Sustainable Water Integrated Management and Horizon 2020 Support Mechanism

This Project is funded by the European Union

EFH-EG-3

Assessment of marine litter in the Egyptian Mediterranean coastline and proposed management options

Literature review on the degradation of plastics in the marine environment

(EFH-EG-3, Task 3)

Version	Document Title	Author	Review and Clearance
1	Literature review on the degradation of plastics in the marine environment (EFH-EG-3, Task 3)	Thomais Vlachogianni	Anis Ismail Michael Scoullos

THE SWIM AND H2020 SUPPORT MECHANISM PROJECT (2016-2019)

The SWIM and H2020 SM is a Regional Technical Support Program, funded by the European Commission, Directorate General (DG) NEAR (Neighborhood and Enlargement Negotiations), that includes the following Partner Countries (PCs): Algeria, Egypt, Israel, Jordan, Lebanon, Libya, Morocco, Palestine, [Syria] and Tunisia. However, in order to ensure the coherence and effectiveness of Union financing or to foster regional co-operation, eligibility of specific actions will be extended to the Western Balkan countries (Albania, Bosnia Herzegovina and Montenegro), Turkey and Mauritania. The Program is funded by the European Neighbourhood Instrument (ENI) South/Environment. It ensures the continuation of EU's regional support to ENP South countries in the fields of water management, marine pollution prevention and adds value to other important EU-funded regional programs in related fields, in particular the SWITCH-Med program, and the Clima South program, as well as to projects under the EU bilateral programming, where environment and water are identified as priority sectors for the EU co-operation. It complements and provides operational partnerships and links with the projects labelled by the Union for the Mediterranean, project preparation facilities in particular MESHIP phase II and with the next phase of the ENPI-SEIS project on environmental information systems, whereas its work plan will be coherent with, and supportive of, the Barcelona Convention and its Mediterranean Action Plan.

The overall objective of the Program is to contribute to reduced marine pollution and a more sustainable use of scarce water resources. The Technical Assistance services are grouped in 6 work packages: WP1. Expert facility, WP2. Peer-to-peer experience sharing and dialogue, WP3. Training activities, WP4. Communication and visibility, WP5. Capitalizing the lessons learnt, good practices and success stories and WP6. Support activities.

Disclaimer:

TABLE OF CONTENTS

LIST OF FIGURES

ABBREVIATIONS

ATR	Attenuated Total Reflectance
COP	Conference of the Parties
D10	Descriptor 10
EC	European Commission
EO	Ecological Objective
EU	European Union
FTIR	Fourier-Transform Infrared Spectroscopy
GES	Good Environmental Status
GPS	Global Positioning System
H2020	Horizon 2020
ICZM	Integrated Coastal Zone Management
IMAP	Integrated Monitoring and Assessment Programme
LBS	Land-Based Sources
MSFD	Marine Strategy Framework Directive
NaCl	Sodium chloride
NAP	National Action Plan
NGO	Non-Governmental Organization
NKE	Non-Key Expert
ROVs	Remotely Operated Vehicles
SCUBA	Self-contained underwater breathing apparatus
TG	Technical Group
UNEP/MAP	United Nations Environment Programme/Mediterranean Action Plan

1 GENERAL INTRODUCTION

Marine litter -any persistent, manufactured or processed solid material discarded, disposed of or abandoned in the marine and coastal environment- is globally acknowledged as a major societal challenge of our times due to its significant environmental, economic, social, political and cultural implications. Marine litter negatively impacts coastal and marine ecosystems and the services they provide, ultimately affecting people's livelihoods and well-being.

Marine litter related information in the Mediterranean, remains limited, inconsistent and fragmented, however it is widely accepted that it is one of the most affected seas by marine litter worldwide. Effective measures to tackle marine litter in the region are seriously hampered by the lack of reliable scientific data. Within this context the need for accurate, coherent and comparable scientific data on marine litter in the Mediterranean countries is evident in order to set priorities for action and address marine litter effectively, thus ensuring the sustainable management and use of the marine and coastal environment of the region.

Within the framework of the SWIM-H2020 SM Egypt has asked for an Expert Facility Activity (EFH-EG-3) in order to assess marine litter in the Egyptian Mediterranean coastline and come up with targeted management options. This activity will support the implementation in Egypt of the obligations and measures relevant to the Regional Plan for Marine Litter Management in the Mediterranean of the Barcelona Convention and will contribute to Integrated Coastal Zone Management (ICZM) within the framework of the implementation of the regional ICZM Protocol of the Barcelona Convention. More specifically, the action will support Egypt in: integrating marine litter measures into the LBS National Action Plan in line with Article 7 of the Regional Plan; assessing marine litter in the Egyptian Mediterranean coastline in line with Article 11 of the Regional Plan; designing a marine litter monitoring programme in line with Article 12 of the Regional Plan; supporting the implementation of Regional Plan through technical assistance and capacity building in line with Article 15 of the Regional Plan.

The assessment of marine litter in the Egyptian Mediterranean coastline and the proposed management options based on the results would trigger positive changes in the design and implementation of the relevant national institutional, policy and regulatory frameworks, which should incorporate marine litter prevention and reduction measures. Furthermore, it will strengthen the regional coherence and cooperation in approaches to marine pollution prevention and control, and sustainable waste management. The areas addressed/covered by the proposed activity include a study/assessment, technical assistance and capacity building.

The overall Activity entails the following tasks:

- Task 1: Carry out marine litter pilot surveys (including a workshop) on the Med Coast of Egypt along with a literature review focusing on strengthening the evidence base concerning marine litter and in particular plastics.
- Task 2: Compile a document with 'best' available techniques and methodologies for monitoring marine litter in the coastal and marine environment and short listing of best environmental practices for management of marine litter.

- Task 3: Carry out a literature review on the degradation process for plastics.
- Task 4: Review the socioeconomic implications of marine litter.

2 AIM AND SCOPE OF THIS DELIVERABLE

Plastics are one of the most widely used materials in the world; they are broadly integrated into today's lifestyle and make a major contribution to almost all product areas. The typical characteristics that render them so useful relate primarily to the fact that they are both flexible and durable. These characteristics are very useful when plastics are used in everyday life. But when plastics end up in the coastal and marine environment they can persist for very long periods of time.

The overarching aim of this document is to provide a concise summary of some of the key issues surrounding the degradability of plastics in the marine environment. In particular, the present document aims to shed light on common misconceptions related to the behaviour of biodegradable plastics in the marine environment and respond to the question whether the adoption of biodegradable plastics will reduce the impact of marine plastics overall, in effort to provide valuable insights for informed and effective decision-making with regards to marine litter management.

3 MARINE LITTER: DEFINITIONS & POLICY CONTEXT

Within this document marine litter is defined as any persistent, manufactured or processed solid material discarded, disposed of or abandoned in the marine and coastal environment. Marine litter can be classified in size classes as follows: macrolitter referring to items above 25mm in the longest dimension; mesolitter from 5mm to 25 mm; and microlitter from 1μm to 5mm. Sometimes the later size class is further broken down to large microplastics from 1mm to 5 mm and small microplastics from 1μm to 1mm.

The main legislative frameworks related to marine litter in the Mediterranean are: the Barcelona Convention Regional Plan for Marine Litter Management in the Mediterranean (UNEP/MAP IG.21/9) and the Ecosystem Approach (COP19 IMAP Decision IG.22/7); the EU Marine Strategy Framework Directive (2008/56/EC, 2010/477/EC, 2017/848/EC) and the EU Plastics Strategy (COM(2018)).

Figure 1. *The Marine Litter Ecological Objective and the respective Indicators within the framework of the Barcelona Convention Ecosystem Approach and the Integrated Monitoring and Assessment Programme.*

Marine Litter and the Barcelona Convention Ecosystem Approach

Ecological Objective 10 (EO10): Marine and coastal litter do not adversely affect the coastal and marine environment.

IMAP Common Indicator 22:

Trends in the amount of litter washed ashore and/or deposited on coastlines (including analysis of its composition, spatial distribution and, where possible, source).

IMAP Common Indicator 23:

Trends in the amount of litter in the water column including micro plastics and on the seafloor.

IMAP Candidate Indicator 24:

Trends in the amount of litter ingested by or entangling marine organisms focusing on selected mammals, marine birds, and marine turtles.

Figure 2*. The Marine Litter Descriptor, Criteria, and respective Indicators within the framework of the EU MSFD.*

Marine Litter within the EU MSFD

Properties and quantities of marine litter do not cause harm to the coastal and marine environment (Descriptor 10)

Criteria D10C1 - Primary:

The composition, amount and spatial distribution of litter on the coastline, in the surface layer of the water column, and on the seabed, are at levels that do not cause harm to the coastal and marine environment.

- ✓ amount of litter washed ashore and/or deposited on coastlines, including analysis of its composition, spatial distribution and, where possible, source (10.1.1)
- ✓ amount of litter in the water column (including floating at the surface) and deposited on the seafloor, including analysis of its composition, spatial distribution and, where possible, source (10.1.2)

Criteria D10C2 - Primary:

The composition, amount and spatial distribution of micro-litter on the coastline, in the surface layer of the water column, and in seabed sediment, are at levels that do not cause harm to the coastal and marine environment.

- ✓ amount, distribution and, where possible, composition of microparticles (in particular microplastics) (10.1.3)

Criteria D10C3 - Secondary:

The amount of litter and micro-litter ingested by marine animals is at a level that does not adversely affect the health of the species concerned.

- ✓ amount and composition of litter ingested by marine animals (10.2.1)

Criteria D10C4 - Secondary:

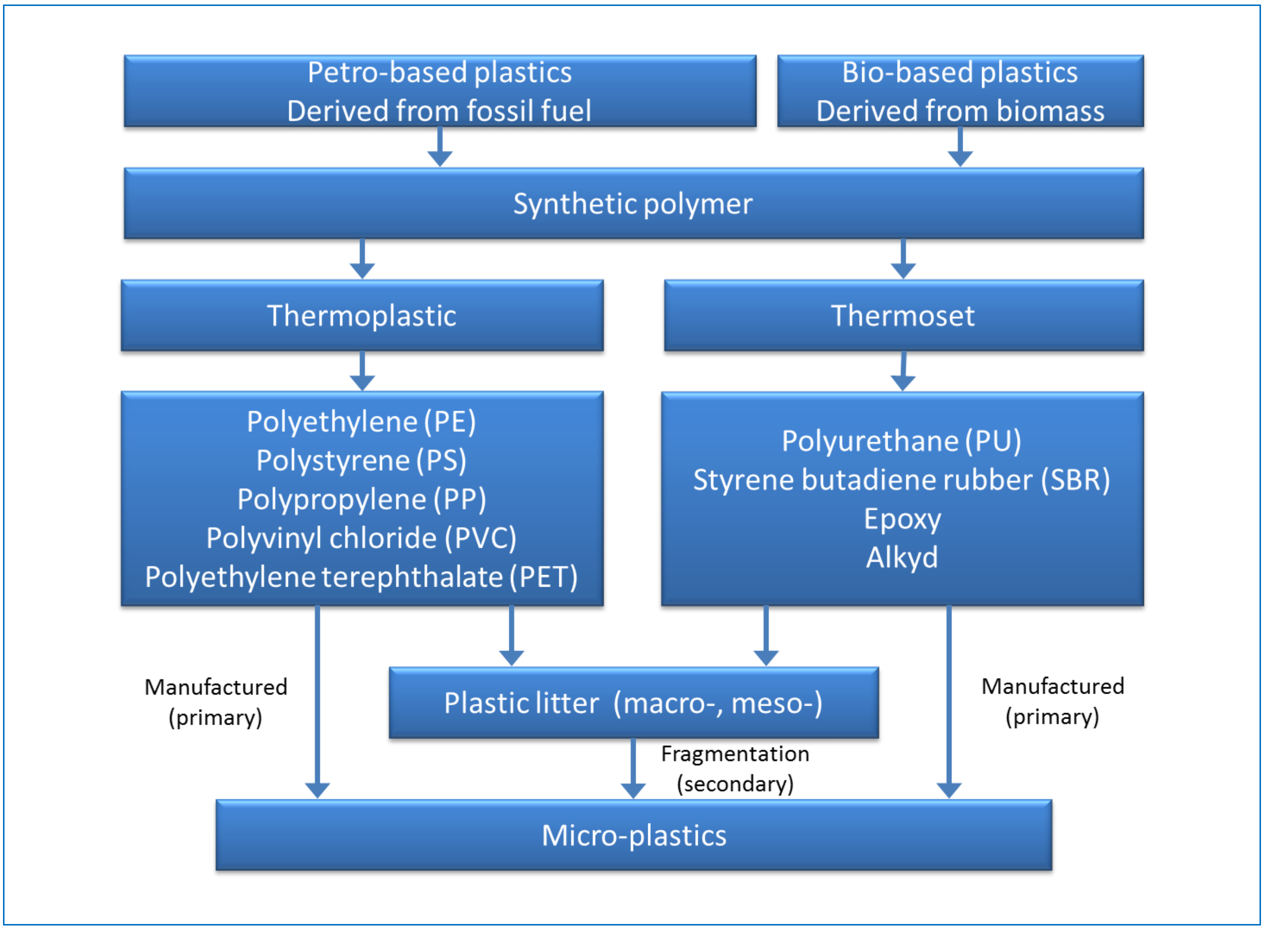
The number of individuals of each species which are adversely affected due to litter, such as by entanglement, other types of injury or mortality, or health effects.

4 POLYMERS AND PLASTICS: TERMINOLOGY & DEFINITIONS

The term plastics, as commonly applied, refers to a wide range of synthetic organic compounds that are produced by polymerization, and these consist of many repeating units (monomers) that come together to create copolymers.

Polymers are large organic molecules composed of repeating carbon-based units or chains that occur naturally and/or can be synthesised. **Naturally occurring** polymers include tar, shellac, tortoiseshell, animal horn, cellulose, amber, and latex from tree sap. **Synthetic polymers** include polyethylene (used in plastic bags); polystyrene (used to make Styrofoam cups); polypropylene (used for fibres and bottles); polyvinyl chloride (used for food wrap, bottles, and drain pipe); and polytetrafluoroethylene, or Teflon (used for non-stick surfaces).

Figure 3. Schematic illustration of synthetic polymer materials based on their material source and types.



There are two main classes of synthetic polymers: **thermoplastic** and **thermoset**. Thermoplastic is capable of being repeatedly moulded, or deformed plastically, when heated; common examples are polyethylene, polystyrene, polypropylene, polyvinyl chloride. Thermoset plastic materials, once formed, cannot be remoulded by melting; common examples are epoxy resins or coatings. Many plastics often contain a variety of additional compounds that are added to alter the properties, such as plasticisers, colouring agents, UV protection, antioxidants, and fire retardants.

Plastics are produced by the conversion of natural products or by synthesis from primary chemicals, generally from oil, natural gas, or coal. Plastics can be referred to as **bio-based plastics** or **bio-derived** plastics that refer to plastics that are made from renewable resources instead of non-renewable petroleum based resources (**petro-based plastics**). These renewable resources can include corn, potatoes, rice, soy, sugarcane, wheat, and vegetable oil. Bio-based plastics are made by creating plastic polymers from these materials, through either chemical or biological processes. Two very common examples of bio-based plastics are bio-polyethylene and poly(lactide). While most of the conventional polyethylenes are produced from fossil fuel, bio-polyethylene a leading bio-based plastic is produced entirely from biomass feedstock (Kershaw, 2015). Similarly, bio-polyamide11 is derived from vegetable oil, while poly(lactide) is a polyester produced from lactic acid derived from agricultural crops such as maize and sugar cane.

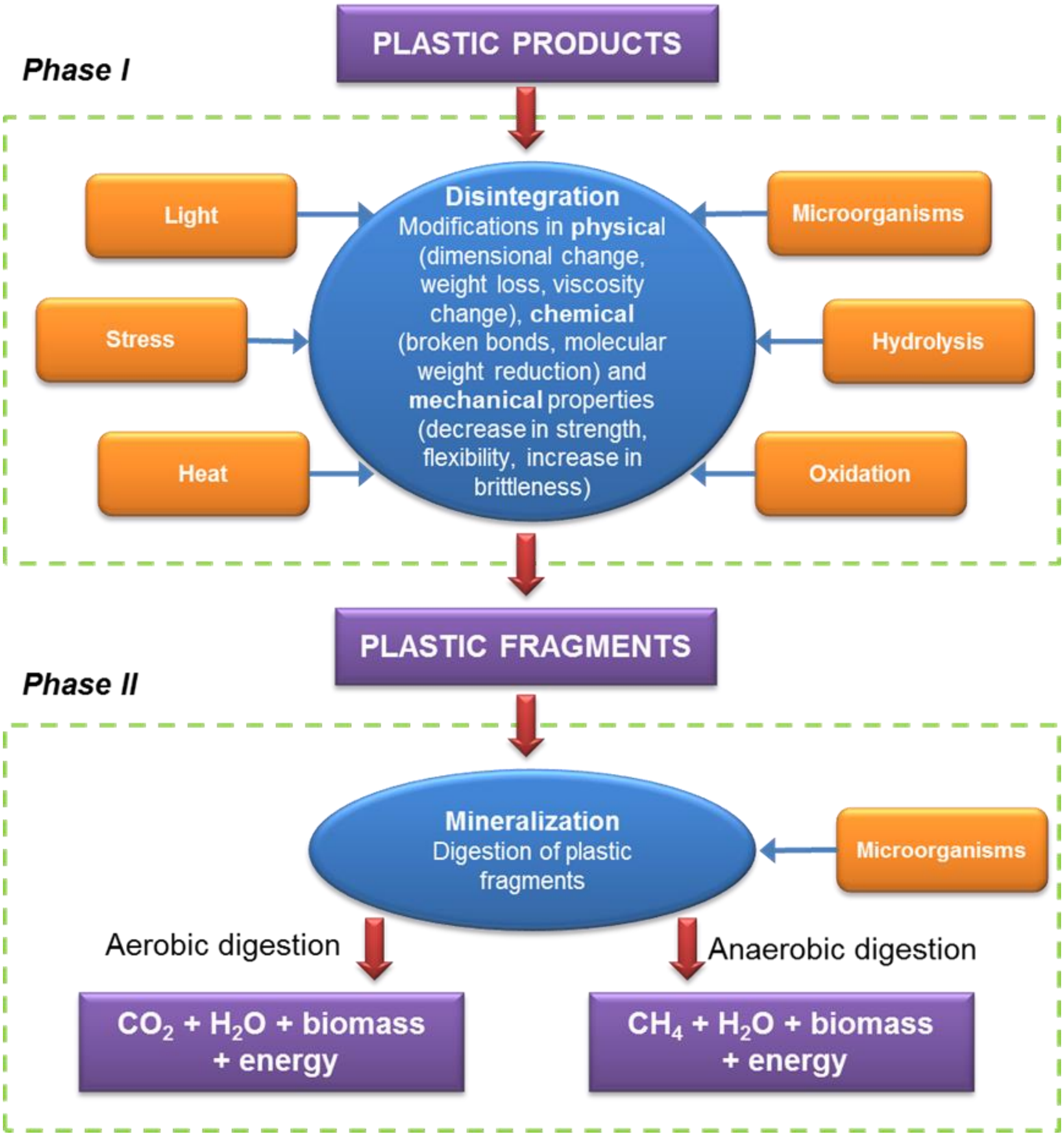
5 DEGRADATION OF PLASTICS

The American Society for Testing and Materials (ASTM) and the International Organization for Standardization (ISO) define degradation as “an irreversible process leading to a significant change of the structure of a material, typically characterized by a loss of properties (e.g. integrity, molecular weight, structure or mechanical strength) and/or fragmentation. Degradation is affected by environmental conditions and proceeds over a period of time comprising one or more steps.

The **degradation** of plastics is defined as the process that induces changes in the polymer properties (deterioration of functionality) due to chemical, physical or biological reactions. The most important modifications are scission and crosslinking of the polymer molecules, producing a change in molecular weight. These modifications of the molecular structure cause changes in the physical properties, such as strength, extensibility, solubility, texture and colour. The changes include bond scission, chemical transformation and formation of new functional groups (Pospisil and Nespurek, 1997).

The degradation process of plastics comprises two phases: **disintegration** and **mineralization** (see Fig.4). The initial phase (Phase I) – disintegration, is significantly associated with the deterioration in physical properties, such as discoloration, embrittlement, and fragmentation. The second phase (Phase II) is the ultimate conversion of plastic fragments, after being broken down to molecular sizes, to carbon dioxide (CO_2), water, cell biomass (aerobic conditions), and methane (CH_4), carbon dioxide (CO_2) and cell biomass in the case of anaerobic conditions.

Figure 4. *Schematic representation of plastics degradation processes in the environment.*



Depending upon the nature of the causing agents, polymer degradations have been classified as thermal- (heat), photo- (sunlight), oxidative- (oxygen), hydrolytic- (water), mechanical- (stress), and bio- (microorganisms) degradation (Krzan et al., 2019).

- **Photo-degradation:** Photo-oxidative degradation is the process of decomposition of the material by the action of light, which is considered as one of the primary sources of damage exerted upon polymeric substrates at ambient conditions.
- **Thermal degradation:** Under normal conditions, photochemical and thermal degradations are similar and are classified as oxidative degradation. The main difference between the two is the sequence of initiation steps leading to auto-oxidation cycle. Other difference includes that

thermal reactions occur throughout the bulk of the polymer sample, whereas photochemical reactions occur only on the surface.

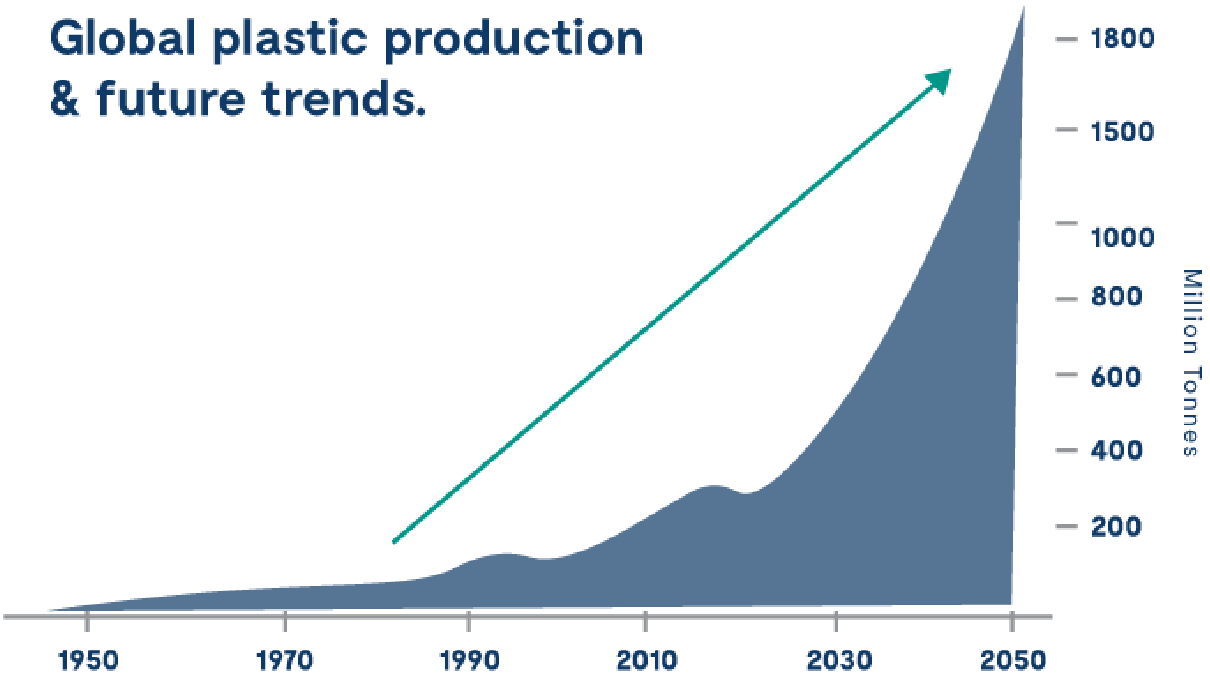
- **Oxidative degradation:** This process is generally coupled with previous thermal and photophysical degradation and involves the reaction of oxygen with the polymer.
- **Mechanical degradation:** This process involves the application of shear forces to break apart the plastics. It is a notable method for size reduction.
- **Hydrolytic degradation:** This process requires the presence of hydrolysable groups such as ester, ether, anhydride or amide groups present in starch, polyesters, polyanhydrides, polycarbonates, polyamides, or polyurethanes. These compounds absorb moisture from the environment leading to hydrolytic cleavage of the polymer chain which can be driven by chemical agents or mediated by enzymes.
- **Biodegradation:** The breaking of polymeric bonds is associated with the action of enzymes (natural catalysts) in the living organisms. The process is greatly affected by the amounts and types of available microorganisms and their microbial activities, which are sensitive to environmental parameters such as temperature, moisture, pH, C/N ratio, and the amount of available oxygen. Biodegradation may lead to partial or complete breakdown of the polymer. Partial biodegradation can lead to the production of nano-sized fragments and other synthetic breakdown products (Lambert et al., 2013). It becomes evident from the above definition that the probability of biodegradation taking place is highly dependent on the type of polymer and the receiving environment.

It should be highlighted that the degradation of plastics is affected by various factors such as the chemical composition of the polymers, their molecular weight, their hydrophobic character, the size of their molecules, the presence of additives and functional groups, their chemical bonding, the way they were synthesized, the effect of substituents and stress, and the environmental conditions (Singh and Sharma, 2008). The biodegradation of polymers depends upon environmental conditions such as moisture, temperature, oxygen, and suitable population of microorganisms (Moharir and Kumar, 2019). In warm climates when the relative humidity exceeds above 70%, the rate of polymer degradation by the microorganisms increases. High temperature and high humidity enhance hydrolytic degradation of the polymers. Even a small increase in solar UV level dramatically accelerates the deterioration processes in plastics at high temperature. Weathering is a degradation process and as such is temperature dependent, i.e. it will occur more rapidly at higher temperatures. The general rule is that for every 10°C increase in temperature the reaction rate will double. Oxygen affects the mechano-chemical degradation of rubber at ambient temperature. For instance, degradation has been found to be almost absent when rubber is masticated in an atmosphere of nitrogen. However, when the process has been repeated in the presence of a small amount of oxygen or air, degradation has been observed very quick and significant.

6 DEGRADATION OF PLASTICS IN THE MARINE ENVIRONMENT

Over the past 50 years the role and importance of plastics in our economy has consistently grown, with the global production of plastics reaching 322 million tonnes in 2015 and expected to double within the next twenty years (Fig. 5). The cumulative waste generation of primary and secondary (recycled) plastic waste totalled 6300 Mt (Fig. 6, Jambeck et al., 2015); 600 Mt was recycled, only 10% of which was recycled more than once (Scalenghe, 2018). Large amounts of plastic waste leak into the marine environment from sources on land and at sea, generating significant environmental and economic damage (Fig. 7). Plastics are estimated to account for over 80% of marine litter. Single-use plastic items are a major component of the plastic leakage and are among the items most commonly found on beaches, representing some 50% of the marine litter found.

Figure 5. *Global plastic production and future trends.*



Source: Ryan, A Brief History of Marine Litter Research, in M. Bergmann, L, Gutow, M, Klages (Eds.), Marine Anthropogenic Litter, Berlin Springer, 2015; Plastic Europe.

Figure 6. *Plastic waste generation waste worldwide.*

Source: Jambeck, J., R., et al., Plastic waste inputs from land into the ocean, Science, 2015

Figure 7*. Plastic waste input from land into the ocean.*

*Tracks percentage of wastewater from households and industry treated before release back into the environment.

** From mismanaged municipal solid waste

Note: only countries with more than 50 000 tonnes of mismanaged plastic waste are shown

Source: Jambeck, J., R., et al., Plastic waste inputs from land into the ocean, Science, 2015

Plastics introduced into the environment end up in different debris pools; floating on the surface, sinking to the seabed or washed ashore (Hammer et al., 2012). When introduced into the marine environment, thermoplastics are not easily biodegradable, so they can last, almost intact, for prolonged periods of time. As a result plastics persist for long periods and build up to high levels in marine habitats (Barnes et al., 2009). Their lifetime depends on both their chemical nature and the characteristics of the environment in which they are located. Compostable plastics, such as blended thermoplastic starches, can degrade within months (Pang et al., 2013) but degradation will take significantly longer for other polymers (Andrady, 2003).

Plastics degradation is especially slow in the marine environment, where degradation primarily is likely to occur by UV-B radiation in sunlight (Andrady, 2011). Once initiated, the degradation can also proceed thermo-oxidatively for some time without the need for further exposure to UV radiation. As long as oxygen is available to the system, the autocatalytic degradation reaction sequence could proceed. Studies show that other types of degradation processes are orders of magnitude slower compared to light-induced oxidation. Due to the deficiency of the solar UV radiation and the low temperature, however, the rate of degradation in the marine environment is especially slower than in the terrestrial environment (Barnes and Milner, 2005; Ryan et al., 2008).

In recent years, a highly debatable issue has been the replacement of conventional plastics with biodegradable ones as a mitigation option for marine plastic litter. Biodegradable plastics in the marine environment will behave quite differently than in a terrestrial setting (soil, landfill, composter) as the conditions required for rapid biodegradation are unlikely to occur. Plastics lying on the shoreline will be exposed to UV and oxidation and fragmentation will occur, a process that will be more rapid in regions subject to higher temperatures or where physical abrasion takes place. Once larger items or fragments become buried in sediment or enter the water column then the rate of fragmentation will slow dramatically (Kershaw, 2016). Balestri et al. (2017) studied the behaviour of biodegradable bags buried in marine sediments. The results of this study demonstrated a negligible degradation of biodegradable bags after six months of exposure to marine sediments confirming that biodegradable bags degrade slowly when buried in marine sediments. The poor bag deterioration may be attributed to environmental conditions, such as the lack of UV-radiation and mechanical abrasion by wave in sediments, which play an important role in promoting degradation in natural habitats (Andrady, 2015).

Some main conclusions related to plastics in the marine environment are:

- Plastic products in the marine environment tend to move and settle in many different habitats. In order to get a complete characterization of the degradation behavior of biodegradable plastics testing is needed in different marine habitats (supralittoral, eulittoral, sublittoral benthic, deep sea benthic, pelagic, buried in the sediments).
- Polymers most commonly used for general applications, with the required chemical and mechanical properties (e.g. PE, PP, PVC) are not readily biodegradable, especially in the marine environment.
- Polymers which will biodegrade in the terrestrial environment, under favourable conditions, also biodegrade in the marine environment, but much more slowly and their widespread use is likely to lead to continuing littering problems and undesirable impacts.

7 REFERENCES/RESOURCES

Andrady, A.L., 2003. Plastics and the Environment. John Wiley and Sons, West Sussex, England.

Andrady, A.L., 2011. Microplastics in the marine environment. Mar. Pollut. Bull. 62, 1596–1605.

Balestri, I., Menicagli, V., Vallerini, F., Lardicci, C., 2017. Biodegradable plastic bags on the seafloor: A future threat for seagrass meadows? Science of the Total Environment, 605–606, 755-763.

Barnes, D.K.A., Milner, P., 2005. Drifting plastic and its consequences for sessile organism dispersal in the Atlantic Ocean. Mar. Biol. 146, 815-825.

COM(2018) 28 final. Communication from the commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. A European Strategy for Plastics in a Circular Economy.

Derraik, J.G.B., 2002. The pollution of the marine environment by plastic debris: areview. Mar. Pollut. Bull. 44 (9), 842–852.

Hammer, J., Kraak, M.H.S., Parsons, J.R., 2012. Plastics in the Marine Environment: The Dark Side of a Modern Gift. Reviews of environmental contamination and toxicology.

ISO, 1993. ISO 472 Plastics – vocabulary, amendment 3 General terms and terms relating to degradable plastics, Geneva.

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Marine pollution. Plastic waste inputs from land into the ocean. Science 347, 768-771.

Lambert, S., Sinclair, C. J., Bradley E. L., Boxall, A. B. A., 2013. Environmental fate of processed natural rubber latex. Environmental Science-Processes & Impacts, 15(7), 1359-1368.

Moharir, R.V., Kumar, S., 2019. Challenges associated with plastic waste disposal and allied microbial. Journal of Cleaner Production, 208, 65-76.

Pang, M.M., Pun, M.Y., Ishak, Z.A.M., 2013. Degradation studies during water absorption, aerobic biodegradation, and soil burial of biobased thermoplastic starch from agricultural waste/polypropylene blends. J. Appl. Polym. Sci., 129, 3656-3664.

Pospisil, J., Nespurek, S., 1997. Highlights in chemistry and physics of polymerstabilization. Macromol Symp, 115, 143–63.

Ryan, P.G., 2008. Seabirds indicate changes in the composition of plastic litter in the Atlantic and south-western Indian Oceans. Mar. Pollut. Bull. 56, 1406–1409.

Scalenghe, R., 2018. Resource or waste? A perspective of plastics degradation in soil with a focus on end-of-life options. Heliyon 4, e00941.

Singh, B., Sharma, N., 2008. Mechanistic implications of plastic degradation. Polym. Degrad. Stab. 93, 561–584.

UN Environment /MAP IG.21/9. Regional Plan on Marine Litter Management in the Mediterranean in the Framework of Article 15 of the Land Based Sources Protocol. UNEP(DEPI)/MED IG.21/9, ANNEX II – Thematic Decisions, pp.143-173.

UNEP, 2015. Biodegradable Plastics and Marine Litter. Misconceptions, concerns and impacts on marine environments. United Nations Environment Programme (UNEP), Nairobi.