MICROPLASTICS IN THE OCEAN

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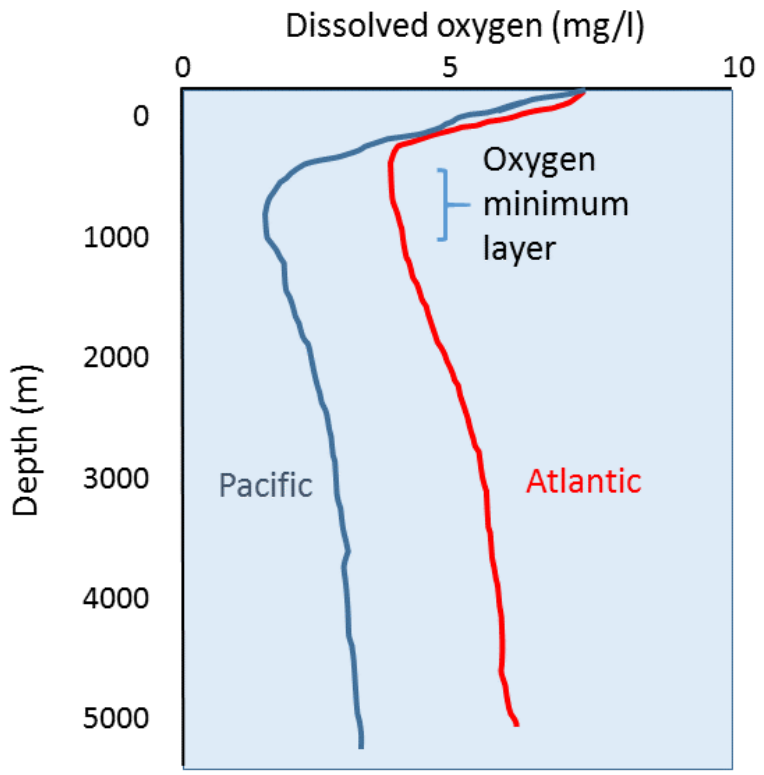
DEGRADATION IS A CHEMICAL PROCESS

- Solar UV Radiation — Same as on land
- Temperature — Decrease
  - Sea water < 30 ^{0}C
  - Plastics in air 70-80 ^{0}C
- Surface fouling — Decrease
  - Surface - colonization of floating plastics
- Dissolved Oxygen — Decrease
  - Only about 5.8 mg/L of O_2 in seawater
  - 20 vol% in air
- Water sorption — Increase?
  - 0.015 wt. % for PE, PP, and PS

AVAILABILITY OF OXYGEN FOR REACTION



Introduction to Oceanography by Paul Webb

O_2 Concentration in coastal Marine Water 2009-2019

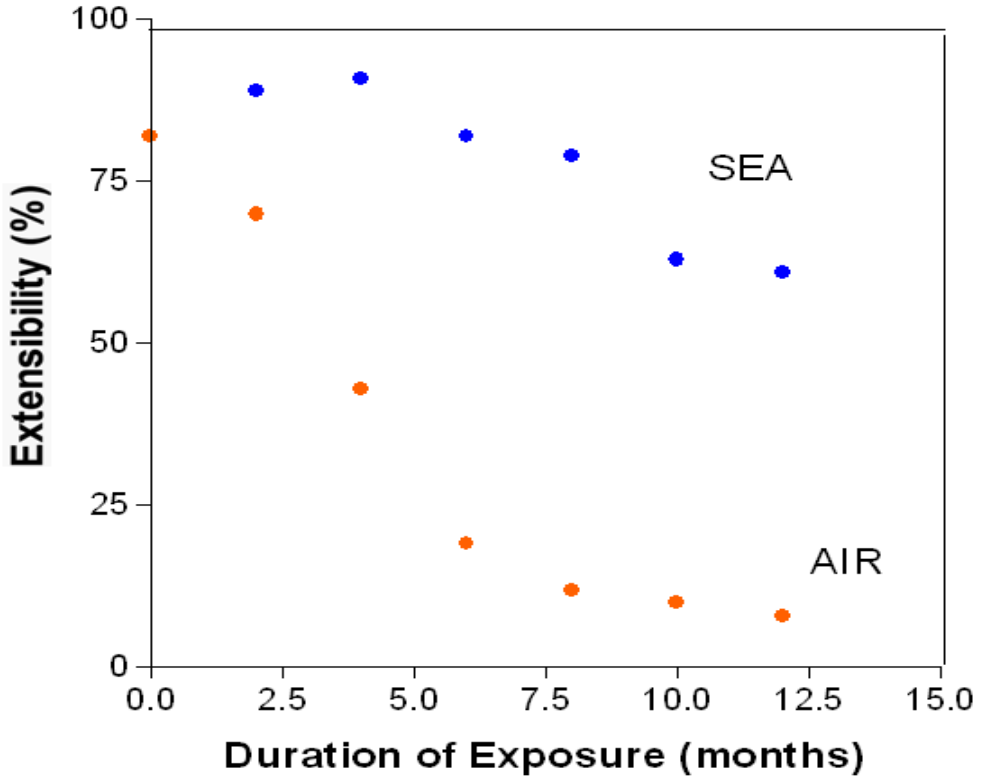
	>6 mg/L	4-6 mg/L	2-4 mg/L
North East Atlantic	94.9	4.1	0.7
Baltic Sea	64.3	18.6	11.4
Mediterranean Sea	79.4	16.0	2.3
Black Sea	62.5	20.8	12.5

European Environment Agency, 2022

Increasing temperature reduces the solubility of oxygen.

Implications for accelerated weathering in Seawater

EXPOSURE TO UV RESULTS IN SLOWER DEGRADATION



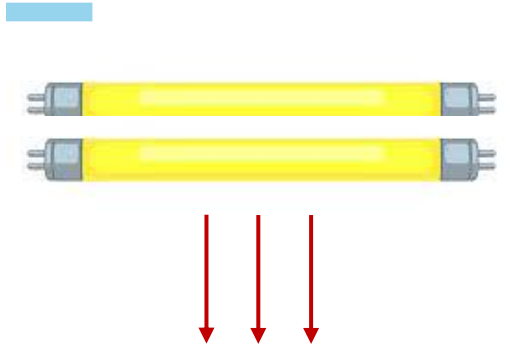
Plastic Tape (PP) exposed in Biscayne Bay

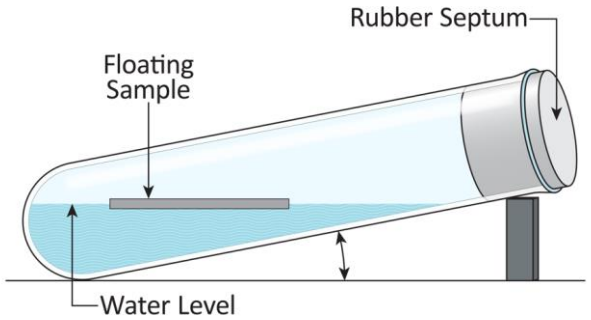
Tensile Elongation at Break (%)

Natural Weathering	Accelerated Weathering
Cartney & Blust, 2021	Andrady et al., 2022
Svendin 2020	Julienne et al, 2019
Biber et al., 2019	Ranjan and Goel, 2019
O'Brine & Thompson, 2010	Tang et al., 2019
Andrady et al., 1993	Andrady et al., 2022
Hsieh et al.,	Julienne et al, 2019
Tosin et al., 2019	Ranjan and Goel, 2019
Leonas & Gordon, 1993	Tang et al., 2018
Aria-Villamizar et al., 2018	Cai et al., 2018

LABORATORY- ACCELERATED EXPOSURE

UV 313 or UV 340 Lamps - 12 hrs Light 12 Hrs Dark





Not to Scale

UV 313 Lamps - 12 hrs Light + 12 Hrs Dark

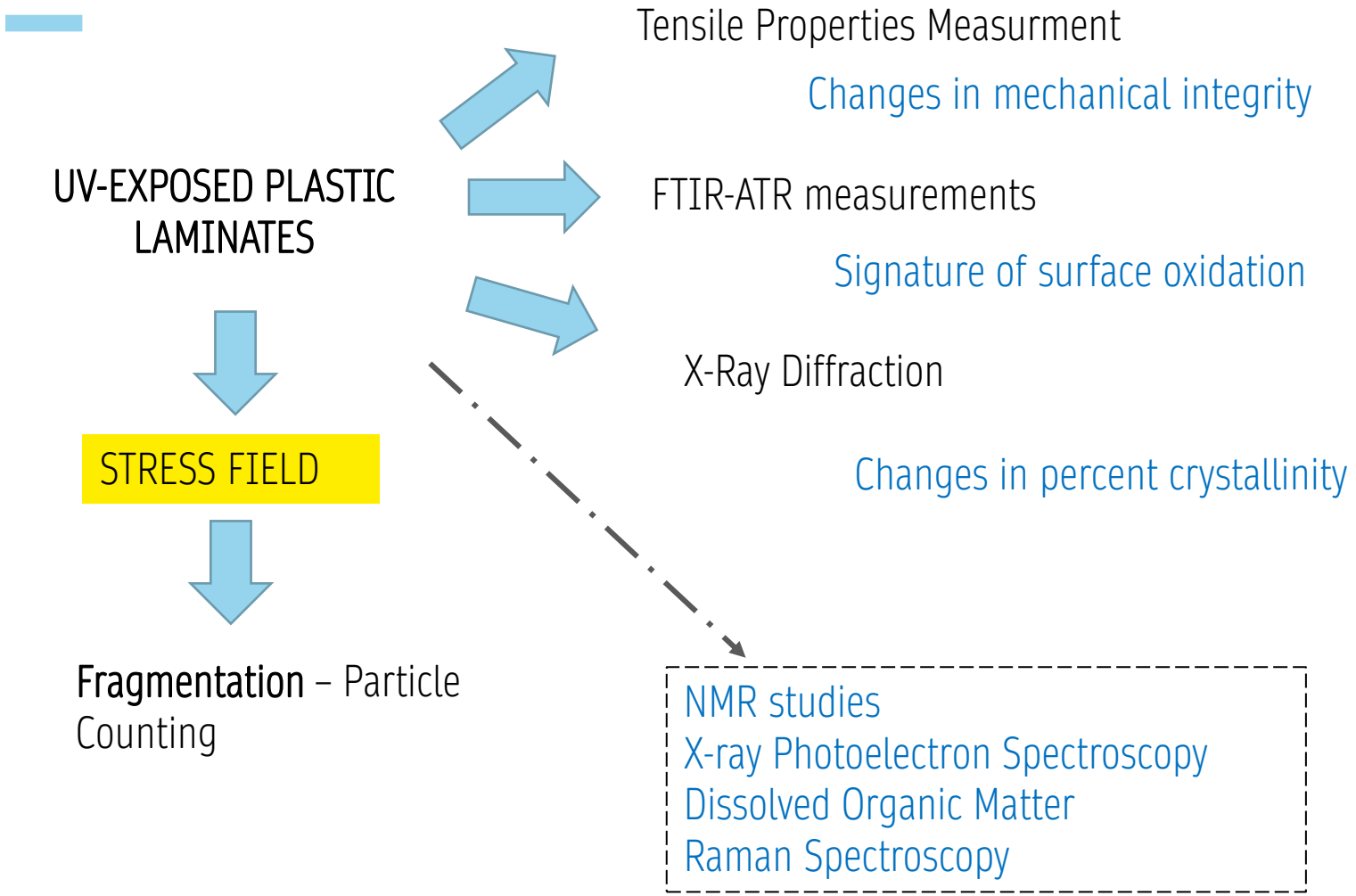
150 mm long 25 mm diameter quartz tubes

Pre extracted silicone rubber septum cap

Sealed with Aluminum tape. Exposed over a sand bath

35 C during light and ~25 C in dark period

TESTING THE UV-EXPOSED PLASTIC SAMPLE



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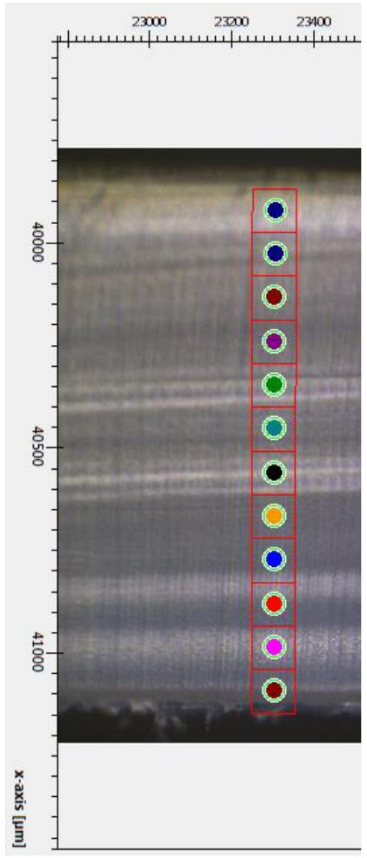
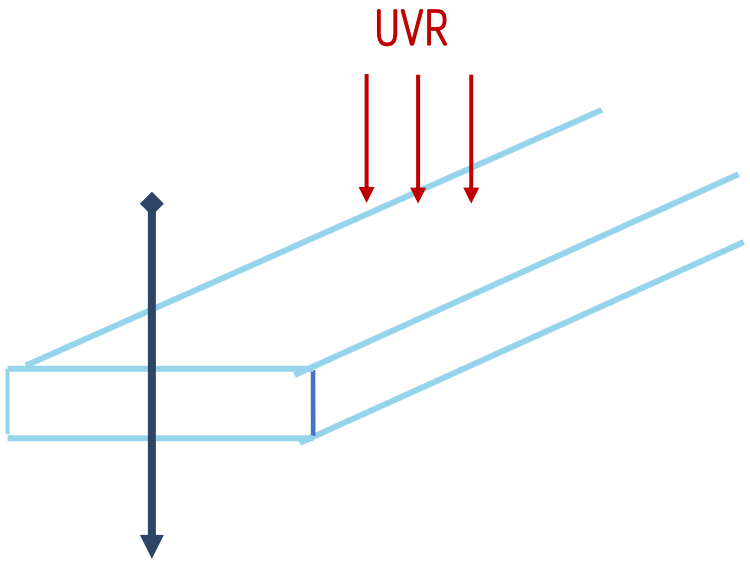
FTIR-ATR OF LDPE EXPOSED TO UV IN AIR

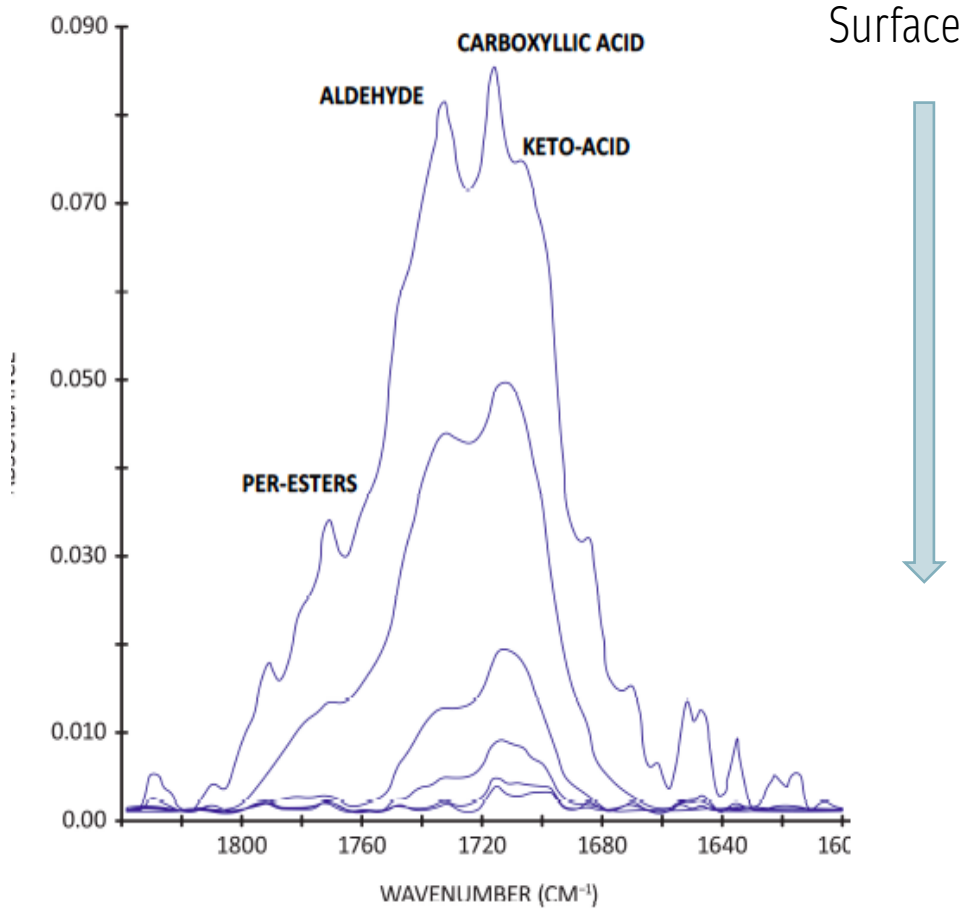




Signature functionalities

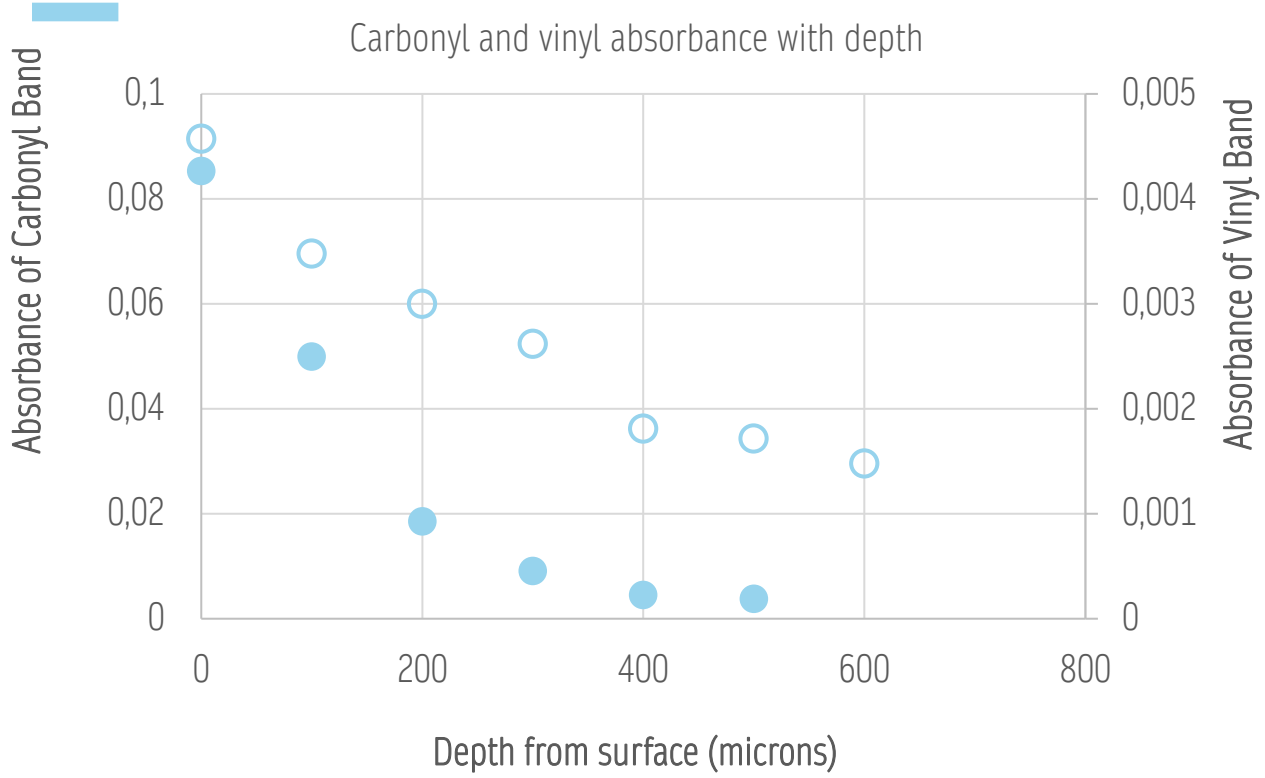
- Carbonyl and Vinyl bands
- Only extend to 400-600 microns

Below that depth virgin plastic

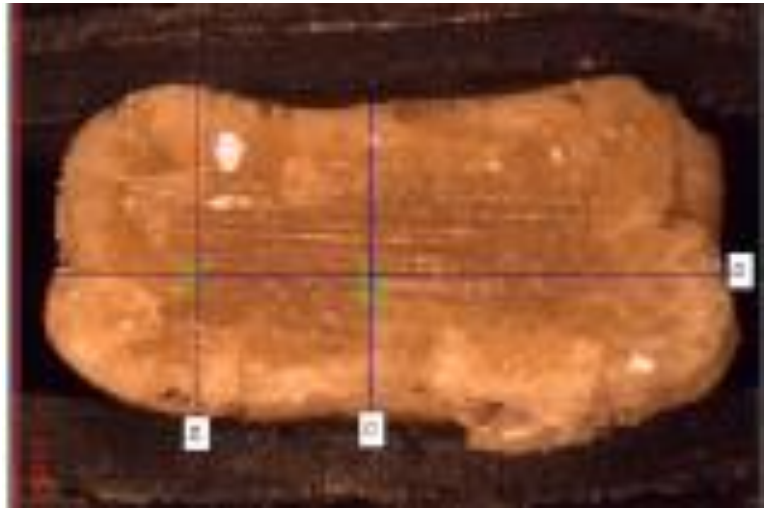


Is the Result the same with samples exposed to UV in seawater?

FRAGMENTATION REQUIRES A STRESS

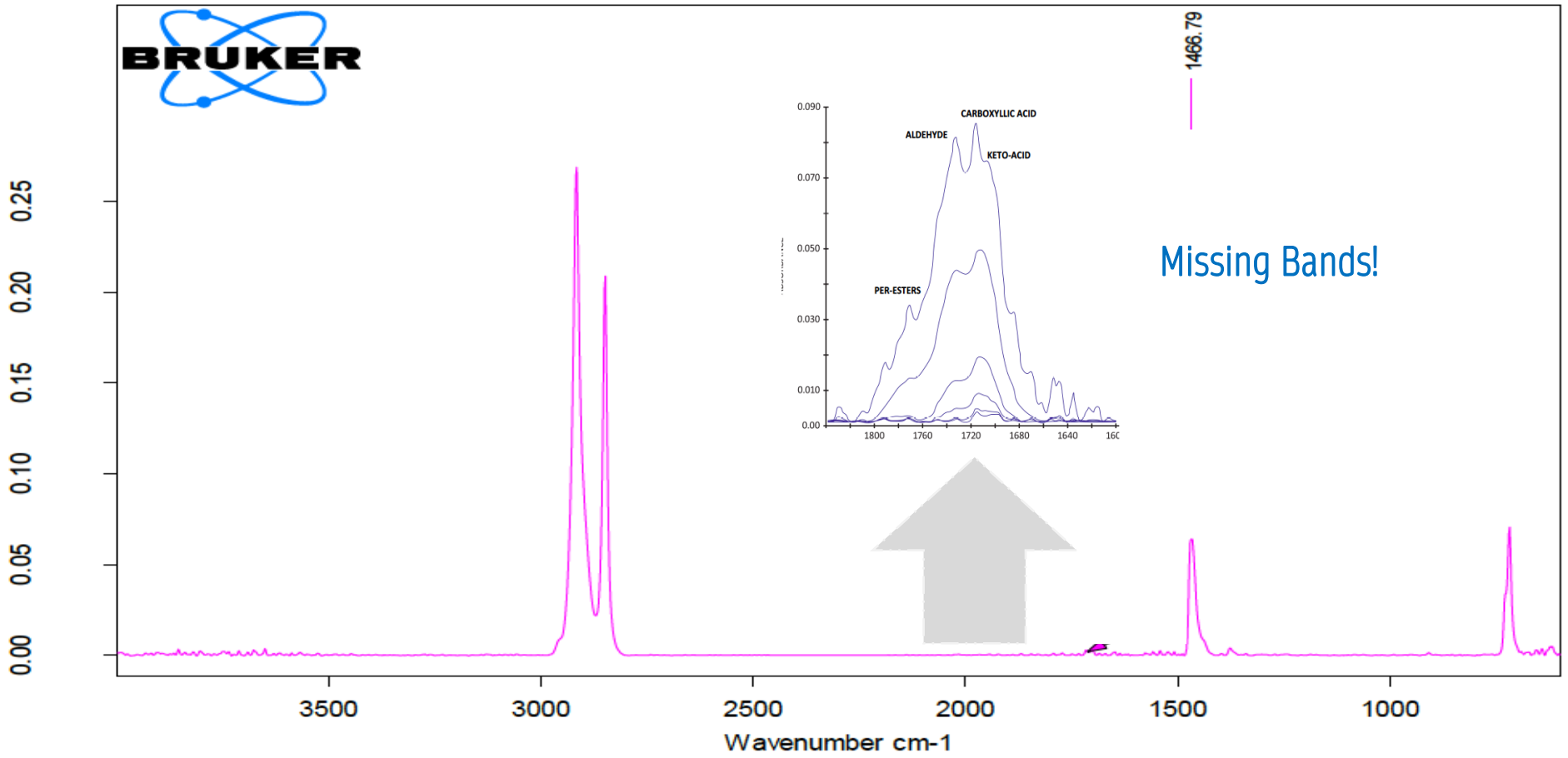


Polyethylene sample from the North Atlantic

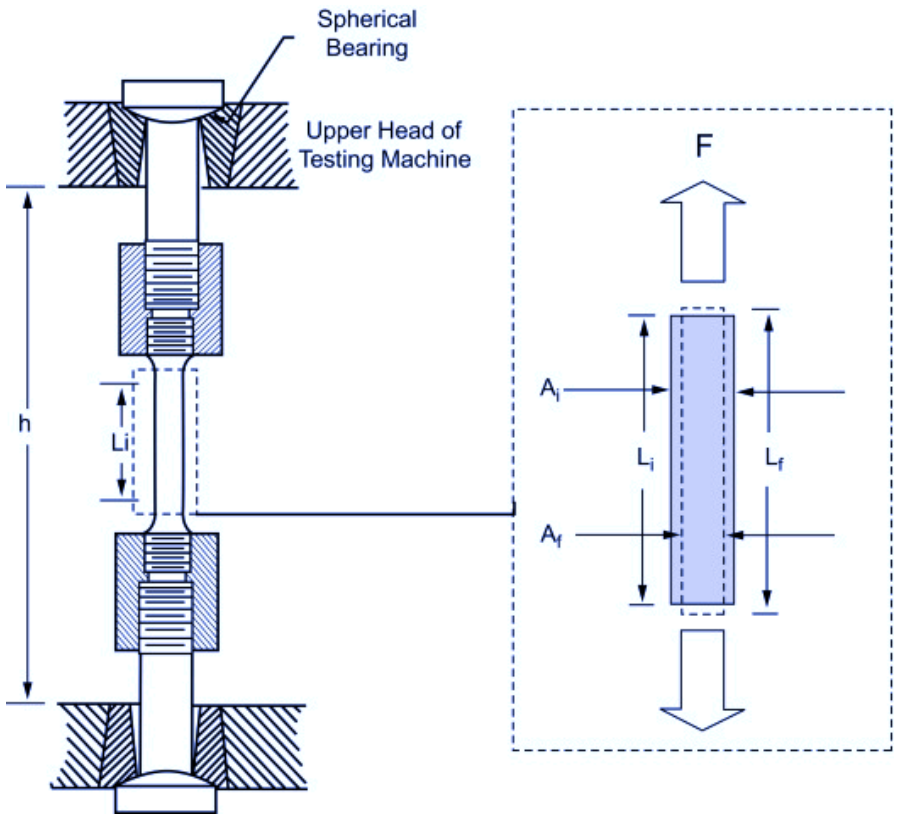


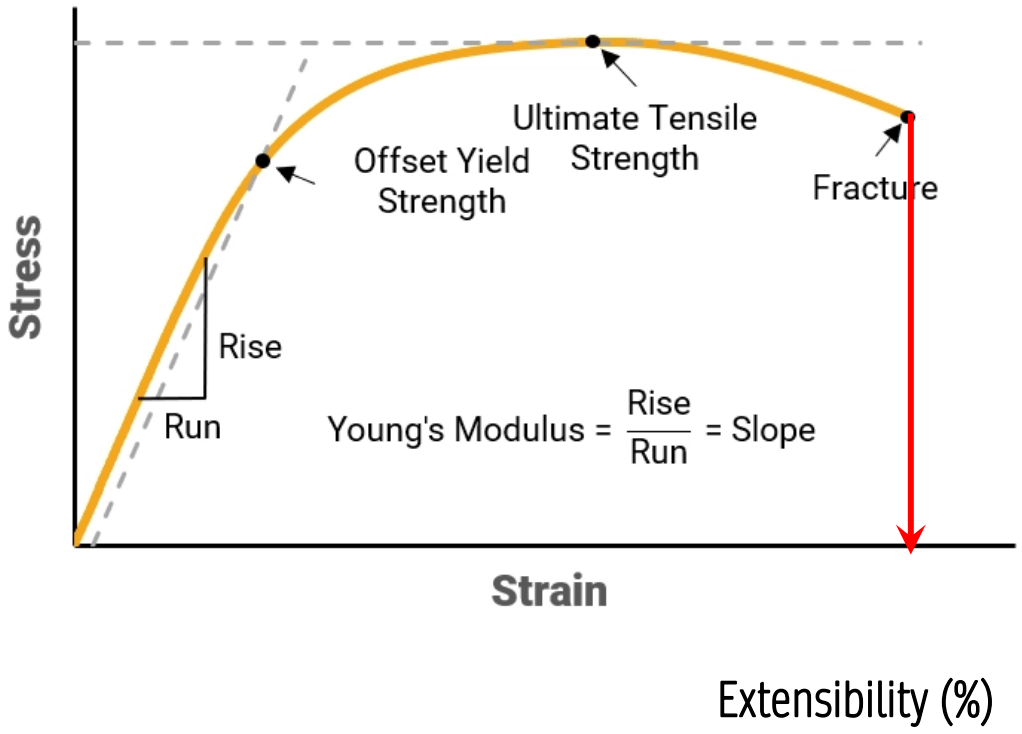
400 μm – ***Long axis***
650 μm - Short axis

FTIR SPECTRUM OF LDPE EXPOSED TO UVR IN SEAWATER



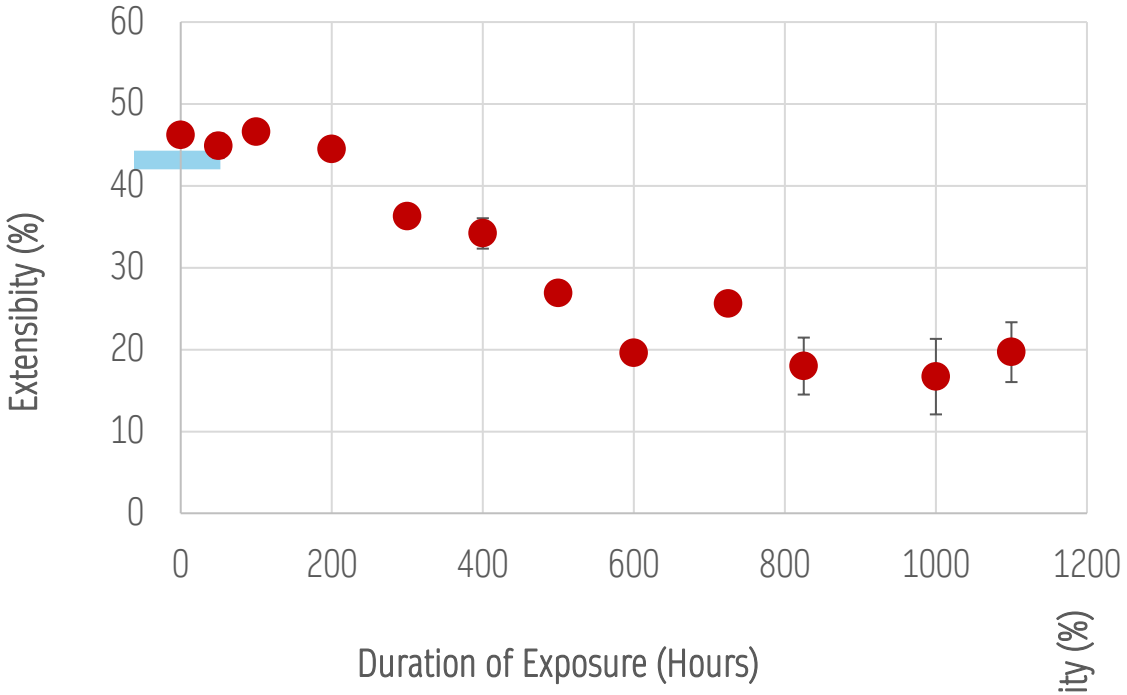
Testing Mechanical Integrity with Tensile Properties



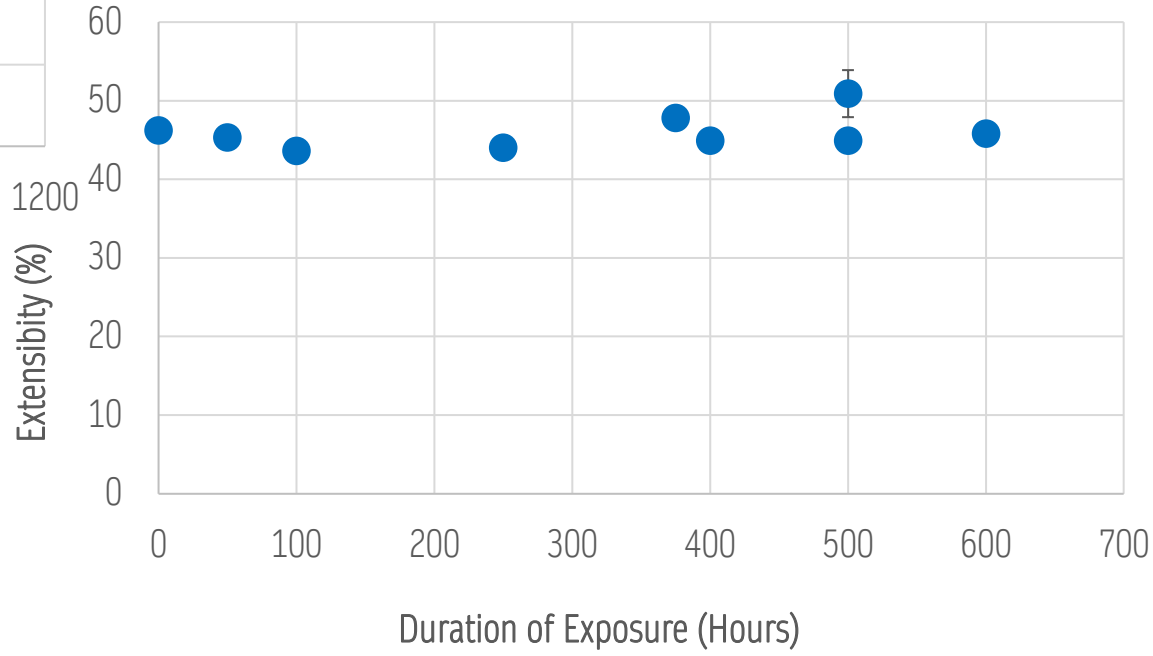


Extensibility (%)

EXTENSIBILITY *VS THE* DURATION OF EXPOSURE



Tensile properties are essentially unaltered during laboratory UV exposure in seawater

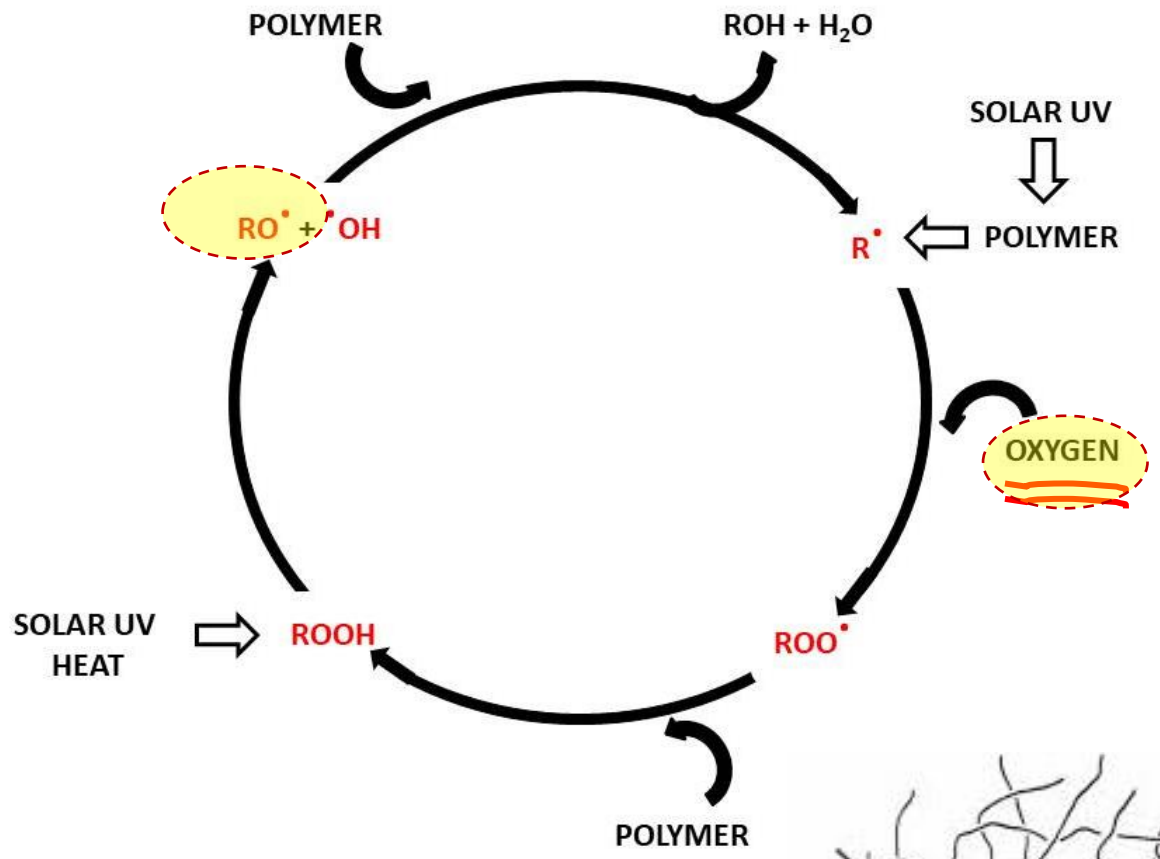


No changes in seawater exposures also for:

Tensile modulus

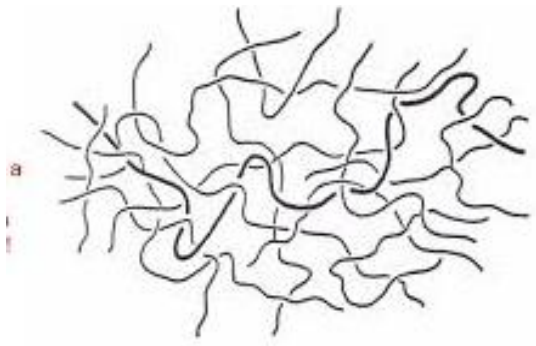
Tensile strength

CHEMISTRY OF LDPE OXIDATION

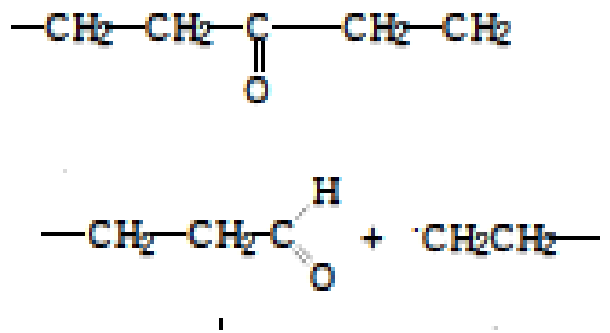


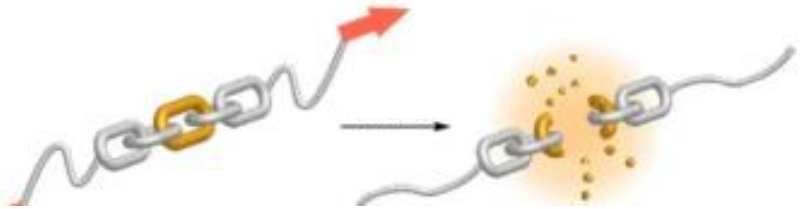
Inter-chain attarcrion (van der Wall's)

Entanglement



CHAIN SCISSION VIA RO. RADICAL



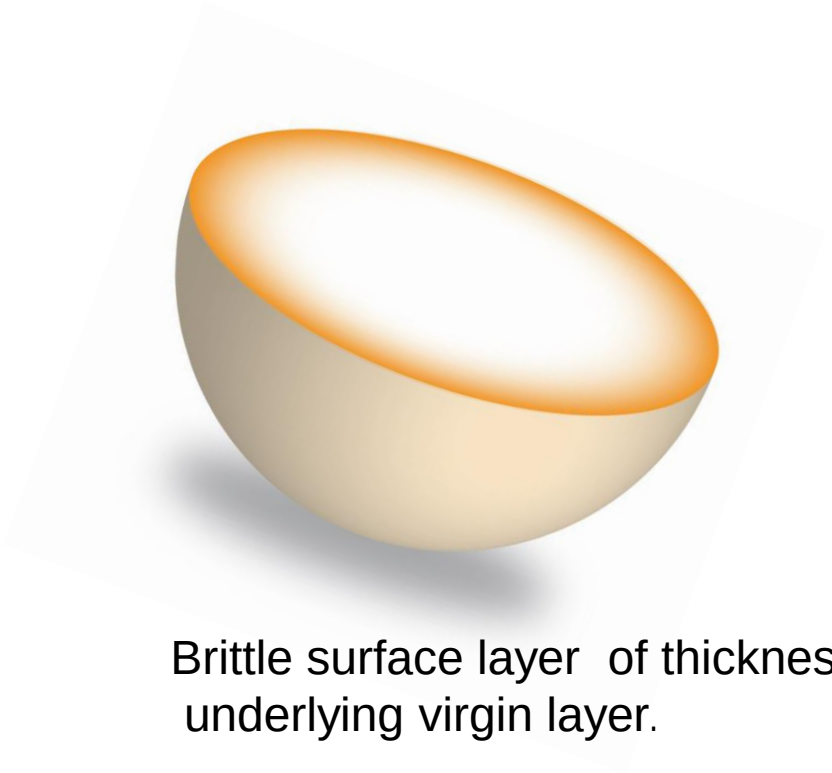


Chain scission

THIN-LAYER DEGRADATION UNDER LOW OXYGEN

$-\{d[O_2]/dt\} \approx (k_3 (r_i/k_6)^{1/2} [PH]$ - High oxygen concentration

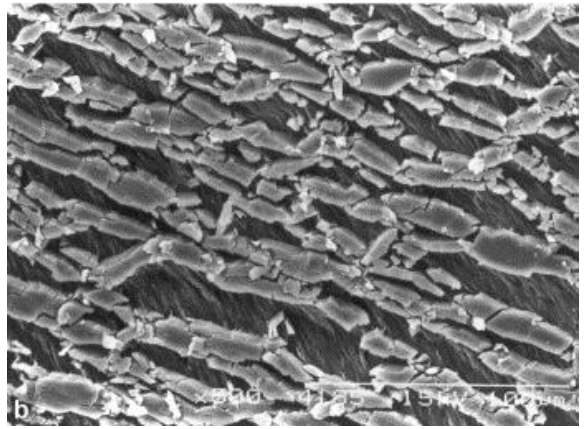
$-\{d[O_2]/dt\} \approx (k_2 (r_i/k'_4)^{1/2} [O_2]$ - Low oxygen concentration



Brittle surface layer of thickness T underlying virgin layer.

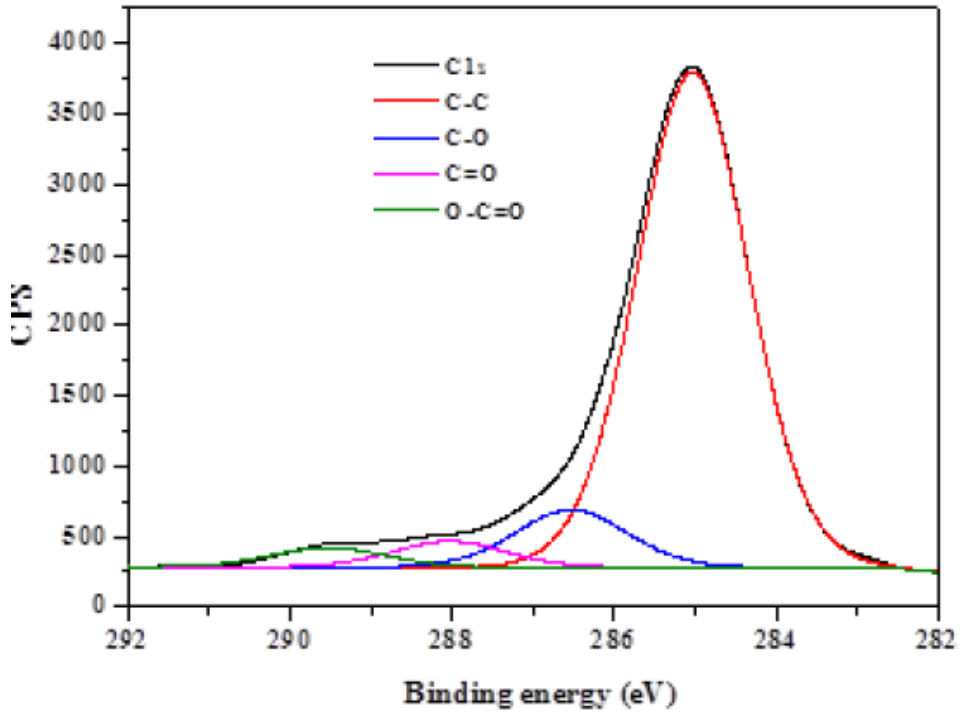
$T \approx \{D.[O_2]/r_i)\}^{1/2} \approx (D/k')^{1/2}$

Value of T must be lower in seawater relative to in air



PP aged and extended uniaxially *(White, 2006)*

SURFACE ANALYSIS SHOWS OXIDATION IN SEAWATER/UVR



FTIR-ATR - ~10^3 nanometers of the surface
Raman - 10^3 nanometers of the surfa

XPS – layer that several nm of the surface

XPS shows that a thin surface layer is oxidized when samples are exposed to UV in seawater.

C1 signal deconvoluted yields:
C-C / C-H at 285 eV
C-O at 286.5 eV
C=O at 288 eV
O-C=O at 289.5 eV.

Note: Soluble products of photooxidation lost in seawater exposures.

FRAGMENTATION RESULTS FROM MECHANICAL STRESS

Plastic Litter → Oxidized Plastic → Meso-, micro-, and nanofragments

SOLAR UV RADIATION

STRESS FIELD

- Wave action in slush zone
- Freeze-thaw
- Encounters with animals
- Wind

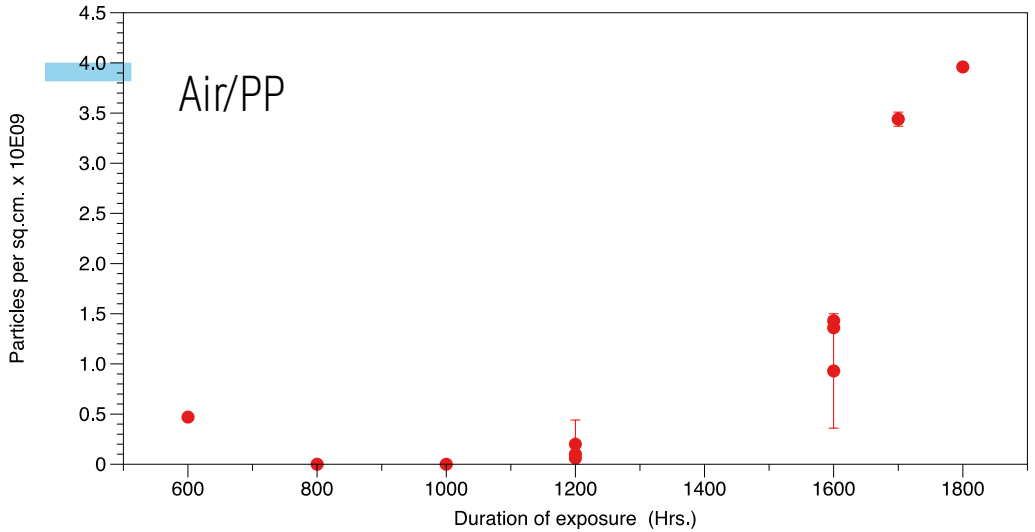
Different techniques for each particle size range

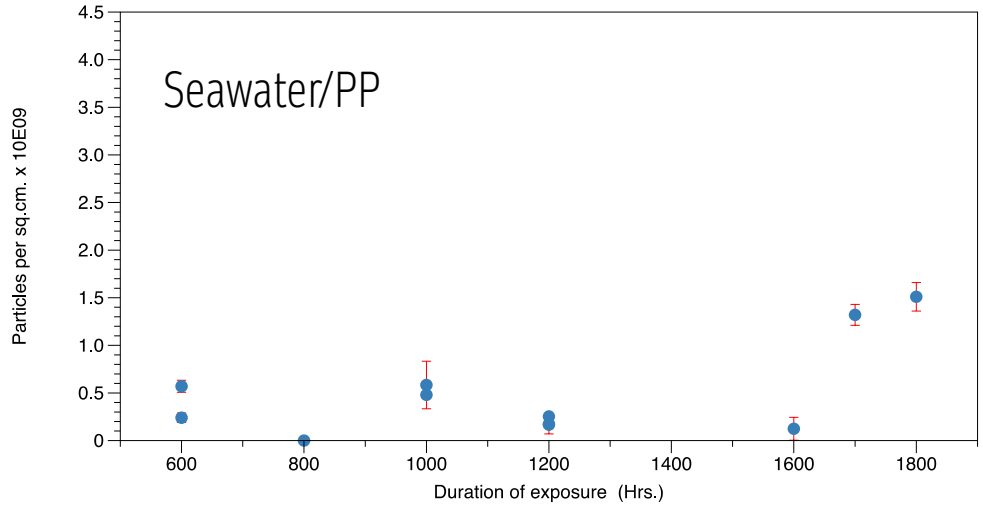
10-2000 nm counted by NTA
(Nanoparticle Tracking Analysis)

Do virgin or relatively undegraded plastics fragment?

Ease of fragmentation increases with the extent of oxidation.

NANOPARTICLE FORMATION PP UNDER UVR IN AIR/SEAWATER





UV exposure under UV-340 lamps.
Mechanical Stress: 15 min. ultrasonications at 35 KHz

All data points corrected for background

~10^9 particles/sq.cm. of plastic film

- Seawater has lower counts

- Particle sizes > 2 microns may have formed.

Summary Findings from Fragmentations Study

1. The data is from laboratory exposures that exclude the retarding effects of lower temperature and fouling in seawater, both tending to decrease fragmentation.

2. Fragmentation was evident in plastics studied. Ranking based on NPS

PP<PS<PLA<LDPE~ECO

PP~ECO<PS~PLA < LDPE

3. Removal of NPs by further oxidation into gaseous or soluble products cannot be ruled out.

4. Plastics tested, including photodegradable LDPE, did not result in large accumulation of particles that are < 2000 nm, especially in air oxidation.

CONCLUDING THOUGHTS

1. Oxidation in seawater weathering of plastics is slower in seawater compared to air because of relatively lower oxygen concentrations. Diffusion-controlled oxidation is localized at the surface.

2. Different exposure protocols and analytical procedures to assess weathering will be needed with seawater exposures.

3. Surface fouling and related sinking will play a significant role in determining the rate of oxidation and, therefore, fragmentation in seawater.

4. Nanoscale fragments {<2000 nm} are formed during both seawater and air exposures of PP to UV radiation. The rate appears to be higher for PP compared to LDPE.

European Environment Agency, 2022

Thanks to : Kara Lavender Law, Jessica Donohue, and Bimali Koongolla

THANK YOU

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