2 Environmental and Socio-Economic Effects

2.1 Description of the Problem

In its quest to solve a big environmental problem, namely food waste, the packaging industry created another one. Flexible plastic packaging offers many benefits: extends food shelf life and minimizes spoilage; reduces waste by preserving and protecting products until they are consumed; reduces material use; minimizes overall size and weight; lowers shipping costs; and generates fewer greenhouse gases (GHG) than alternative packaging. At the same time, the growth in consumption and disposal of flexible plastic packaging raises environmental concerns. Flexible plastic packaging, like rigid plastic packaging, is derived from nonrenewable resources, and increased amounts of waste end up in landfills and the environment.

It is estimated that about 300 million metric tons (MMT) of plastic are produced annually, and half of this is used once; about 40% of the total sum of the plastic produced is used for packaging. A large part of that amount ends up in nature [1]. The uncontrolled disposal of flexible plastic packaging, and the lack of legislation and effective recycling technologies can have dire consequences on the environment. Because of its longevity, sheer volume, and difficulty to be recycled profitably, plastic packaging in general, and flexible packaging in particular, has become a global environmental problem [2]. According to Barlow and Morgan [3] the environmental impact of packaging is more dependent on material volume than recyclability.

Thin-film products, such as plastic wrap and shopping bags, are a particular subset of flexible packaging items that are frequently littered. These items are extremely light and mostly enter the marine environment through wind transfer into oceans or rivers when incorrectly or poorly disposed of [4]. Another subset of flexible packaging is pouches and sachets. Both of them are currently used in the packaging of a wide variety of products, from food and beverage to cleaning supplies and other household items. Despite their numerous benefits, pouches and sachets pose a serious waste problem. These multilayer flexible packaging materials are used once and thrown away, ending up in landfill or in

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waterways and oceans [5]. It is estimated that single-use plastics, such as crisp packets and sweet wrappers, food containers, and cutlery, make up about 60% of the plastics found in beaches worldwide [6].

Most types of flexible plastic packaging have complex structures (e.g., laminates), and with the exception of clean monolayer polyethylene films, they are not currently recycled and have little or no economic value.

In spite of the damage flexible plastic packaging causes to marine ecosystems and human activities, such as fishing, shipping, recreational activities, and tourism, there is no much literature on the fate of these plastic items in seawater [7].

Bioplastics (including biodegradable and/or biobased plastics) are alternative materials to conventional plastics (e.g., polyolefins) in flexible packaging with the potential to improve environmental performance. However, biodegradable plastics might be half the solution, because the favorable degradation conditions required for the composting of these materials are not always achieved in the sea and other natural environments. A further complication arises from the fact that although the bioplastics should degrade rapidly in natural environments, they should not degrade during their shelf and service life [8]. Biodegradable plastic packaging may also release methane when disposed of in a landfill, whereas nonbiodegradable packaging is inert. Further, biobased polymers, which are not biodegradable, have to be recycled in the same way as their counterparts [9].

2.2 Degradation of Plastics in the Environment[1]

2.2.1 Environmental Degradation Modes

Degradation is the partial or complete breakdown of a plastic under the influence of one or more environmental factors, such as water, heat, light, microbes, and mechanical action. There are five degradation modes by which plastics can degrade in the environment:

- hydrolytic degradation;
- thermooxidative degradation;
- photodegradation;

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[1] This section is based on Chapter 3 of the book "Management of Marine Plastic Debris", Niaounakis M. William Andrew-Elsevier, 2017.

- biodegradation; and
- mechanical degradation.

In the diverse marine habitats, including beaches, the sea surface, the water column, and the seafloor, plastic debris is exposed to different environmental conditions that either accelerate or decelerate the degradation of plastics. The degradation of plastics in the sea or on the beach is affected by many factors, such as exposure time, the intensity of UV radiation, temperature, biological degradation, and physical abrasion. The degradation is more intensive on the beach and to a lesser degree at the sea surface as the result of solar UV-radiation-induced photooxidation. The degradation of plastic materials occurs slower in the sea than on land, because seawater, which is a good heat sink, inhibits the thermal loading that accelerates degradation on land. In the water column, plastics degrade very slowly, especially at the seafloor [10].

The length of time that the various plastic materials persist in the sea is not reliably known [11]. The degradation times of most flexible plastic debris, such as plastic bags, films, and six-pack rings, is estimated to be tens of years. Most of the estimated life spans of the various plastic debris are hypothetical, and they do not reflect the actual lifetime of plastic debris in the marine environment. Most of these estimations are based on degradation studies of various plastics exposed in different environments and are focused on the early stages of degradation that impact the useful lifetime of the product [12]. Furthermore, there is limited or fragmented information on the weathering of plastic debris floating in seawater, stranded on shorelines, submerged in seawater or sediment [13,14]. The effects of variables, such as mechanical impact, salinity, temperature, hydrostatic pressure, presence of pollutants, such as oil in seawater and biofouling (reducing UV exposure) on the degradation rates of various types of plastic items are virtually unknown [12]. While a pure polymer can be more degradable than others, its overall degradation behavior can be altered by the incorporation of additives (e.g., antioxidants, UV stabilizers, and the like), blending of other polymers, after-treatment processing, etc.

2.2.2 Hydrolytic Degradation

Polyolefins, including polyethylene, polypropylene, and most of their copolymers, are hydrophobic and are not expected to hydrolyze in the water environment. In general, polymers with pure carbon backbones are particularly resistant to most types of degradation, including hydrolysis, while vinyl polymers carrying aromatic carbocyclic rings, such as polystyrene tend to be more resistant to hydrolysis [15].

Polymers that contain heteroatoms in the backbone, including various polyaddition or condensation polymers, such as polyesters and polyamides show higher susceptibility to hydrolysis. While this is often true, aromatic polymers tend to be resistant to degradation, despite the presence of bonds that are normally readily hydrolyzed [15,16]. Poly(ethylene terephthalate) (PET) is a typical example of such a polymer; the ester bonds that form part of the polymer chain are potentially hydrolyzable, however, due to its aromatic groups, the polymer is essentially nondegradable under normal conditions [17].

Hydrolysis is usually not a significant mechanism in seawater for the degradation of most commercial fossil fuel-derived plastics [13].

2.2.3 Thermooxidative Degradation

The temperatures and oxygen levels encountered in seawater are not adequate to initiate thermooxidative degradation. The relatively low temperatures and low oxygen concentration in water environments, as well as the biofouling of plastics, inhibit the heat build-up and retard the thermooxidative degradation [13,18]. The situation is different when the same plastic is stranded on the beach where it is subjected to higher temperatures. Certain plastics will fragment more rapidly in regions subject to higher temperatures, such as those in tropical beaches. High temperatures increase the rate of chemical reaction, generating greater degradation.

Given the relatively low specific heat of sand (664 J/kg-°C), sandy beach surfaces and the plastic debris on it can heat up to temperatures of about 40 °C in summer. In dark-colored plastic debris, the heat build-up due to solar infrared absorption can raise the temperature even higher [19]. The light-initiated oxidative degradation is accelerated at higher temperatures by a factor depending on the activation energy (Ea) of the process; for example, for an Ea of about 50 kJ/mol, the rate of degradation doubles when the temperature rises by only 10 °C [13].

2.2.4 Photodegradation

Photodegradation is the dominant environmental degradation mode of most plastic debris. The ultraviolet (UV) radiation portion (400−10 nm) of sunlight plays a key role in plastic degradation through photooxidation. It is primarily the UV-B radiation (280−315 nm) in sunlight that initiates the photooxidative degradation of common polymers, such as low-density polyethylene (LDPE), high-density polyethylene (HDPE, polypropylene and aliphatic polyamides (nylons) that are exposed to the marine environment. The mechanism of photodegradation is one of photooxidative degradation rather than of direct photolysis [20]. Once initiated, the degradation can also proceed through thermooxidative mechanisms for some time without the need for further exposure to UV radiation. The autocatalytic degradation reaction sequence can progress as long as oxygen is available to the system. In photodegradation, the molecular weight of the polymer is decreased, and oxygen-rich functional groups are generated in the polymer. Higher temperatures and oxygen levels both increase the rate of fragmentation, as does mechanical abrasion [21]. However, the other types of environmental degradation are several orders of magnitude slower compared to UV-induced degradation.

The initial photooxidative degradation of plastic debris usually starts at the outer surface of the plastic [13]. This localized degradation is because of the high extinction coefficient of UV-B radiation in plastics, the diffusion-controlled nature of oxidation reaction [22] and the presence of fillers that impede oxygen diffusion in the plastic [23,24]. The deterioration of the surface takes the form of discoloration, pitting, crazing or cracking, erosion or embrittlement. This degraded fragile surface is susceptible to fracture by stress, induced by humidity or temperature changes, as well abrasion against sand [25], which may result in the fragmentation of plastic into smaller pieces [13,26].

The extent of photodegradation depends primarily on the presence within the polymer of light-absorbing structures. Polymers containing aromatic or carbonyl groups in their backbone are likely to absorb the sunlight (wavelength, $\lambda > 290$ nm), and usually become photosensitive materials. On the other hand, polymers that do not possess any chromophore group in their backbone, absorbing above 250 nm, like polyolefins, still appear to be degraded by sunlight during outdoor exposure. This finding implies that those polymers must contain chromophore groups absorbing the solar radiation either as impurities (catalyst residues, organic contaminants, and thermal oxidation products, such as hydroperoxides) or as functional groups incorporated into the polymer backbone [27]. Actually, many aliphatic polymers are more sensitive to UV radiation than most aromatic polymers in spite of the fact that the latter is capable of absorbing much more solar UV radiation; for example, polyolefins and poly(vinyl chloride) (PVC) are less stable than aromatic polyesters, like PET [28].

PVC exhibits the highest sensitivity toward UV radiation. The UV sensitivity of PVC is attributed mainly to the C–Cl bond, which together with the saturated bonds C—C and C—H, absorb in the far ultraviolet region, at wavelength below 200 nm. PVC articles exposed to UV radiation degrade and become embrittled and readily crack or shatter. Moreover, as photodegradation is primarily a superficial process due to the limited penetration of UV radiation, the surface properties of the degraded polymer are substantially modified. Most commercial PVC products are effectively protected by the incorporation of adequate stabilizers [27].

Polypropylene is liable to chain degradation from exposure to UV and will become brittle and weak if left for long periods in the sun. Degradation shows up as a network of fine cracks and crazes that become deeper and more severe with exposure over time [29].

Little is known about the fate of plastics that sink to the seafloor. It is postulated that the plastics at the seafloor are largely impervious to photodegradation once shielded from UV radiation [30]. The lack of UV-B (rapidly attenuated in seawater) to initiate the process, the low temperatures and the lower oxygen concentration relative to that in air, makes extensive degradation far less likely than for the floating plastic debris [31]. On the other hand, plastic debris stranded on the beach, and exposed to high levels of UV radiation, degrade more readily [32,33].

In most cases, the photodegradation of plastics is accompanied by a change in color turning them into yellow, brown, or even white, or acquiring gray tons [34—38]. Yellowing of plastic debris is most likely the result of quenching, which derives from the capture of free radicals on the plastic surface by the action of UV light stabilizers, particularly phenolic antioxidants, which absorb UV radiation, quench the free radicals that are generated in the polymer and prevent oxidation. The action of quenching leads to the formation of yellow byproducts, such as quinonoid structures [35]. Yellowing may constitute a qualitative measure to determine exposure time in the marine environment [36].

For white plastics, it should not be assumed that this color pertains exclusively to plastic debris with a short residence time in the marine environment. Plastic debris, which appears to have turned white, may correspond to plastics that have been exposed for a long period of time in the marine environment and have been subjected to extensive degradation [34].

Pigmented plastics usually lose some of their original colors and become lighter. Sometimes, surface darkening gives plastics a gray ton, likely owing to the progress of oxidation that fosters small cracks and holes. These facilitate the adhesion of various kinds of materials that end up darkening the plastic surface. In general, paints, pigments, and dyes on plastic surfaces provide protection from UV radiation and diminish the extent of photooxidation. Photooxidative processes, however, were found to degrade polymers when artificial fractures (scoring) were induced on colored polymer surfaces [39].

2.2.5 Biodegradation

Most conventional polymers used in packagings like polyethylene, polypropylene, PET, nylons, and PVC have very slow biodegradation rates, and thus, remain semi-permanent when disposed of in the sea [10]. The microbial species that can metabolize these polymers are rare in nature.

Several features of polyethylene make it resistant to biodegradation. Among these features are: (1) polyethylene's highly stable C−C and C−H covalent bonds; (2) its high molecular weight, which makes it too large to penetrate the cell walls of microbes; (3) its lack of readily oxidizable and/or hydrolyzable groups; and (4) its highly hydrophobic nature [40,41].

The biodegradation of polyethylene can be compared with the biodegradation of paraffin. The biodegradation of the latter starts with the oxidation of the alkane chain to a carboxylic acid, which later undergoes β-oxidation [42]. An initial necessary abiotic step is the oxidation of the polymer chain; once hydroperoxides have been introduced, a gradual increase in keto groups in the polymer is followed by a decrease in keto groups when short-chain carboxylic acids are released as degradation products to the surroundings [8−10]. Photooxidation enhances the rate of biodegradation of polyethylene. It leads to the scission of the main chain in the polymer, thereby leading to the formation of low molecular weight products. This results in the generation of large surface area due to its embrittlement and also a greater degree of hydrophilicity due to the introduction of carbonyl groups. All these factors further promote the biodegradation of polyethylene [43]. However, the biodegradation proceeds at a very slow rate. A laboratory study reported degradation rates of LDPE of 1, 1.5, and 1.75 wt% after 30 days of incubation with *Kocuria palustris* M16, *Bacillus pumilus* M27, and *Bacillus subtilis* H1584, respectively, isolated from marine waters present at high microbial densities [44]. A field study reported degradation rates of LDPE, HDPE, and polypropylene after 1 year in seawater off the Indian coast of 1.9 w, 1.6 wt, and 0.65 wt%, respectively [45].

Synthetic polyamides, and in particular aliphatic polyamides (nylons), are resistant to degradation in the natural environment because of the high symmetry of their molecular structures and strong intermolecular hydrogen bonds [46].

Unlike fossil fuel-derived plastics, which have very slow rates of biodegradation, biodegradable polymers have been designed to degrade in compost under specific conditions within a certain time span. However, the extent to which these bioplastics decompose in the sea has not been adequately investigated. There is no concrete evidence that they will degrade readily in seawater [47], where the average temperature of the ocean surface water is about 17 °C, while the deep ocean water is between 0 and 3 °C at least in the time span foreseen by the relevant international standards [7]. Most bioplastics, such as PLA, are heavier than seawater and will sink, where the low water temperature, the lack of UV, and the lower oxygen concentration are expected to further retard their degradation. Biodegradable plastic packaging may also release methane when disposed of in a landfill, whereas nonbiodegradable packaging is inert.

The most versatile bioplastic, poly(lactic acid) (PLA), degrades slowly in water over a period from several weeks up to about 1 year. Compared to water-soluble or water-swelled polymers, which fall apart quickly in water, PLA-based polymers can only be classified as moisture-sensitive because they degrade slowly. For instance, after a month's immersion in water, PLA and certain copolymers thereof show no reduction in molecular weight; but after 6 months, the physical properties drop significantly.

Poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-*co*-3-valerate) (PHBV) films disposed of in seawater disappeared within 8 weeks [48].

PHBV and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB) solvent-cast films exposed in seawater for a 3-week period (22 + 3 °C) were degraded via surface dissolution. The rate of surface erosion was almost independent of the copolymer compositions of PHBV and P3HBP4HB samples, but markedly dependent upon the temperature of the seawater. A simple hydrolytic degradation process did not contribute to the degradation of the polyhydroxyalkanoates in the marine environment [49].

Several microorganisms have been identified that can degrade polyhydroxyalkanoates (e.g., PHB, PHBV) in freshwater [50,51] and marine environments [49,50,52–54]. Among them are the bacteria Pseudoalteromonas sp. NRRL B-30083, Marinobacter sp. NK-1, *Alcaligenes faecalis* AE122, and the actinomycetes *Nocardiopsis aegyptia* and Streptomyces sp. SNG9.

The biodegradabilities of eight aliphatic polyester films: PHB, PHBV, P3HB4HB, poly(ε-caprolactone) (PCL), poly(ethylene succinate) (PES), poly(ethylene adipate) (PEA), poly(butylene succinate) (PBS), and poly(butylene adipate) (PBA) were studied in different natural waters from a river and a lake, and in seawater, from bay and ocean for 28 days at 25 °C under aerobic conditions [55]. PHB films were eroded at a relatively fast rate in freshwater from river and lake, and the weight loss was almost 100% after 28 days. By contrast, the biodegradation rate of PHB in seawater, from both the bay and the ocean, were slower than those in freshwater. PHBV films were degraded at a rapid rate in all the natural waters used, and the weight-loss and BOD (biochemical oxygen demand) of the PHBV films were 100 and 78 ± 8% for 28 days, respectively. PES films were eroded completely in freshwater within 10 days, whereas the PES films were hardly eroded after 28 days in seawater. PCL films were degraded in freshwater from river and lake, and in seawater from the bay, in which, the weight-loss and BOD were 100 and 80%, respectively. PEA films were completely degraded in freshwater and seawater from a bay, and the weight-loss were almost 100%. PBS films were hardly eroded in natural water, except for freshwater from lake, in which, the weight-loss and BOD were 22 ± 14 and 12 ± 8%, respectively. The weight-loss and BOD of PBA films in freshwater from the lake were 80 ± 13 and 50 ± 10%, respectively. The biodegradation rates of PBA films in freshwater from the river and in seawater from the bay and ocean were slower than that in freshwater from the lake [55].

A series of studies compared the deterioration of carrier bags made of Mater-Bi® (Novamont), which is believed to consist of corn starch, vegetable oils, and poly(butylene adipate-*co*-terephthalate) (PBAT), in two aquatic ecosystems, a littoral marsh and seawater, in soil and compost. Little deterioration was observed in specimens exposed to water of a littoral marsh and of the Adriatic Sea or buried in soil under field conditions. Conversely, results from the laboratory study indicated that after 3 months of incubation Mater-Bi® carrier bags were rapidly deteriorated in soil and compost with weight loss of specimens of 37 and 43%, respectively [56]. A Mater-Bi® film, thought to contain corn starch and PCL, underwent a severe deterioration in its tensile properties during aging in seawater for at least 8 months [7].

A further study investigated the degradation of oxodegradable, compostable, and conventional plastic carrier bags in the marine environment [57]. Four types of polymers that are used as carrier bags were compared. The first two bags were made from two oxodegradable polyethylenes. The first polyethylene used the d2w™ self-destruct oxodegradable plastic additive manufactured by Symphony Plastics (UK), and the second polyethylene used the Totally Degradable Plastics Additives (TDPA®) manufactured by EPI Environmental Products, Inc. The third bag was made from Mater-Bi®. The fourth bag was made from standard polyethylene containing 33% recycled material. Tensile strength of all materials decreased during exposure, but at different rates. Mater-Bi® degraded more than all the other polymers with 100% surface area loss between 16 and 24 weeks, while the other polymers lost only approximately 2% after 40 weeks. Some polymers required UV light to degrade. The transmittance of UV light through oxodegradable and standard polyethylene decreased as a consequence of fouling, such that, these materials received approximately 90% less UV light after 40 weeks. The data indicate that Mater-Bi® degrades relatively quickly compared to oxodegradable polyethylene and conventional polyethylene. While biodegradable polymers offer waste management solutions, there are limitations to their effectiveness in reducing hazards associated with plastic debris; some biodegradable polymers may not degrade quickly in natural habitats. On the other hand, oxodegradable formulations could merely disintegrate into small pieces that are not in themselves any more degradable than conventional polymers.

Another study examined the degradation of oxodegradable, compostable, and conventional shopping bags in the gastrointestinal fluids of sea turtles [48]. The conventional plastic bags were made of HDPE; the oxodegradable plastic bags were made of polyethylene with prooxidant (d2w™); and the compostable plastic bags were made of Mater-Bi® and manufactured by BioBag (US). After 49 days, the weight losses of the HDPE and oxodegradable plastic bags were negligible. The compostable bags showed a weight loss between 3 and 9 wt%. This is much slower than the degradation rates claimed by the manufacturers for industrial composting.

2.2.5.1 Biofouling

Biofouling is the colonization of an interface by a diverse array of organisms affecting the surfaces, the materials they are made of and their properties. Biofilm formation leading to biofouling develops in four stages: (1) adsorption of dissolved organic molecules; (2) attachment of bacterial cells; (3) attachment of unicellular eukaryotes; and (4) attachment of larvae and spores [58]. Bacterial attachment is a highly controlled and regulated process whereby attached cells produce extracellular polymers to form structured and complex matrixes [59]. Microbial biofilms can subsequently trigger the attachment of specific invertebrates and algae, which increases the degree of biofouling [14,60].

Biofouling depends on the surface properties of the plastic debris, such as surface roughness, surface energy, and hydrophobicity [45]. Biofouling also depends on the concentration of bacteria and nutrients in the marine environment. Biofouling fluctuates depending upon the season, geographic location, substrate, and age. Cursory calculations estimate a range of 1000−15,000 MT of microbial biomass harbored on plastic debris. The biofouling of plastic surfaces is more extensive in warmer climates [39].

Most of the plastic debris consists of hydrophobic plastics, such as polyethylene and polypropylene that promote microbial colonization and biofilm formation. With a hydrophobic surface rapidly stimulating biofilm formation in the water column, plastic debris can function as an artificial "microbial reef" [61]. The accumulation of micro and macroorganisms covering the surface of floating plastic debris, substantially, reduces the amount of UV-light reaching the plastic and increases its density, which decreases the plastic buoyancy. Using nitrogen as a proxy for biomass, which is absent in virgin polyethylene and polypropylene, it has been shown that the change in density is caused by the attached biomass. Initial rate of biofouling depends on the surface energy of the plastic; materials with surface energy between 5 and 25 mN/m are minimally fouled [62]. Once the density of biofouled plastic debris reaches that of seawater, it can sink well below the water surface. Microbial biofilms that developed early on plastic debris would become less hydrophobic and more neutrally buoyant so as to sink below the sea surface [63]. Polyethylene food bags (20 cm × 28 cm) submerged in seawater displayed a well-developed biofilm within 1 week, which continued to increase throughout a 3 week exposure period. By the third week, the polyethylene food bags had started to sink below the sea surface, indicating neutral buoyancy [63]. Typically, the density of seawater increases with depth. Therefore, neutrally drifting or slowly sinking plastic debris would remain suspended at a certain depth in which density is equal to that of plastic debris. Field experiments, however, have shown that biofouled plastic debris would undergo rapid defouling by other organisms or other mechanisms when submerged that can decrease its density causing the plastic debris to return back to the surface [64]. Fouled plastic debris may increase in density enough to ultimately reach benthic regions [65−67].

There are early indications that the formation of a biofilm on the surface of plastic debris may promote the biodegradation process. Bacterial diversity upon polyethylene and polypropylene samples collected from geographically distinct areas from the North Atlantic Subtropical Gyre and analyzed with scanning electron microscopy (SEM) and next-generation sequencing (pyrotag sequencing) revealed a diverse microbial community of heterotrophs, autotrophs, predators, and symbionts

[61]. Pits visualized in the plastic debris surface conformed to bacterial shapes suggesting active hydrolysis of the polyolefins. Small-subunit rRNA gene surveys identified several hydrocarbon-degrading bacteria, supporting the possibility that microbes play a role in degrading plastic debris. Some of the microbes may be opportunistic pathogens, such as specific members of the genus Vibrio that dominated one of the plastic samples. SEM has also been used to explore how microbial diversity (measured in terms of morphology) on polyethylene, polystyrene, and polypropylene particles from the North Pacific Gyre varies with location and polymer type, showing "Bacillus" bacteria and pennate diatoms to be most abundant on the plastic, with highest abundances on expanded polystyrene [68]. Despite the reports of plastic degrading microbes in biofouled plastic debris, the degradation rates are extremely slow.

2.2.6 Mechanical Degradation

Mechanical shearing has been suggested as a possible degradation mechanism of plastic debris [69]. The mechanical forces exerted on plastic debris are more intense on the beach than at sea [70]. Mechanical degradation may happen through the combined efforts of wave and tide action, and abrasion from sediment particles, which can scratch the surface of plastic debris and increase its rate of fragmentation. Surface alterations in plastic fragments resulting from environmental erosion increase the overall surface area and polarity and can facilitate the sorption of persistent organic pollutants (POPs) [37,71] (see Section 2.4.5.1).

Plastic debris particles sampled from the beaches of Kauai, Hawaii, and analyzed by SEM were found to contain fractures, horizontal notches, flakes, pits, grooves, and vermiculate textures. The mechanically produced textures provide favorable sites for oxidative processes to occur, which further weaken the polymer surface leading to embrittlement. Fourier transform infrared spectroscopy (FTIR) results suggest that, compared to polypropylene, polyethylene marine debris are more liable to surface oxidation, which occurs in pits and fractures created during collisions [72].

2.2.7 Combined Degradation Processes

The degradation of most common plastics encountered in the marine environment is attributed to the combined action of sunlight, atmospheric oxygen, and seawater [69]. Among the degradation processes involved, the most important is photooxidation, followed by mechanical action, and thermal oxidation, and to a lesser degree biodegradation and hydrolysis.

Andrady [73] compared the loss of mechanical integrity of several common packaging and fish gear-related plastics—including LDPE film, polypropylene stripping tape, rubber latex balloons, expanded polystyrene sheet, and rapidly degradable polyethylene[2] and six-pack ring—exposed while floating in seawater with those exposed in air at the same sites. LDPE film and polypropylene tape were found to degrade at a significantly slower rate on seawater, with marked differences in elongation at break after 1 year of exposure. The marked retardation of the degradation process in these types of plastic materials might be attributed to lack of heat buildup in samples exposed on seawater and the shielding action of surface biofouling, which reduces the light availability [13,28]. Enhanced degradable polyethylene six-pack ring material is degraded in about the same time scale under both air and seawater exposure.

Plastic debris stranded on the beach degrades more readily through the combined action of exposure to high levels of UV radiation, and particle-particle collisions associated with physical processes as saltation and dragging. Polyethylene marine debris appears to be more conducive to breakdown via both weathering processes than polypropylene, which occur in pits and fractures created during collisions [28]. While IR spectra of sampled and experimentally degraded polymers indicate that polypropylene is more conducive to photooxidative degradation relative to polyethylene, SEM results indicate that the combined effects of chemical and mechanical degradation processes may degrade polyethylene preferentially to polypropylene [39].

According to Rochman [74], the prolonged weathering of plastic debris can increase its surface area, generate oxygen groups (i.e., increase polarity) [37,75], and induce biofouling (increase electrical charge, roughness, and porosity) [45], and allow plastic debris to accumulate increasingly larger concentrations of chemical contaminants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and trace metals [37,76–78], the longer the plastic is exposed in the marine environment, the higher the concentration of adsorbed contaminants [79]. Presently, there are no reliable methodologies to assess the exposure time of plastic debris in the marine environment. While the degree of degradation of plastic debris can be quantified by FTIR, the duration of its exposure cannot be deduced from such information [12].

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[2] Ethylene-carbon monoxide copolymer.

2.3 Environmental Effects in Land

According to Flexible Packaging Association (FPA), the estimated amount of flexible packaging waste generated in the United States is 5.8 MMT per year. After a single use, 95% of flexible plastic packaging material ends up in landfills, as roadside litter, and eventually in the sea. Nearly, a third of this plastic packaging waste does not even make it to landfill, and instead, is littered on land or swept into the ocean, while only 14% of the plastic packaging waste is recycled. Flexible plastic packaging films and bags are thin and lightweight, and it is easy for flexible packaging material to become airborne after use, and scatter on land or be washed into storm drains, and pollute water bodies and aquatic ecosystems.

Consigning plastic waste to landfill is one of the most traditional methods of waste disposal, and it remains a common practice in most countries. However, older, poorly managed landfills can create a number of adverse environmental impacts, such as wind-blown litter, attraction of vermin, and generation of landfill gas, mainly composed of carbon dioxide and methane, which is produced as organic waste from food waste breaks down anaerobically. For overcoming these problems, many landfills are covered with earth to prevent attracting vermin and to reduce the amount of wind-blown litter. Furthermore, space in landfills is at a premium, and the cost of dumping waste material is calculated on a weight basis. It is disadvantageous to dispose of untreated flexible plastic waste materials in a landfill because these waste materials are bulky, and therefore, the cost of transporting them to the landfill is high.

2.4 Environmental Effects at Sea[3]

More than 8 MMT of plastic waste enters the oceans every year wreaking havoc on the wildlife and generally degrading the landscape [80]. Flexible plastic packaging films and plastic bags are the most prevalently found marine plastic pollution. Plastic bags have the tendency to float because of entrapped air. Approximately 70% of the carry plastic bags make their way to the ocean floor, where conditions are such that they prevent plastic bags from biodegrading [47]. A plastic bag and sweet wrappers were found even on the seabed of the Mariana Trench, the

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[3] This section is based on Chapter 2 of the book “Management of Marine Plastic Debris”, Niaounakis M. William Andrew-Elsevier, 2017.

deepest place in the Pacific Ocean [81]. It is estimated that 150 MMT of plastics are currently residing in the world's oceans.

Plastic packaging accounts for more than 60% of the plastics recovered in coastal cleanup operations [82]. Plastic bags and food plastic packaging are the next most common item, after cigarettes butts, removed from beaches during the annual International Coastal Cleanup campaigns, but they have a much greater potential impact than cigarettes butts [83].

The bulk of flexible plastic packaging debris found floating in the sea is composed mainly of LDPE, linear low-density polyethylene (LLDPE) and HDPE (e.g., plastic shopping bags, packaging films, or six-pack rings); polypropylene (e.g., films, or food containers) because of their inherent buoyancy, broad utility, and high production volumes. Floatable plastic debris items, once they enter the ocean, are carried away via oceanic currents and atmospheric winds. Oceanic features, such as gyres, eddies, and frontal meanders, trap marine debris in accumulation zones, often referred to as "garbage patch," "plastic soup," "trash island," or "ocean landfill." Because of the longevity of plastic debris, once it enters a gyre system, it can remain for long periods of time. The largest garbage patch is the "Great Pacific Ocean Garbage Patch" also known as "Eastern Garbage Patch." The size of the patch has been estimated to be from 700,000 km^2 (270,000 mi^2) to more than 15,000,000 km^2 (0.4–8% of the size of the Pacific Ocean).

Polyethylene is the most common type of plastic packaging debris and has recently been recognized as a major threat to marine life. There are reports that polyethylene fragments and particles cause blockages in the intestines of fish, birds, and marine mammals. In addition, the entanglement of marine animals in polyethylene packaging debris, such as carrier bags and films, has endangered hundreds of marine species [47]. Negative media publicity with upsetting images of dead marine animals after ingesting or being entangled in plastic debris heightened the awareness about the negative impacts of plastic debris on marine life.

2.4.1 Entanglement

Polypropylene packaging straps, HDPE six-pack rings, and LDPE bags are also a major source of entanglement found around the bodies (neck-collars) of marine animals. Although the packaging straps and six-pack rings account for only a tiny fraction of the marine plastic debris, they are responsible for the deaths of hundreds to thousands of seabirds and marine mammals [84].

2.4.1.1 Mammals

It is estimated that 45–46% (52–53 of 115) of all marine mammals have been entangled in plastic debris.

The pinniped with the most references to plastic debris entanglement in the U.S. waters is the northern fur seal (*Callorhinus ursinus*) followed by the Hawaiian monk seal (*Monachus schauinslandi*), the California sea lion, and the northern elephant seal (*Mirounga angustirostris*). Pinnipeds were generally observed to be entangled around the head and appendages in net fragments, monofilament line, packing straps, rope, and rubber products [85]. The decline in the populations of the northern sea lion (*Eumetopias jubatus*), endangered Hawaiian monk seal [86,87] and northern fur seal [88] seems at least aggravated by the entanglement of young animals in derelict fishing nets and packing bands. Page et al. [89] reported that New Zealand fur seals were commonly entangled in loops of packing tape.

2.4.1.2 Sea Turtles

Sea turtles tend to align themselves with oceanic fronts, convergences, rip and drift lines, where marine debris often occur [90]. As such, sea turtles are susceptible to entanglement in marine debris that can form loops and openings that could catch on and appendages [85]. Hawksbill turtles show a tendency to entangle in plastic bags and sacks [91]. Entanglement accounts for 10–11.8% of all turtles (including brackish turtles) species. Bjorndal et al. [92] reported that 5% of 1500 observed sea turtles worldwide were entangled in marine debris.

2.4.1.3 Birds

It is estimated that 25–26% (79–80 of 312) of all marine birds have been entangled in plastic debris [93]. Besides the risk of entanglement from derelict nets and fishing gear, marine birds are also susceptible to entanglement from plastics and other synthetic materials that they may gather for making nests [85].

2.4.2 Ingestion

The negative effects of ingested plastic debris can be divided into three categories [31]: physical damage to the digestive system [32,33]; impairment of digestive and foraging efficiency [34]; and the release of toxic chemicals [35–37]. Most of plastics found in the stomachs of marine animals are characterized by shape (e.g., plastic fragments, pellets, pieces of films, threads or nets) and/or color.

2.4.2.1 Mammals

Baulch and Perry [94] listed 48 cetacean species (56% of all) having ingested marine debris, with rates of ingestion as high as 31% in some populations. Items ingested by cetaceans were most commonly plastic (47%), with fishing gear (e.g., nets, hooks, lines, etc.) (25%), and miscellaneous items (28%) constituting the remainder [95].

Flexible plastic packaging debris (films, bags, and bands) was also found in the ingestion system of 68 Franiscana dolphins (*Pontoporia blainvillei*) out of 106 examined (64%) [96].

A Cuvier's beaked whale (*Ziphius cavirostris*) found on the west coast of Norway in January 2017 had its stomach filled with 30 plastic bags, and many smaller pieces of plastic (see Fig. 2.1). Another dead whale that swallowed 40 kg of plastic was found in the Philippines in March 2019. The stomach of this juvenile Cuvier's beaked whale contained 16 rice sacks, 4 banana plantation-style bags, and many plastic bags [98]. A pregnant sperm whale washed ashore in Italy's island of Sardinia in April 2019 with almost 23 kg of plastic in its stomach, including plastic bags, plastic plates, fishing lines, etc. [99].

2.4.2.2 Turtles

Marine turtles are known for consuming plastic bags at sea. It is assumed that these neutrally buoyant bags are mistaken by the turtles for food items, such as salps and medusa (jellyfish), the major food items of leatherback turtles [100–102].

Mrosovsky et al. [103] studied the autopsy records of 408 leatherback turtles (*Dermochelys coriacea*), spanning 123 years (1885–2007). The first mention of plastic in the gastrointestinal tract was for 1968. Of the 371 autopsies from that year and onwards, 37.1% revealed the presence of plastics. Blockage of the gut by plastic was mentioned in some accounts [7].

Balazs [90] listed 79 cases of turtles whose guts were full of various sorts of plastic debris. Plotkin and Amos [91] necropsied 111 turtles that were found stranded on the south Texas coast from 1986 through 1988.

Figure 2.1 Plastic films and bags found in the stomach of a whale stranded at Sotra, Bergen, in January 2017 (the University of Bergen Copyright) [97]. *Photo: Christoph Noever.*

Plastic debris was found in the stomachs or intestinal tracts of 60 (54%) of the turtles. Plastic debris was present in 52% of the loggerhead turtles (*Caretta caretta*), 47% of the green turtles (*Chelonia mydas*), and 87.5% of the hawksbill turtles.

Lazar and Gračan [104] analyzed the gastrointestinal tract of 54 loggerhead sea turtles found stranded or incidentally captured dead by fisheries in the Adriatic Sea. Plastic debris was present in about 35% of turtles, 68% of which have ingested soft plastics.

Santos et al. [105] analyzed the impact of plastic debris ingestion in 265 green turtles (*Chelonia mydas*) over a large geographical area and different habitats along the Brazilian coast. It was found that a surprisingly small amount of debris (about 0.5 g for juveniles and about 47% of adults) was sufficient to block the digestive tract and cause the death of juvenile green turtles. A large part of the ingested debris might come from disposable and short-lived plastic products.

2.4.2.3 Fishes

Davison and Asch [106] reported that at least 9.2% of fish in and below the Great Pacific Garbage Patch had plastic debris in their stomachs, and the researchers estimated that fish in the North Pacific are ingesting 12,000 to 24,000 tons of plastic every year.

The occurrence of microplastics in the stomachs of fish poses several environmental concerns. Ingested microplastics are passed through in the feces, retained in the digestive tract, or translocated from the gut into body tissues via the epithelial lining [107,108]. Negative effects on fish health are due to the plastic itself and to other pollutants in the marine environment absorbed by plastic debris.

2.4.3 Rafting

Floating and submerged marine plastic debris were reported to act as rafts for the transport of alien and invasive species to distant or remote areas. Some types of debris, such as plastic bags and films, are completely submerged and remain just below the surface where they are transported by currents. Furthermore, because of their hydrophobic nature, plastics act as "sponges" and absorb a wide range of inorganic and organic compounds from the marine environment [77]. A wide variety of POPs can sorb from the marine environment (i.e., seawater and sediment) on and/or in the plastic matrix. These contaminants have a greater affinity for the plastic matrix than the surrounding seawater leading to an accumulation onto the plastic particle. Polymer type plays an important role in this contamination accumulation: under identical sorption conditions, PCBs and PAHs are consistently found in a higher concentration on HDPE, LDPE, and polypropylene, compared to PET and PVC [77]. In this way, marine plastic debris may act as a transport vector of chemical pollutants to marine organisms [75,109].

2.4.4 Loss of Biodiversity and Habitat

Plastic debris poses a serious threat to marine habitats and wildlife. When settled on the seafloor marine debris alters the habitat, either by introducing substrates where none was available before or by overlaying the sediment, inhibiting gas exchange and interfering with life on the seabed. If relatively static on the seabed, or buoyant but retained in oceanic gyres, plastic debris will still become colonized, providing additional habitat having the potential to influence the relative abundance of organisms within local assemblages [110].

Ecosystem impacts can also occur in the intertidal. For example, microplastics and debris fragments on beaches have been reported to alter the porosity of the sediment and its heat transfer capacity. It has been suggested that increased plastic debris loads could lead to reduced subsurface temperatures, potentially affecting organisms, such as sea turtles whose sex-determination relies on temperature [38]. Nesting beaches for sea turtles, frequently, are sinks for plastic debris. As a result, nesting females may have difficulty in ascending to lay their eggs, or debris could act as obstacles for emerging hatchlings. Moreover, the physical properties of nesting beaches, particularly, the permeability and temperature of sediments, are known to be altered by the presence of plastic fragments. Such alterations could ultimately have implications for sex ratios, which are influenced by nest conditions, and for nest success rates when pollution is severe [111].

2.4.5 Toxicity

The plastic polymers are considered to be biochemically inert due to their large molecular weight, and are, therefore, not considered to be hazardous for the marine environment. However, unreacted monomers, oligomers, residual catalysts, and solvents can be found in plastic products as a result of incomplete polymerization [112]. Plastics also contain several additives that have been added to endow the plastics with certain desirable properties. While at sea, several of these chemical compounds and additives can be released from the plastic in the marine environment as a result of degradation and/or incomplete polymerization.

As mentioned earlier, plastic debris has the tendency to adsorb contaminants that are present in water, particularly those that are hydrophobic. Many of the hydrophobic contaminants are concentrated at the sea surface, and their levels are up to 500 times greater than in the underlying water column [113]. The plastic debris can either transport the contaminants to other areas and if washed up, the contaminants could be transferred to shoreline sediment or could be ingested by marine organisms and potentially transferred to their tissues and further up the food chain. Plastic debris could be subject to fouling and then sink to the bottom, where it becomes part of the sediment or is eaten by benthic organisms that live on the sea bottom [114].

2.4.5.1 Persistent Organic Pollutants

A wide variety of POPs can sorb from the marine environment (i.e., seawater and sediment) on/in the plastic matrix. The presence of such POPS on plastic debris has been demonstrated for a wide variety of chemicals and for different geographic areas [75,115]. These contaminants have a greater affinity for the plastic matrix than the surrounding seawater leading to an accumulation onto the plastic. Polymer type plays an important role in this contamination accumulation: under identical sorption conditions, PCBs and PAHs are consistently found in a higher concentration on HDPE, LDPE, and polypropylene, compared to poly(-ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC), while phenanthrene sorbs more to polyethylene than polypropylene or PVC [77,116]. As a result, the possible effects of both the polymer and associated contaminants have to be considered when assessing the potential risks of plastic debris.

Rochman et al. [77] measured sorption of PCBs and PAHs throughout a 12-month period to the five most common types of mass-produced plastic: HDPE, LDPE, polypropylene, PVC, and PET. For PAHs and PCBs, PET and PVC reach equilibrium in the marine environment much faster than HDPE, LDPE, and polypropylene. Most importantly, concentrations of PAHs and PCBs sorbed to HDPE, LDPE, and polypropylene were consistently much greater than concentrations sorbed to PET and PVC. These data imply that products made from HDPE, LDPE, and polypropylene pose a greater risk than products made from PET and PVC of concentrating these hazardous chemicals onto fragmented plastic debris ingested by marine animals.

Plastic fragments (~ 10 mm) collected from the open ocean and from remote and urban beaches were analyzed for organic micropollutants. PCBs, PAHs, DDE and its metabolites (DDTs), polybrominated diphenyl ethers (PBDEs), alkylphenols and bisphenol A were detected in the fragments at concentrations from 1 to 10,000 ng/g. Concentrations showed large piece-to-piece variability. Hydrophobic organic compounds, such as PCBs and PAHs were sorbed from seawater to the plastic fragments. PCBs are most probably derived from legacy pollution. Nonylphenol, bisphenol A, and PBDEs came mainly from additives and were detected at high concentrations in some fragments both from remote and urban beaches and the open ocean [115].

2.5 Socio-Economic Effects

The social impacts of plastic litter include a deterioration in the quality of human life, reduced recreational opportunities, loss of aesthetic value, and loss of nonuse or vicarious value[4] [117]. Socially, the plastic garbage

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[4] Knowledge that quality coastal ecosystems exist.

patches affect the health and lives of people living along coasts that border the ocean gyres [118]. Most of the socio-economic impacts of plastic debris are intertwined, and it is not always easy to distinguish one from another [119].

2.5.1 Tourism

There are few studies in the literature to consider the economic effects of marine plastic debris on tourism. Ofiara and Brown [120,121] found that marine debris wash-ups in New Jersey, United States, decreased beach attendance by 8.9−18.7% in 1987 and by 7.9−32.9% in 1988. A study in South Africa found that a decrease in beach cleanliness could decrease tourism spending by up to 52% [122]. It is further estimated that the tourism on the Skagerrak coast of Bohuslän in West Sweden decreased by 1−5% as a result of beach litter, resulting in a calculated annual loss of $23.4 million [123]. In the Goeje Island of South Korea, marine debris led to lost revenue of €29−37 from tourism in 2011. The number of people visiting the island decreased by 63% from 2010 to 2011 were probably due to the marine debris pollution [124].

Cleanups of beaches and waterways can be expensive. The cost of cleaning the beaches in Bohuslän, in just 1 year was reportedly at least $1,550,200 (or 10 million SEK). In the Netherlands and Belgium, about $13.65 million per year is spent on removing beach litter. The annual cleanup costs for municipalities in the UK amounted to $23.62 million in 2011 [119]. The municipality of Ventanillas in Peru has calculated that it would have to invest around $400,000 a year in order to clean its coastline, while its annual budget for cleaning all public areas is only half that amount [125].

A cost analysis on a hypothetical cleanup scenario was developed by NOAA (National Oceanic and Atmospheric Administration) based on the following assumptions [126]:

- cleaning up less than 1% of the North Pacific Ocean (a 3-degree swath between 30° and 35°N and 150° to 180°W), which would be about 1,000,000 km^2
- using nets or net-like devices to collect the plastic debris
- hiring a boat with an 18 ft (5.5 m) beam and surveying an area within 100 m off of each side of the ship. If the ship travels at 11 knots (20 km/h), and surveys during daylight hours (about 10 h a day), it would take 67 ships 1 year to cover that area.

At a cost of $5000–20,000 per day, it would cost between $122 million and $489 million per year only for boat time, without taking into account equipment or labor costs; and yet, not all debris can be swept up with a net [126]. The costs for cleaning the seafloor of the coasts are also especially expensive.

The deposit of macro- and microplastics along beaches, aside from having an ecological impact, has a significant economic impact on local businesses and property owners there along. Ocean resorts and hotels must maintain their property for guests, keeping up the appearance of the beach for continued use and for aesthetic reasons. Therefore, the burden of cleanup of these microplastic deposits shifts to the local businesses and property owners, which can be both incredibly costly and time-consuming.

Tourism and recreational usage of beaches can be a significant source of litter to the marine environment, especially during summer, when seaside resorts receive their greatest number of visitors. A study correlated the debris levels with visitor density on beaches in Brazil and found that the daily litter input to the beach was significantly higher in the regions frequented by people with lower annual income and literacy [127].

2.5.2 Aesthetics

The social cost of marine plastic debris is not known, but it seems likely that the largest component of this cost is the reduced aesthetic value of fouled shorelines. The presence of floating, submerged, and stranded plastic debris can negatively affect the aesthetic appeal of beaches, reduce its recreational value [128], and lead to serious economic problems for regions that are dependent on tourism and marine activities [120]. The degradation of the aesthetic appeal of beaches has a serious effect on many user groups, such as recreational fishers and boaters, sport divers and tourists, who visit and enjoy these areas, and value the coastal scenery and landscape [129]. Floating plastic debris is an aesthetic issue for swimmers, mariners, coastal, and inland water body dwellers, and submerged debris is an aesthetic issue for divers [130]. The absence of marine litter has been identified as a desirable beach quality in beach users priorities [131,132]. A survey assessing the value of clean beaches to users and the socio-economic impacts of beach litter on South Africa beaches found that 85% of both tourist and residents would not visit beaches if they had more than two items of debris per meter [133].

Although it is difficult to convert the aesthetic value into a monetary equivalent, coastal litter causes economic losses, including the decline of tourism and generation of cleanup costs, and furthermore, may be translated into a social issue, such as distrust of governments [117]. The effects of aesthetic issues on the amenity value of marine and riverine environments have been defined by the World Health Organization (WHO) as loss of tourist days; resultant damage to leisure/tourism infrastructure; damage to commercial activities dependent on tourism; damage to fishery activities and fishery-dependent activities; and damage to the local, national, and international image of a resort [134].

2.5.3 Human Health

Flexible plastic packaging debris, such as film residues, plastic bags, and straps, can be a navigational hazard to boats and can threaten the safety of the occupants. Film fragments carrying or adsorbing toxic compounds, such as PCBs or pathogenic pollutants and being ingested by fishes and shellfishes can enter the human food chain and may (might) affect the health of the food consumers [135].

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