



Technical Report 3

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

Curtin Corrosion Centre

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Experimental validation of role of marine sediments

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Abstract

A model (developed in a preceding report, TR-RES-62365-2) shows that sand abrasion can play a considerable role in the degradation of synthetic polymers in marine environments, especially considering the relatively long lifespan of synthetic polymers in the ocean. Building on this modelling observation, this study aimed to validate the abrasion (degradation) model of synthetic polymers associated with subsea infrastructure if left in situ at varying continental shelf depths in Australia's offshore waters.

Conducted by Curtin Corrosion Centre, this report presents the results of sand abrasion experiments of selected synthetic polymers in simulating conditions, providing information on how sand erosion influences the degradation of synthetic polymer components of oil and gas infrastructure in the ocean. The outcome is expected to support the NDRI research programs and support decisions regarding decommissioning.

Revision History

Revision	Description and Record of Changes
0.1	Initial Release
1.0	Revised version based on NDRI industry participants and the ISAB

Executive Summary

This project has been executed for the National Decommissioning Research Initiative (NDRI) within National Energy Resources Australia (NERA) to provide an understanding of the degradation rates and processes for non-metals (synthetic polymers) in subsea infrastructure.

Following the outcomes of a preceding study (see TR-RES-62365-2), this report presents the findings of the experimental validation of the mechanical sand abrasion model, to provide information on how buoyant sand sediments can influence the degradation of synthetic polymers associated with subsea infrastructure if left in situ at varying continental shelf depths, in Australia's offshore waters. The objectives are (i) to experimentally measure the rate of abrasive erosion of the synthetic polymers in simulating conditions and (ii) to characterise the formation of microplastics.

According to the previous study, synthetic polymer components based on polyethylene (PE), polypropylene (PP), and epoxy (EP) chemical frameworks are prone to underwater sand abrasion. The experimental results in the current study highlight that at a very low sand concentration (and low water current velocity), the abrasion rates are, on average, in the same order of magnitude as those calculated from the model (see TR-RES-62365-2). Additionally, the particle sizes of the microplastics, formed during abrasion of the synthetic polymers, are less than the size of the sand grains. Although the numerical values of abrasion rate are small, the effects could be significant considering the large degradation timeframe (i.e., lifespan) of the synthetic polymers in offshore environments. The outcomes are significant to understanding the influence of transport of marine sediments on abrasive degradation of synthetic polymer post-decommissioning.

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Glossary of Terms, Abbreviations, and Acronyms

AFM	Atomic force microscopy
EP	Epoxy thermoset
FBBP	Fusion bonded black polyethylene
FBE	Fusion-bonded epoxy
HBE	High build epoxy
HDPE	High-density polyethylene
MP	Microplastic
PA	Polyamide
PE	Polyethylene
PP	Polypropylene
PU	Polyurethane
PUF	Polyurethane foam
XLPE	Cross-linked polyethylene

1. Introduction

1.1. Background

Previous reports have described the degradation mechanism of synthetic polymer components of oil and gas infrastructure in the Australian offshore environments and presented the model developed for estimating the degradation rates of synthetic polymers associated with subsea infrastructure, lifespan, and formation of microplastics. In brief, the synthetic polymers will degrade into smaller fragments and dissolved-organic products via biotic and abiotic mechanisms. The aerobic biotic degradation mechanism involves microbial activities.¹⁻³ On the other hand, abiotic degradation can follow two pathways in the ocean. Firstly, chemical degradation can be initiated by temperature (thermal degradation), solar radiation (photodegradation), and water (hydrolytic degradation), depending on various factors such as the inherent functional groups in the polymer, polymer structure (i.e., backbone), molecular weight, and exposed surface to volume ratio.⁴⁻⁶ The second abiotic form of degradation in the ocean involves mechanical stimuli (hence, termed mechanical degradation) like impacts due to wind, waves and tidal current, and marine sands.^{4,6,7}

In subsea environments, the mechanical degradation channel (due to ocean currents and suspended sand loads) has gained popularity in terms of qualitative understanding of fragmentation of synthetic polymers into microplastics,⁷⁻⁹ but remains unquantified. There are some published results for high-velocity air-borne sand abrasion of synthetic polymers,^{10,11} which may not explain the mechanism of sand erosion of plastics in water at relatively low current velocities and low sand concentrations. A few studies on the water-borne sand erosion of some epoxy thermoset and plastic coatings^{12,13} focused on aggressive industrial conditions, i.e., high velocity (above 20 m/s) and high sand load (2.1 wt. %, or 21 g/L). Our model (see TR-RES-62365-2) relied on the literature data measured under air-borne sand conditions and high impact velocities. We projected the data to low impact velocity, typical ocean currents and low sand concentration. However, experimental measurements were needed to validate the abrasion model.

1.2. Purpose and objective

Project 2.2 seeks to develop an overarching understanding of the degradation rates and processes for non-metallic materials (synthetic polymers) to inform the assessments of the rates at which structures will degrade and facilitate potential leaching of contaminants, and the formation of macro- and microplastics. Following a comprehensive literature review (TR-RES-62365-1); and the development sensitivity analysis of a model for estimating the degradation rates of synthetic polymers associated with subsea infrastructure, lifespan, and formation of microplastics (TR-RES-62365-2); the purpose of this study is to experimental validate the abrasion part of the model by fulfilling the following objectives:

- To experimentally measure the influence of transport of marine sediments on abrasive degradation of synthetic polymer associated with offshore oil and gas infrastructure.
- To characterise and evaluate the formation of microplastics (i.e., fragments less than 5mm in size). The data acquired from the first objective will enable the quantitation of the formation of microplastics.

1.3. Scope of work

According to the problem statement from NERA,¹⁴ the synthetic polymeric components of Australian offshore infrastructure can be categorised based on the intended functions such as (i) insulating

material, e.g., polyurethane foam (PUF); (ii) 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); and (iii) materials used in flexible flowlines and umbilicals, e.g., polyamide 11, cross-linked polyethylene (XLPE) pressure sheath and PE sheaths. Our previous study has shown that only the synthetic polymers comprising of polyethylene, polypropylene, and epoxy chemical backbones are susceptible to sand abrasion. Therefore, tested materials include high-density polyethylene (HDPE), polypropylene (PP) and high-build amine-cured epoxy thermoset, which are susceptible to sand erosion. Synthetic polymers from decommissioned offshore oil and gas pipelines were also tested.

2. Basic principle and methodological approach

Sand sediments can be transported by the ocean current, waves and celerity, storm surges and nearshore currents. As shown in Figure 1, the size and shape of the sand may vary and impact the erosion rates of plastic materials in the marine environment differently. Moreover, the impact energy of the sand and water (hence, the erosion rate of plastics) depends on the depth-corrected current velocity, which can be estimated based on the velocity profile in Equation 1; 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 combined current velocity at the surface v_0 (m/s) at the surface.¹⁵ The power law is usually taken to be of the 1/7th order (i.e., $\alpha = 7$).¹⁶ The typical average surface velocity of ocean current varies between 0.5 – 3 m/s.¹⁷

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

The concentration of suspended sand represents another important parameter. The necessary theory for estimating the sediment concentration and transport phenomenon has been documented separately by Soulsby,¹⁸ and Camenen and Larson.^{19,20} For sediments under the influence of current, 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:¹⁸

$$w_s C = -K_s \frac{dC}{dz} \quad (2)$$

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:

$$C_z = C_a \left(\frac{z_s}{z_a} \right)^{-b}; \quad b = \frac{w_s}{\kappa u_*} \quad (3)$$

Where C_a denotes the sediment reference concentration at height z_a , b is the Rouse number, or suspension parameter, κ represents the von Karman's constant = 0.40, and u_* refers to the total friction velocity or total skin friction of the sediment. Due to the complexity of the seabed, the estimation of C_a ($\times 2650$, conversion factor to kg/m^3)¹⁸ depends on the weight distribution of (e.g., $d_{50} = 0.20$ mm) of the rippled bedload, and the depth-average flow velocity is needed to calculate the drag coefficient and

the total skin factor. The concentration of sand sediments can also be obtained directly from the measured data, or estimated from a correlation of relevant turbidity information, e.g., as reported by Cooper et al.²¹

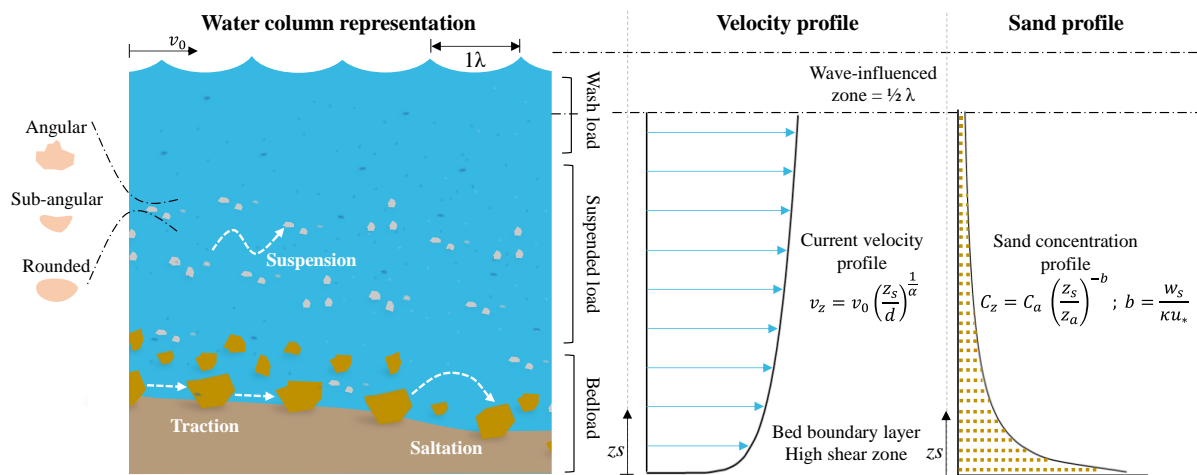


Figure 1. Representation of water column illustrating the suspended (buoyant) sand sediments, and descriptions of velocity profile and sand concentration profile.

Therefore, the sand-water abrasion of synthetic polymer specimens was conducted under the characteristic water velocities and sand concentrations estimated from the respective profiles described above. Figure 2 illustrates the mechanical abrasion rig used in this study.

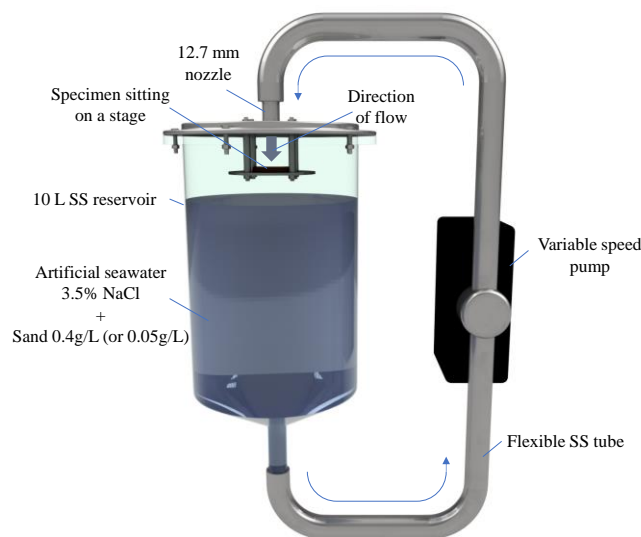


Figure 2. Experimental setup for abrasion of synthetic polymers at low velocity and sand concentrations.

As listed in Table 1, we maintained relatively low velocity and sand concentrations that are representative of marine (and subsea) environments. We maintained the sand-water velocity at 2 m/s to keep the experimental programs within the budgeted timeframe; however, it should be noted that this velocity is relatively low enough to validate the model. The tested materials include HDPE, PP, and EP

which are susceptible to sand erosion. Synthetic polymers from decommissioned offshore oil and gas flowlines (courtesy of Chevron) were also tested.

Table 1. Characteristic test conditions

Sediment	Silica sand
Sediment (sand) size (μm)	210 – 297
Sediment (sand) shape	Rounded + subangular
Medium	Artificial seawater
Salt (NaCl) concentration wt.%	3.5
Water-sand velocity (m/s)	2
Sand concentration (g/L)	4; 0.05
Temperature and Exposure period	Ambient and 5 days

The specimens ($40 \times 40 \times 6$ mm) were weighed before and after the experiments in a microbalance (with readability down to $1 \mu\text{g}$) to obtain the bulk erosion rate ($\mu\text{g/y}$) and linear surface erosion rate ($\mu\text{m/y}$), according to Equations 4 and 6, respectively.

$$ER = \frac{\Delta w}{t} \times 365 \quad (4)$$

$$LER = \frac{\Delta w}{A\rho t} \times 365 \quad (5)$$

Where Δw denotes the mass loss (based on the initial and final mass of the specimens), t corresponds to the test duration (5 days), A is the affected surface area (approximated from the diameter of the incompressible water jet) and ρ represents the density of the synthetic polymer. Each experiment was conducted indoors for 5 days; sustained enough to allow measurable data (because low velocity and sand concentration will result in a relatively slow erosion rate), but considerable short to limit the effects of other degradation mechanisms. After each experiment, the sand-water mixture was drained, allowed to settle, and a portion of the water was passed through a $1.2 \mu\text{m}$ glass microfibre filter to examine the microplastics using a dissecting (stereo) microscope.

3. Results and discussion

3.1. Samples and extent of surface oxidation before abrasion test

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) produced the IR spectra of the samples. As shown in Figure 3, the pristine samples have neither any form of contamination nor oxygenated (carbonyl) functional groups. However, in Figure 4, the decommissioned HDPE samples have undergone some degree of surface oxidation due to prolonged exposure to

seawater during the service life. Such degradation will impact the surface properties,²²⁻²⁴ e.g., mechanical hardness, enabling relatively higher susceptibility to sand abrasion.

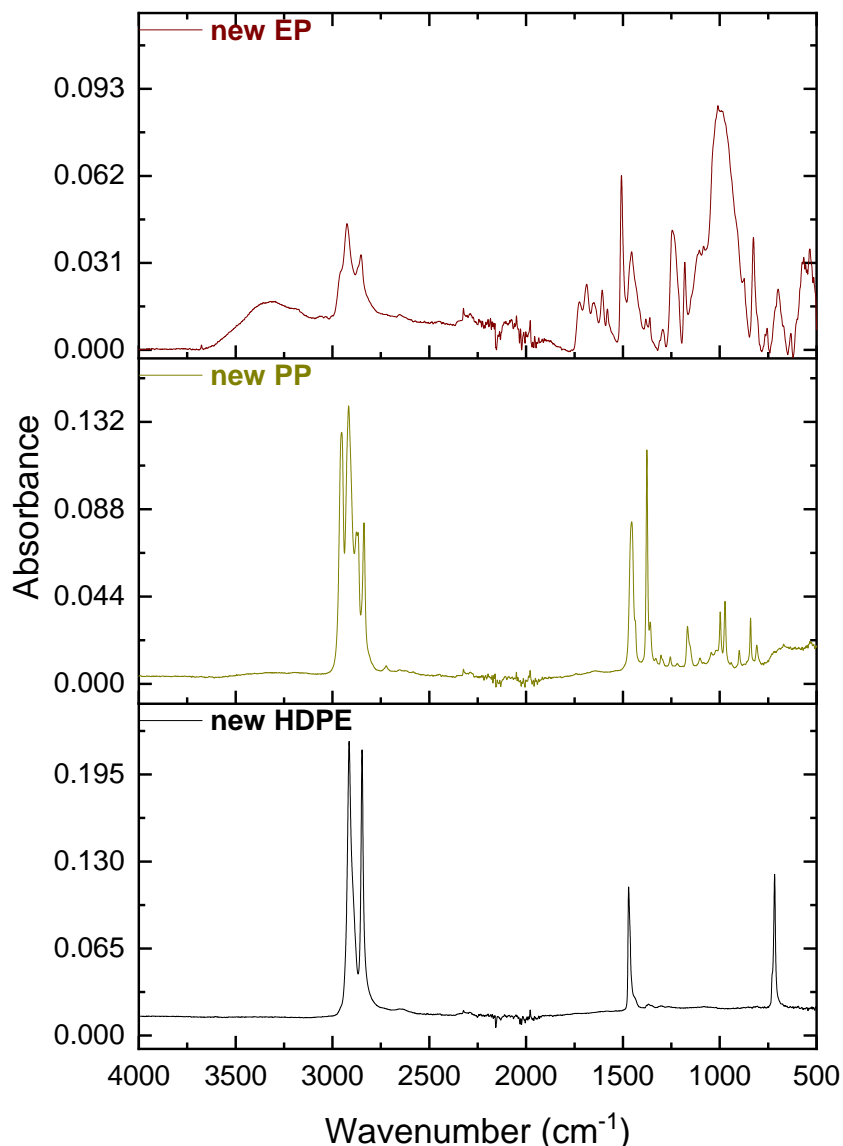


Figure 3. FTIR spectrum of the pristine synthetic polymer specimens.

The observation in Figure 4 supports our surface degradation modelling approach (TR-RES-62365-2), showing that the diffusion coefficient of the degradation agents (i.e., water, dissolved O₂, and ions) into the synthetic polymer is relatively slow compared to the reaction rate constant, and the diffusion of the enzymes into the bulk structure of the polymer structure is restricted by the large molecular size of the microbial enzymes. Therefore, only the surface (or thickness closed to the surface) of the decommissioned HDPE experiences degradation. The core of the material (depicted by “inner depth 3” in Figure 4) remains intact.

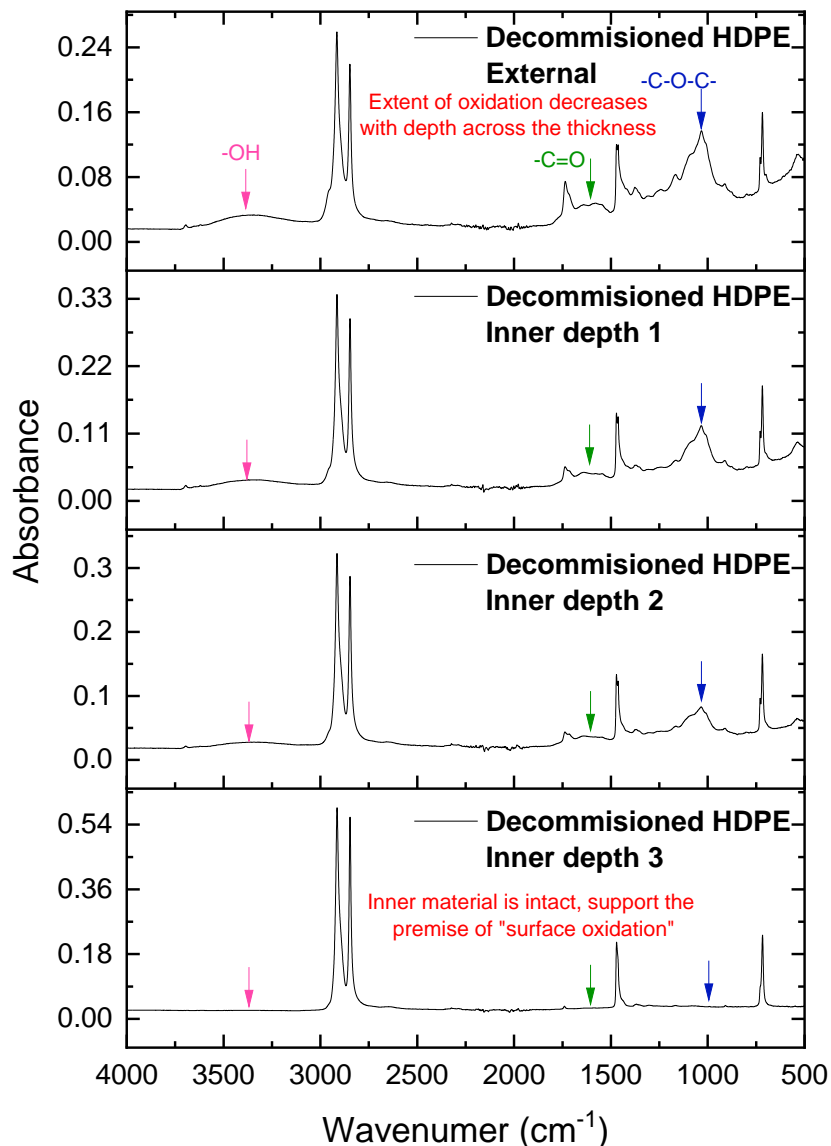


Figure 4. FTIR spectrum of the decommissioned HDPE (external sheath of flexible flowline) specimens.

3.2. Effect of water velocity and sand concentration on surface erosion rate

As mentioned above, we maintained the sand-water velocity at 2 m/s to keep the experimental program within the budgeted timeframe. In practice, the subsea velocity can range from 0.2 – 2 m/s. However, the velocity of 2 m/s is relatively less than those used in previous studies (above 20 m/s) and should be contributory to validating the model.

The results in Figure 5 indicate that the performance of the model is somewhat comparable to the experimental values, especially for the decommissioned HDPE. The numerical values will be much lower in conditions of velocities approaching 0.2 m/s and are presented in the previous Report. At low sand concentrations (e.g., 0.5 g/L), the experimental data are somewhat higher than the model. This is because of sand water density; while the literature model does not consider the effect of the carrier fluid (i.e., water in this case), the normal force acting on the surface of the synthetic polymer is influenced by the density of the sand-water mixture.

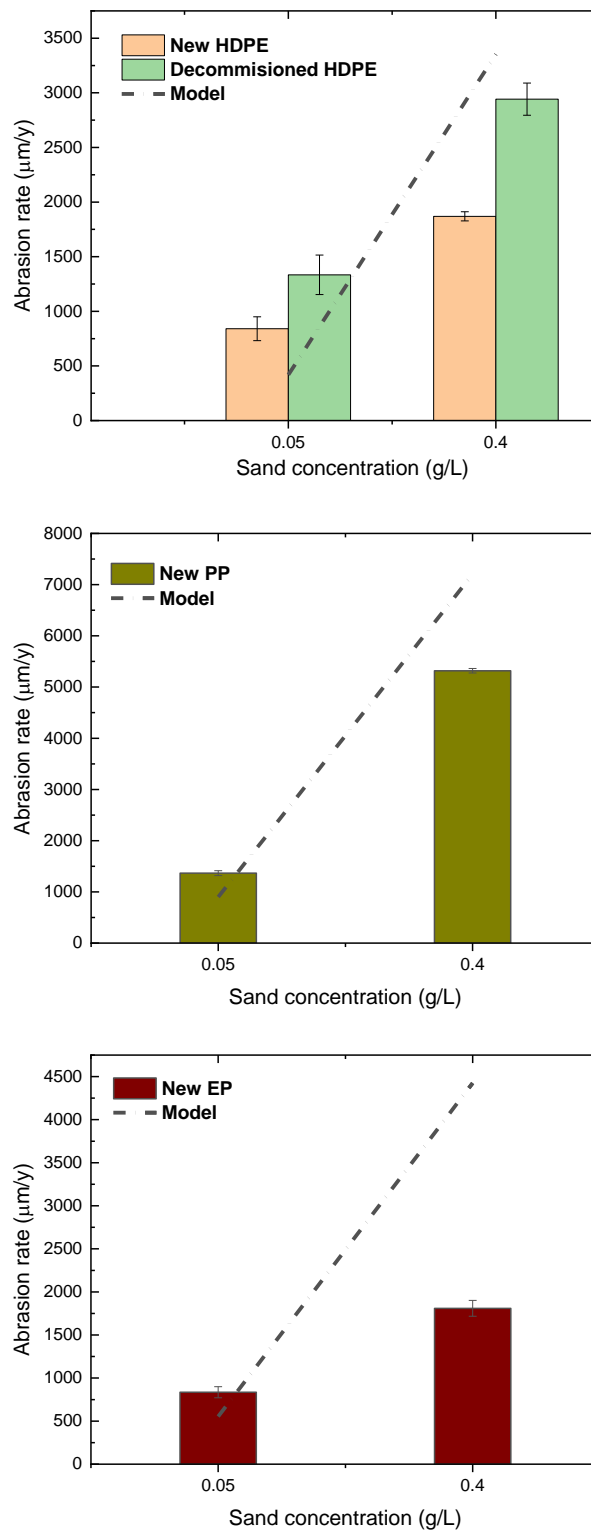
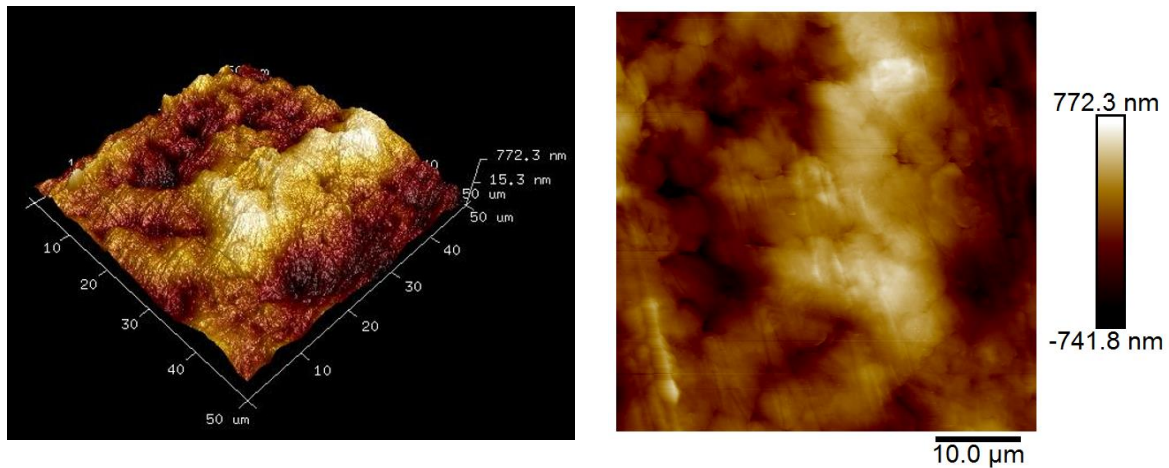


Figure 5. Experimentally measured abrasion rates of the synthetic polymer samples compared to the modelling results. Details of the model are presented in Technical Report 2 (TR-RES-62365-2).

Based on the data presented in Figure 5, the combined average correction factor of the model amounts to 1.07. This value can be used to correct the abrasion rates in technical Report 2; however, it will make a trivial statistical difference.

Furthermore, the atomic force microscopy (AFM) image (Figure 6) reveals the surface topography at the centre of the HDPE sample before and after 5 days of sand-water abrasion. The surface roughness of the sample increased, confirming the mass-loss data. The AFM images are very localised and cannot be used to quantitate degradation rates at the macro scale.

HDPE surface before sand-water abrasion



HDPE surface after sand-water abrasion

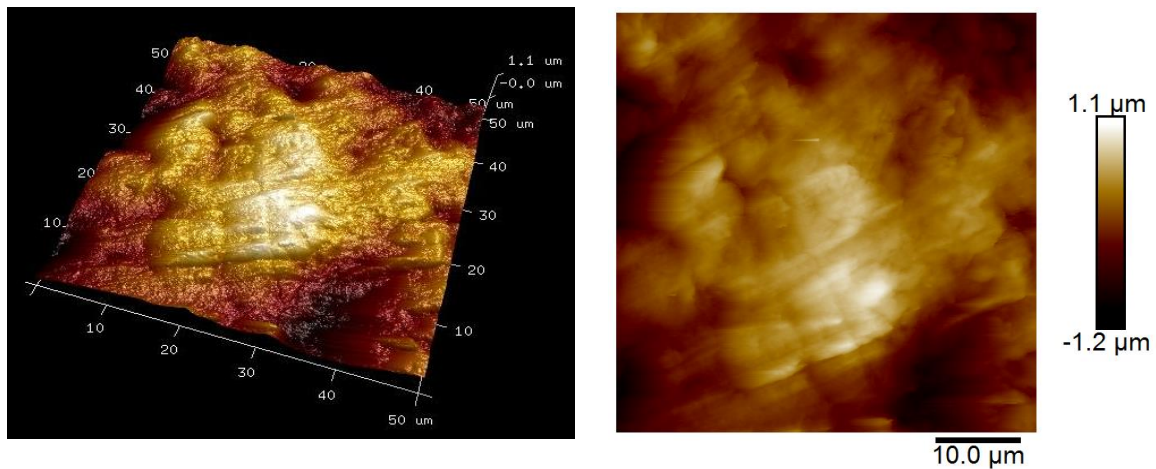


Figure 6. AFM images showing the surface topography of new HDPE sample before and after sand-water abrasion.

3.3. Characteristics and formation of microplastics

The experimental program has been designed without irradiation and to be relatively short (i.e., 5 days) to impede other chemical degradation mechanism and ensure that microplastic is the only degradation product. Therefore, based on the experimental data, the measure mass loss equals total microplastic formation. Figure 7 depicts the size and shape of the typical microplastics identified based on the colour of the original sample (HDPE) and the hot-needle test. It is shown the microplastics (except for one) are less than 100 μm, agreeing with our premise in the Technical Report 2 that the size of the microplastics will be less than the particle size of the abrasive sand sediments.

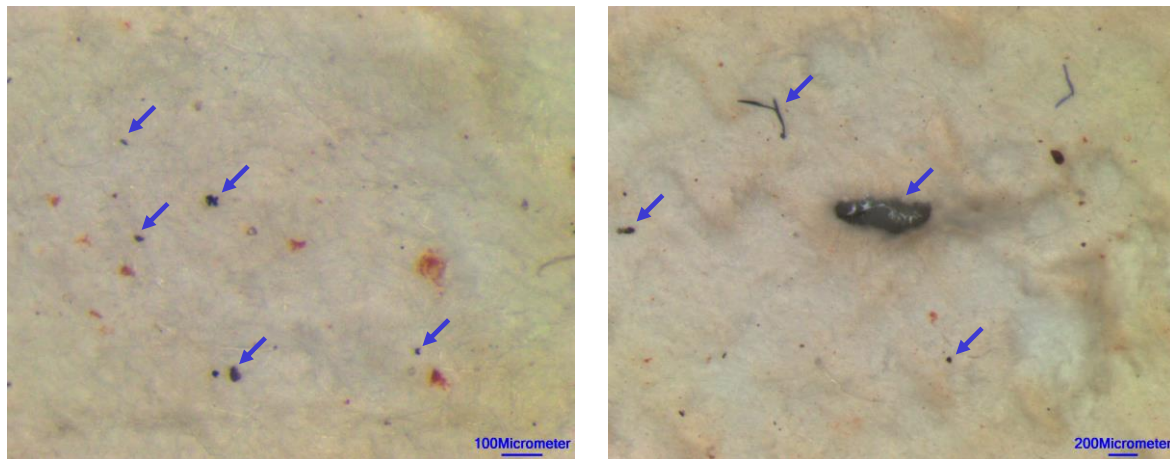


Figure 7. Examples of microplastics detected in the sand-water mixture after 5 days abrasion test.

4. Summary and implications on long-term exposure prediction

The prime objective of this study is to experimentally verify the synthetic polymer abrasion model proposed in the Technical Report 2 (see TR-RES-62365-2) as part of a comprehensive degradation and lifespan model for synthetic polymer in subsea environments. The results show that the abrasion model is reliable as its result is averagely close to the experimental data.

Even if the numerical values of the abrasion rate of synthetic polymers are small (see TR-RES-62365-2 for details), the effects on long-term exposure could be significant considering the large degradation time scale. Therefore, the impact of abrasion due to buoyant sand sediments on the long-term exposure of synthetic polymers associated with oil and gas infrastructure should be considered for decisions regarding decommissioning.

Regarding the formation of microplastics, most of them will be formed due to fragmentation of the synthetic polymers associated with oil and gas infrastructure, and their formation (and respective degradation) can be predicted with the model ((see TR-RES-62365-2).

For future studies, a marine campaign is needed to measure the rate of degradation of the plastics at varying ocean depths. This can be achieved by placing synthetic polymer coupons in different depths of the ocean, followed by retrieval (after a period of one or two years) for mass loss and surface characterisation. The test program would need to simultaneously measure sediment concentration and the current velocity at the sample location, and would also need to account for fouling of the samples. Such data are currently not available but will be highly instrumental in validating the depth-controlled kinetic model.

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