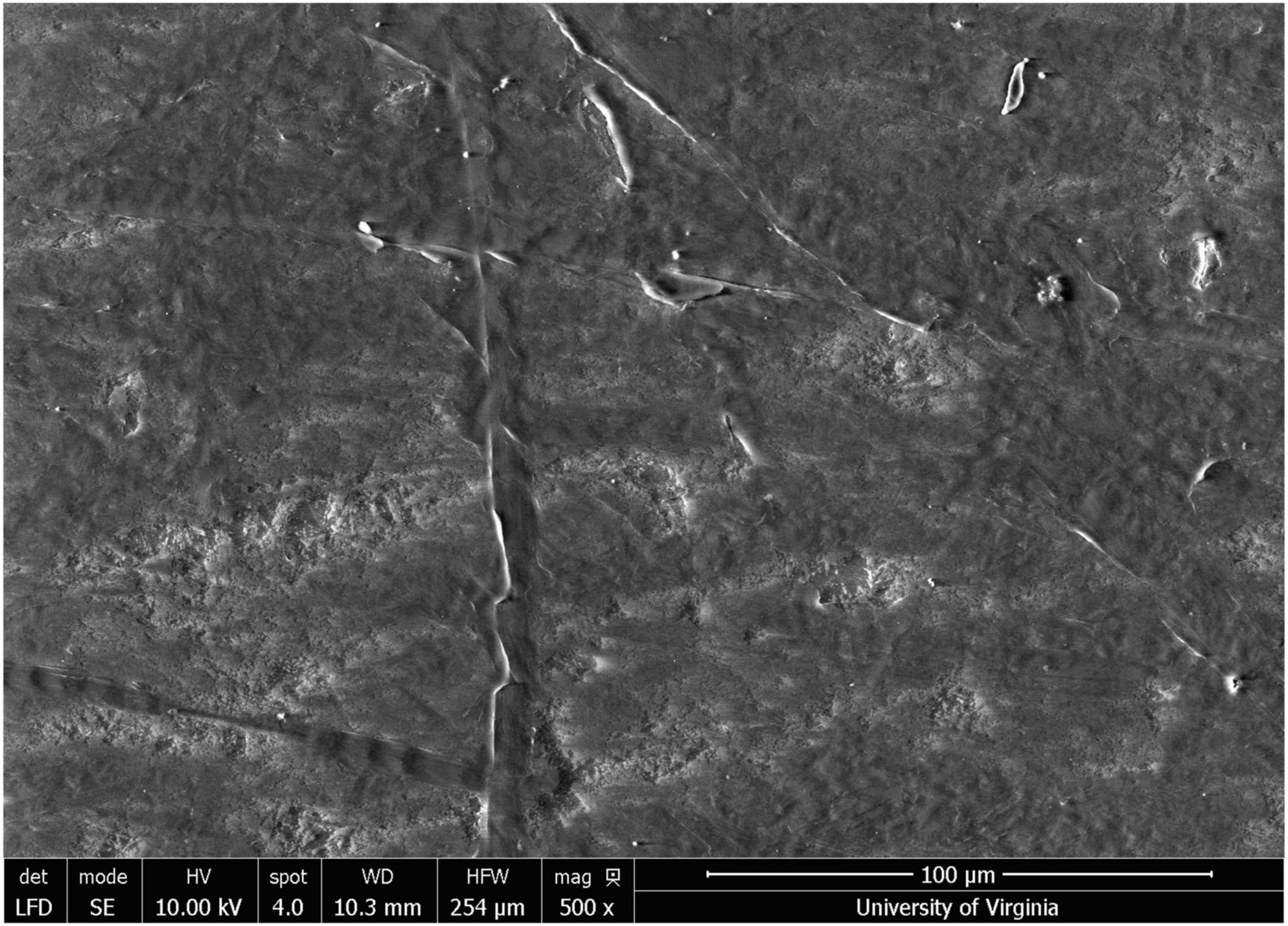


Figure 4.10 HDPE Surface After 5 Months of Exposure. Image was captured in the low vacuum mode. This sample was located at the surface with an average salinity of 7 ‰. Aside from typical scarring artifacts produced during extrusion, the surface appears oxidized in some areas.

Lynton HDPE Below Sample (7 ‰)

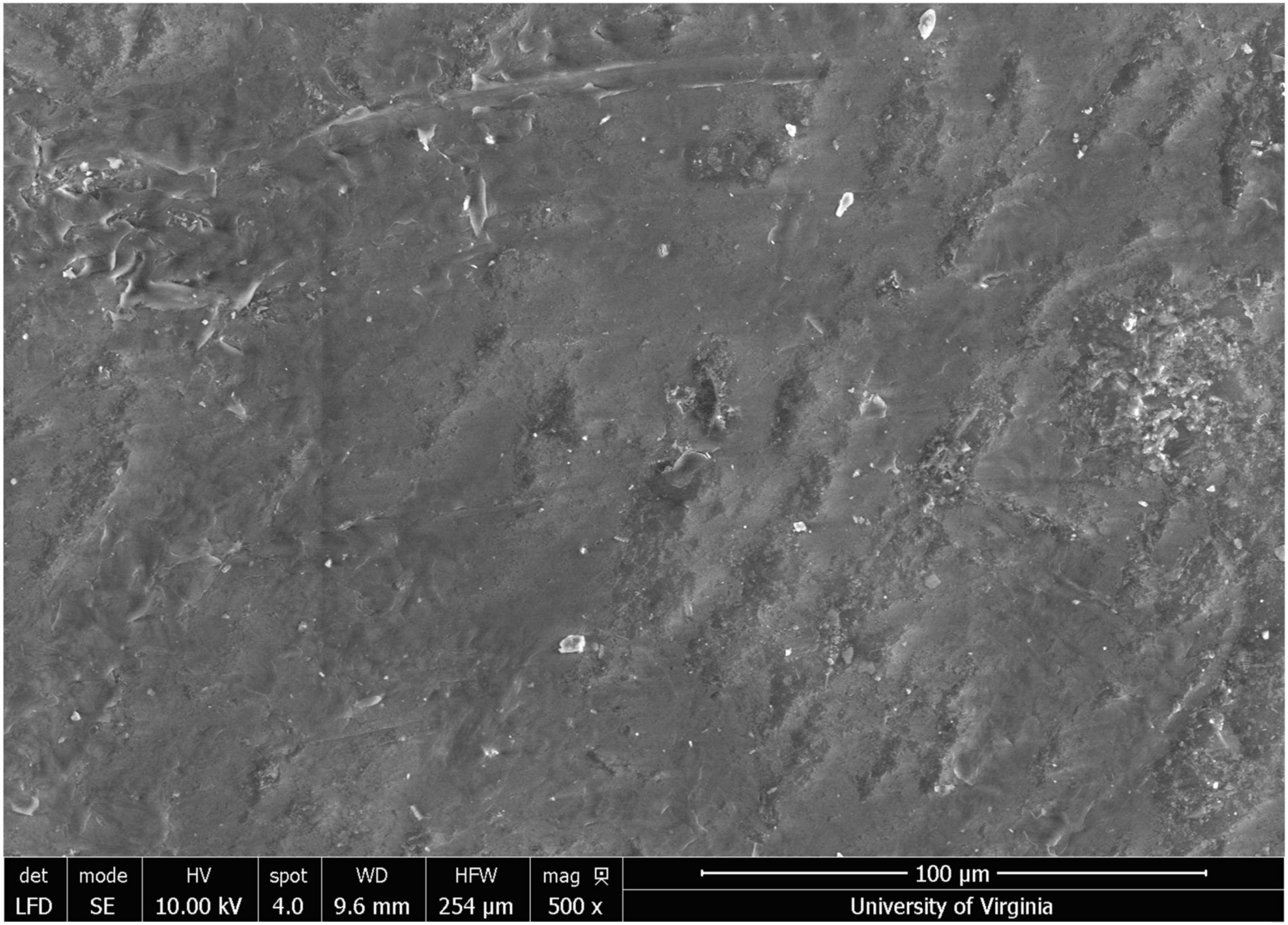


Figure 4.11 HDPE Surface of Sample Below the Surface. This sample appears to have a greater amount of surface oxidized compared to the one located the surface. Exposure time was 5 months. Image taken in LV mode.

Lynton PETE Sfc. Sample (7 ‰)

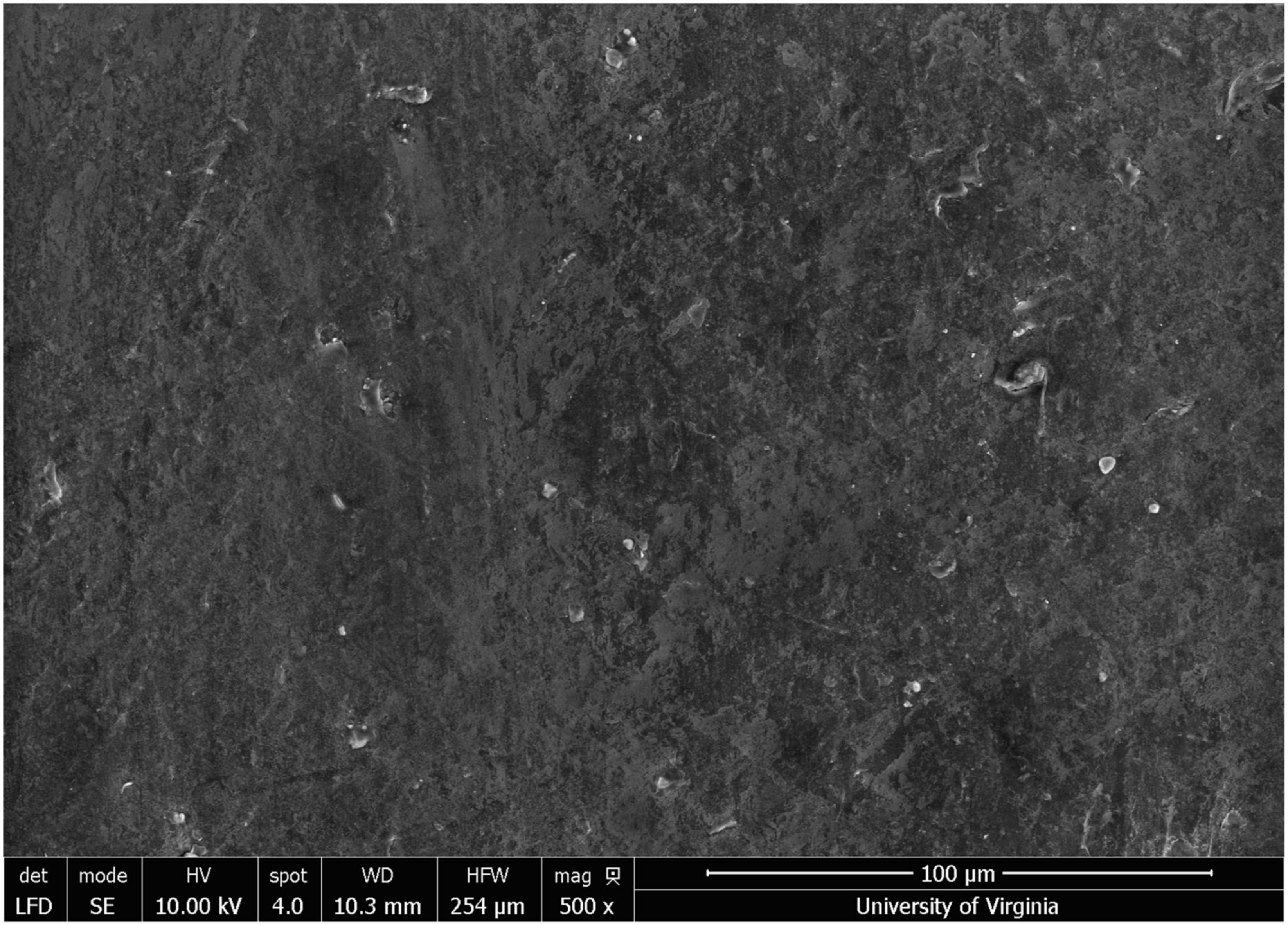


Figure 4.12SEM Image of PETE Sample Located at the Surface. The surface of this sample appears to be considerably more oxidized than either of the HDPE samples. This may be due to the oxygen content in its molecular structure, making it slightly less stable and more conducive to oxidizing in more direct sunlight.

LTER Dock (26 ‰)

The heavy presence of seaweed and biofouling reduced the UV light exposure of samples.

Samples were randomly selected for analysis during each sampling visit. Displayed in this section are images taken after just 5 months of exposure. Despite the shorter length of time, samples in this environment appear to have altered their surface features greatly compared to those obtained at Lynton's. Considering the shorter time frame and that the salinity is almost 4 times as great, this may be an indication that salinity does indeed increase the degradation of plastic polymers.

HDPE – 5 Months

After just five months and despite the heavy covering of seaweed, the surface of HDPE samples appear to be heavily oxidized. This was noticeable upon visual inspection but even more apparent in the SEM image (Fig. 4.13). Oxidation appears to have occurred over multiple layers and throughout much of the viewable surface.

PETE – 5 Months

At the Lynton site, the PETE sample along the surface appeared to be more oxidized than the HDPE samples taken from the surface and below. While the PETE sample from the LTER site shows significant signs of oxidation (Fig 4.14), it does not appear any greater than that of the HDPE sample.

Conclusions cannot be made as to whether the blanket of seaweed had any impact on the rate of degradation. The oxidation being observed could have occurred at the beginning of the experiment before the plant life amassed prior to the first sampling period. It is possible that radicals formed in surrounding waters can still interact with the samples.

LTER HDPE Sample (26 ‰)

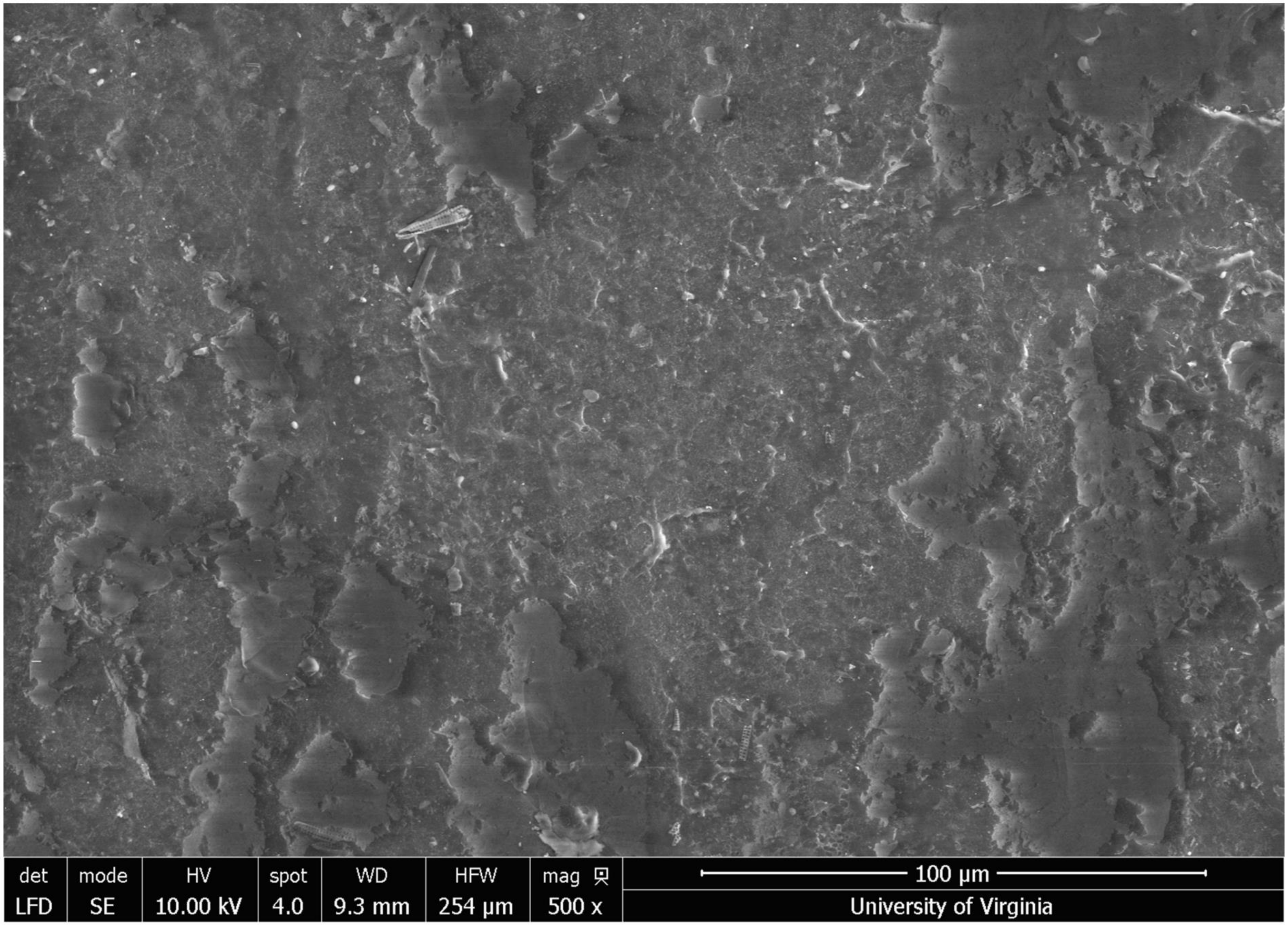


Figure 4.13 SEM Image of HDPE Surface After 5 Months. The surface of the sample is considerably oxidized despite the relatively short exposure time. The increase in salinity found at this location may cause degradation to occur more readily. Image taken in LV mode.

LTER PETE Sample (26 ‰)

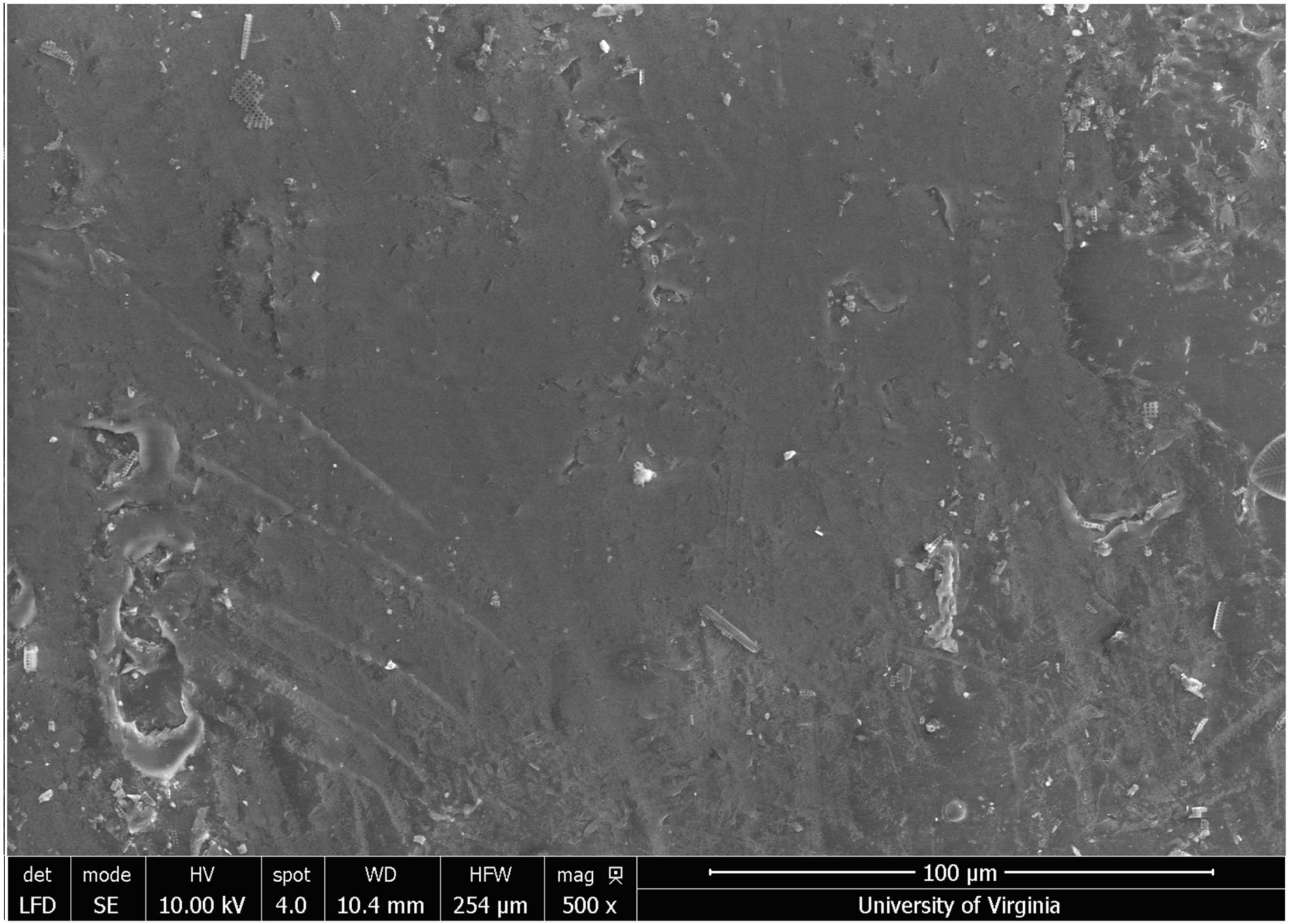


Figure 4.14 SEM Image of PETE Polymer Surface. The surface of this sample shows significant oxidation. Skeletons of diatoms can also be seen contaminating the surface (top left and middle right). Image taken in LV mode.

3.4 Fourier Transform Infrared

The SEM images depicted significant changes in the physical surface of various plastic polymers exposed to marine aquatic environments. Fourier Transform IR (FTIR) analysis reveals details of chemical changes. All FTIR analysis was performed using well-documented characteristic group absorption assignments of organic molecules[2]. Samples of HDPE will be provided first as these spectra are less complicated in general, and consist solely of carbon and hydrogen atoms.

3.4.1 Laboratory HDPE FTIR Spectra

Laboratory experiments were conducted under a variety of conditions for different polymers including those exposed to air or water environments as well as changes in salinity. Samples were removed periodically (every 6 months) to be analyzed via FTIR and then returned to the experiment as soon as possible.

Different Conditions

The average of the initial FTIR spectra is presented in Figure 4.15. In the "new" HDPE spectra four peaks are observed which are assigned as different C-H vibrations. The first band is referred to as an asymmetric C-H stretch (2950 cm-1), while the second is from symmetric C-H stretching (2900 cm-1). The next peak that appears (around 1465 cm-1) in the spectra of hydrocarbons is attributed to a specific type of bending vibration coined scissoring. The final band that appears as a doublet (720 cm-1) is the result of a second type of vibrational bend known as the methylene rocking vibration. These various vibration modes were all described in 3.3.1.

The absence of new peaks or zero changes to pre-existing peaks is indicative that no chemical changes are observed. However, the formation of peaks indicative of oxygen-containing bonds (i.e. hydroxyl, carbonyl groups, etc.) describe that oxidation is indeed occurring. An overlay of spectra for HDPE polymers exposed to a variety of conditions in the laboratory is depicted in Figure 4.16. Polymer samples exposed to air alone (no water) did show some changes to the spectra with the addition of a peak forming around 1720 cm-1 which is typical of a carbonyl stretch or a carbon doubly bound to an oxygen (i.e. ketone). Samples of HDPE polymers retrieved from the laboratory degradation experiments exposed to 0 ‰ salinity displayed no changes to the spectra over

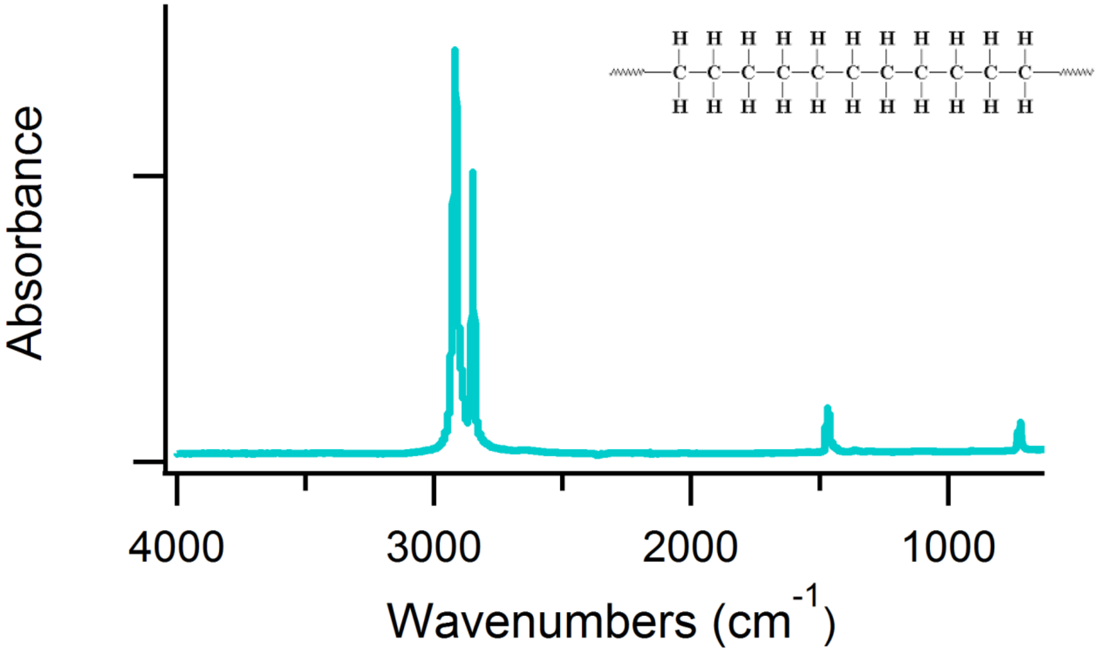
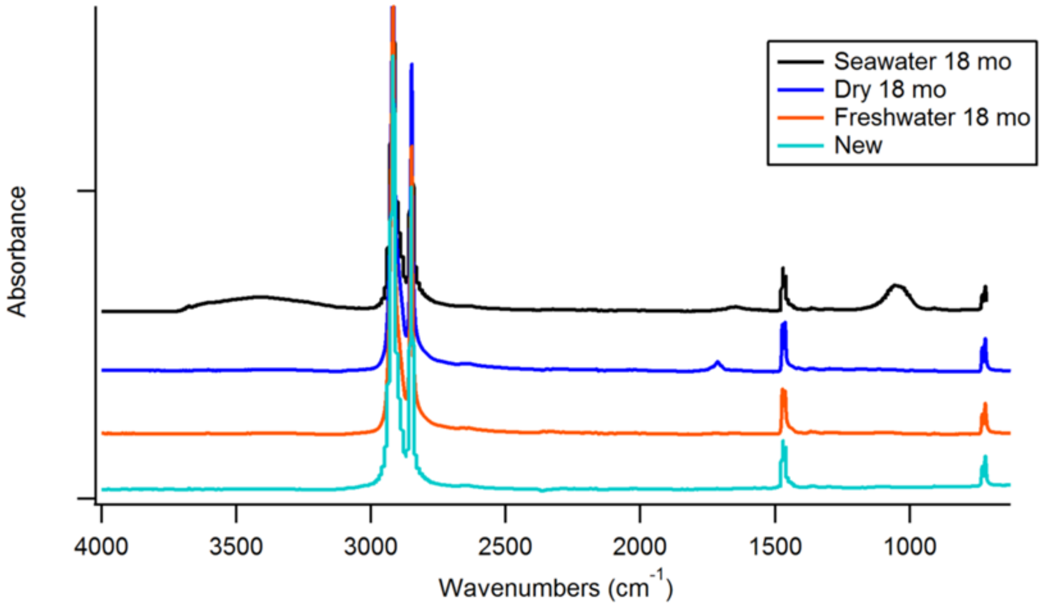


Figure 4.15 New HDPE FTIR Spectra. The four zones of bands are attributed to different C-H bond vibrations, asymmetric and symmetric stretches, scissoring vibrations, and rocking.

time. Although samples exposed to freshwater displayed no change in spectra, three additional stretches were observed for HDPE polymers exposed to seawater. The broadest peak represents the intermolecular hydrogen bonded O-H stretch (3331 cm^{-1}). The stretch around 1100 cm^{-1} is characteristic of C-O bonds which are likely connected to the OH groups being observed as well. The smallest stretch, but still statistically quite significant, is the carbonyl which absorbs around 1680 cm^{-1}. The slight shift in C=O peak compared to the "dry" spectra is likely due to interactions with the hydroxyl groups present[2]. A table listing the treatment of HDPE samples and their various FTIR vibrations assignments of each are presented in Table 4.1.



Y-Axis Offset

Note:
O-H stretch developing around 3500 cm^{-1}
C=O stretch developing around 1700 cm^{-1}
C-O stretch developing around 1100 cm^{-1}
Indicates the plastic surface is being oxidized

Figure 4.16 FTIR Spectra for HDPE Polymers Exposed to Various Conditions. Note that increases in oxygen containing bonds are more prevalent in marine water environments compared to dry and non-existent in freshwater systems.

Table 4.1 Assignments for HDPE FTIR Spectra.

Treatment	Peak Range (cm^{-1})	Center Peak (cm^{-1})	Assignment
New	2980-2905	2950	C-H(υ_{as})
	2905-2895	2900	C-H(υ_{sym})
	1490-1330	1465	C-H($\delta_{scissor}$)
	734-609	720	C-H(ρ_{rock})
Freshwater	2970-2830	2920	C-H(υ_{as})
	2830-2650	2850	C-H(υ_{sym})
	1490-1360	1465	C-H($\delta_{scissor}$)
	734-688	718	C-H(ρ_{rock})
Dry	2980-2860	2920	C-H(υ_{as})
	2860-2650	2850	C-H(υ_{sym})
	1490-1380	1460	C-H($\delta_{scissor}$)
	735-635	718	C-H(ρ_{rock})
	1730-1630	1710	C=O
Seawater	2970-2860	2920	C-H(υ_{as})
	2860-2670	2850	C-H(υ_{sym})
	1490-1370	1470	C-H($\delta_{scissor}$)
	735-652	717	C-H(ρ_{rock})
	3600-3200	3420	O-H
	1700-1610 1610-1510	1680 1580	C=O
	1160-1000	1035	C-O

Utilizing an X-axis offset and examining alterations in the two largest C-H stretches, asymmetrical and symmetrical, signify that there may be a trend in decreasing C-H population stretches for HDPE polymers exposed to seawater (Fig. 4.17). This trend is even more apparent if the spectra for marine lab samples are displayed over time.

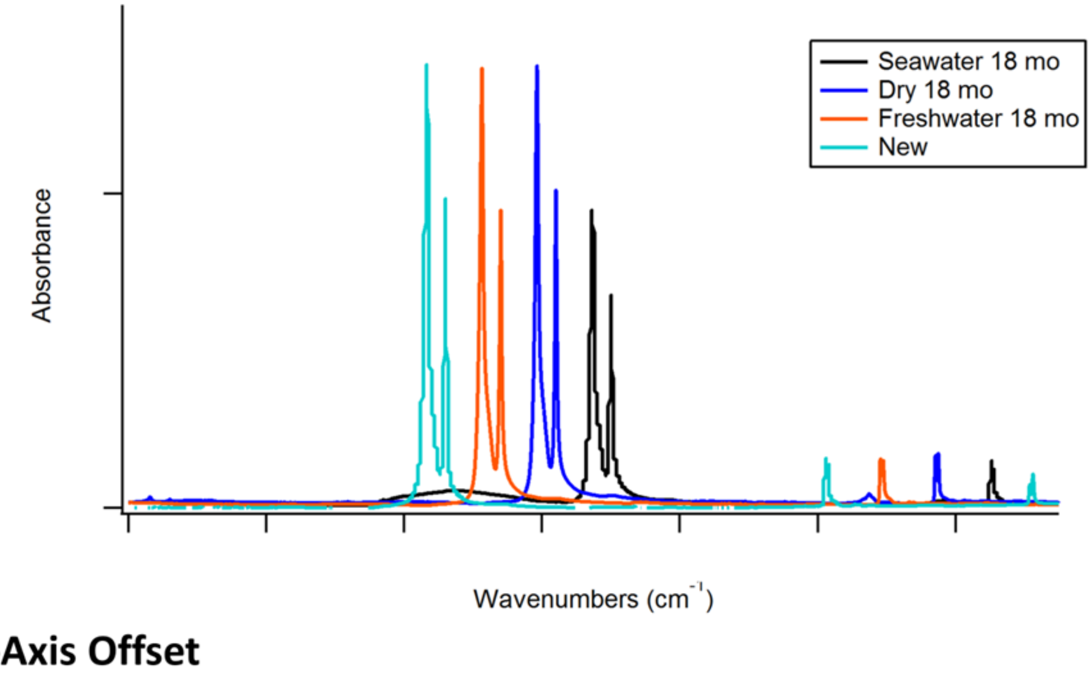


Figure 4.17 X-axis Offset of HDPE Spectra. The prominent peaks account for the asymmetric and symmetric C-H stretches. Note that after 18 months of seawater and UVexposure, the C-H stretches have significantly reduced in height, while those exposed to freshwater and UV did not.

Time Series

Spectra taken throughout the degradation experiment have been overlaid to depict bond formation over time (Y-axis offset), as well as decreases in C-H stretches (X-axis offset). An apparent trend is observed (Fig. 4.18) showing the formation of O-H, C-O, and C=O groups over time. The decreases in C-H stretches over time (Fig. 4.19) suggest that oxygen replaces hydrogen at these sites along the surface of polymers. The small sharp peak present in the broad O-H stretch is characteristic of “free” OH groups, such as terminal alcohols or those not involved in intramolecular bonding[2].

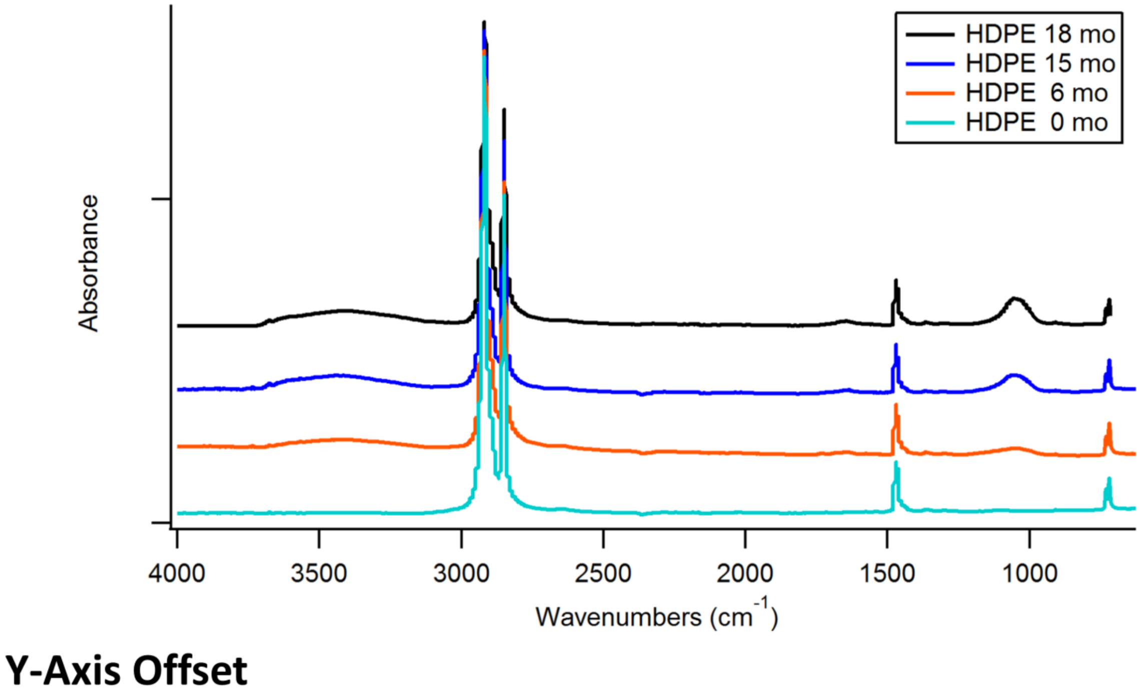


Figure 4.18 Time Series Overlay of FTIR Spectra. The formation of oxygen containing bonds can be seen progressing throughout the duration of the experiment. The most prominent stretches are notably the O-H and C-O bends.

Plots depicting the trends in hydroxyl, carbonyl, and C-O bond formed over time is displayed below. The reduction in C-H bond absorbance is also portrayed in Fig. 4.20.

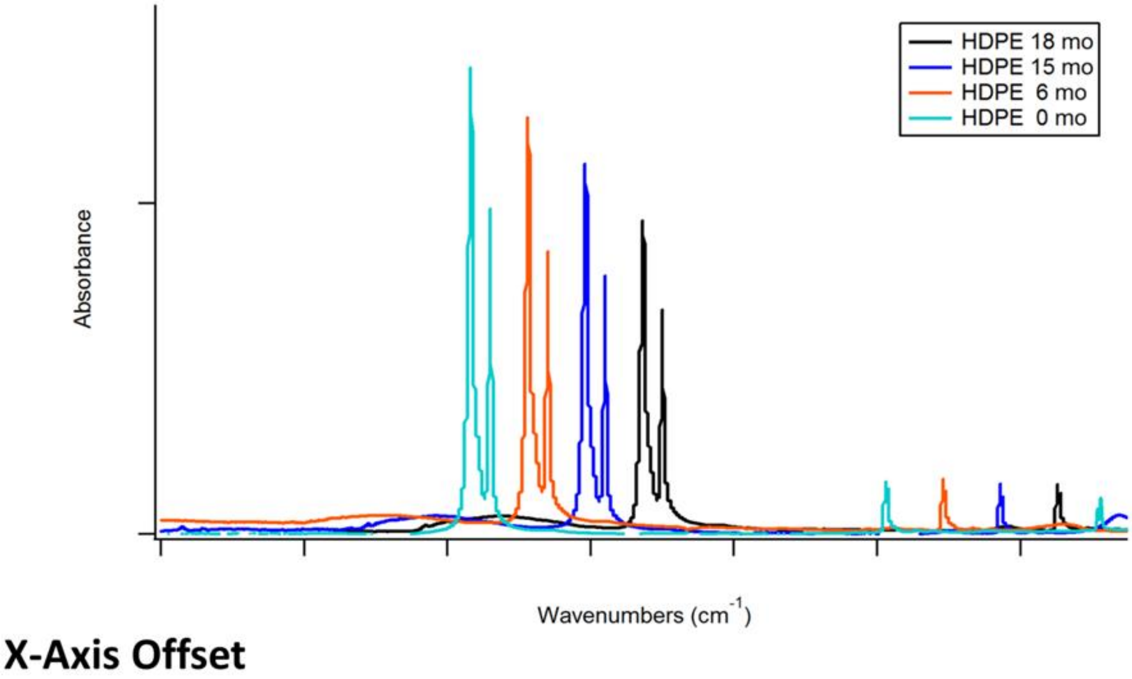


Figure 4.19 Offset Spectra of HDPE Over Time for C-H Stretches. An apparent trend is apparent in the decreasing absorbance associated with C-H asymmetric and symmetric stretches. This is likely the result of hydrogens being replaced with oxygen over time.

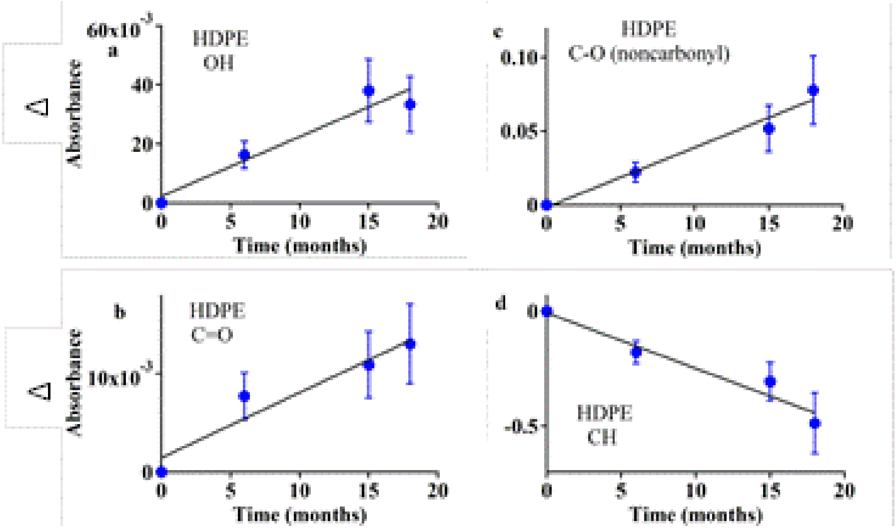
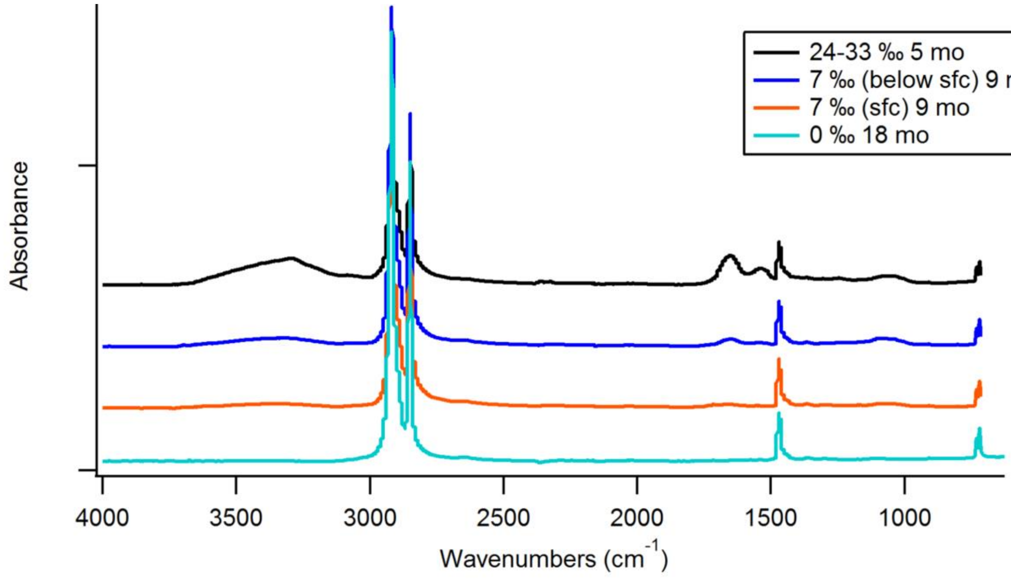


Figure 4.20 Relative changes in FTIR Absorbance for HDPE Over Time. An apparent trend showing an increase in O-H, C-O and C-O (noncarbonyl) is observed. As these new functional groups arise, there is a decrease in C-H stretch absorbance.

4.4.2 Field HDPE FTIR Spectra

Different Conditions

Comparisons are made between FTIR spectra under various salinties. Minor changes exist for HDPE polymers exposed to aquatic environments with average salinities of 7 ‰, but these changes are consistent with those observed in Lab experiments, namely O-H, C-O, and C=O stretch formation. Samples extracted from Lynton's dock positioned 8 inches below the surface displayed a greater increase in absorbance for oxygen containing groups. This result is consistent with the SEM images. Despite the relatively short exposure times of LTER samples, the greatest observable changes in FTIR spectra were noted as shown in Figure 4.21. Again, the trends in bond formation are similar

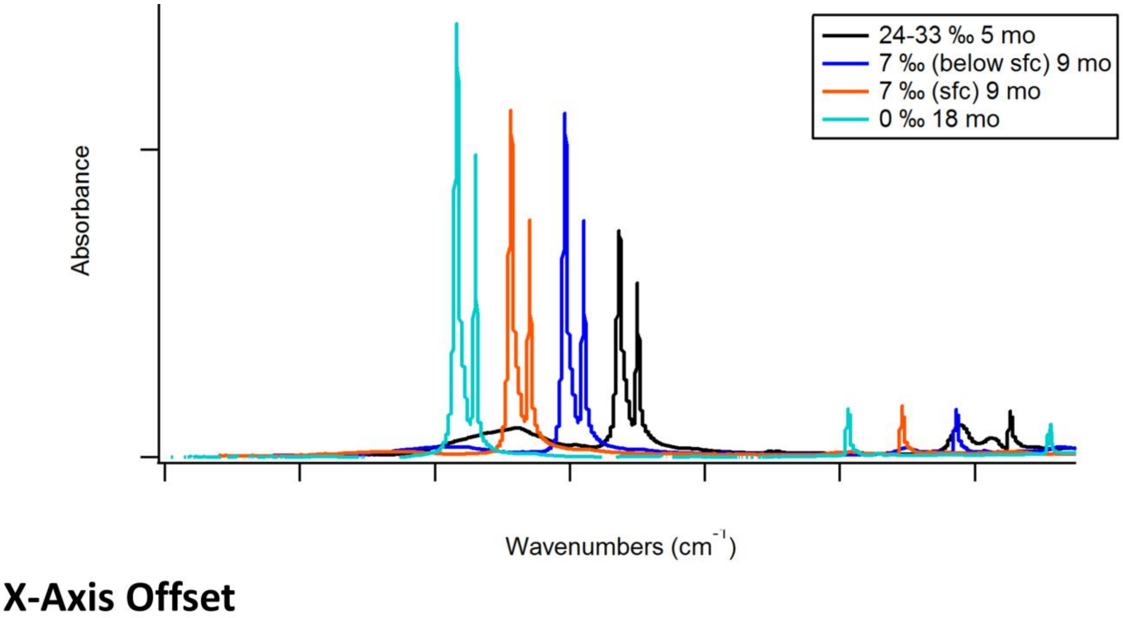


Y-Axis Offset

Figure 4.21 Overlay of Spectra Representative of Various Salinity Exposures. Similar trends in O-H, C-O, and C=O stretches are evident. Despite shorter exposure times, polymers exposed to greater salinities displayed the greatest absorbance of these oxygen containing groups. Also of note is the increase in absorbance for samples located at Lynton's dock which were below the surface. The increased oxidation was also evident in SEM images.

to those observed in laboratory experiments.

The FTIR spectra utilizing an X-axis offset exhibits similar trends to those observed in lab HDPE samples. As salinity increases, a 50% decline occurs in the absorbance of C-H stretches due to increasing oxidation of the polymer surface (Fig. 4.22).



X-Axis Offset

Figure 4.22 Field HDPE Spectra with X-axis Offset. As seen in laboratory experiments of HDPE degradation, C-H stretches show significant decreases in absorbance. The greatest decrease occurs for HDPE polymers subjected to more saline environments despite less exposure times.

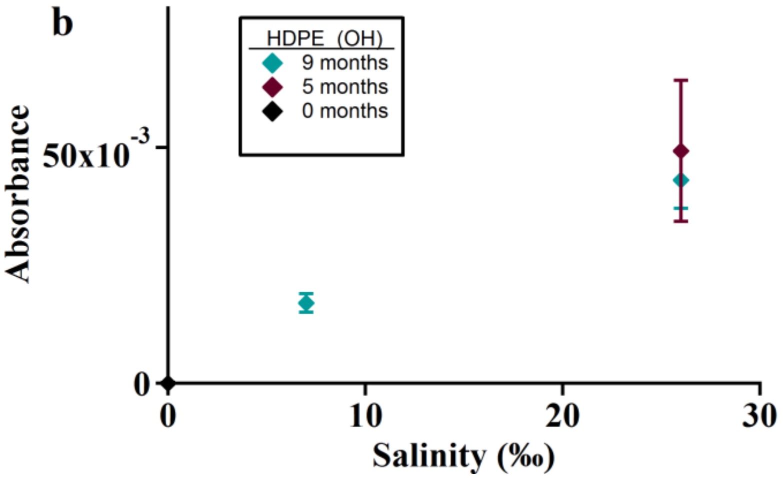


Figure 4.23 Changes in O-H Stretch Absorbance VS. Salinity. Despite shorter exposure times, HDPE polymers floating in 26 ‰ seawater displayed the greatest absorbance.

4.4.3 Laboratory PETE FTIR Spectra

As previously mentioned, PETE spectra are considerably more complicated compared to HDPE spectra. This is due to additional signal contributions from the aromatic rings and oxygen atoms present in the molecular structure. Figure 4.24 demonstrates the additional complexity found in the spectra. Crowding of these signals occurs in the area classified as the “finger print” region. Less prominent in PETE compared to HDPE are the absorbance bands for asymmetric and symmetric C-H stretching (2950 cm^{-1} and 2900 cm^{-1} respectively). Another characteristic which differs from the spectra observed in HDPE is the strong absorbance for the C=O stretch (1720 cm^{-1}). The stretches observed between 1600 and 1400 cm^{-1} are indicative of ring C=C bonds in aromatic structures. The two stretches located around 1285 and 1125 cm^{-1} are due to vibrations from C(=O)–O stretch and the O–C=O asymmetrical stretch. The small band appearing between 900-850 cm^{-1} regions can be attributed to asymmetrical ring stretching in which the C-C bond is stretching at the same time the C-O bond is experiencing contraction^{2}. The final stretch to note is a prominent stretch located at 760 cm^{-1}. This stretch results from out-of-plane bending of C-H groups.

Only samples exposed to seawater are displayed as these showed the greatest chemical modifications among HDPE polymers. Comparing the spectra over time a couple of observations can be made despite the more challenging initial spectra. Similar to what was observed in HDPE spectra, there is a formation of the O-H stretch around the 3400 cm^{-1} region (Fig. 4.25). Another reported trend is a decrease (20%) in absorbance of C=O stretches, 1720 cm^{-1}, (Fig. 4.26) with a 30% decrease in absorbance with C-H stretches as well, although less dramatic than those observed in HDPE (Fig. 4.24). Aromatic ring stretches also showed decreases in absorbance.

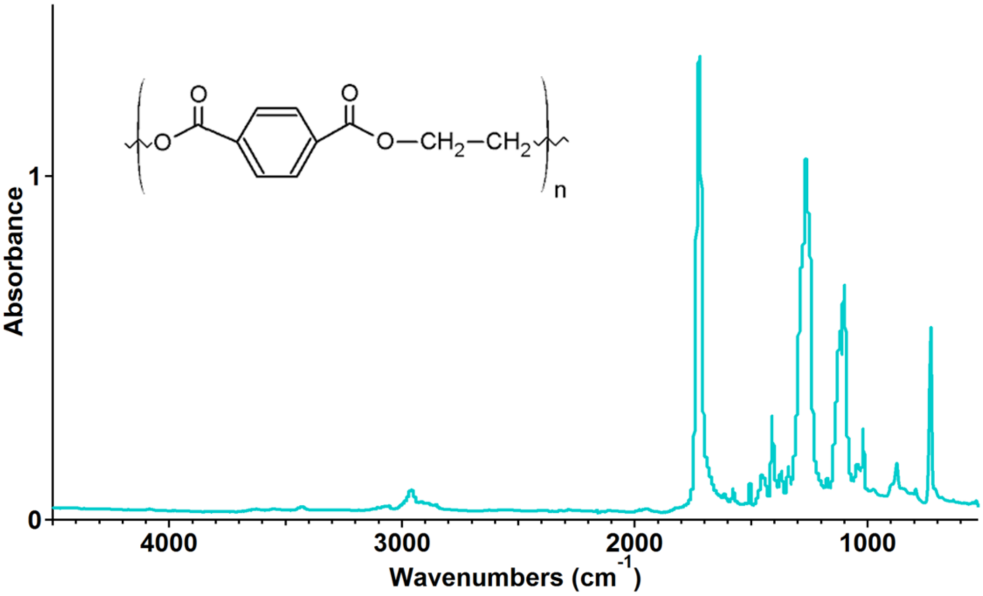
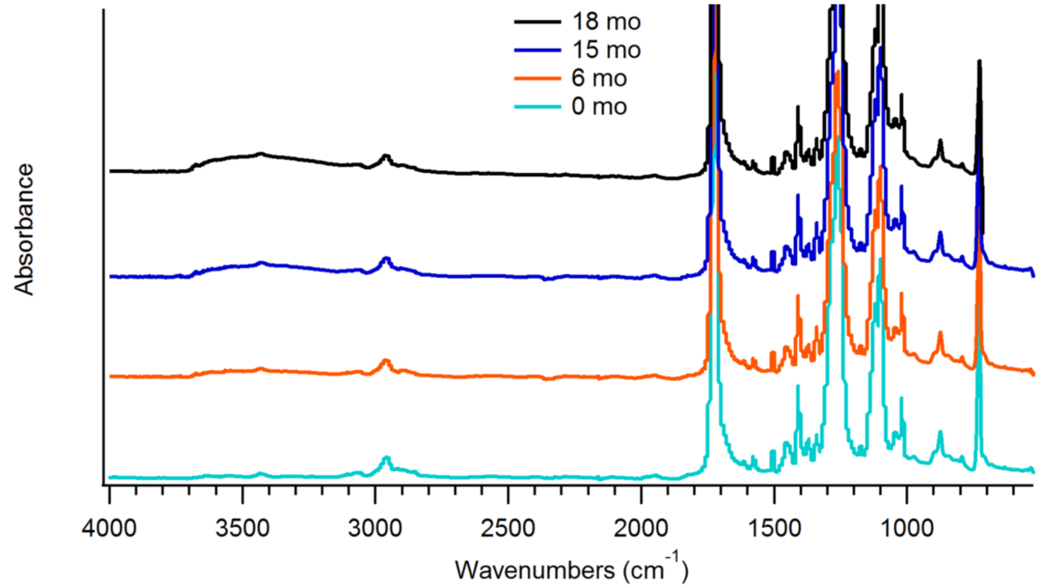
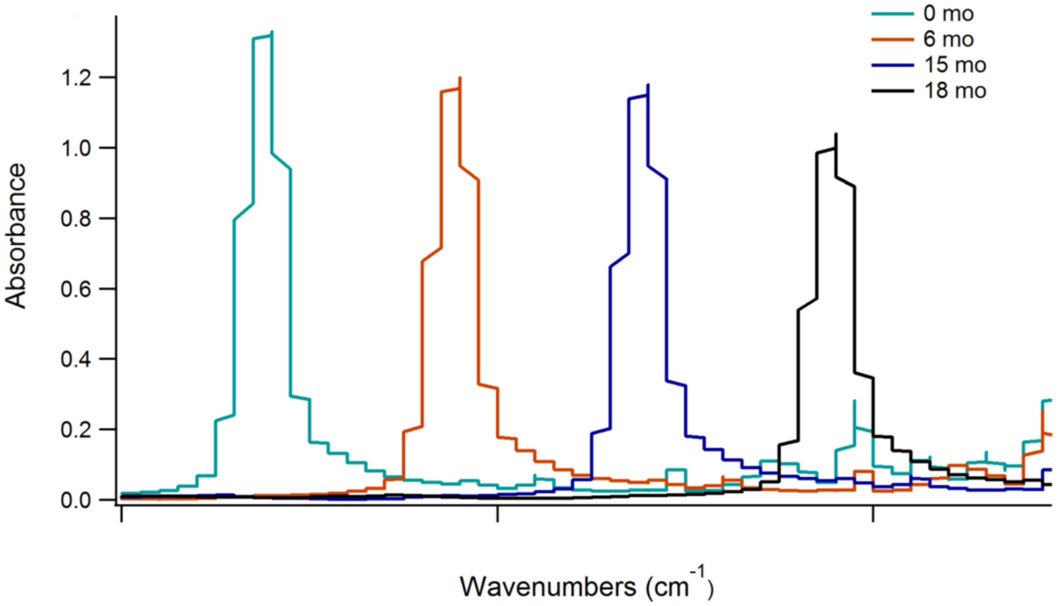


Figure 4.24 Average Spectra for New PETE Polymers. The molecular structure has been provided as an aid to recall bond-linkage and type. The small C-H stretches in the 2950 cm^{-1} region are the result of CH_2 bonds, while the more muted and broad peaks between 3100-2850 cm^{-1} are indicative of aromatic C-H stretches. The sharp absorbance located at 1720 cm^{-1} represents the C=O stretch. Aromatic ring C=C stretches are observed between 1600-1400 cm^{-1}. The C(=O)–O stretch and the asymmetric O–C=O stretch are found at 1285 and 1125 cm^{-1} respectively. Small bands between 900-950 cm^{-1} are the result of asymmetrical ring C-C stretching. The sharp absorbance featured at 760 cm^{-1} is characteristic of out-of-plane C-H stretching.



Y-Axis Offset

Figure 4.25 Time Series of Lab PETE FTIR Spectra. An overlay of PETE spectra affords little observable changes aside from the formation of the broad O-H stretch.



X-Axis Offset

Figure 4.26 Side by Side Comparison of Carbonyl Absorbance Over Time. A trend displaying slight decreases in absorbance for carbonyl groups is present. Although small, it is still statistically significant.

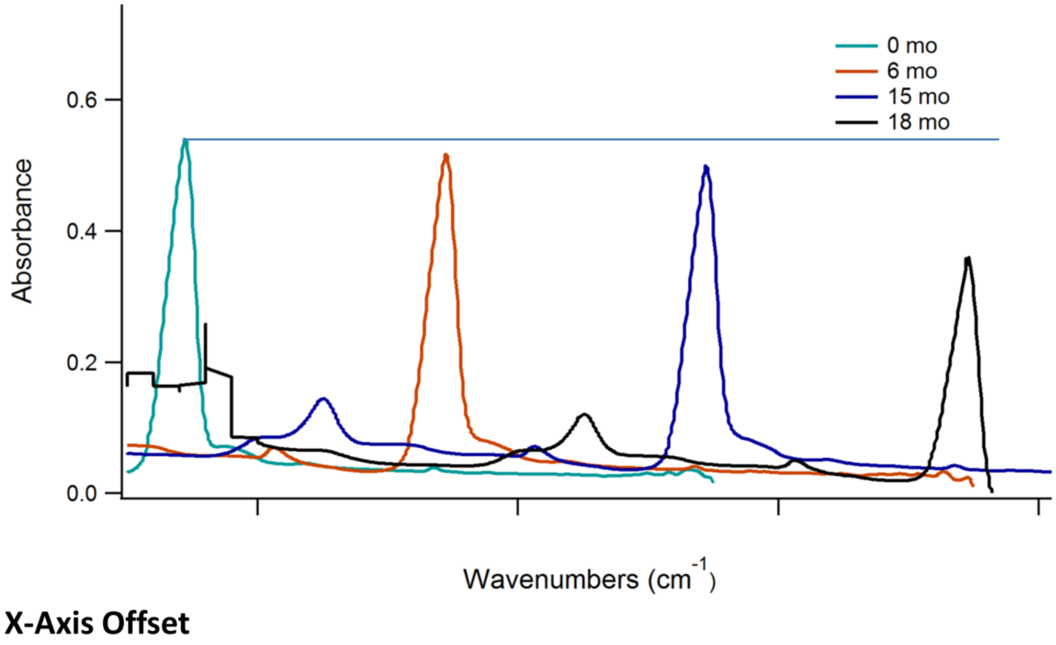


Figure 4.27 X-Axis Offset Comparing Absorbance of CH Stretch Over Time. After 18 months there is a 30% decrease in absorbance. The thin blue line is there to guide the eye line as the decrease in absorbance is minimal until the end of the experiment.

4.4.4 Field PETE FTIR Spectra

The greatest changes observed in field experiments for any polymer investigated occurred in the more saline waters located off the LTER dock. A direct correlation between the concentration of salinity and the increase in O-H absorbance exists, in agreement with PETE polymers employed in lab experiments. A slight increase (8%) in absorbance was observed for samples obtained from the LTER site (26 ‰) compared to the less saline location despite almost double the exposure time in the 7 ‰ waters (Fig. 4.28). A decrease (32%) in the C=O stretch observed for field samples is similar to that reported in the laboratory experiments, however there was not a significant difference between the absorbance observed from the two locations (Fig. 4.29). Moving down field in the spectra, the C-H stretch (760 cm^{-1}) decreases in absorbance by approximately44 % from both field sampling sites for PETE polymers (Fig. 4.30).

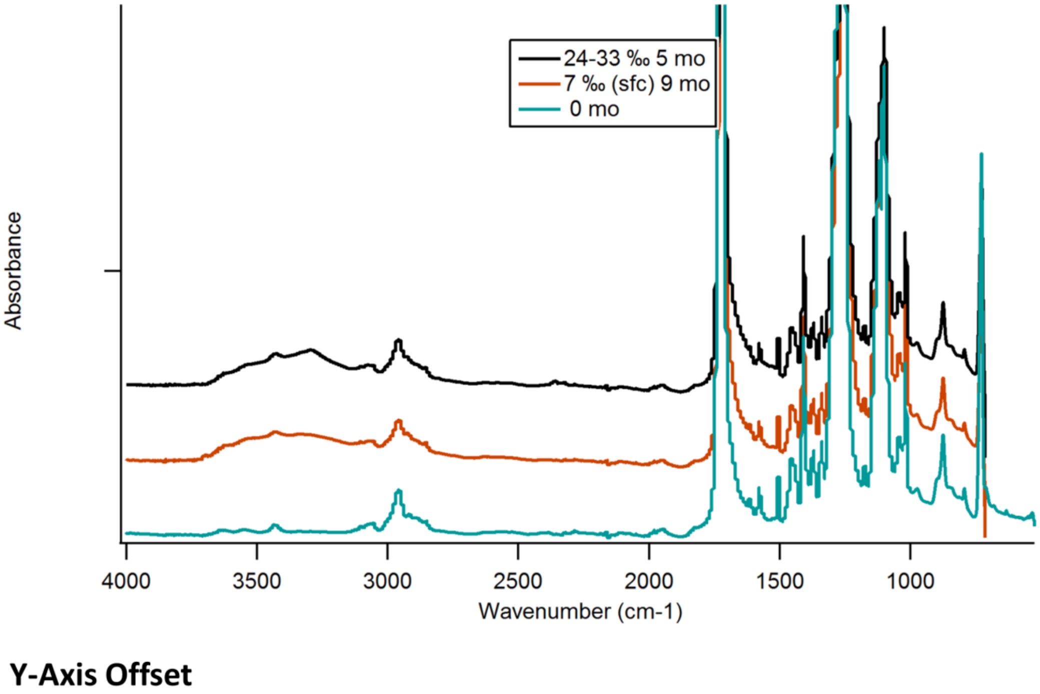


Figure 4.28 Field Sample FTIR Spectra of PETE Polymers. Formation of a broad O-H stretch is observed in both field locations. There is a slight (8%) increase in absorbance noticed for samples exposed to greater salinity despite less time.

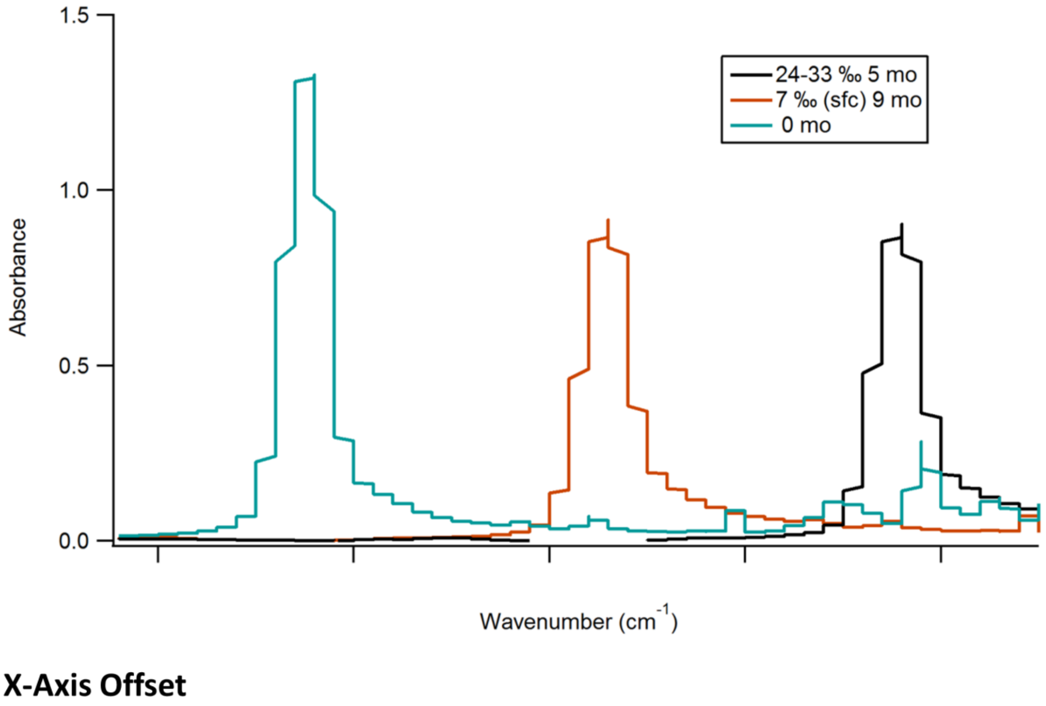


Figure 4.29 Side By Side Comparison of Carbonyl Stretches. Samples retrieved from both locations experience a decrease in absorbance of the 1720 cm^{-1} C=O stretch.

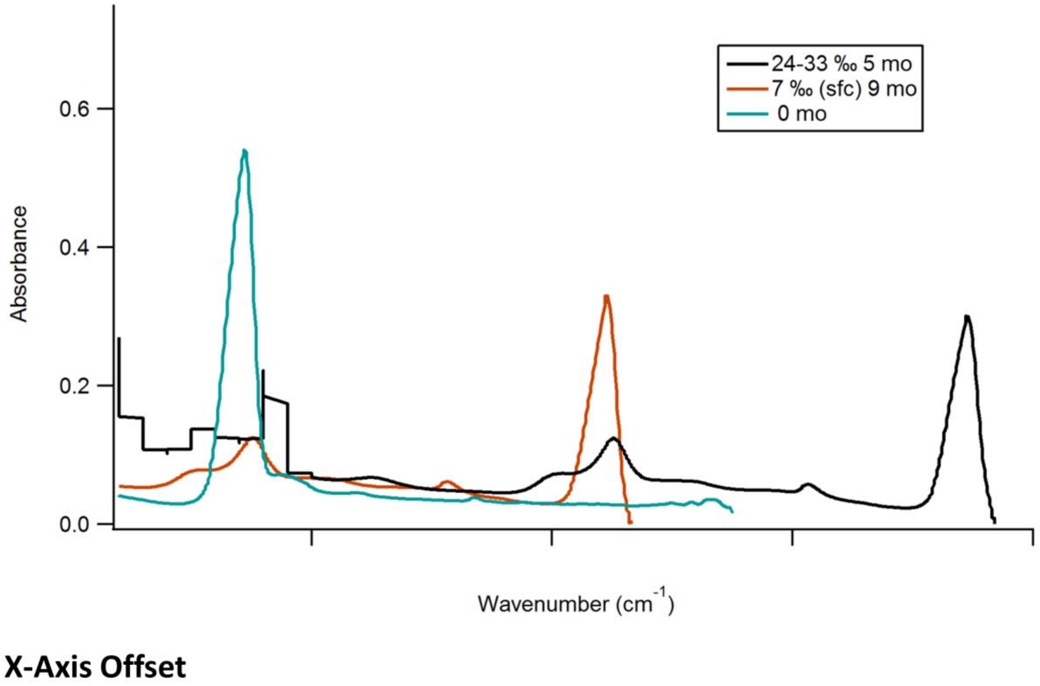


Figure 4.30 Decreasing CH Stretches Observed in Field PETE Samples. The decrease in C-H stretches is likely the result of the increasing oxidized surface observed in polymers exposed to UV light and saline waters.

4.4.5 Laboratory PC FTIR Spectra

Polycarbonate has a slightly more complicated molecular structure due to additional aromatic and methyl groups, as well as oxygen, in the monomeric subunit. Additional vibrations are created in the presence of the additional aromatic rings and conjugation with other bonds also occurs more readily. The FTIR spectra however, are very similar to those obtained for PETE (Fig. 4.31).

The same trends persist for polycarbonate samples as were seen in other polymers investigated that were exposed to seawater and UV light. Formation of the O-H stretch, decrease in aromaticity, decrease in C=O absorbance stretches and C-H stretches (Fig. 4.32) were all observed. The C=O absorbance reduces 70% over the period of the laboratory experiment (Fig. 4.33).

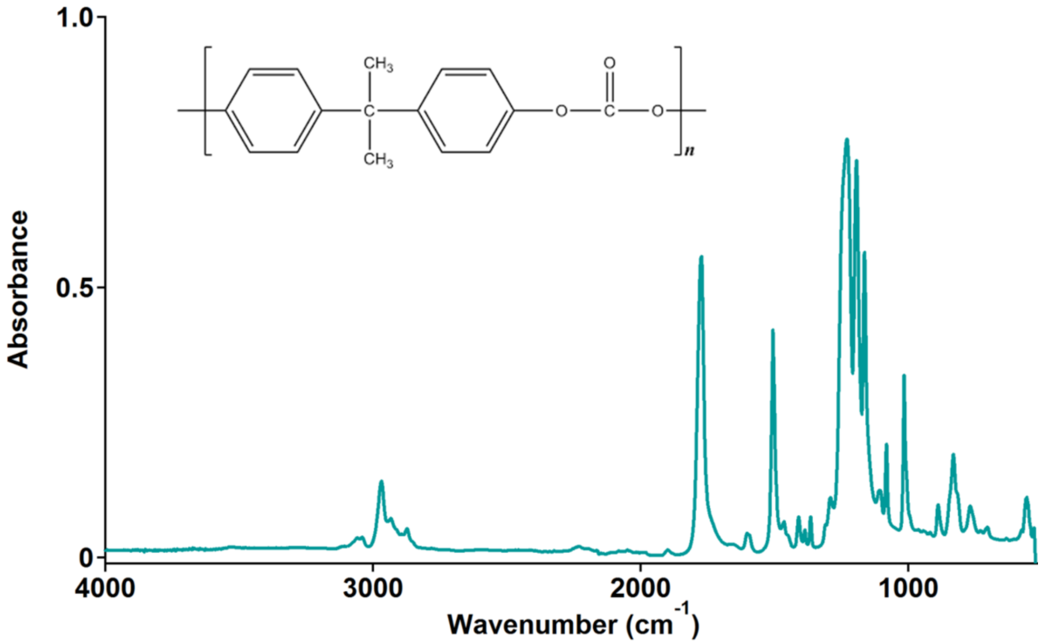
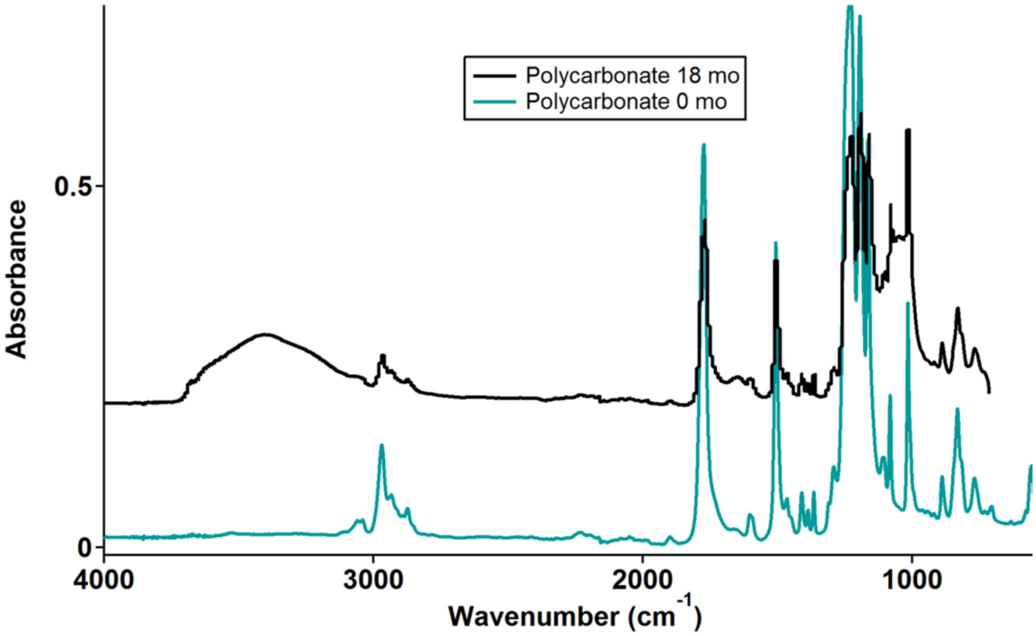
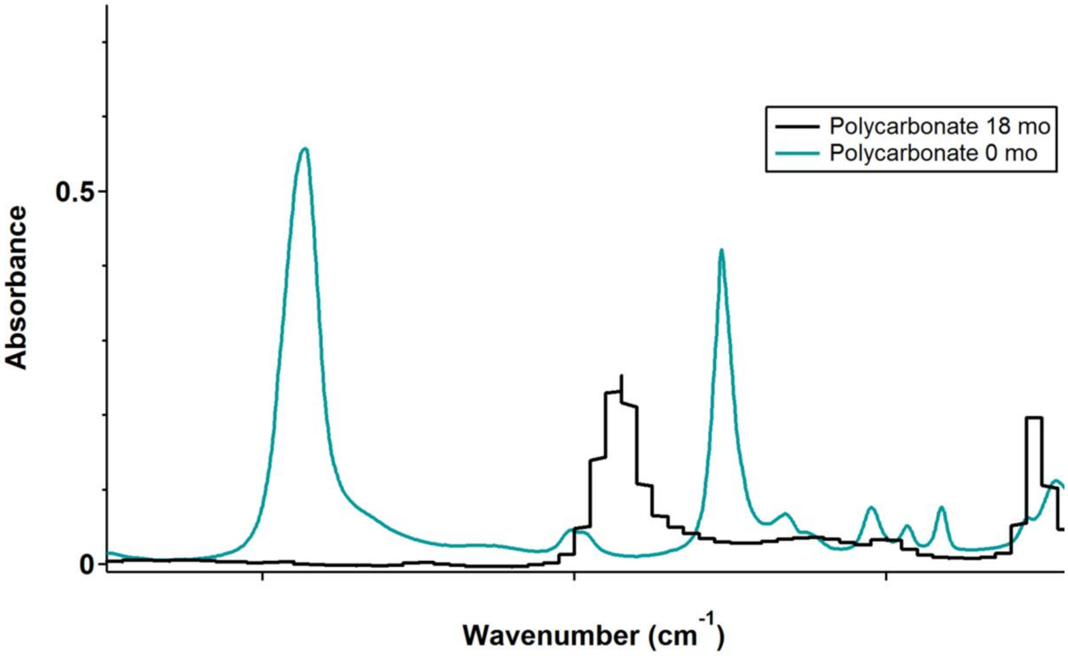


Figure 4.31 Normal FTIR Spectrum of Virgin Polycarbonate. The asymmetric and symmetric stretches affiliated with the methyl groups are located 2972 cm^{-1} and 2951 cm^{-1}. Additional signals in the 3000 cm^{-1} region are attributed to aromatic C-H stretches.



Y-Axis Offset

Figure 4.32 Formation of O-H Stretch in Polycarbonate Plastics. A large stretch in the O-H region of the spectra is observed, indicative of the surface oxidized after exposure to seawater and UV light in laboratory experiments.



X-Axis Offset

Figure 4.33 Reduction in Carbonyl Absorbance in PC Samples. The absorbance of the C=O stretch reduces by 70% over the course of the experiment.

4.4.6 Field PC FTIR Spectra

Samples obtained from the surface of the Lynton experiment did not show signs of hydroxyl formation as previously observed in laboratory experiments. Polycarbonate samples were the only polymers examined that did not display any oxidation in this regard as per their FTIR spectra, but the surface did appear oxidized via SEM imaging (Appendix I). Additionally, no changes observed for any of the other bond types by FTIR analysis. Samples obtained from the LTER location did show some OH formation but was not nearly as apparent as the laboratory studies (Fig. 4.34). Other alterations in absorbance reduction or formation were not observed by FTIR spectra for polycarbonate samples.

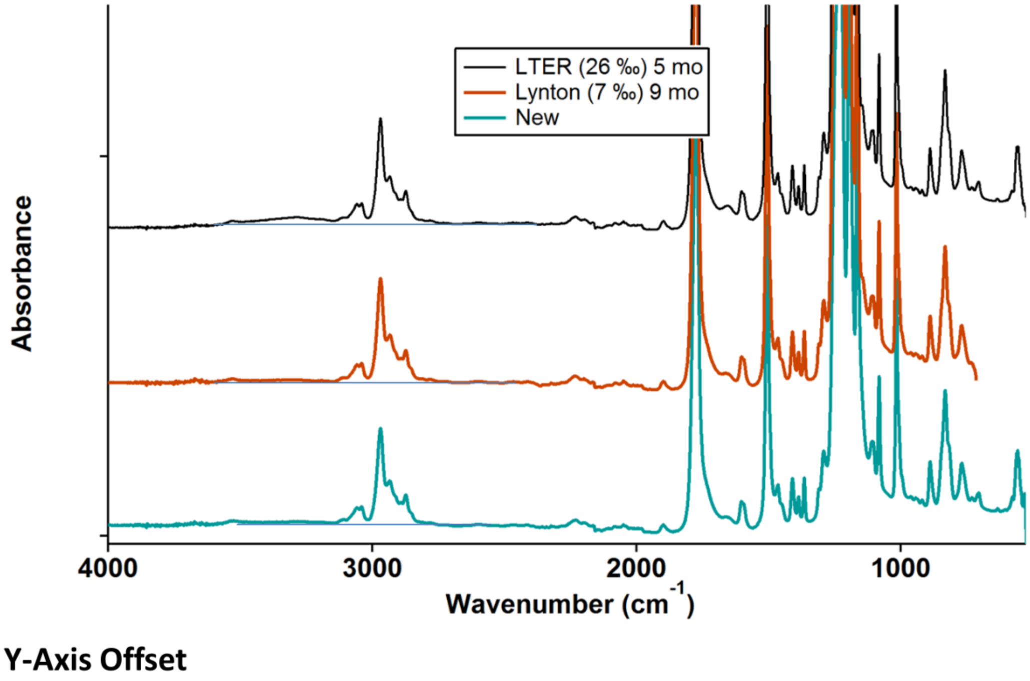


Figure 4.34 Field Sample FTIR Spectra of Polycarbonate. Guidelines were added beneath the O-H stretch region to help visualize any absorbance in these areas.

4.4.7 Particulate FTIR Spectra

Particulates were collected prior to analysis using vacuum filtration with a 0.45 micron filter. Particulates were rinsed carefully with DI water and left to dry gently. The filter containing particulates was tented using aluminum foil. After drying, particulates were simply flaked from the filter and collected for analysis. A blank filter was analyzed by FTIR to control for filter fiber contamination in samples. Filters did not respond to the IR signal which remained flat throughout the scanning process. Remarkably, particulates collected from the three different polymers were nearly identical in their FTIR spectra (Fig. 4.35). Strongest absorbance is observed in the O-H, C=O, and C–O stretch regions, the same areas observed in the oxidized surfaces of the parent materials. Weak absorbance in the C–H regions are present upfield and downfield in the spectra, suggesting that the

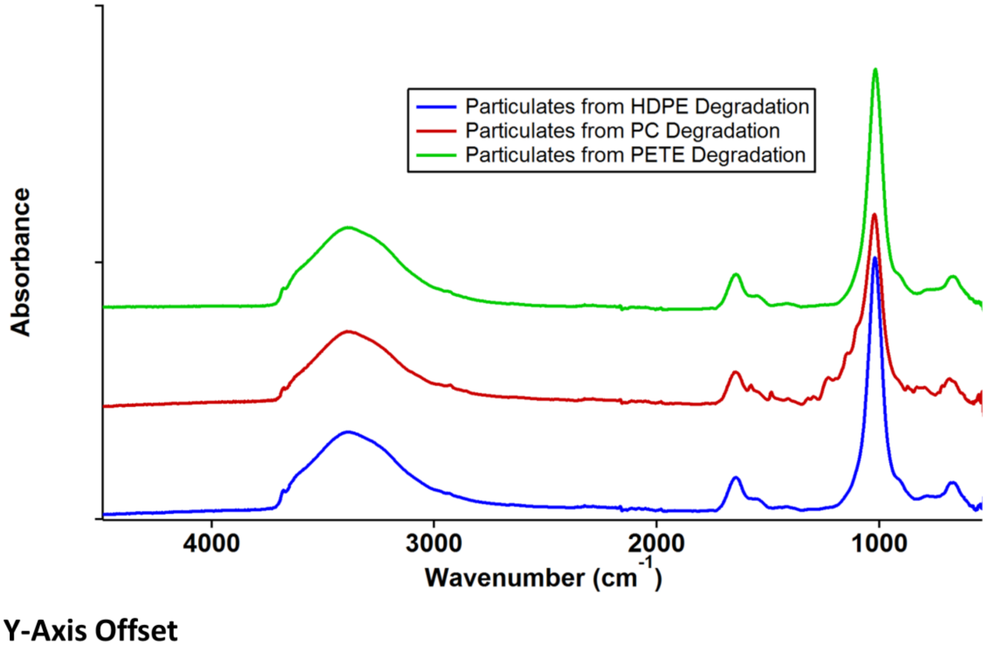


Figure 4.35 Fourier Transform IR Spectra of Plastic Particulates. Displayed are spectra for particulates collected from the three polymers investigated.

surface of the particulates were heavily oxidized.

3.5 Particle Size Coulter Counter

A Beckman Coulter Counter was employed to determine the sizes of particulates produced during laboratory degradation experiments. Analysis began using a 40 micron limit, meaning only particles 40 μm and larger would be counted. The target size eventually reduced to 5 microns. Using a 100 μm aperture gave an operation limit of 2 microns[3]. To ensure we stay within the limits of this apparatus, particulates below the 5 micron threshold were not measured.

Analysis of the plastic particulates produced upon degradation of the parent material was performed. For all three polymers investigated, the largest population fell between the 5-10 micron ranges. Polyethylene and phthalate measured similarly in populations, while polycarbonate had the greatest number of particulates in the 5-10 micron range (Fig. 4.36).

Concerned that dust contamination was responsible for a portion of particulates measured, water samples from the “freshwater” beakers were analyzed. These beakers were housed in the same degradation chamber and for the same amount of time the seawaters were exposed. Any dust collected in the seawater beakers would similarly contaminate the freshwater beakers. As further controls, samples of autoclaved seawater and the deionized water used to reconstitute evaporated water in both types of beakers were examined. Seawater contained the greatest amount of particulates, mostly in the 5-10 micron range. Deionized water had the least amount. Figure 4.37 describes the size and population distribution for the water samples. From an examination of the freshwater samples, dust cannot be attributed to the massive population of particulates measured in degraded plastic seawater.

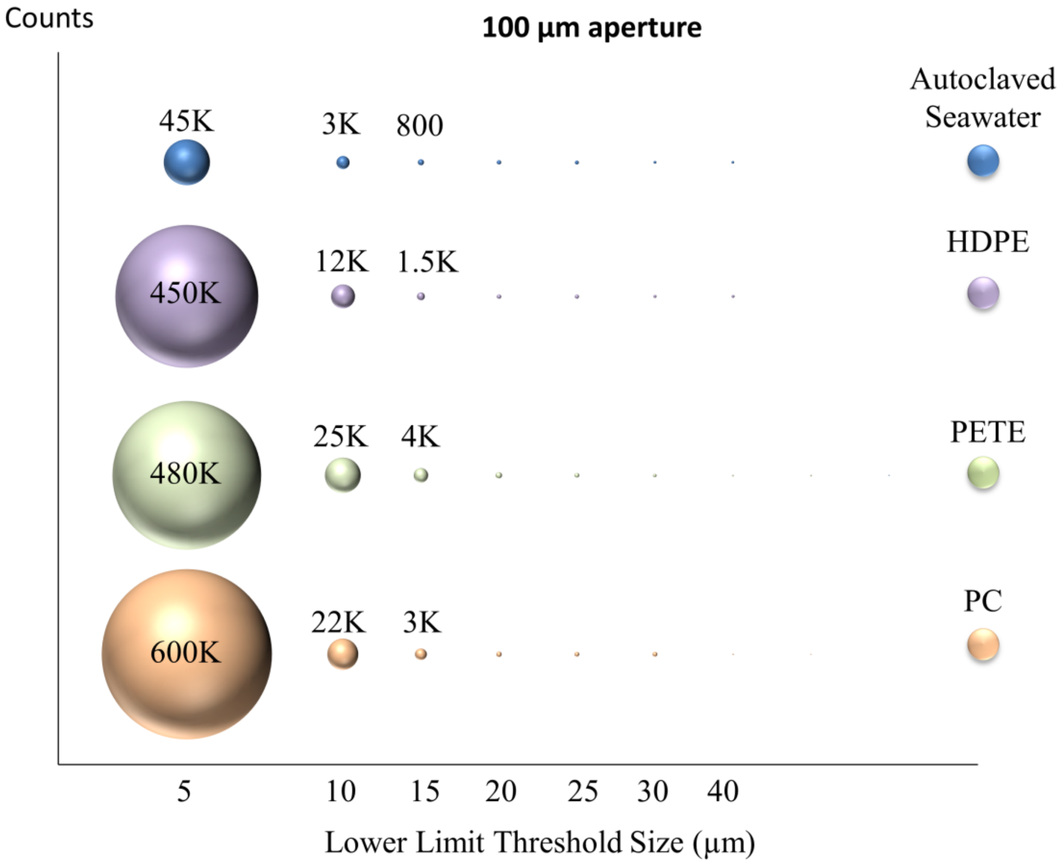


Figure 4.36 Particle Size Distribution. Particulates collected over the course of the degradation experiment were evaluated to determine the sizes of debris produced. Using a 100 micron aperture limited measurements to 5 microns.

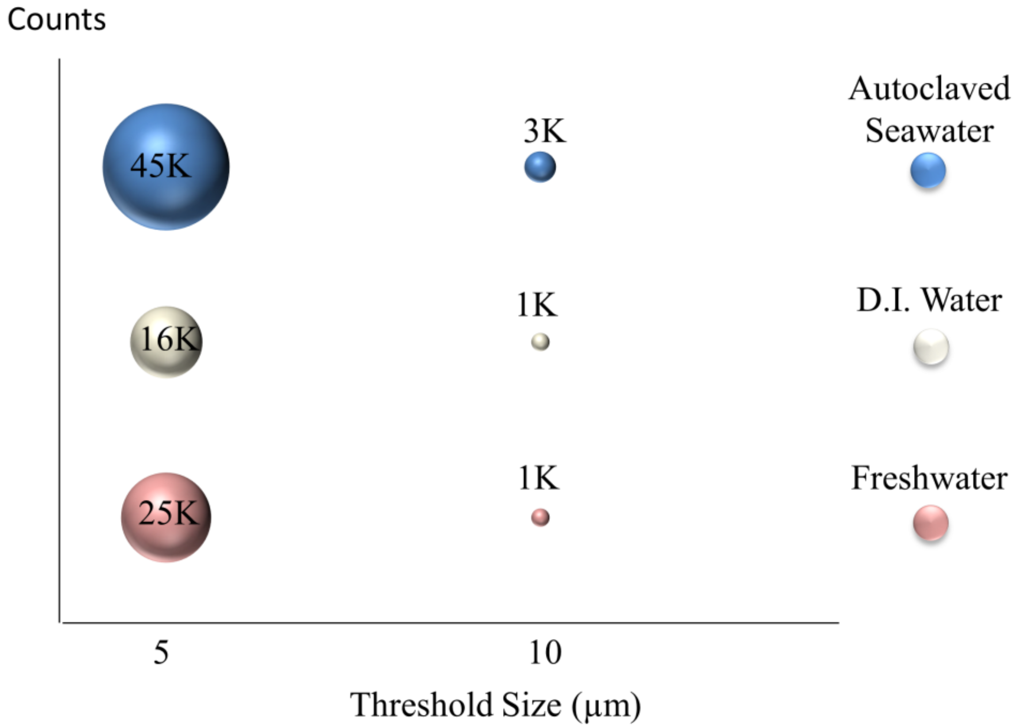


Figure 4.37 Particle Size Distribution of Water Samples. Samples of water were analyzed to ensure particulate populations observed in polymer degraded water could not be attributed to dust. It is apparent from the freshwater samples in the same degradation chamber as the seawater samples and for the same length did not have a significant population of micro-particulates.

3.6 Elemental Analysis Isotope Ratio Mass Spectrometry (EA-IRMS)

Recall that a natural abundance of isotopes exist for carbon atoms, where 98.9% of carbon nuclei house 6 neutrons (^{12}C) and 1.07% are found with 7 neutrons (^{13}C). Initial Analysis of isotope composition displayed an apparent trend resulting in the parent material becoming isotopically depleted with respect to ^{13}C in HDPE polymers (Fig. 4.38). After eighteen months of degradation exposure the isotopic composition decreased by nearly 2 per mil (‰), suggesting a rate of depletion around 0.1 per mil/month. However, this trend does not appear to be linear. Counterintuitive to expectations that ^{12}C-^{12}C bonds would break and be removed first, leaving the residual material more enriched with ^{13}C. The isotope composition of particulates produced upon degradation was also analyzed. The particulates show a slight enrichment compared to the surface scraping of HDPE polymers after 18 months of degradation. However, the isotope signatures do not vary greatly from experimentally measured HDPE polymers. Particulates produced from PETE and PC polymers have isotope signatures in the ranges observed for their respective parental polymers as well. A table of these values is provided in Appendix I.

Analyzing random samples of clear plastic for each polymer showed variations in isotope composition within each polymer classification. Deviations of 3 per mil were measured in materials made from HDPE polymers. Plant based materials were more enriched in ^{13}C compared to oil based materials. However, this enrichment is not surprising (Figure 4.39) given the relative isotope compositions of the starting materials (corn vs. fossil fuels).

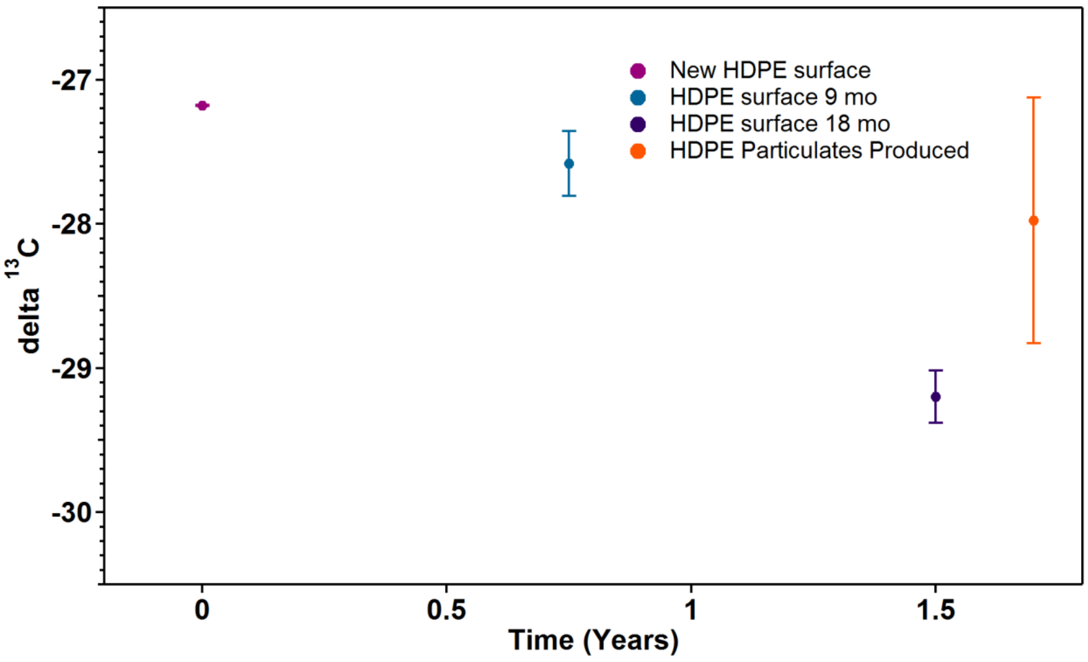


Figure 4.38 Isotope Composition of HDPE as Oxidation Occurs. The polymer becomes depleted with respect to ^{13}C over time based on surface scrapings. This is counter to what was initially proposed. The isotope composition of resulting particulates register about 1 per mil more enriched than the surface of the polymer after 18 months of degradation.

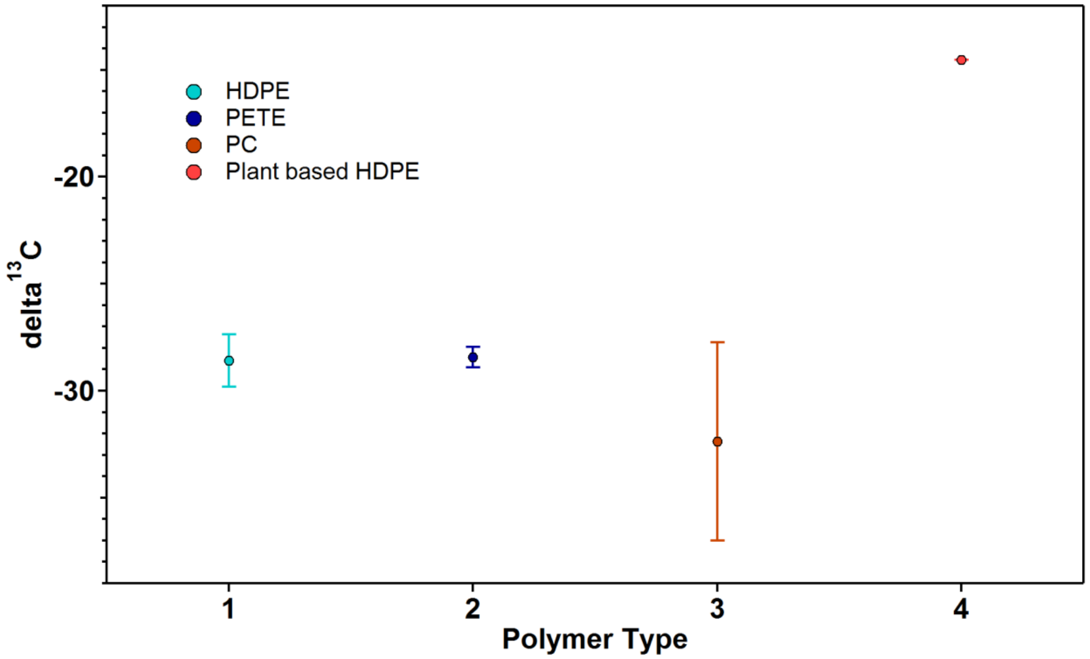


Figure 4.39 Variations within Polymers. Starting materials affect the isotope composition; plant based plastics tend to be more enriched with 13C compared to fossil fuel based polymers. Isotope compositions varied by more than a per mil amongst similar polymer types.

4.7 References

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CHAPTER 5

Discussion, Conclusions, and Implications

5.1 Introduction

The current mass production and future projections demonstrate the large volume of plastic produced globally per year (300 MT) and that these production rates are likely to increase[1]. The inadequate rate of recycling and mismanaged waste of disposed plastic was also addressed. Many of these disposed plastics eventually make their way into aquatic systems. Current studies suggests that plastic, once in an aquatic environment will not degrade as readily as similar material on beaches or other terrestrial settings[2,3]. Other research has suggested that microbes are responsible for degradation of plastic adrift in the ocean[4].

The mission of this study to investigate whether plastic reacts to water environments differently, based on constituents that may be present (i.e. salts) which could influence the chemistry of degradation. Ultra-violet (UV) light is a well-known catalyst for a plethora of organic chemical reactions. Under conditions similar to those observed in marine environments (pH >5, SO_4^{2-}, Cl^-) and in the presence of UV light, small alkane compounds can oxidize[5]. The mechanism proposed uses a sulfate radical based oxidation scheme. As much of the plastic produced is made from hydrocarbons, like alkanes, it is feasible that they will behave chemically similar.

Field and laboratory experiments, were designed and implemented to address these degradation chemical patterns of change.

5.2 Results

It is obvious from both field and laboratory experiments that a greater amount of oxidation was present amongst the surface of each plastic polymer studied when it was exposed to seawater. This was physically observed by the production of microplastics in laboratory experiments, changes in surface roughness as depicted in S.E.M. images, and by FTIR spectra that monitored chemical changes. The laboratory study demonstrated that there was greater surface oxidation of polymers in seawater than experienced by those polymers that were not submerged in freshwater and then those only subjected to the UV light. This suggests that oxidation does occur despite attenuation of UV light as it descends the water column, and that some other chemical degradation process (aside from photo-degradation) is being demonstrated.

Probably the most intriguing result was the oxidation of polyethylene samples exposed to seawater and UV light. This polymer has been previously thought to be the least reactive of all polymers due to the lack of reactive functional groups. Despite polyethylene terephthalate and polycarbonate both containing oxygens in their molecular structures which should make neighboring bonds weaker along the backbone, polyethylene degraded just as quickly, and produced similar amounts of particulates in laboratory experiments.

Plastics in freshwater and waters with lower salinities had the least if any oxidative degradation. According to literature, this was the obvious scenario as UV light attenuates as soon as it penetrates surface waters. The low temperatures these samples were exposed to also align with what was believed to be another reason why plastic floating debris in water degrades at a more retarded rate than those on land. However, these predictions did not hold true when plastic samples were exposed to seawater.

The increased number of oxygen type bonds observed in FTIR spectra indicate that the S.E.M. images showing roughening of the surface is due to oxidation as samples are exposed to seawater and UV light. Oxidation is also apparent based on quick Energy Dispersive Spectroscopy (EDS) analysis as samples were being imaged by SEM, a technique that offers information as to the type of elements present as well as quantity. Data from these supplemental experiments are presented in Appendix I.

Although a decrease in C-H absorbance is observed in FTIR spectra, oxidative species increase indicating that the hydrogen atoms along the surface are being replaced with hydroxyl groups.

5.2.1 Degradation: Abiotic or Biotic

To address one of my central questions - whether degradation was the primary result of abiotic or biotic processes, surface seawater collected from the coast of Virginia was autoclaved. Autoclaving uses extreme pressures and temperatures which inactivate microorganisms (including bacteria, viruses, fungi, and spores) present in the natural water samples. The removal of microorganisms helps to ensure that only abiotic processes were observed. Despite no observable biofilm that could indicate microbes were present, cultures of water samples (Appendix I) were performed at the end of the experiment and displayed no growth after 72 hour incubation, suggesting that no oceanic bacteria colonized water samples after autoclaving or as the experiment progressed. Lack of microbial growth was also confirmed by SEM imaging which did not show any signs of microbes present on the plastic surfaces observed. Many oceanic bacteria fall in the 1-2 μm range[6] and would be visible by SEM if present. Therefore, the conclusion can be drawn that any biotic processes that may have been present were reduced to a minimum by both autoclaving and the UV light, leaving abiotic processes as the primary degradation pathway.

Interactions between the polymers, UV light, and seawater produced small particulates to flake from the parent material after just a couple of weeks as observed in the laboratory. The production of microplastics (and quite possibly nanoplastics) may have gone unnoticed if laboratory studies were not performed which retained the particulates, allowing their observation. Just visual inspection of the parent material would not have informed the viewer that potentially millions of microplastics were released into the water.

The oxidized surface of plastic polymers exposed to seawater and UV light may be a source of carbon to microbes as well, and may explain why prior investigators observed a slightly elevated population of microbial communities on the surface of marine plastic debris. As the surface begins to degrade, the degree of crystallinity is likely to reduce, as well as the molecular weight. Therefore, microbial communities may take advantage of the abiotic process and continue with degradation, and possibly utilizing it for biomass.

5.2.2 Salts Facilitate Oxidation

The increased absorbance in spectra from FTIR experiments translate to the number of oxidized bonds produced in all polymer types exposed to seawater in lab and field tests. Conclusions can be made using the spectra obtained for LTER and Lynton samples that the degree of oxidation is directly affected by the salinity of the water to which the sample is exposed. Based on laboratory experiments UV light is also a major factor contributing to the amount of oxidation that occurs along the surface of a polymer. Knowing that chloride and sulfate are key components found in seawater, that the pH of seawater is greater than 5 (pH 8.1), and availability of UV light suggest that the proposed mechanism observed in laboratory settings[5] regarding the oxidation of alkanes is likely occurring in natural settings for compounds of similar chemistries.

As stated previously, the biggest surprise was the reaction of polyethylene as it is considered the most inert of the plastics. Production of hydroxyl radicals, facilitated by various salts present and UV light, are likely attacking the surface of these polymers and allowing for quicker oxidative degradation to occur than what has been previously reported.

FTIR spectra all display the production of a broad O-H stretch. The decrease in C-H stretches overtime suggests that fewer C-H groups are present at the surface of polymers and that these groups are being replaced by hydroxyl groups. These assignments were determined based on the relative position of the stretches. The carbonyl stretch in HDPE samples exposed to seawater, are slightly lower in frequency (cm^{-1}) than what is typically observed, and is likely the result of intramolecular hydrogen bonding and an increase in the electronegativity of neighboring atoms. For example, a typical C=O stretch might be observed closer to 1720 cm^{-1} but is downshifted here to 1680 cm^{-1}. This falls near where an alkene stretch should occur but the absence of the sp^2 hybridized C-H stretch (sharp stretch above 3000 cm^{-1}) that would accompany a C=C bond suggests that it is not an alkene but more likely a downshifted carbonyl. Another clue is the roundness of the peak that suggests hydrogen bonding is occurring.

As the surface oxidizes, the topography of the surface becomes more embrittled, fracturing, and releasing small particulates. A schematic depicting the proposed surface chemistry of oxidized HDPE is provided in Figure 5.1. As oxygens are added to the structure, they bring instability and provide sites for

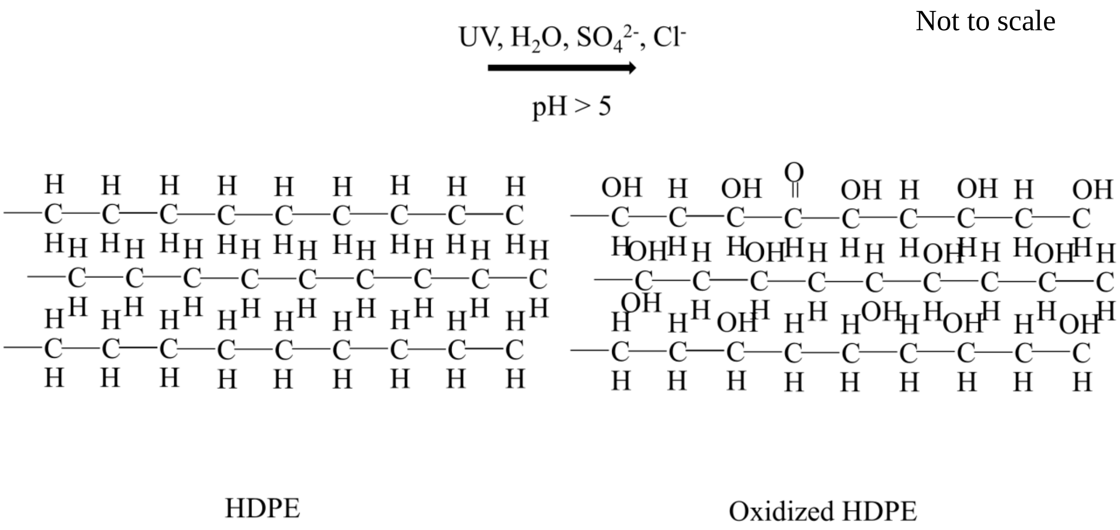

Figure 5.1 Oxidized Surface of HDPE Polymers. This schematic is not to scale but suggests how surface polymers may become oxidized in seawater.

potential cleavage. Knowing FTIR is capable of penetrating samples up to 5 microns, it is proposed that the degree of oxidation also extends at least that distance as observed by spectra. The typical length of a C-H bond is about 1 angstrom (Å) or 0.1 nm. A rough approximation proposes that a 5 micron distance (FTIR penetration depth) translates to 50 C-H bond lengths or that polymers stacked up to 25 layers deep may be subjected to oxidation.

5.2.3 Particulate Sizes Produced

The smallest particle sizes that could be measured with confidence using a 100 micron aperture in the Coulter counter used were 5 microns in diameter. It is possible that particles were present measuring in the namometer range which could not be registered with the affixed aperture. The secondary microplastics produced from the oxidation of the various polymers investigated fell within the 5-10 μm scale and are much smaller than many of the microbeads used in plankton studies[7]. Conclusions can be made that these particulates are small enough to be ingested by a variety of zooplankton. It is not known if the particulates produced from the oxidation will have the same negative effects observed by Cole et al. including issues with adherence and egestion. It may be possible that the oxidation allows the material to be more readily digested with the addition of oxygen but this is mere speculation as it is not known if the molecular weights have been reduced to allow for metabolism.

Millions and perhaps billions of particulates were produced from a single 1 inch square sample. A casual observer may have only noticed that the material became more opaque as it was not obvious that the material lost any significant mass. The introduction of particulates into the water column may impact ecosystems and organisms. Plastic have been a persistent contaminate in our oceans for decades, and it is currently impossible to predict how much secondary microplastics have been produced from the oxidation of these polymers while at sea.

5.2.4 Isotopes as Geochronometers

The covalently bound ^{13}C requires more energy to rupture its bond compared to a ^{12}C bond. In other words, the rate of dissociation for bonds containing ^{12}C atoms should be faster than those containing ^{13}C. This is known as a kinetic isotope effect (KIE). Predictions were made that as a plastic polymer begins to degrade, the ratio of ^{13}C/^{12}C of the bulk material would become more enriched with respect to ^{13}C as more ^{12}C is removed. Experimentally, the opposite appears to occur for laboratory samples. One explanation as to why the residual material seems to become isotopically depleted with respect to ^{13}C is that perhaps as bonds are being broken and formed; it is the lighter isotope that forms the bonds more readily. This would suggest a transfer of carbon atoms is occurring along the surface of the polymers.

The secondary plastics produced measure just slightly more enriched than the residual bulk material. However, the isotopic composition ranges greatly and in some instances matches that of the initial samples. A compilation of random samples collected for the various polymers investigated demonstrated that isotopic composition can vary by more than a couple per mil within polymer type. The deviation exceeds the change observed in the degradation experiment.

Although the trend of depletion in ^{13}C appears real, this small variation may not be significant enough to be useful as a geochronometer as it does not transcend the error observed from sampling. As polymers oxidize material is removed and exposes new layers of virgin polymer. It is reasonable to assume that the newly exposed layer will have an isotope composition close to that of the starting material. Scrapings of the surface would have a net isotope composition of the oxidized material (depleted ^{13}C) and the newly exposed layers (more enriched ^{13}C). Without knowing the proportions of the fractions, it would be challenging to utilize isotopes as a geochronometer.

5.3 Conclusions

Previous studies have suggested that degradation becomes retarded when plastic is submerged in aquatic environments. Reasons for the delay were attributed to attenuated UV light and relatively lowered temperatures found in aquatic systems[2,3]. The metric used however, only measured changes in tensile strength. As discussed in Chapter 2, many degradation processes could occur that remove material, yet leave the residual component stronger due to either new bond formations or cross-linking. Oxidation of the surface for all polymers investigated was observed when samples were exposed to waters containing salt. The greatest oxidation occurred in samples subjected to waters with the highest salinity and exposed to natural sunlight. The data obtained and analyzed from this experiment indicate that degradation of plastic polymers does occur in estuarine or marine systems despite UV attenuation and relatively lowered temperatures. It also suggests that salts help facilitate the degradative oxidation as well.

The processes occurring in our experiment are likely similar to those observed in other. Studies using small alkanes. The autoclaved seawater used and bacterial cultures performed in laboratory studies make evident that these processes are indeed abiotic and cannot be attributed to microbial activity. Literature has reported that even when polymers are doped with starch that only the starch is degraded by microorganisms, and that the remainder of the plastic polymer is left unperturbed[8]. Some speculation was made regarding specialized marine bacteria capable of degrading plastic but offered no concrete evidence, providing only a slight increase in population compared to surrounding water as primary reasoning[9]. Another recent article in *Science* reported the isolation of a specialized bacterium capable of producing an enzyme that degrades polyethylene terephthalate (at elevated temperatures), allowing assimilation to occur[11]. The investigators were able to isolate the genes required for the enzyme production after noticing subcultures lost the ability. Although this finding is remarkable, it should be noted that the PETE material the bacterium were exposed to were not the highly crystallized polymers present in consumer goods but the low-crystalline PETE fibers which were trace contaminants in sediment, soil, wastewater, and sludge from a PETE recycling site[11].

As abiotic processes occur, smaller molecular weight material, lacking in crystallinity, is likely produced that can be assimilated by microbial communities. As most plastic does not offer a nitrogen source, any microorganisms will need to have the capability of fixing nitrogen themselves or live symbiotically with others that can provide the additional nutritional requirements for survival. The decreased crystallinity and molecular weight as these polymers undergo oxidative degradation when exposed to seawater and UV light may provide a new carbon source however.

The secondary plastics produced from the oxidation of polymers contaminate the water. The smallest sizes were 5 microns in diameter, much smaller than the microbeads recently used to investigate plankton ingestion of microplastics[7]. It is not known if the oxidized material formed is benign or harmful to primary consumers as the microbeads were reported by Cole *et al.*. Although Cole *et al.* studied zooplankton, microplastics may adhere to external appendages or flagella, limiting mobility and potentially threaten primary producers in this way as well.

The sheer volume of secondary material produced means that more polymer surface area is available to absorb toxic persistent organic pollutants (POP) contaminating ocean waters. These POP compounds have been shown to concentrate in plastic material allowing bioaccumulation to occur along trophic levels[10]. If digestion of microplastics does not kill the organism, then the levels of POP absorbed may.

A surprising result from this study was that despite the low reactivity reported for polyethylene in literature, these polymers appear to degrade at a rate similar to those containing oxygen in their backbone structures. It was postulated that the additional oxygens would cause areas of instability around these bonds in PETE and PC. The production of plastic particulates recorded for each polymer by the Coulter counter was of similar magnitudes. Polycarbonate did produce roughly 15 % more particulates than the other two, but PETE only produced 4 % more particulates. Oxygen containing polymers do degrade producing marginally greater secondary material compared to hydrocarbons.

The potential use of isotope composition as a geochronometer seems unlikely based on this study. The oxidized surface flakes away, leaving a virgin layer possessing the original isotope ratios which is likely the reason for the large variations observed in particulate isotope compositions. This challenge would also present itself in SEM and FTIR analysis as well. During the second sampling (8.5 months) and analysis of LTER samples, oxidation was still quite apparent (Appendix I) but the peak absorbance observed were not as strong as the first visit (5 month). The constant turnover of oxidized and exposure of virgin polymer add to the difficulty in determining a proper technique which could allow stable isotope composition change to be used as a geochronometer.

5.4 Future Research

Additional laboratory studies varying in salt content and concentration should be performed to determine if chloride and sulfate are indeed the necessary reagents for the hydroxylation to occur. Field studies in limnetic systems should be conducted to determine if other degradative processes may be occurring. It is possible that those systems containing high organic content may provide reactants that could affect the surface chemistry of polymers. For example, hydroxyl radicals can be produced during the oxidation of ferrous iron by hydrogen peroxide (H_2O_2)

Although we did not observe any oxidation in our freshwater laboratory experiments, freshwater systems with sufficient UV exposure may be able to produce enough hydroxyl radicals to react with polymers.

Further chemical characterization of the secondary particulates formed in laboratory experiments could offer insight as to the mechanism(s) responsible for the oxidative products. Molecular weight (MW) determination has previously been achieved using a number of methods including membrane osmometry, gel permeation chromatography, viscosity analysis, or mass spectrometry. Advancements in Nuclear Magnetic Resonance (NMR) of large organic polymers has increased substantially over the past few years, offering an easier alternative to determine MW as well as offering information as to bond linkage, and monomer formula weights. Knowing the molecular weight (average chain length) can answer whether polymer surfaces are solely being oxidized or are polymers actually degrading into smaller molecular weight compounds.

5.5 Summary

Plastic endures in our oceans, taking decades to degrade in order to form secondary microplastics based on prior studies[10]. The data produced as a result of this work have demonstrated that interactions do occur between the common plastic materials, seawater, and UV light. These interactions not only oxidize the surface of these polymers but produce micro- and possibly nanoplastics within weeks. The extent of oxidation and the concentration of salts present are strongly correlated. Although the bulk of material persisted after the completion of our experiments, micro-particulates were released into the surrounding water.

Anecdotal tales exist from ocean voyagers who have travelled the oceans extensively. Descriptions of a gooey layer persisting deep in water columns have been relayed. Perhaps the strange layer of milky material is a collection of secondary plastic material, a residue produced from decades of oxidizing plastic debris that has entered into our oceans. With the new discovery that plastic does interact with seaater and UV light, a greater attempt to remove and and prevent these materials from entering these marine waters is needed. For the plastic already present, further studies during removal processes may help elucidate further problems that may arise from the the particluates produced that may have been previously overlooked.

5.6 References

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Appendix I.

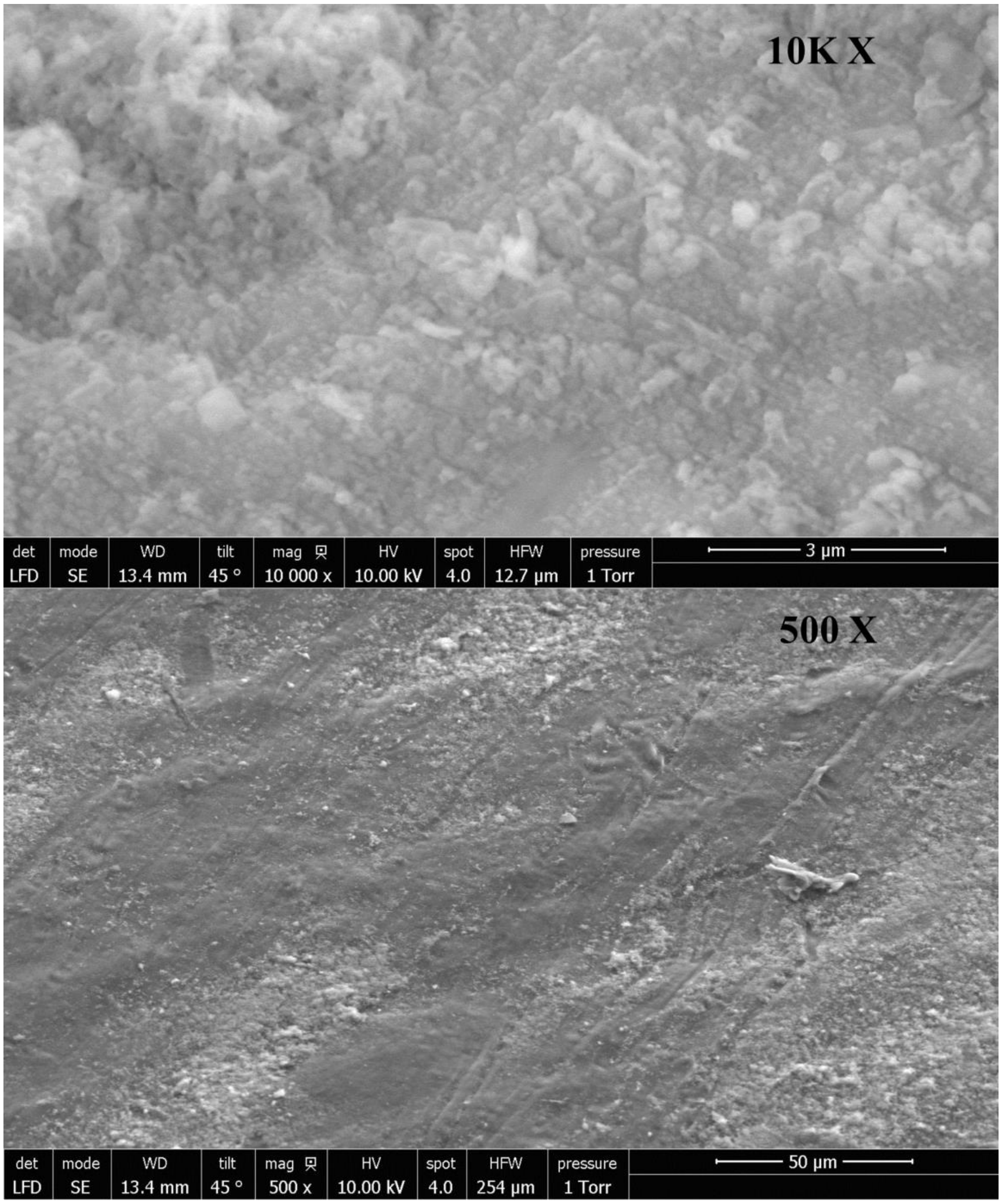


Figure S1. SEM Image of HDPE After 15 Months of Lab Experiment.

Magnification was 10,000 X and 500 X. These images depict the roughness of the surface after oxidation.

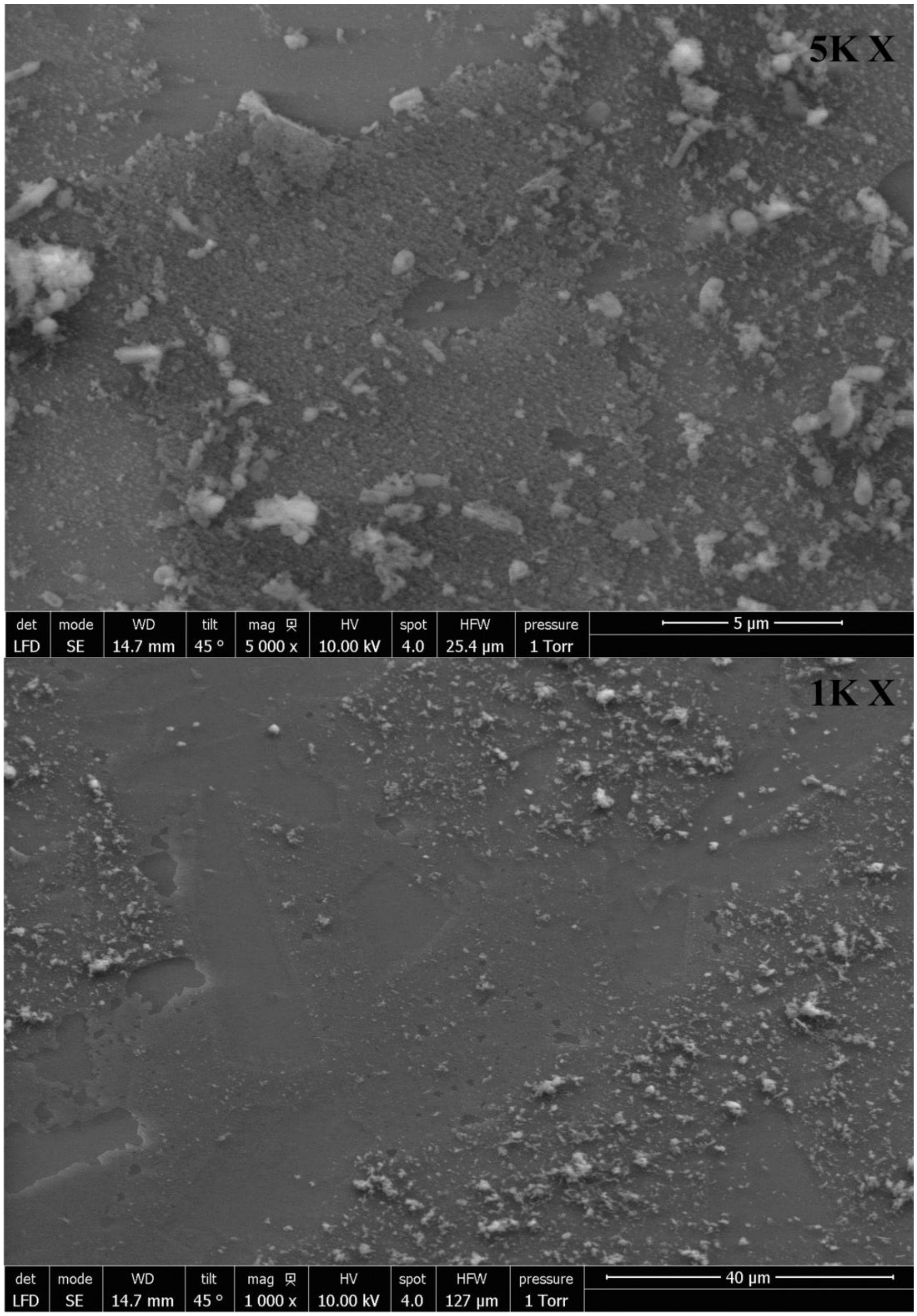


Figure S2. SEM Image of PETE After 15 Months of Lab Degradation. Surface changes and removal of surface layers are obvious in multiple sections. Magnifications are 5000 X and 1000 X, respectively.

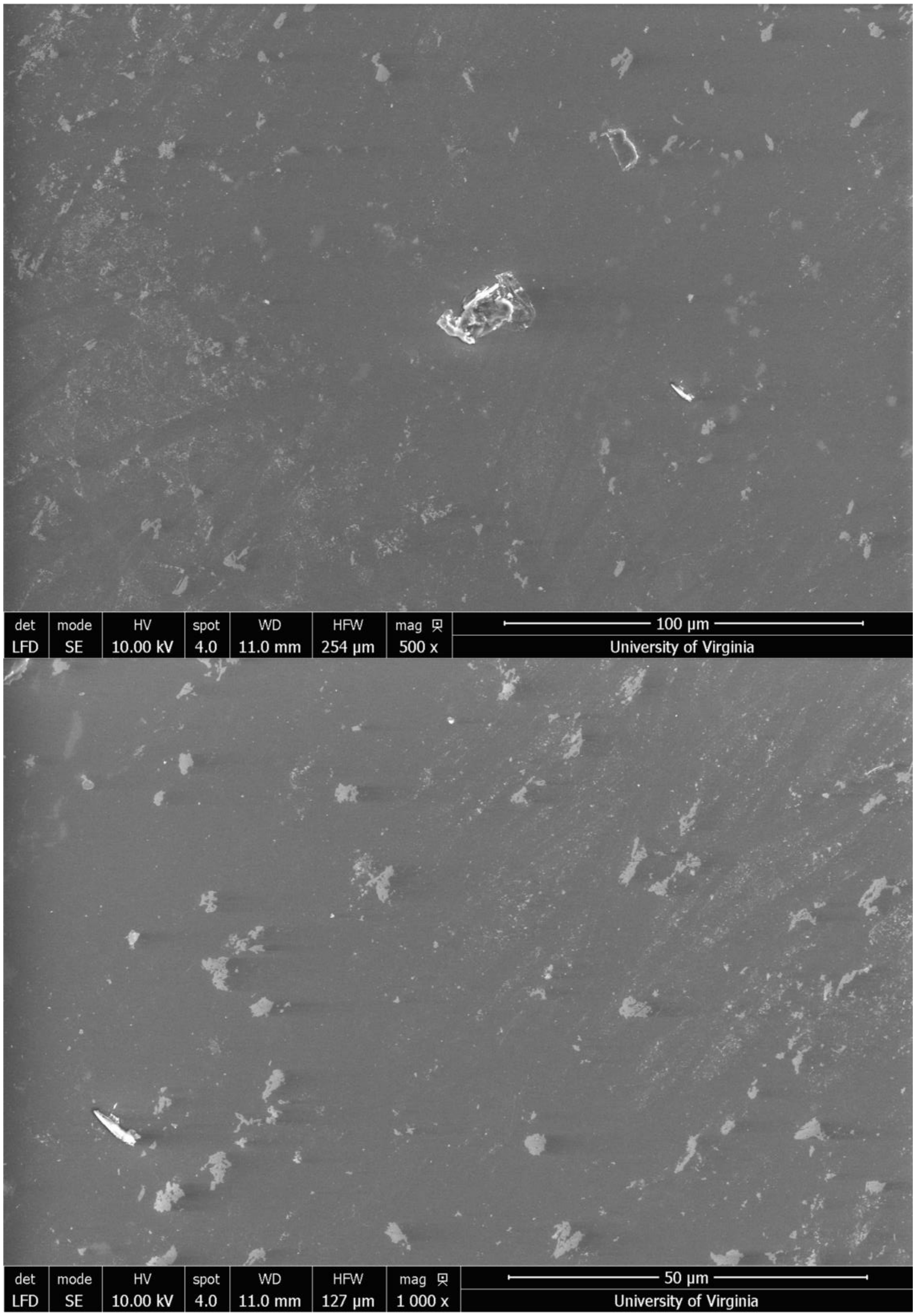


Figure S3. SEM Image of Polycarbonate After 5 Months of Degradation at LTER Site. Similar to what is observed for the other polymers investigated, there are obvious signs of degradation and particulates present on the surface.

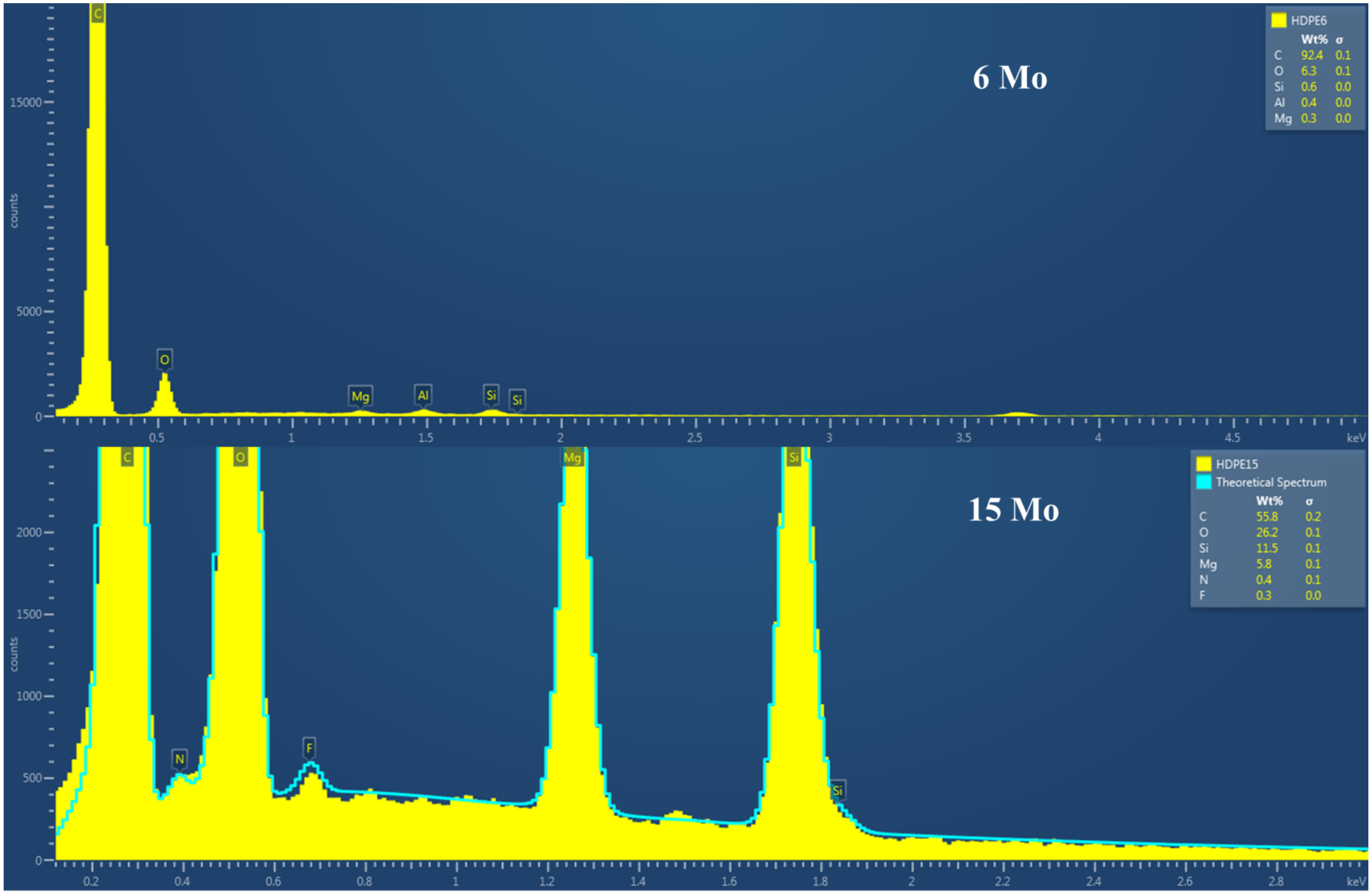


Figure S4. Energy Dispersive X-ray (EDS) Spectra of HDPE After Degradation. A. Six months and polymer displays 6.3% oxygen content and 92.4% carbon. B. After 15 months the oxygen content has increased to 26.2 % and carbon has dropped to 55.8%.

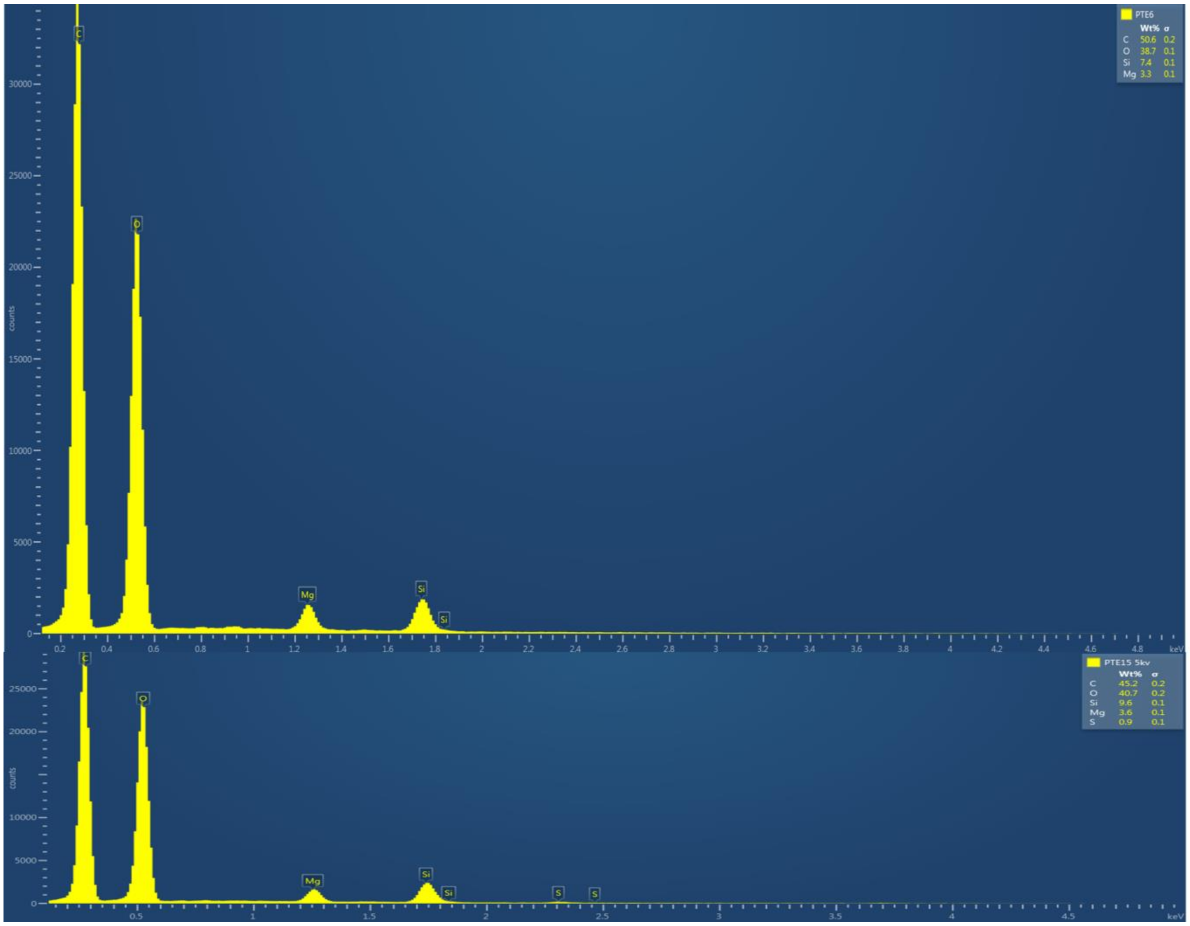


Figure S5. Energy Dispersive X-ray (EDS) Spectra of PETE Polymers After Degradation. The molecular structure of PETE comprises of oxygen. At 6 months the oxygen content registers at 38.7 Wt.% and carbon measures at 50.6 Wt. %. After 15 months the EDS spectra (bottom) displays 40.7 Wt. % for oxygen and 45.2 Wt. % for carbon.

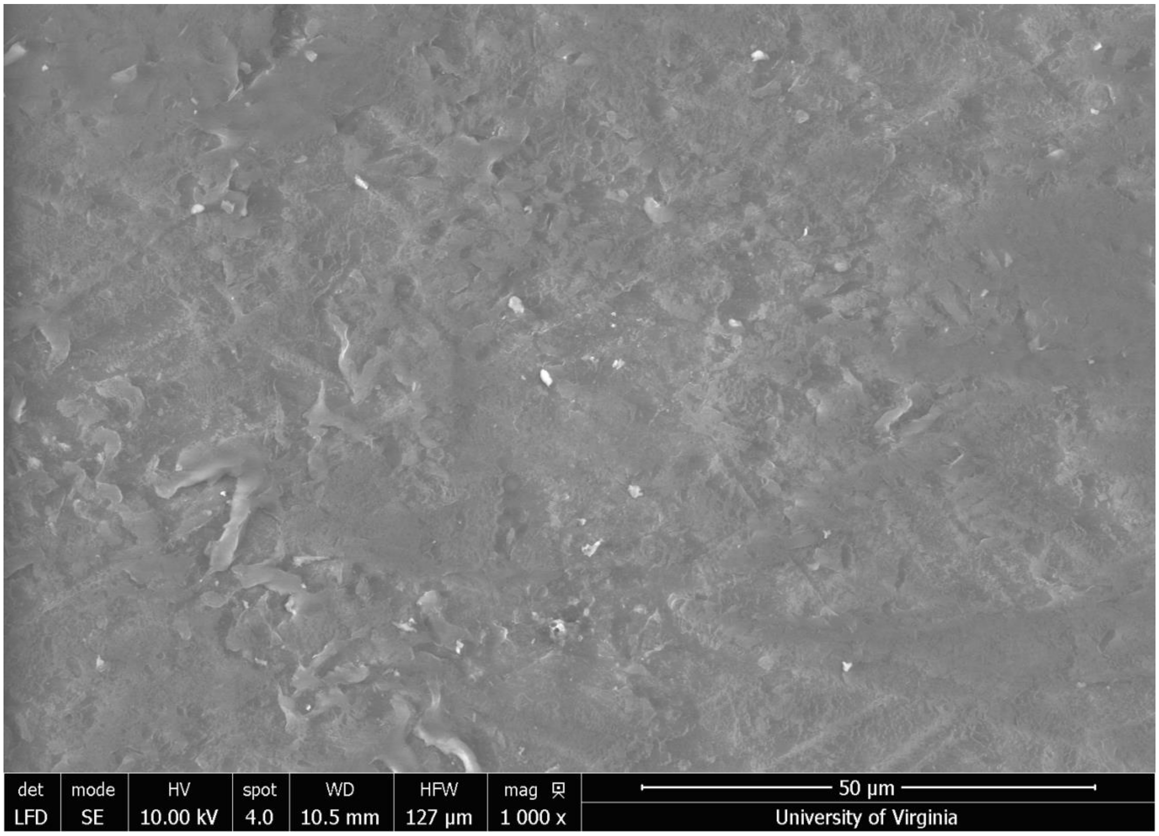


Figure S6. SEM Image of Degraded Polyethylene After 5 Months at LTER Site. Similar to what is observed in polyethylene polymers in lab experiments, the surface topography is rough.

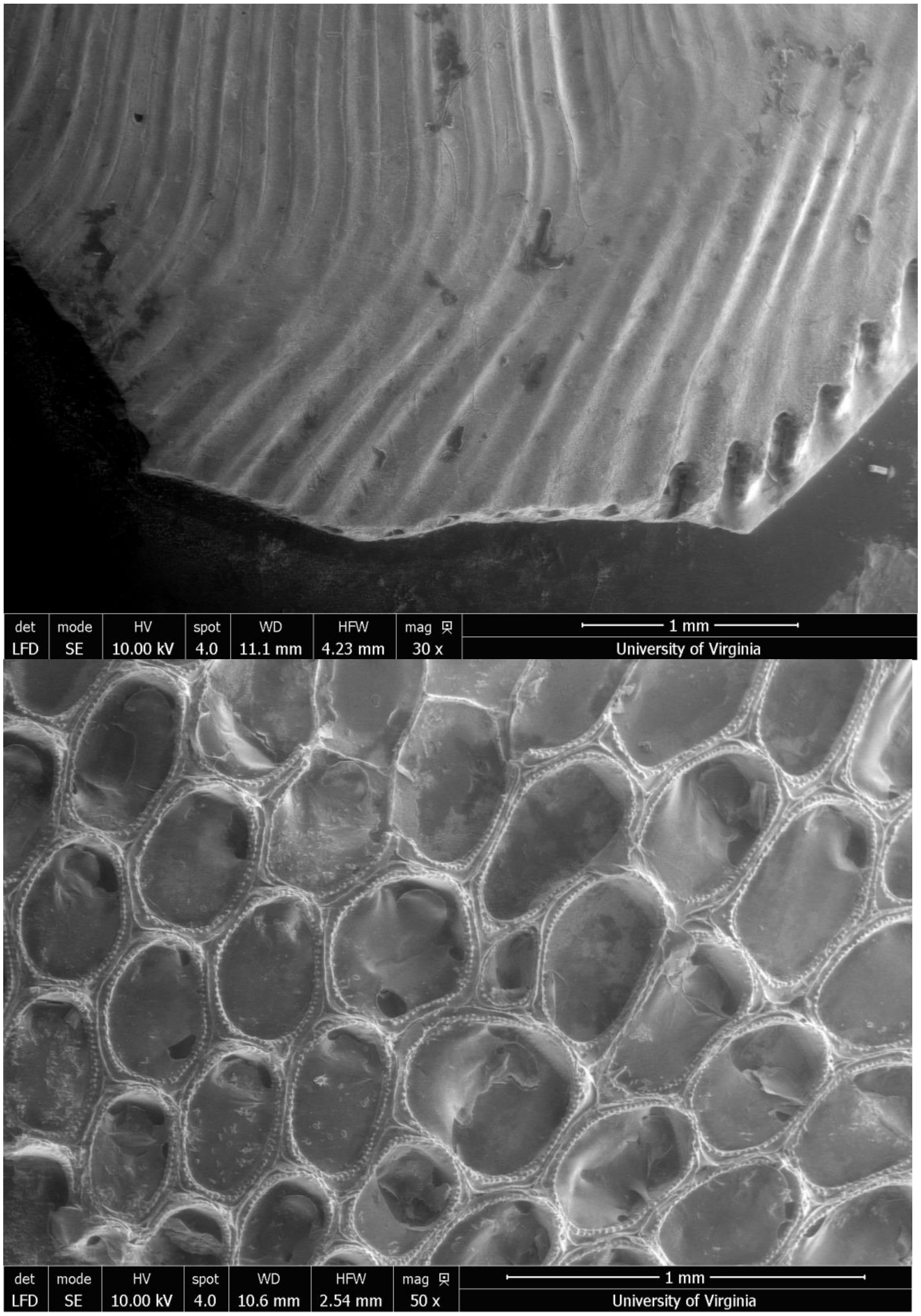


Figure S7. SEM Image of Biota Remains Found on the Surface of Some Polymers Retrieved from LTER. The shell formation, likely from an oyster, was present on some of the samples collected from the LTER site (TOP). Possible egg sacs were also spotted on one of the samples surface (BOTTOM).

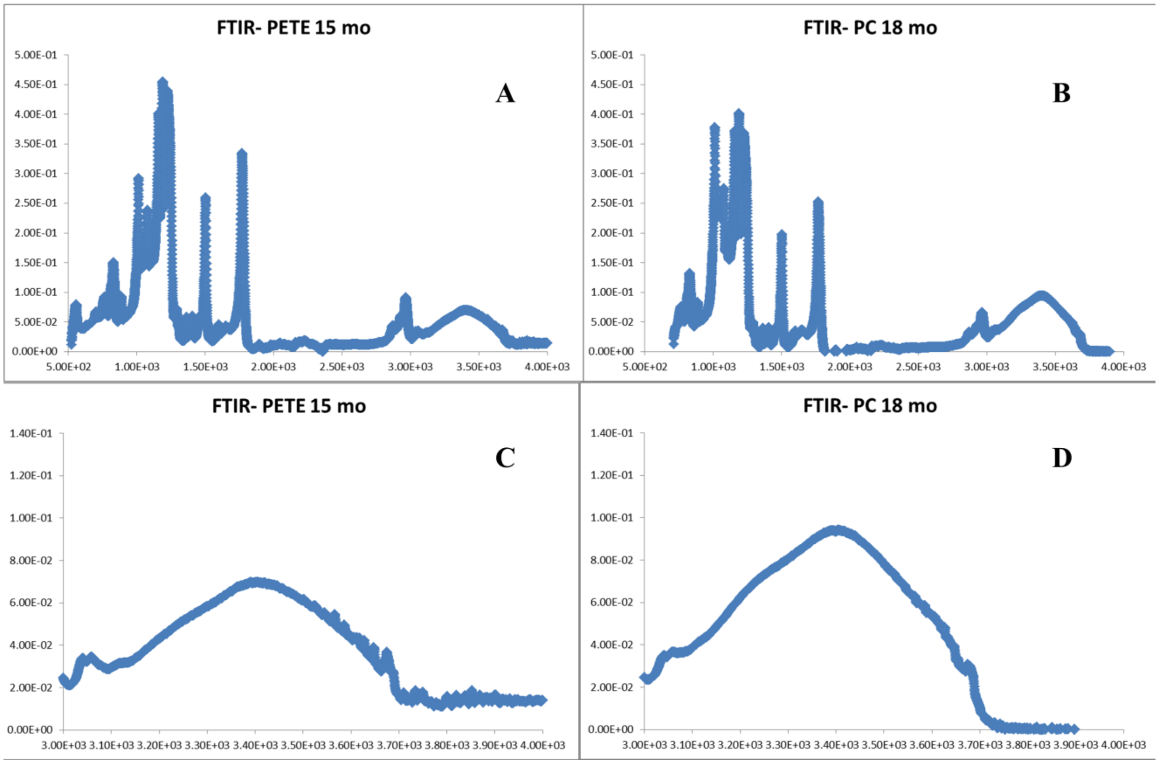


Figure S8. Infrared Spectra of Polycarbonate Samples Post Degradation. All spectra are displayed with wavelengths opposite from those reported within Chapter 4. A and B represent the entire spectra obtained for PC after 15 and 18 months, respectively. C and D are zoomed in images of the hydroxyl peaks.

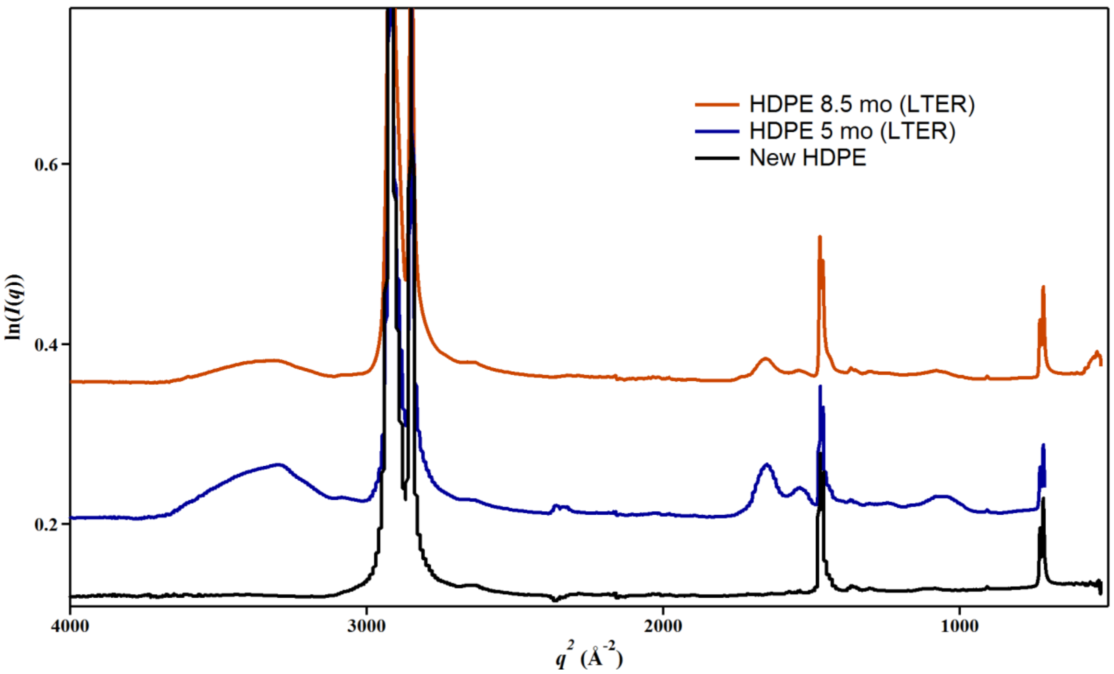
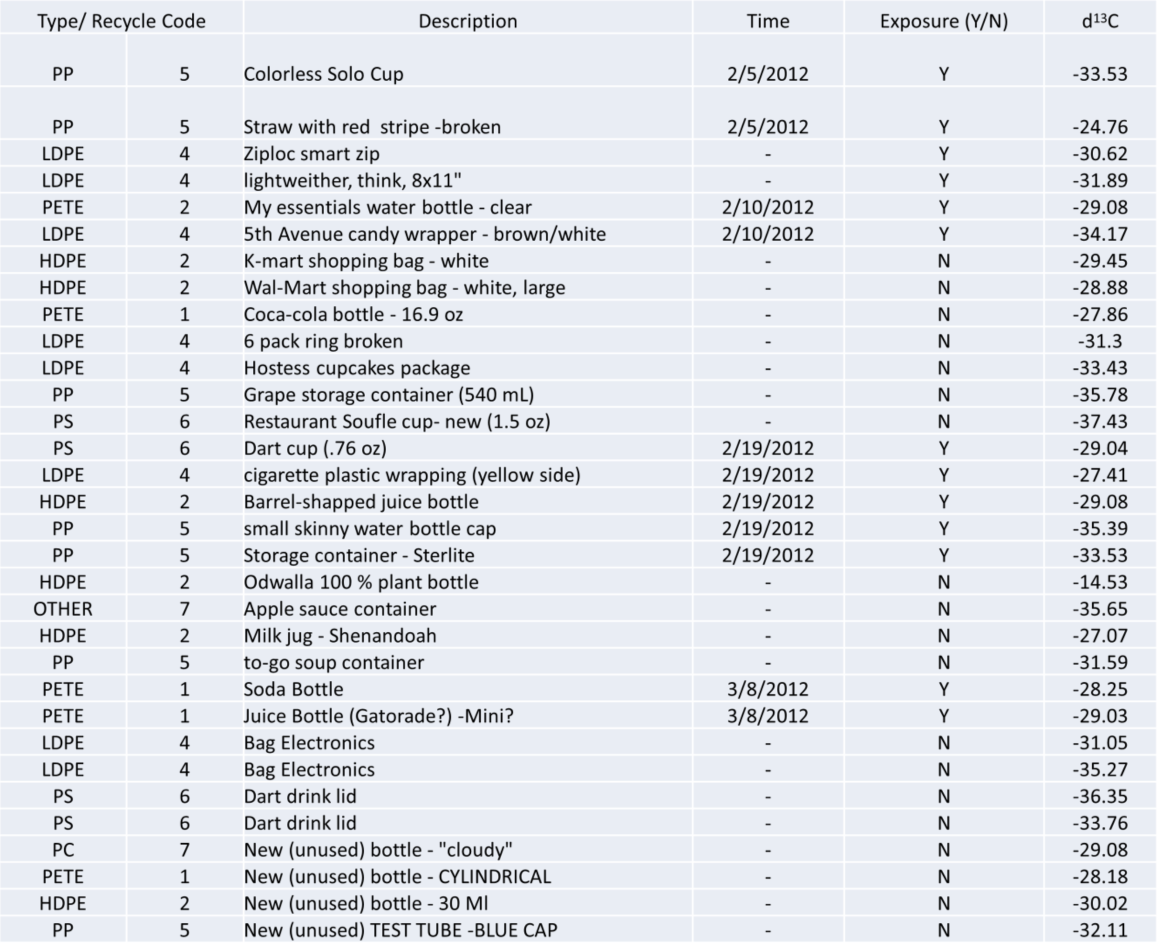


Figure S9. Fourier Transform IR Spectra of HDPE from LTER Experiment. The formation of O-H, C=O, and C-O bonds are observed after exposure to the 26 ‰ (avg.) salinity waters found at the LTER. There is a slight decrease in the average absorbance peaks for the three oxygen containing stretches. This is likely attributed to the changing surface as oxidized material is removed and newer virgin polymer is exposed.



Type/ Recycle Code		Description	Time	Exposure (Y/N)	d^{13}C
PP	5	Colorless Solo Cup	2/5/2012	Y	-33.53
PP	5	Straw with red stripe -broken	2/5/2012	Y	-24.76
LDPE	4	Ziploc smart zip	-	Y	-30.62
LDPE	4	lightweither, think, 8x11"	-	Y	-31.89
PETE	2	My essentials water bottle - clear	2/10/2012	Y	-29.08
LDPE	4	5th Avenue candy wrapper - brown/white	2/10/2012	Y	-34.17
HDPE	2	K-mart shopping bag - white	-	N	-29.45
HDPE	2	Wal-Mart shopping bag - white, large	-	N	-28.88
PETE	1	Coca-cola bottle - 16.9 oz	-	N	-27.86
LDPE	4	6 pack ring broken	-	N	-31.3
LDPE	4	Hostess cupcakes package	-	N	-33.43
PP	5	Grape storage container (540 mL)	-	N	-35.78
PS	6	Restaurant Soufle cup- new (1.5 oz)	-	N	-37.43
PS	6	Dart cup (.76 oz)	2/19/2012	Y	-29.04
LDPE	4	cigarette plastic wrapping (yellow side)	2/19/2012	Y	-27.41
HDPE	2	Barrel-shapped juice bottle	2/19/2012	Y	-29.08
PP	5	small skinny water bottle cap	2/19/2012	Y	-35.39
PP	5	Storage container - Sterlite	2/19/2012	Y	-33.53
HDPE	2	Odwalla 100 % plant bottle	-	N	-14.53
OTHER	7	Apple sauce container	-	N	-35.65
HDPE	2	Milk jug - Shenandoah	-	N	-27.07
PP	5	to-go soup container	-	N	-31.59
PETE	1	Soda Bottle	3/8/2012	Y	-28.25
PETE	1	Juice Bottle (Gatorade?) -Mini?	3/8/2012	Y	-29.03
LDPE	4	Bag Electronics	-	N	-31.05
LDPE	4	Bag Electronics	-	N	-35.27
PS	6	Dart drink lid	-	N	-36.35
PS	6	Dart drink lid	-	N	-33.76
PC	7	New (unused) bottle - "cloudy"	-	N	-29.08
PETE	1	New (unused) bottle - CYLINDRICAL	-	N	-28.18
HDPE	2	New (unused) bottle - 30 Ml	-	N	-30.02
PP	5	New (unused) TEST TUBE -BLUE CAP	-	N	-32.11

Table S1. Isotope Compsotion of Random Plastic Samples Collected. Various samples of plastic material display differences in their respective isotope composition among polymer type. Polymers used in this study such as HDPE vary by more than 2 per mil while PC can vary up to over 5 per mil.

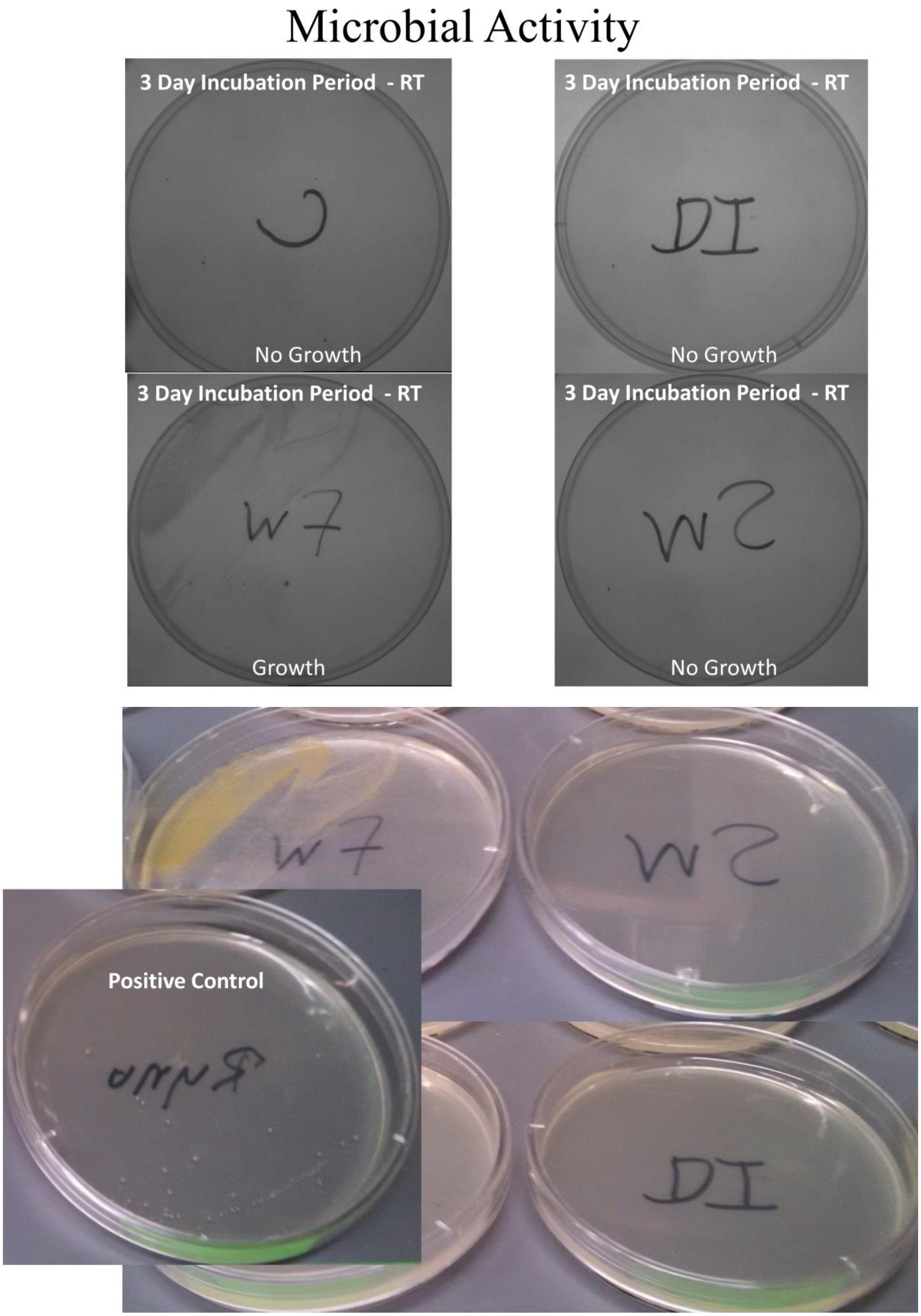


Figure S10. Bacteria Culture Plates of Seawater and Freshwater from Laboratory Experiments. (Top) Plates observed under UV light show growth only in the freshwater sample. (Bottom) Plates viewed in natural light.