



# Technical Report 1

## AN INVESTIGATION INTO THE DEGRADATION OF NON-METALLIC COMPONENTS OF OIL AND GAS INFRASTRUCTURE IN THE OCEAN

Curtin Corrosion Centre

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**Abstract**

The decommissioning of oil and gas infrastructure requires an accurate understanding of the degradation mechanisms, pathways, and lifetime of the various components, including the non-metals, to understand how long the materials will last in marine environments.

Conducted by Curtin Corrosion Centre, this report collates the outcome of a literature review of relevant studies on the degradation of synthetic polymers. The report identifies essential parameters in the offshore marine environment that influence the degradation model of engineering polymers.

## Revision History

<b>Revision</b>	<b>Description and Record of Changes</b>
0.1	Initial Release
1.0	Revised version based on NDRI industry participants and the ISAB.

## Executive Summary

This project has been executed for, and on behalf of, the National Decommissioning Research Initiative (NDRI) within National Energy Resources Australia (NERA), with Phase 1 comprising of two main activities: a desktop study and a conceptual proof of concept.

This report presents the findings of the first activity, i.e., the desktop study, a critical assessment of the state-of-the-art on physical and environmental degradation mechanisms and rates of non-metallic components used in oil and gas infrastructure in the ocean. The objective of the desktop study is to (i) evaluate all the essential parameters pertinent to the Australian offshore environments and (ii) appraise the degradation mechanisms of the engineering polymers used in the oil and gas infrastructure. This literature review collates relevant studies on the degradation of polymers in marine environments to identify factors and their likely relative importance on the breakdown (i.e., degradation mechanism) of synthetic polymers when left in marine environments. The comparative assessment shows that photothermal initiation plays a significant role in the degradation of C-C backbone polymers; however, most polymers with heteroatom backbones are susceptible to hydrolytic initiation. Since the current literature data are limited to the surface environments of the ocean, this study has identified some essential physicochemical parameters and explored how they will influence the rate of degradation of the infrastructure.

The structure of this report has been organised systematically. The first section provides an introductory background of engineering polymers, their application in the oil and gas sector, and the geography of the Australian offshore environment. The subsequent section assesses the essential factors, including temperature, pressure, light intensity, etc., affecting polymer degradation in marine conditions. Finally, Section 4 details the degradation mechanisms of each of the selected polymers. The review and the complementing results are significant for assessing the degradation rate and lifetime of polymers in subsea infrastructure, especially during decommissioning. In addition, the outcomes of this study will fit into the proof-of-concept mathematical model to predict the lifetime of synthetic polymers in oceanic conditions.

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## Glossary of Terms, Abbreviations, and Acronyms

CP	Cathodic protection
CSIRO	The Commonwealth Scientific and Industrial Research Organisation
CTE	Coal tar enamel
DGEBA	Diglycidyl ether of bisphenol A
DOC	Dissolve organic carbon
DOM	Dissolved organic matters
DON	Dissolved organic nitrogen
EIA	Environmental impact assessment
FBBP	Fusion bonded black polyethylene
FBE	Fusion-bonded epoxy
HBE	High build epoxy
HDPE	High-density polyethylene
IMOS	Integrated Marine Observing System
LDPE	Low-density polyethylene
MP	Microplastic
NP	Nano-plastic
NRS	National reference stations
PA	Polyamide
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyls
PBDE	Polybrominated diphenyl ethers
PE	Polyethylene
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid

PP	Polypropylene
PSE	Photosensitising efficiencies
POP	Persistent organic pollutant
PU	Polyurethane
PUF	Polyurethane foam
ROS	Reactive oxygen species
SA	Surface area
Tg	Glass transition temperature
XLPE	Cross-linked polyethylene

## 1. Introduction

### 1.1. Background

Synthetic polymers (or plastics) remain widely deployed in many applications, including packaging, insulations and civil infrastructure.<sup>1,2</sup> While sustainable campaigns endeavour to shift the public interest from synthetic polymers, some key application areas will continue to rely on them for polymeric protective coatings, insulation purposes and other structural functions. Offshore oil and gas production is a crucial field where biodegradable polymers cannot replace environmentally resistant synthetic polymers, where plastics are used, e.g., for external corrosion resistance, as well as thermal insulation of subsea infrastructure. The former ensures the protection of metals (e.g., pipelines) against seawater corrosion.

Regardless of the source, plastics entering the ocean exhibit various environmental concerns. Numerous stakeholders and policymakers consider critically the input of plastics and debris into the ocean, due to the direct and flow-on effects in the marine ecosystem.<sup>3,4</sup> The issue exacerbates owing to the relatively high durability and persistence of the polymeric materials in the environment,<sup>5-7</sup> and the detrimental formation of microplastics, the potent carrier of persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs),<sup>8</sup> that end up in the food web.<sup>9-11</sup> Examples of POPs include polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), perfluorooctanoic acid (PFOA), and perfluorooctanesulfonic acid (PFOS). However, further environmental impact assessment (EIA) is crucial to evaluate the influence of the non-metallic material employed in subsea oil and gas infrastructure on the marine ecosystem (flora and fauna), especially during the decommissioning periods of such facilities. This kind of assessment requires an accurate understanding of the degradation rate and fates of the non-metallic materials, considering the amount and capacity been used. The fate of plastics in subsea and offshore infrastructure will rely on the operational, physical, photochemical and biological drivers in the marine environment.<sup>12,13</sup> Therefore, it is necessary to develop a suitable model accounting for all the characteristics of environmental fluxes, to describe the mechanism, and predict the degradation of polymers in subsea infrastructure.

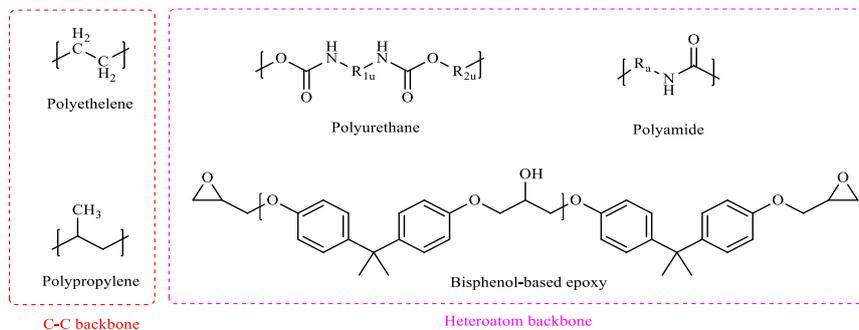
### 1.2. Polymers in oil and gas applications

Speciality polymers, including those used in engineering and functional purposes, have found diverse applications in offshore and deep-sea infrastructure. Thousands of kilometres of rigid and flexible flowlines and umbilicals lying undersea carry considerable amounts of polymers that have reached or will soon be nearing the end of their service-life. This is of great interest to the environmental regulators, industry, and community, considering the sizable impacts of these class of materials on global biogeochemical cycles. There are thousands of offshore infrastructure worldwide with varying environmental impact,<sup>14,15</sup> primarily being managed by the oil and gas, maritime, and civil sectors. According to the problem statement from NERA, the polymeric components of Australian offshore infrastructure can be categorised based on the intended functions such as:

- Pipeline insulating material, e.g., polyurethane foam (PUF).
- Pipeline coatings providing external corrosion protection, e.g., fusion bonded black polyethylene (FBBP), high build epoxy (HBE), high-density polyethylene (HDPE), Coal tar enamel (CTE), solid polyurethane, fusion-bonded epoxy (FBE).

- Flexible flowlines and umbilicals, e.g., polyamide 11, cross-linked polyethylene (XLPE) pressure sheath and PE sheaths.

Moreover, Figure 1 categorises the polymers based on their chemical structure, namely, the C–C backbone and the heteroatom framework.



**Figure 1.** Chemical frameworks of polymers employed in coatings and insulation applications. The symbols  $R_{1U}$  and  $R_{2U}$  denotes isocyanate and polyol fragments in polyurethane. The  $R_a$  in polyamide varies depending on the composition – however, the aliphatic  $(CH_2)_{10}$  main chain (Nylon 11) is used in subsea applications.

### 1.3. Geographical considerations

The areas of interest comprise Australian offshore waters with geolocations identified in Figure 2. Most of the offshore infrastructure at these locations were commissioned between 1965 (e.g., in the Bass Strait) and 1980s, and therefore nearing their end of service life. For Bass Strait (near Tasman Sea, Pacific Ocean), the depth generally ranges from shore to 95m, with one subsea development reaching ~400m. For Northwest (near the Indian Ocean), water depths typically range from 5 m to 1500 m. In Figure 2, the red circles show wells drilled by the oil and gas industry in the Australian marine environment between January 2001 and January 2021 (not to scale; data from <https://nopims.dmp.wa.gov.au/Nopims/>); the numbers of structures are indicative based on publicly available information and are derived from Advisian (2020); the diversity of marine environments in which these operations have occurred is shown by IMCRA v4.0 bioregions (pastel colours; Commonwealth of Australia, 2006); and Commonwealth waters are those that are more than three nautical miles offshore.

The methodology compiled in the following sections can be adapted to any specific location in the global marine system, while sourcing the relevant data (i.e., oceanography, meteorology, and biology information) from the local database.

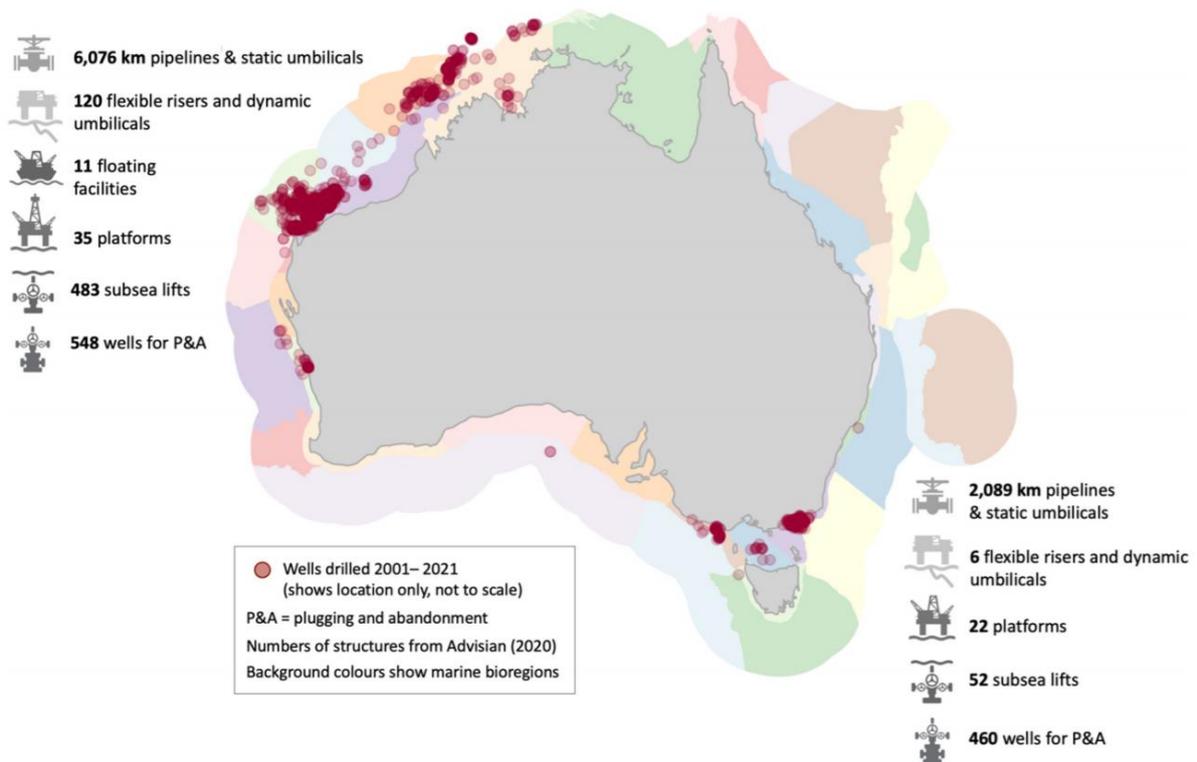


Figure 2. Geographical location of the Australian offshore Oil and Gas activities.<sup>16</sup>

## 2. Methodology

Document analysis, a form of qualitative research method, has been used in this study. The procedure involved a systematic review of both printed and electronic materials from the open literature. We catalogued and categorised a number of resources of representative studies into thematic sections below.

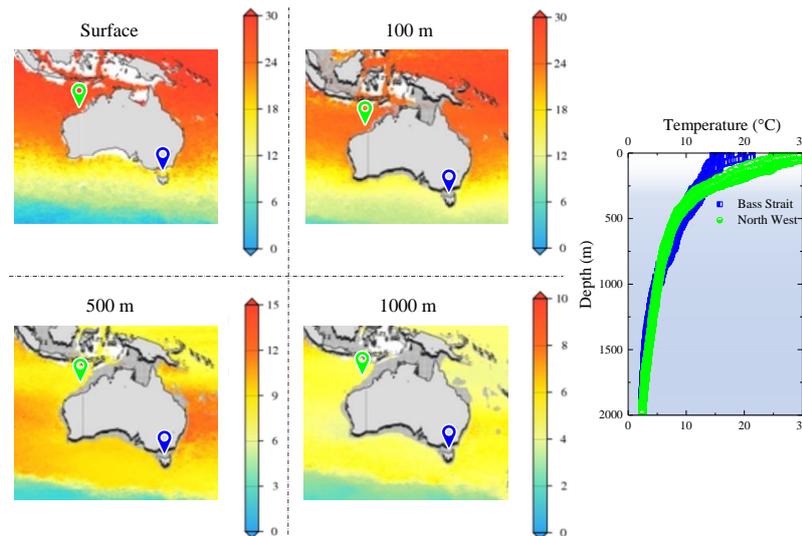
Furthermore, location-specific data were sourced from open databases such as the National Oceanic and Atmospheric Administration (NOAA) and the Open Access to Ocean Data. Subsequently, we fit the data into regression models to obtain the depth-profile relations.

## 3. Essential factors affecting degradation rates in marine environments

Besides chemical composition, molecular weight, hydrophilicity, and additive contents of the polymers,<sup>17</sup> the following physical, chemical, and biological parameters in offshore waters will contribute to the degradation of the materials. Unlike previous works conducted on floating plastics in the marine environment, one must consider the stratification of the ocean because marine infrastructure can often penetrate beyond the ocean surface into the deep-sea depths.

### 3.1. Temperature variation

Temperature plays a vital role in reaction kinetics and enzymatic activities.<sup>18</sup> The variation of temperature with water depth is a key parameter controlling the degradation of polymers, depending on the latitude, season, and oceanic turbulence (mixing). As shown in Figure 3, the surface layer (i.e., the epipelagic zone) and the thermocline layer represent the region of interest for offshore Oil and Gas infrastructure in our case study. Figure 3 provides the temperature profile of Australia offshore waters<sup>19</sup> at a selected depth, as well as the scattered plot of the temperatures acquired from various float stations<sup>20</sup> relatively to the mid-latitude and tropical oceans.



**Figure 3.** World Ocean atlas climatology for annual temperatures (statistical mean from 2005 – 2012) of Australian offshore waters at selected depths as compared to the typical ocean temperature-depth profile for a mid-latitude and tropical region. The iso-surface reveals temperature in °C.<sup>19</sup> The temperature-depth data has been acquired from Argo Australia’s Open Access to Ocean Data, with minor transformation of the hydrostatic pressure values into depth.<sup>20</sup> Argo Australia acquired the data from 2005 to 2020 by real-time monitoring through an array of profiling floats that measure temperature, salinity and pressure down to 2000m every 10 days in real-time.

A numerical fitting of the temperature-depth profile yields the following exponential parameters (Equation 1) for estimating the temperature of the offshore waters at Northwest and Bass Strait regions.

$$T_z = y_0 + Ae^{-rz} \tag{1}$$

Noting that,  $T_z$  is the temperature (°C) at a distance  $z$  from the surface, i.e., the depth in the ocean;  $y_0$  denotes a constant (e.g., 3.07462 for Northwest region, and 1.86693 for Bass Strait region);  $e$  is the natural log;  $A$  represents a constant (e.g., 26.14008 for Northwest region, and 19.69527 for Bass Strait region);  $r$  corresponds to the decay factor (e.g., 0.00307 for Northwest region, and 0.002 for Bass Strait region); and  $z$  is the distance from the sea-level, i.e., the required depth for plastic degradation.

### 3.2. Pressure changes

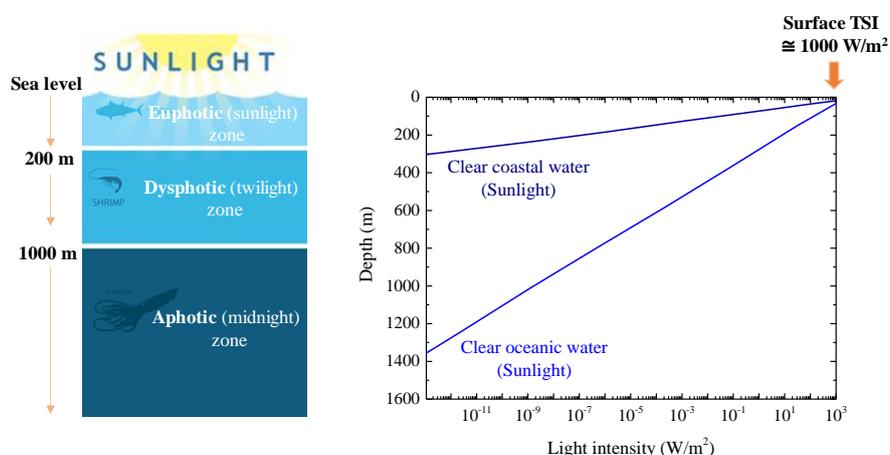
The depth profile results in shifts in hydrostatic pressure and can be estimated from the products of ocean density, acceleration due to gravity and water depth. However, due to the lack of direct gas-

phase, reversible, and precipitation reactions, the variation in pressure will have trivial effects on the photo and thermal degradation of the plastics.<sup>21</sup> However, hydrostatic pressure will influence hydrolytic and enzymatic reactions.<sup>22-24</sup> Furthermore, the impact of pressure on the marine environment can also manifest in the thermodynamic constants, especially for solubility of ion products of water such as the (bi)carbonate system in the ocean, and on the dissociation constants of acids.<sup>25</sup> Although the pressure impacts the gas dissolution, marine nutrients (silicates, phosphates, and nitrates), as well as the microbial compositions and activities through solubility thermodynamics,<sup>26</sup> one can indirectly account for it by using the depth-resolved values, e.g., for dissolved oxygen and CO<sub>2</sub> contents.

Pressure will contribute to the solubility of degradation products, e.g., CO<sub>2</sub>, resulting in the local acidification of the offshore waters. Excess CO<sub>2</sub>(aq) may alter the local equilibrium of the marine system to favour the Ca<sup>2+</sup>(aq) and HCO<sub>3</sub><sup>-</sup>(aq), while decreasing CaCO<sub>3</sub> concentrations. Dissolved CO<sub>2</sub>(aq) is acidic and can react with the strongest base present in significant concentrations, e.g., CO<sub>3</sub><sup>2-</sup>(aq), and upsets the carbonate buffer system. The effect of local CO<sub>2</sub>/carbonate dissolution from the degradation of polymers might have an impact on the marine ecology and, therefore, should be considered in a degradation model.<sup>27-31</sup> One can employ a simple carbon balance to calculate metric tonnes of CO<sub>2</sub>. Nonetheless, the slow-release rate may offset the effect.

### 3.3. Solar radiation penetrating the offshore waters

The intensity (actinometry) and wavelength of the solar radiation is another critical factor. Solar radiation within the ultraviolet and visible light regions initiates the photo-oxidation of organic substrates, including polymers.<sup>12,32-34</sup> It has been reported that light-induced oxidation is orders of magnitude higher than other types of degradations in marine systems.<sup>35</sup> Therefore, the profile of the intensity of solar radiation at the required water depths should be considered. The direct estimation of the radiation intensity based on the optical properties of the ocean will yield incorrect values due to the additional photochemical activities of marine organisms and infrared heating of the ocean. The literature provides a detailed account of the percent drop (relative to surface intensity) of solar irradiance in the ocean.<sup>36</sup> As depicted in Figure 4, the regions can be portioned into the euphotic zone (i.e., the upper 200 m part of the ocean that receives bright and clear sunlight), the dysphotic zone (i.e., water layer beneath the euphotic zone, extending to about 800 m with a significant drop in light intensity), and the aphotic zone (i.e., the water layer below 1000 m where there is no visible sunlight). The UV-A (320 – 400 nm) radiation can reach the depth of 70 m, while the light penetrating beyond the euphotic zone is the blue-green (450 – 550 nm) radiation.<sup>37</sup>



**Figure 4.** Penetration (attenuation, logarithmic scale) of solar radiation in oceanic waters. The surface total solar irradiance (TSI) varies from about 55 – 70 % of the earth's atmosphere irradiance (1366 W/m<sup>2</sup>) depending on the location and season.<sup>38</sup> The intensity values are digitalised daily average values from different ocean stations.<sup>39,40</sup> 1 W/m<sup>2</sup> = 4.57 Photon μmol/m<sup>2</sup> s.

It is worth noting that most of the laboratory simulations of photo-degradation reactions are conducted with light intensities within the euphotic/dysphotic range. Hence, a correction factor based on the depth–actinometry information may not be necessary. The light intensity, at the required depth, can be estimated based on Equation 2, which corrects the degradation rates as explained in the later sections:

$$I_z = I_0 e^{-kz} \quad (2)$$

Where  $I_z$  is the light intensity at a distance  $z$  from the surface;  $I_0$  denotes light intensity at the surface, e.g., 1000 W/m<sup>2</sup>;  $e$  represents the natural log;  $k$  is the light attenuation coefficient, amounting to 0.023 m<sup>-1</sup> and 0.056 m<sup>-1</sup> for oceanic and coastal waters, respectively, based on the numerical fittings of the data presented in Figure 4; and  $z$  = distance from the sea-level, i.e., the required depth for plastic degradation.

### 3.4. Changes in water column chemical composition

The ocean can also be stratified based on the changes in chemical composition, i.e., the chemocline. The changes in salinity, pH, and dissolved oxygen and other gases dictate the chemical nature of water column.<sup>39</sup> Although these parameters could be impacted by the bathymetry,<sup>40</sup> their variations in depth will have a trivial impact on the degradation of underwater plastic structures. For instance, the dissolved oxygen varies from approximately 3 mL/L to 8 mL/L of ocean water up to the depth of 4000 m.<sup>20,40</sup> Relatively to the plastics, the concentration of oxygen is in excess resulting in pseudo-first-order degradation kinetics. Moreover, the degradation of some plastics, e.g., polyurethane, follows hydrolysis-initiated reactions by water. Wherever possible, the data should be sourced from experiments conducted using typical ocean/seawater, to account for implicit effects of dissolved ions and oxygen.

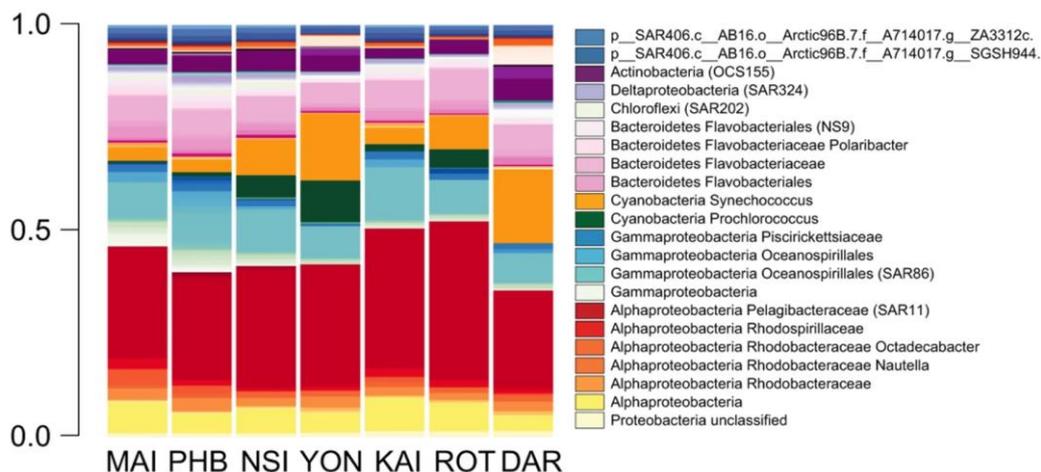
The photosensitising property of aquatic systems represents another factor to consider. The dissolved organic matters (DOM) in the ocean can generate reactive oxygen species (ROS) that are particularly known to initiate chemical reactions. DOM consists of riboflavin and pteridine derivatives, chlorophyll derivatives, fulvic acids, bile-type pigments, and humic materials derived from the dead cells of plants, bacteria, and algae.<sup>41,42</sup> Whereas, the formation of ROS transpires via light excitation of complex DOM molecules, which decay subsequently to their ground state by transferring the energy into triplet (oxygen) species. Typical examples of ROS include singlet delta oxygen ( $O_2^1\Delta_g$ ), hydroxyl radical (OH), superoxide anion ( $O_2^-$ ), and hydrogen peroxide ( $H_2O_2$ ), with hydrospheric concentrations well documented in the literature.<sup>43</sup> Considering the relatively high dissolved oxygen concentration and the low DOM concentration, the major ROS species formed by Type II photodynamic is the singlet oxygen.<sup>41</sup> Momzikoff investigated the photosensitising efficiencies (PSE) of samples of seawater;<sup>41</sup> based on the regression function computed by the author, the effect of ROS remains strongly active down to the depth of 500 m and mildly beyond. This is reasonably expected as the formation of ROS relies on the abundant dissolved oxygen, as well as light penetration. Therefore, kinetic corrections based on radiation attenuation should also account for the variations in photosensitising efficiencies, and the relative impact of degradation of the polymers.

### 3.5. Microbial composition

Microorganisms contribute to the degradation and biofouling of polymers. The process may include fungal, bacterial, and enzymatic degradations.<sup>44</sup> The generic aerobic biotic activity in plastics involves the secretion of extracellular enzymes that adhere to the polymer surface, leading to surface degradation (via erosion and mineralisation). Therefore, microbial enzymes often act as biocatalysts in degradation reactions.<sup>45</sup>

Furthermore, temperature alteration and hydrostatic pressure of the marine environment can affect microbial activities. Hochachka<sup>46</sup> worked on the enzyme mechanism in temperature and pressure adaptation of off-shore benthic and mesopelagic organisms. The author concluded that at physiological substrate concentrations and poikilothermic enzyme reaction rates are controlled by key kinetic parameters rather than energy volume relationships. The enzyme-substrate affinities often are adjusted to compensate for the unidirectional effect of temperature changes. However, the impact of pressure (which is not unidirectional) is maintained at a minimum. In other words, the benthic (occurring at the ocean floor) and mesopelagic (existing between 200 m to 1000 m ocean depth) organisms supply sufficient mechanisms for avoiding uncontrollable effects of high pressure on chemical reactions. Moreover, another study on the effect of hydrostatic pressure and temperature on the activity and synthesis of extracellular enzymes (i.e., chitinases) by psychrophilic and psychrotrophic marine bacteria led to a similar conclusion. It was shown that the effect of pressure becomes significant around hydrostatic pressure of 400 bars (395 atm, equals about 4000 m seawater depth), with the growth of psychrophilic strains showing moderately barophilic character, as compared to severely restricted growth of psychrotrophic strains. The extracellular chitinases were active up to 1000 bars at neutral pH.<sup>26</sup> Studies have shown that the composition of bacterial decreases with depth,<sup>47</sup> with the majority existing as members of the free-living plankton in low-nutrient ocean ecosystems.

A direct approach is to identify the microorganism inhabiting the sites and account for their respective effects on degradation rate based on the available published data. CSIRO's data collates the marine pelagic microbiota (up to a depth of 100 m) by the Australian Marine Microbial Biodiversity Initiative.<sup>20,48</sup> As shown in Figure 5, Alphaproteobacteria and Cyanobacteria which are known to degrade polymers are identified at all the seven Integrated Marine Observing System (IMOS) national reference stations (NRS). These results are in agreement with those identified in the southern hemisphere in another study.<sup>49</sup> The database also contains information on nutrients and other relevant oceanographic information. Specific published information for each polymer is discussed below in Section 4. However, one should bear in mind that time, and climate changes could pave the way to the adaptation and evolution of highly active enzymes.<sup>50,51</sup>



**Figure 5.** Relative abundance of bacterial retrieved from surface waters at seven IMOS NRS around Australia. The acronyms MAI, PHB, NSI, YON, KAI, ROT, and DAR denote Maria Island, Port Hacking, North Stradbroke Island, Yongala, Kangaroo Island, Rottnest Island, and Darwin, respectively.<sup>48</sup>

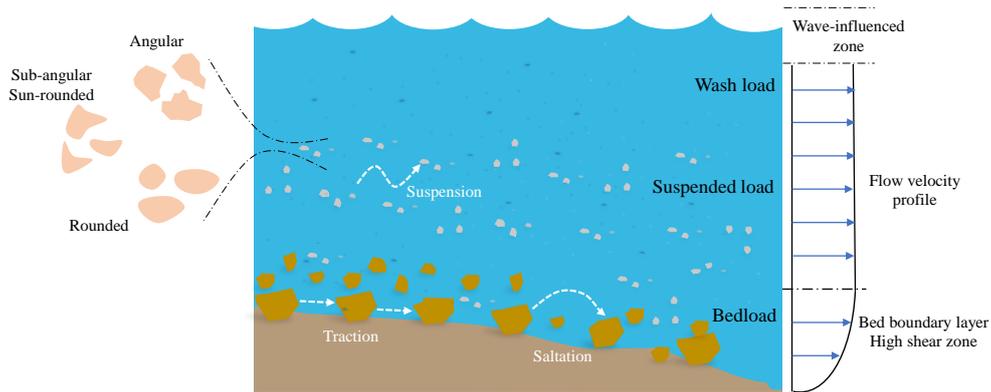
### 3.6. Abrasive wear

Abrasive wear (or mechanical erosion) occurs due to waves, winds, and residues of suspended particles in the ocean. This factor contributes to the fragmentation of plastics by breaking the larger plastics into smaller pieces of micro- and nano-plastics (i.e., MP, with sizes less than 5 mm, and NP, with sizes below 0.1  $\mu\text{m}$ ). The subsequent degradation of the nano or microplastics will then follow other pathways (see sections below).

The fragmentation due to stresses from water<sup>52</sup> can be accounted for by considering degradation data acquired from flowing a stream of water. Moreover, waves have trivial impacts on the mechanical fragmentation plastic residing at depths below half the wavelength because the circular motion (kinetic energy) of water due to waves becomes approximately zero at depth  $\geq 0.5 \times$  wavelength.<sup>53</sup>

Despite confirming the natural occurrence of abrasion of plastics due to oceanic particles (fine grains of sand),<sup>17,54,55</sup> the literature lacks information on how to model and estimate the abrasive fragmentation of plastics in the natural marine environment. However, wherever such data are not available, reasonable postulations can be made based on the paradigmatic principles of abrasive wear. We develop an approach to estimate the rate of abrasion of polymers in a water column due to marine particles in the following paragraphs.

Oceanic sediments arise through geological fluid dynamics,<sup>56</sup> such as weathering and coastal accretion or erosion. They are subsequently transported by ocean currents, waves and celerity, storm surge and nearshore currents, as depicted in Figure 6. The size and shape of the particulates (See Figure 6) can have an impact on the abrasion rates of plastic materials in the deep ocean.



**Figure 6.** Mobility and transportation of particulates (sands) in the marine environment, and shape classification of the suspended loads. Bedload represents the fraction of the sediment transport that rolls, slides or bounces along the bottom of a waterway; Suspended load resides above the bed as a result of water flow and turbulence, and settling velocity, i.e., a function of drag force and gravitational force; Wash load is a subset of suspended load that remains permanently afloat due to ultra-fine particle size of about 1.95  $\mu\text{m}$  (classified as very fine clay-sized sediment in Wentworth scale<sup>57</sup>). The velocity profile and amount of loads are required to estimate the abrasion rates of subsea plastics.

According to the theory of abrasion, e.g., Hutching equation, the steady-state erosion (abrasion) rate can be ascertained from the dimensionless wear coefficient ( $k_w$ ), the density of the material being eroded (i.e., plastics), the impact velocity ( $v^2$ ) of the particles (i.e., sediment loads), and the hardness of the material surface ( $H$ , Pa).<sup>58,59</sup> In Equations 3 and 4, the erosion rate has been defined as the ratio of mass loss suffered by eroding material to the mass of erodent ( $E_m$ , g/g) or in terms of volume lost per unit mass of erodent ( $E_v$ ,  $\text{m}^3/\text{kg}$ ). The impact function  $f(\theta)$ , accounting for the angle at which the erodent hits the surface, is sometimes assumed to be unity for simplicity, but  $f(\theta) = \sin^2 \theta$  results in better accuracy. The term sand erosion can describe processes involving solid particles to up to approximately 1000  $\mu\text{m}$  in size.<sup>60</sup>

$$E_m = \frac{k_w \rho v^2}{2H} f(\theta) \quad (3)$$

$$E_v = \frac{k_w v^2}{2H} f(\theta) \quad (4)$$

For the erosion of common polymers, the value of  $k_w$  lies typically in the range of  $10^{-3}$ – $10^{-4}$ , with exact values reported in the literature.<sup>61,62</sup> However, the application of Equation 3 or 4 in the marine environment will require knowing the numerical values of the impact velocity of the sediment loads. This challenging parameter can be resolved by assuming the sediment grains travel at the same velocity as the water. Subsequently, the impact velocity follows the velocity-depth profile of the ocean current that can be evaluated from any of Equations 5 – 8, depending on the available data. For offshore engineering structures, where the total depth below the surface is  $d$  (m), and the height above the seabed is  $z_s$  (m), the velocity of current  $v_z$  (m/s) can be calculated as a function of  $z_s$  from the velocity of the tidal current  $v_{ct_0}$  (m/s) and the velocity of the wind current  $v_{cw_0}$  (m/s) at the surface.<sup>63</sup> The power law is usually taken to be of the 1/7th order (i.e.,  $\alpha = 7$ ).<sup>64</sup> In Equation 6,  $v_0$  represents the combined current velocity at the surface. The velocity decreases with depth due to friction (drag) from the seabed.

Moreover, the velocity of current  $v_z$  can also be estimated from the bed roughness ( $\beta = 0.32$ ), the total water depth and the depth-averaged velocity  $\bar{v}$ , as shown in Equation 7.<sup>65,66</sup>

$$v_z = v_{ct_0} \left( \frac{z_s}{d} \right)^{\frac{1}{\alpha}} + v_{cw_0} \left( \frac{z_s}{d} \right) \quad (5)$$

$$v_z = v_0 \left( \frac{z_s}{d} \right)^{\frac{1}{\alpha}} \quad (6)$$

$$v_z = \bar{v} \left( \frac{z_s}{\beta d} \right)^{\frac{1}{\alpha}} \quad (7)$$

The typical average surface velocity of ocean current varies between 0.5 – 3 m/s.<sup>20</sup> Webster<sup>67</sup> provide the actual measurements of velocities in the deep-water ocean. The latter study presents a simplified equation for estimating the velocity of currents in a deep-water ocean (Northwest Atlantic) below 10 m depth, as described in Equation 8, which is very useful if there is no information regarding the surface current. The parameter  $h$  (cm) is measured positively downward from the surface.

$$v_z = 670 h^{-0.4} \quad (h \text{ in cm, and } v_z \text{ in cm/sec}) \quad (8)$$

It is important to express the steady-state abrasion rate in the same unit as the chemical degradation rate (e.g., in mass per unit time). Such transformation requires specific information regarding the amounts of sediment loads and the volumetric flow rate of the water, preferably based on depth dependencies. The abrasion rate,  $E_{m_r}$  in mass per unit time (g/s), of a stationary material being eroded by sediment loads in flowing offshore water then becomes:

$$\frac{dm_r}{dt} = E_{m_r} = E_m C_z Q = E_m C_z v_z \times SA \quad (9)$$

where  $E_m$  has been defined as the ratio of mass loss suffered by eroding material to the mass of sediment-erodent (g/g),  $C_z$  denotes the concentration of sediments (g/m<sup>3</sup>), and  $Q$  defines the volumetric flow of water in direct contact with the plastic surface (m<sup>3</sup>/s) – approximated as the surface integral of the  $v_z$  with respect to the area, approximated as the dot product of the  $v_z$  and the surface area ( $SA$ ) of eroding material. The physical interpretation of Equation 9 implies that a volume of water carries a particular amount of sediments loads over a stationary material (e.g., plastic-coated pipelines) in a unit measure of time. Equation 9 can be reformatted into Equation 10, with  $k_{SSE} = (E_m C_z v_z) / \rho$ , where  $\rho$  is the density of the polymer material. Ideally,  $k_{SSE}$  should also reflect the fraction of the total surface area that is interacting with the stream.

$$\frac{dm_r}{dt} = E_{m_r} = k_{SSE} \cdot \rho \cdot SA \quad (10)$$

The necessary theories for estimating the sediment concentration and transport phenomenon have been documented in the application book by Soulsby.<sup>65</sup> For the deep-water application, we limit this to sediment under the effect of current. In a sand suspension, the settling of the grains towards the bed counterbalances the diffusion of the sands upwards due to turbulent water motion based on the following governing equation:

$$w_s C = -K_s \frac{dC}{dz} \quad (11)$$

where  $w_s$  corresponds to the settling velocity of sediment grains,  $C$  the volume concentration of sediment at height  $z_s$  above the bed, and  $K_s$  the eddy diffusivity of sediment. Assuming the eddy diffusivity increases linearly with height, then the corresponding concentration obeys a power-law profile:<sup>65</sup>

$$C_z = C_a \left( \frac{z_s}{z_a} \right)^{-b} ; b = \frac{w_s}{\kappa u_*} \quad (12)$$

where,  $C_a$  denotes the sediment reference concentration at height  $z_a$ ,  $b$  is the Rouse number, or suspension parameter,  $\kappa$  represents the von Karman's constant = 0.40, and  $u_*$  refers to the total friction velocity or total skin friction of the sediment.

The geology of the seabed is very complex. For simplicity,  $b = 0.811$ ,  $z_a = 1.30 \times 10^{-3}$  m, and  $C_a = 6.81 \times 10^{-3}$  ( $\times 2650$ , conversion factor to  $\text{kg/m}^3$ )<sup>65</sup> based on the shearing of a rippled bedload with 50 % weight distribution of  $d_{50} = 0.20$  mm (i.e., fine to medium sand, needed to calculate the grain settling velocity) and depth-average flow velocity of 1 m/s (needed to calculate the drag coefficient and the total skin factor). The concentration of sand sediments can also be used directly from the measured data, or estimated from a correlation of relevant turbidity information, e.g., as reported by Cooper et al.<sup>68</sup> It is worth noting that Equation 12 yields concentration values that are well comparable to those measured from depth-specific marine systems.<sup>68,69</sup> Even if the numerical values of abrasion rate are small, the effects could be significant considering the large degradation time scale and the relatively low hardness of the plastic materials. Future experimental plans should investigate further the abrasive wear of materials in marine systems.

### 3.7. Miscellaneous parameters

The service conditions, including working temperature, static loads (inducing local strains) and protection mechanisms such as cathodic protection (CP), may influence the degradation of plastic components in offshore infrastructure. The CP system, for instance, results in the build-up of calcareous deposits. Such deposits are formed on bare metal components due to the alkalinity produced on cathodically protected surfaces in the presence of calcium and magnesium salts (e.g., carbonates).<sup>70</sup> The effect of CP on plastic coatings should be minimal as very little deposition of calcareous materials are expected on plastics coatings.<sup>71</sup> However, the presence of holiday defects on the polymer coating can result in cathodic disbondment (CD), i.e., delamination of polymer coating from the metallic substrate.

Various mechanisms have been proposed for CD, including the dissolution/reduction of the oxide layer in the steel-polymer interface,<sup>72-75</sup> mechanical lifting of the coating by  $\text{H}_2$  gas generated in the interface,<sup>76</sup> aqueous displacements of the coating,<sup>77</sup> and enhanced degradation on polymer coating.<sup>75,78-81</sup> The degree of CD has been found to be influenced by the negative potentials achieved by Al-Zn-In sacrificial anodes (i.e., the industry standard CP choice) which accelerates electrochemical reactions and production of hydroxyl ions ( $\text{OH}^-$ ),  $\text{H}_2$  gas, and reactive oxygen species, i.e., short-lived oxygen-containing radicals such as superoxide ( $\text{O}_2^-$ ), peroxide ( $\text{H}_2\text{O}_2$ ) and hydroxyl radical ( $\text{OH}^\cdot$ ). Based on their high reactivity, it is more probable that the free radicals are responsible for the detachment of the polymer coating from the steel pipe.<sup>81-85</sup> The rate of growth of disbondment areas

can be used to estimate the exposed surface area when calculating the lifetime of the polymer. However, the thickness of the coating material on the flowlines, ranging from about 1 - 3mm (for rigid pipelines) or above 3 mm (for flexible flowlines), can hinder the formation of holidays that penetrates deep into the metal substrate.

The presence of marine growth that is rapidly colonized by algae and other marine biotas, including encrusting organisms,<sup>12,86</sup> may inhibit the mechanical abrasion of subsea material but should have minimal negative effect on the degradation mechanism due to enzymatic activities of biofoulants.<sup>87</sup> Furthermore, components buried under the seabed should encounter rates similar to those recorded for underground degradation, and may be influenced by the bathymetry, the existence of benthic organisms, as well as the pronounced effect of the abrasion due to moving ocean-bed particles. There is currently no literature information on the degradation of polymers buried under the seabed. However, a realistic approach assumes the degradation will proceed at a rate similar to materials located on the seabed, but without the effect of sand abrasion. This assumption is based on the fact that (i) like to underwater buried condition, the material on the seabed is already experiencing a near-zero light intensity (see Figure 4 of the report), (ii) the temperature below the seabed can be represented by the bulk temperature of the seabed, (iii) due to the poroelastic nature of the seabed, water can diffuse to a considerable depth (e.g., more than 20 m) below the (porous) seabed.<sup>88,89</sup> In fact, beyond the porous seabed depth, the so-called rigid impermeable bottom is also made of porous materials;<sup>89</sup> therefore, all the hydrolytic (and consequential biotic) degradation channels will persist in underwater buried condition.

Another factor may involve the interference of metallic corrosion as ions from corroding metal may scavenge/promote radical species in polymer degradation. There are no precise literature data in this regard. Therefore, future experiments should investigate the effect of proximity of corroding metal, e.g., on the formation of persistent free radicals and promotion (or inhibition) of plastic's degradation rate.

### 3.8. Design and size factors

Apart from the marine environment, another critical parameter is the design (e.g., geometry) and size of the plastic components. As will be discussed later, the geometry and size of a material have a strong influence on the kinetics of degradation proceeding along the surface front. The geometry and design of subsea cables, integrated service umbilicals, flexible and rigid flow lines are very different from one another.<sup>90</sup> Ideally, this information should be considered while estimating the lifetime of plastic components of the infrastructure.

In summary, the essential parameter discussed in this section will control the degradation of polymeric components of offshore oil and gas infrastructure during both service operation and decommissioning periods. The empirical relation for estimating the depth-resolved temperature profiles of offshore waters in the two regions will be highly instrumental in translating the effect of depth temperature into the kinetic model. Similarly, the respective quantitative relations for pressure and light attenuation will serve to adjust the degradation rate in the kinetic model. The effect of microbial activities is best captured by using only the literature data acquired in experiments performed in marine water containing specific microbes available in the Australian offshore waters. The method of assessing the abrasion due to marine sediments is conservative and should be further tested experimentally.

From an application point of view, temperature, pressure, solar irradiance, and abrasion would play the most significant role in the degradation of polymers in offshore waters. The methods described above can be used to determine the magnitude of the temperature, pressure quantitatively, and solar irradiance at a particular water depth of interest, followed by an appropriate chemical kinetic transformation to predict the degradation of the polymers. In comparison, the miscellaneous parameters would have a relatively minor effect.

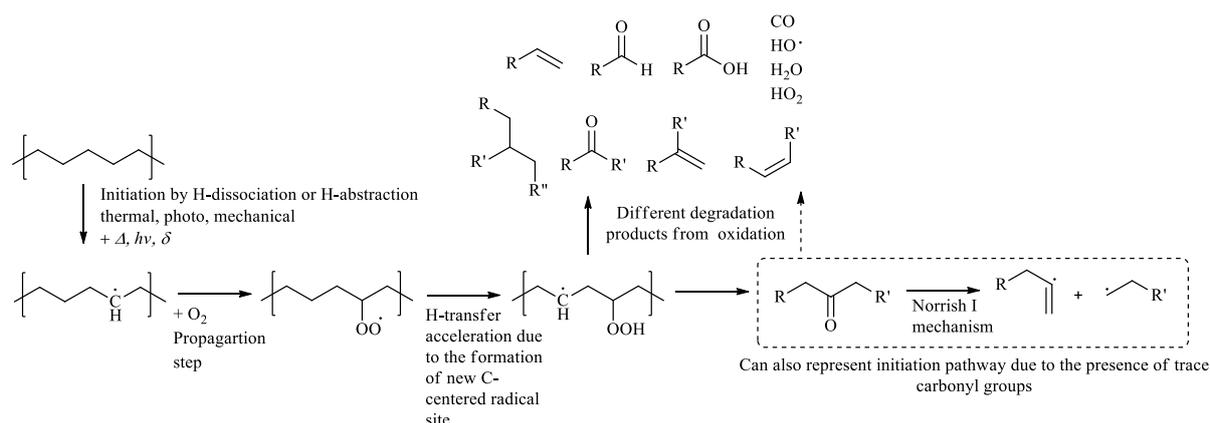
#### 4. Degradation mechanisms and role of the physicochemical parameters

The degradation mechanisms of plastics have been widely reported. Although many definitions exist in the open literature, we describe “degradation” as the loss in mass per unit time, especially for lifetime predictions. The international standards define polymer degradation as a deleterious change in the chemical structure, physical properties, or appearance of a polymer, which may result from chemical cleavage of the macromolecule forming a polymeric item, regardless of the mechanism of chain cleavage.<sup>91,92</sup> While this kind of definition remains helpful in understanding the chemical, structural and mechanical changes in a polymer, the rate obtained may not necessarily imply direct mass loss. Proper numerical and empirical rate transformations should be used to convert such rate expressions into mass-loss per unit time.

The mode of degradation of synthetic polymers can follow integrated pathways, including solar-induced photo-degradation, thermal oxidation reactions, ozone-induced degradation, hydrolysis, catalytic degradation, mechanical wear (see abrasive wear above), and microbial-induced biodegradation.<sup>17,93</sup> The chemical degradation of plastics at ambient environmental conditions involves either oxidation (from dissolved oxygen) or hydrolysis (from marine H<sub>2</sub>O), both of which can be accelerated by microbial activities, heat, light, or their respective combinations.<sup>94</sup> The following subsections summarise the degradation mechanisms of the selected commercial plastics, highlighting how the marine ambient factors influence the degradation pathways.

##### 4.1. Polyethylene

Polyethylene (PE) has been characterised as the most inert synthetic polymer due to its extremely slow degradation rate in the natural environment. Hence, PE serves as the most common coating material in offshore applications. The inertness of PE stems from the C–C single bonds backbone that is resistant to hydrolysis and photo-oxidative attacks due to lack of UV–visible chromophores. However, mechanical shears, structural defects, and the presence of production impurities such as trace unsaturated (C=C) bonds, peroxides, carbonyl and hydroperoxides can influence the initiation of photo-oxidative pathways.<sup>93,95-97</sup> Therefore, low-density polyethylene (LDPE) having a relatively higher frequency of reactive branch sites degrades faster than the analogous high-density polyethylene (HDPE).<sup>98</sup> Figure 7 captures the degradation pathways of PE in an abiotic environment as described in various studies.<sup>95,99-102</sup> The initiation reaction is solely limited to photo, thermal, or mechanical stimuli, with the addition of oxygen and molecular transfer of hydrogen atom being the propagation and auto acceleration steps, respectively, for the formation of the primary oxidation products. The presence of free chlorine and hydroxyl radical can accelerate the initiation reaction.<sup>103</sup>

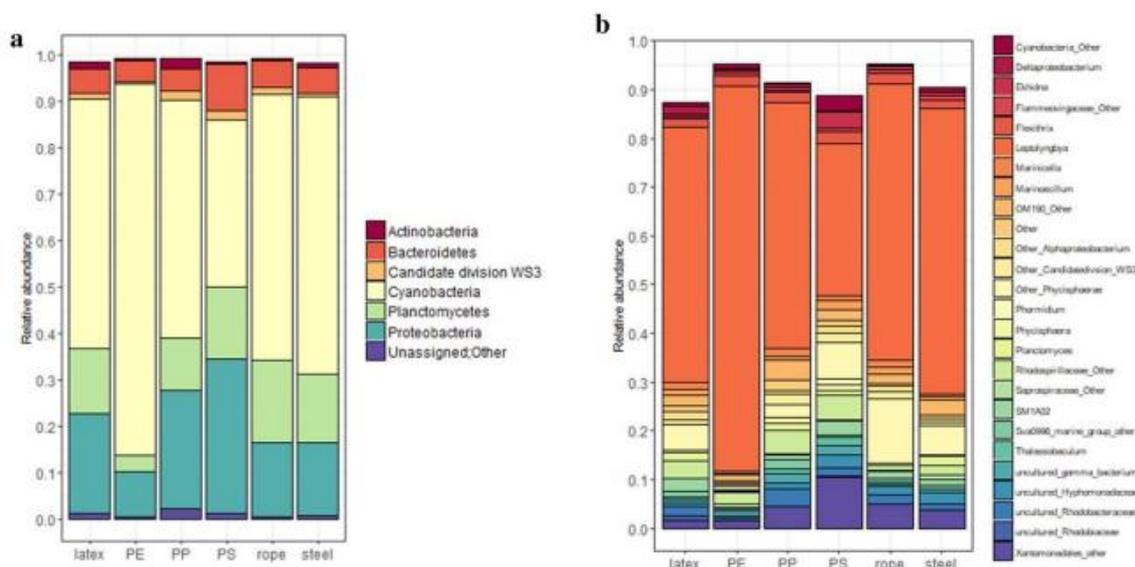


**Figure 7.** Initial degradation pathways of polyethylene and formation of common products. The notation R, R', and R'' represent polymer chains of different lengths. Norrish II mechanism and termination steps are not shown here.

Considering a marine medium with temperatures below 30 °C (i.e., much less than 100 °C), the photolytic reactions remain the most critical initiation channel.<sup>13,100</sup> Lifetime prediction in marine environments should rely on initial rate data acquired under identical temperatures, requiring no (or minor) temperature-extrapolation (e.g., to 16 °C) due to the depth variations. Likewise, the service temperature impacts the degradation rate of plastics, even during the after-service-life period. This is because moderate heating, in the presence of oxygen, enhances rates of polyolefin oxidative degradation significantly, as it increases the hydrophilicity due to the incorporation of oxygen-containing functional groups that facilitate surface attachment of microorganisms. A previous study has shown that thermal pre-treatment of PE at 80 °C for ten days increases the marine bacterial colonisation 4 to 7 times compared to no thermal treatment. The same study recorded higher mass losses for thermally pre-treated LDPE and HDPE (17 % and 5.5 %, respectively), compared to the untreated materials (10 % and 1 %, respectively) over the same time period.<sup>104</sup>

At any given temperature and water content, the rate of weathering and degradation increases with increasing solar radiation UV flux.<sup>17</sup> The UV-visible light spectrum of 300 nm – 500 nm carries enough energies, equivalent to 400 kJ/mol – 240 kJ/mol, to break various bonds in PE structure. It is worth noting that the bond dissociation enthalpies for C–H and C–C in polyethylene amount to about 410 kJ/mol and 290 kJ/mol, respectively, depending on the chemical identity of adjacent functional groups,<sup>96,105</sup> presence of radical sites<sup>106-108</sup> and ionic interactions.<sup>109</sup>

Furthermore, the effect of microorganism is important under biotic conditions present in water, mainly in the form of surface erosion by extracellular enzymes and rarely by intercellular activities. Many scientific papers have identified some microbe (including bacterial and fungi) specially isolated to target effective and rapid degradation of PE.<sup>110-120</sup> Enzymes such as laccase,<sup>121,122</sup> hydrolases,<sup>123</sup> esterase,<sup>124</sup> depolymerases, cutinase, and lipase<sup>113,125</sup> are significant in PE degradation, producing humus, CO<sub>2</sub> and H<sub>2</sub>O as the ultimate products. However, in the natural marine environment, microbial activities will be limited to the presence of the naturally occurring organisms. In Figure 8, Gerritse et al. have shown that Cyanobacterial and Proteobacteria (which are abundant in Australian offshore waters, see Figure 5) dominates the biofilms of PE degrading in typical seawater.<sup>7</sup> The mechanism of biological degradation of PE via enzymatic hydrolysis has been documented elsewhere.<sup>126,127</sup>



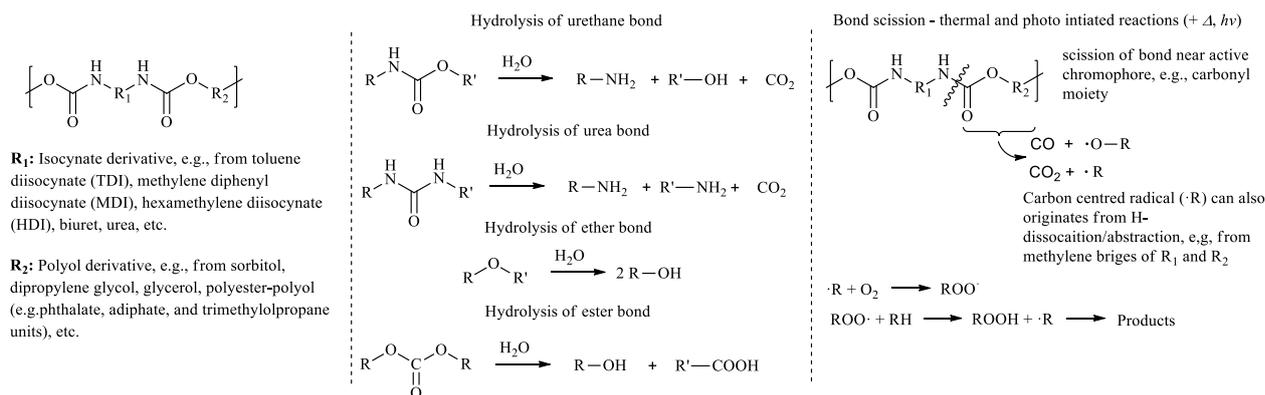
**Figure 8.** Relative abundance of 16S rRNA genes of biofilm growing on plastics in seawater microcosm at (A) phylum level and (B) genus level. Figures show only those phyla/genera, which represent at least 1% of the total community in at least one sample.<sup>7</sup>

#### 4.2. Polypropylene

The degradation mechanisms of polypropylene (PP) appear similar to that of PE.<sup>33,128,129</sup> However, PP has relatively lower stability than PE due to the presence of tertiary carbons (refer to Figure 1) that are more prone to abiotic degradation than secondary carbons in PE. The initiation stems from the formation of PP radical due to hydrogen abstraction/dissociation and trace impurities. The radical reacts with oxygen, yielding random chain scission, cross-linking, and predominately forming lower molecular weight fragments.<sup>130,131</sup> Although the tertiary carbons promote abiotic degradation of PP, they decrease the susceptibility of the polymer to microbial (biotic) degradation.<sup>132</sup> This is logical because the relative abundance of 16S rRNA genes of biofilm on PP differs compared to PE.<sup>50</sup> Therefore, PP degrades relatively slower in natural seawater as compared to PE.<sup>7,133</sup>

#### 4.3. Polyurethane

Unlike PE and PP, polyurethane (PU) can undergo hydrolysis. Therefore, the degradation of PU is much faster in seawater. Hydrolysis represents another chemical degradation mechanism. In order to suffer splitting by H<sub>2</sub>O, the polymer must have functional groups containing hydrolysable covalent bonds, e.g., ester, ether, anhydride, amide, carbamide (urea), ester amide (urethane) etc.,<sup>94</sup> as in PU.<sup>134,135</sup> Factors including temperature, pH, and water activity can affect the rate of hydrolysis of a polymer. As shown in Figure 9, the hydrolysis proceeds via ester linkages and polar groups in the side chain of PU. Apart from the ester bond, urethane and urea bonds can also undergo hydrolytic cleavage, but at relatively slower rates.<sup>136</sup> The presence of ions (e.g., in seawater) can promote hydrolytic degradation of PU. Parallel to hydrolysis, alternative abiotic solar radiation (or heat) can induce oxidative degradation through radical reaction pathways.<sup>33,135,137,138</sup>

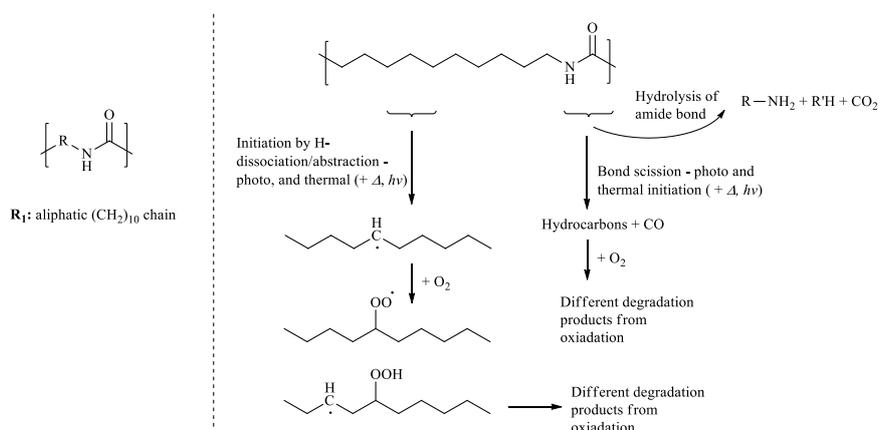


**Figure 9.** Initial degradation pathways of polyurethane via hydrolysis and photo (and thermal) initiated pathways. The notation R and R' represent polymer chains of different lengths.

The biotic degradation process of PU is also limited to the surface due to the diffusion limitation of enzyme into the bulk polymer, and it favours fungal biodegradation<sup>44,139</sup> more than bacterial attack.<sup>114,140-143</sup> Moreover, it has been shown that the microbial degradation of the polyester segments of PU proceeds faster than that of the ether groups. Bacteria (e.g., *Pseudomonas*) known to degrade PU produce polyurethanes degrading enzymes, such as polyurethane-esterases with effective intracellular and extracellular activities on the carbonyl and adipic carbons in the PU chain.<sup>139,140</sup>

#### 4.4. Polyamide

Polyamide (PA) typifies a group of polymers with repeated amide linkages. The most relevant PA in the marine application is polyamide 11 (PA 11), otherwise known as nylon 11 or Rilsan.<sup>144</sup> Although PA 11 is an example of bioplastic being produced from a renewable raw material (i.e., 11-aminoundecanoic acid), it can resist biodegradation. Similar to PU, PA 11 is very sensitive to water (hydrolysis),<sup>145</sup> and the rate of degradation should be comparable to that of PU.<sup>146</sup> Previous studies monitored the hydrolytic and oxidative degradation of PA 11 by recording the change in molecular weight with time at fairly high temperatures between 90 °C to 110 °C.<sup>145,147-151</sup> This kind of molecular weight model can be adjusted into other forms of degradation representations by using appropriate mathematical transformations.<sup>145,152</sup> Figure 10 summarises abiotic degradation mechanisms of PA 11,<sup>153</sup> illustrating different initiation channels in the aliphatic and amide functional groups.



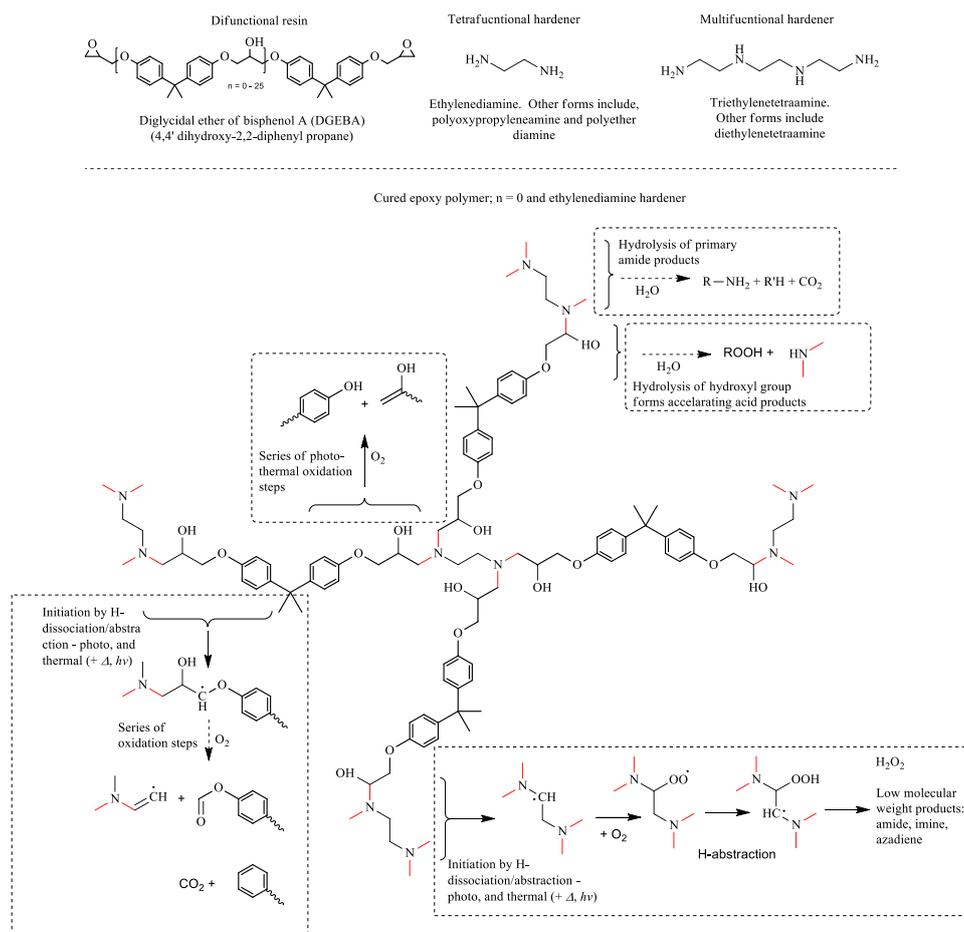
**Figure 10.** Initial degradation pathways of polyamide 11 via hydrolysis and photo (and thermal) initiated pathways. The notation R and R' represent polymer chains of different lengths.

While natural polyamides such as proteins and natural silk can easily undergo enzymatic degradation, there is no microorganism known to fully degrade high molecular weight PAs.<sup>50</sup> Studies have identified bacteria acting on the short-chain oligomers of PA. This includes hydrolases and aminotransferases of *Flavobacterium* sp. (recently named *Arthrobacter* sp.) strain KI72 grown in the waste wastewater system of nylon factories.<sup>154,155</sup> While no data exist for PA 11; the literature records three main enzymes essential for the hydrolysis of linear and cyclic 6-aminohexanoate (from PA 6.6 or nylon 6.6) oligomers.<sup>156-164</sup> Manganese-dependent peroxidase (an enzyme originated from rot fungus) appears to be the only enzyme that has so far been reported to act on high-molecular-weight nylon fibres.<sup>165</sup> Species of *Pseudomonas*, such as *P. aeruginosa* and evolved strain PAO1 been reported to be able to degrade 6-aminohexanoate-dimers by utilising it as a sole carbon and nitrogen source.<sup>154,166,167</sup> Whereas, in marine environments, *Bacillus cereus*, *Bacillus sphaericus*, *Vibrio furnissii*, and *Brevundimonas vesicularis* have been reported to degrade nylon 6 with a significant mass loss over a period of three months.<sup>168</sup>

#### 4.5. Epoxy polymer

Epoxy polymers are complex thermoset admixture containing the resin and the cure that represents a functional blend of hardener and other components such as plasticiser, preservative, and chain-terminating agent. Although the resin, on its own, can be polymerised to a reasonable extent, the application of hardeners improves the chemical resistance and material properties of epoxy polymers.<sup>169</sup> Epoxy resins acquire their name from the presence of epoxide functional group in their respective structures. Most marine applications usually rely on diglycidyl ether of bisphenol A (DGEBA) and other phenolic analogues as the primary epoxy resin, and aliphatic amines and polyamides (see Figure 11), as the curing agents (i.e., hardener).<sup>170,171</sup> Other common hardener includes cycloaliphatic amines, aromatic amines, amidoamines, and anhydrides.<sup>171,172</sup> The use of amines results in an epoxy polymer having low glass transition temperature ( $T_g$ ) as compared to anhydride curing agent, favouring application in ambient environments. However, adhesion and CD performances can be improved by modification of the epoxy network, e.g., bromination of the phenyl functional groups.<sup>173</sup> FBE<sup>174</sup> and HBE have emerged as the most preferred options in marine environments due to their performance and favourable resistance to water diffusion.<sup>175</sup> Zargarneshad et al. reviewed the mass transport of H<sub>2</sub>O in epoxy coatings and provided insights on probabilistic models to relate the likelihood of failures based on the declining properties of the coatings.<sup>175</sup> It has also been shown that the surface degradation of epoxy is relatively faster than the bulk degradation.<sup>175,176</sup>

The structure of epoxy polymers allows for deterioration by hydrolysis, as well as photo/thermal stimuli. As illustrated in Figure 11, the photo-thermal degradation pathway can be initiated both in the resin and the hardener,<sup>177-180</sup> leading to fragmentation of the cross-linked structure and the formation of low-molecular-weight species. Hydrolysis, on the other hand, depends on the hydrophilic groups, mainly secondary hydroxyl and amide ends. Most works have focused on water uptake and depreciation of the mechanical properties of the material rather than surface erosion.<sup>172,181</sup> The mechanism involves migration of water unto the surface, resulting in swelling (due to disruption of the hydrogen bonding within the matrix) and subsequent degradation of the molecule<sup>169,172</sup> into products including acids. The effect of acid has been reported to increase the degradation rate of an epoxy polymer.<sup>182</sup> Moreover, seawater should facilitate the formation of inorganic salts within the polymer matrix.<sup>182,183</sup>



**Figure 11.** Initial degradation pathways of epoxy polymer via hydrolysis and photo (and thermal) initiated pathways. The notation R represents polymer chains.

There are only a few studies on microbial degradation of an epoxy polymer in natural environments despite its widespread applications in protective paints,<sup>184-186</sup> adhesives, composites, and varnish coatings. The most common isolated bacteria from surfaces coated with epoxy belong to phylum Firmicutes, Proteobacteria, *Pseudomonas*, and Actinobacteria.<sup>184,187</sup> The presence of *Pseudomonas putida*<sup>188</sup> and *Bacillus flexus*<sup>189</sup> in seawater has been demonstrated to degrade epoxy polymers, with a mechanism centring on the microbial attack of the hydroxyl to form biodegradable carbonyl groups.<sup>188</sup> Other research works involved bacteria isolated from soil,<sup>190,191</sup> bacterial activities during soil burial degradation,<sup>192</sup> and degradation due to mixed culture of fungi<sup>193</sup> and black yeast fungi.<sup>187</sup>

#### 4.6. Evolution of microplastics

In addition to the produced  $\text{CO}_2$  (carbonate), and dissolved organic carbon (DOC) and nitrogen (DON), the formation of microplastics (and nanoplastics) in the marine environment stems from both shearing (i.e., abrasive wear) and chemical degradation pathways, which are coupled under realistic conditions. As photochemical degradation (weathering) proceeds in time, the structural integrity of the plastics deteriorates, allowing for a faster rate of abrasive wear.<sup>7,35,54,194</sup> Similarly, chemical degradation unzips the polymer into low molecular weight fragments, contributing to the fragmentation of the plastics along the surface cracks and fissures.<sup>35,195-197</sup>

While there has been an attempt to detect the onset of microplastic generation in marine system,<sup>198</sup> and the role of water in fragmentation of plastics,<sup>52</sup> there exists no literature information on the mass balance of plastics' degradation into product and fragmentation species. In other words, there is no information on the number of microplastics generated per unit mass of the parent plastic degradation in the ocean. Gerritse et al., while investigating the fragmentation of plastics in a microcosm experiment, reported that microplastic generation was responsible for portions of the detected gravimetric weight loss.<sup>7</sup> More data are required to estimate the amount of microplastics generated from plastic degradation in the ocean. It can be assumed that microplastics fraction can be estimated based on the ratio total degradation rate to rate of fragmentation/abrasion. This kind of approximation will be influenced by the type of plastic, discontinuities in the form of voids and cracks in the structure of the plastics, and the environmental degradation factors.

Once formed, microplastics interact inevitably with chemical pollutant, acting as vectors to transport harmful heavy metals, persistent organic pollutants (POPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), antibiotics, pathogens, invasive species, etc.<sup>35,199-201</sup> From an environmental point of view, microplastics may have adverse effects on the marine biota, human health, and migration of microorganism species depending on the concentration.<sup>120,196,199,202</sup> The microplastics will persist for decades (see Modelling Report for details) and may accumulate mostly along the shorelines, coastal regions, and offshores.<sup>203</sup>

## 5. Outlook on lifetime modelling

The essential parameters and the relevant literature data reviewed in this study will facilitate the development of a proof of concept for lifetime prediction based on the mathematical modelling of the degradation rates.

The prime objective was to review all relevant information to assist in modelling the degradation rate and lifetime of the polymers during decommissioning. The activity focused on:

- i. Defining empirical relations to evaluate some essential parameters as a function of marine water depth.
- ii. Defining the possible degradation mechanisms of polymeric components and coatings in subsea environments.
- iii. Identifying available data sets, models, and methodologies.

Considering the range of the identified essential parameters, the lifetime of each of the respective polymers will be location- and depth-specific. The effect of the service conditions can be envisaged in the form of irreversible bulk transformation within the polymer matrices. Such reactions may influence the decommissioning of the polymers by accelerating the degradation rates. Furthermore, a functional mathematical modelling approach should also address the impact of the design and size factors, e.g., the large surface area of the infrastructure. The identified essential parameters will be employed to correct the degradation rates of the selected polymer, allowing an appropriate lifetime prediction at a specific water depth or burial condition.

A subsequent report will document the development of a fully functional model that relies on literature information and all the essential physicochemical parameters described in this report to predict the degradation profiles of different configurations of polymers. This kind of model will enable accurate sensitivity analysis to explore how the model inputs (i.e., the essential parameters) will contribute to the output uncertainties of the model (i.e., the degradation rates and lifetime).

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