



Degradation and Fragmentation of Polyethylene in Seawater

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Weathering of Plastics

OXIDATION



Incorporation of oxygen-containing groups in the polymer
Associated chain-scission and crosslinking
Release of water-soluble and gaseous products

DEGRADATION



Change in appearance and physical properties such as color
Change in material properties such as strength or crystallinity
Loss in molecular level properties (Avg. Molecular Mass)

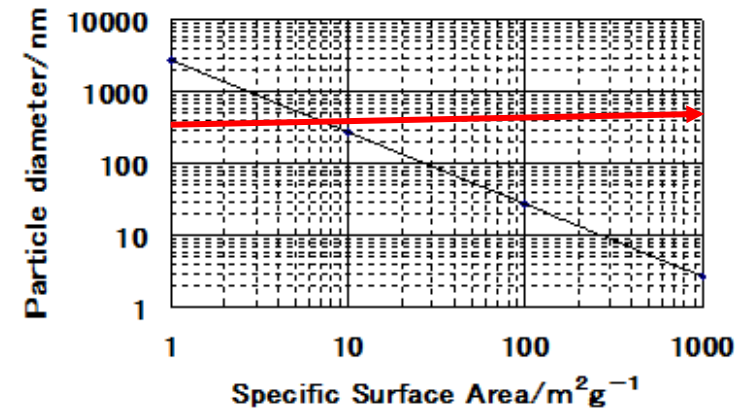
FRAGMENTATION



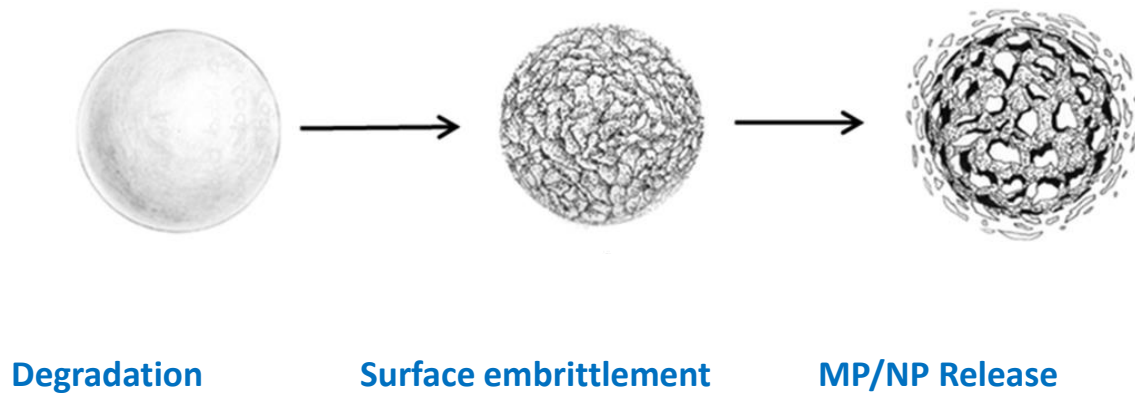
Macro-fragmentation in to meso- and microplastics
Micro- nano-plastics by surface-ablation

MINERALIZATION

Conversion into inorganic carbon, biomass and water



Micro-fragmentation by Surface Ablation



FRAGMENTATION

- High extent of degradation (embrittlement)
- Energy to dislodge particles from surface

Recent work: In the 'swash zone' mechanical force alone is sufficient to generate MPs

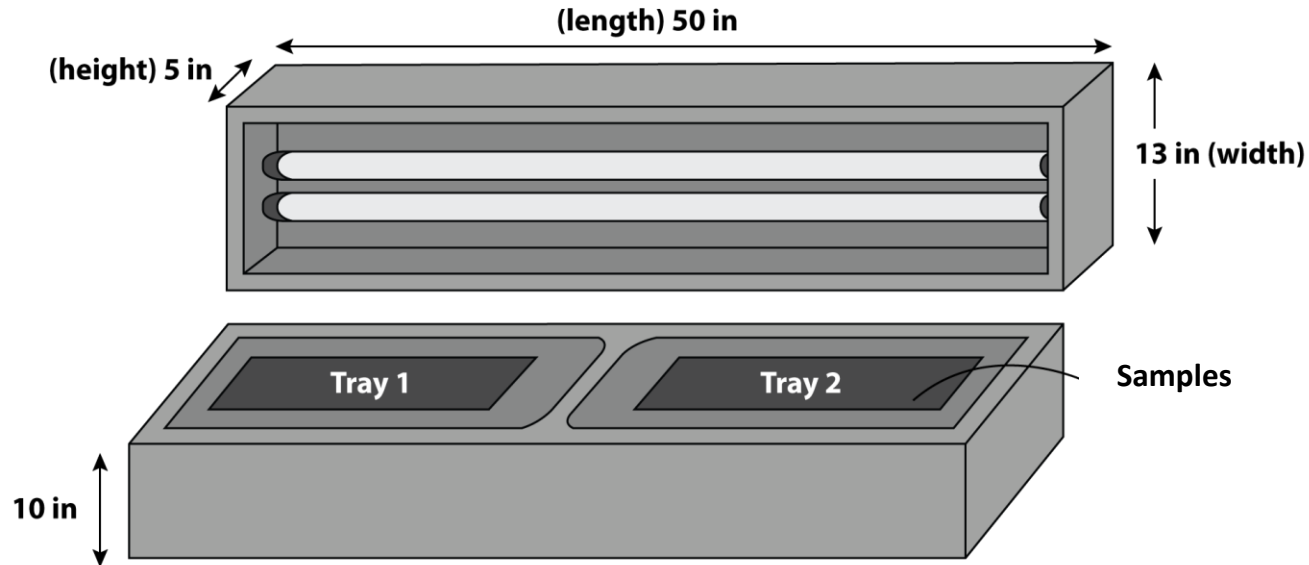
Work on Polyethylene:

To assess the development of the highly-degraded surface layer in weathering

To compare degradation of polyethylene in air and seawater

Observe a field sample of ocean-degraded polyethylene

Exposure to UV-313 Lamps

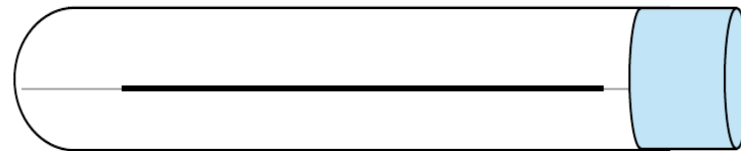


ASTM G154-12 Test Protocol

UV 313 Lamps with higher UV-B content

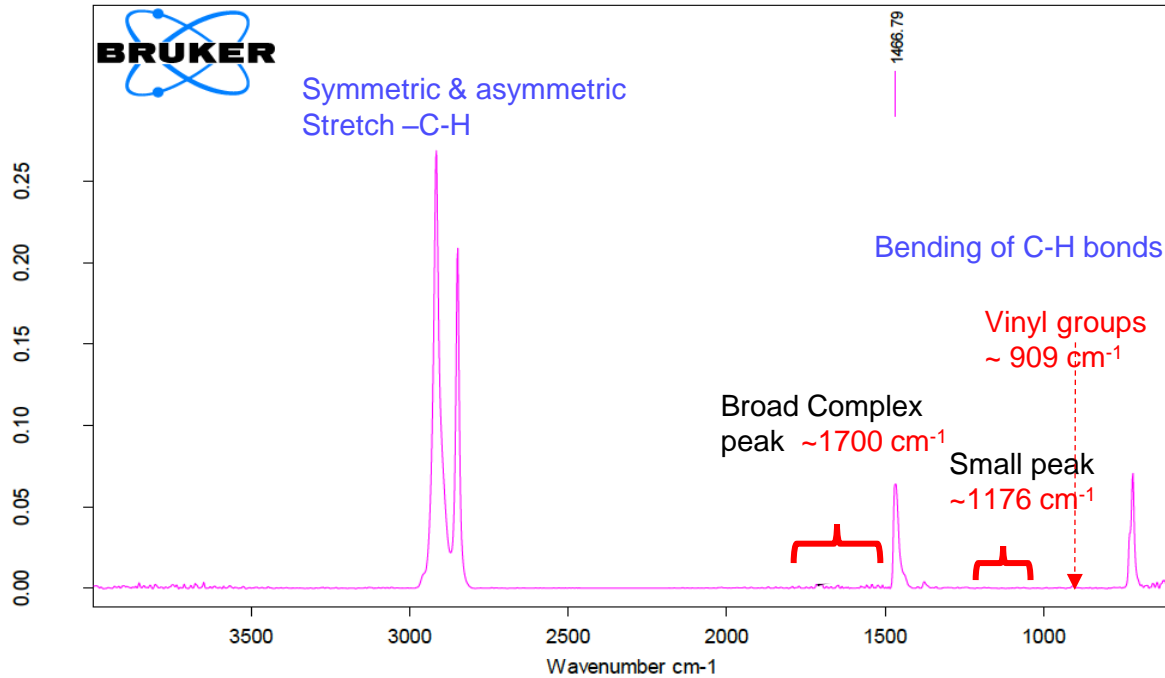
Higher temperature

12 hour light/ 12 hour dark exposure

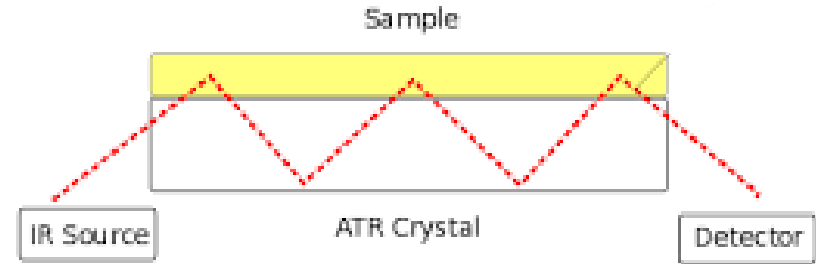


- UV-313 Lamps (2.45 ± 0.25 mW/sq.cm.)
- 12 hour light/12 hour dark
- Temp. 50 C/~ 25 C
- ASTM Type IV test pieces
- Artificial sea water.

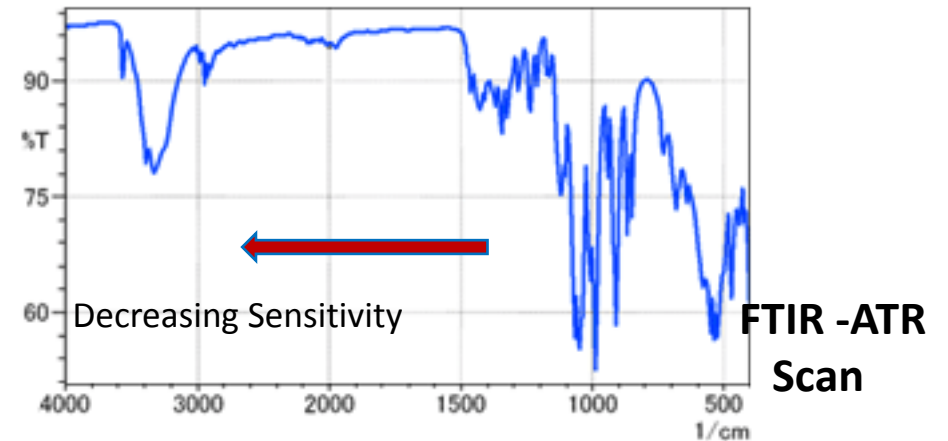
FTIR Spectroscopic Analysis



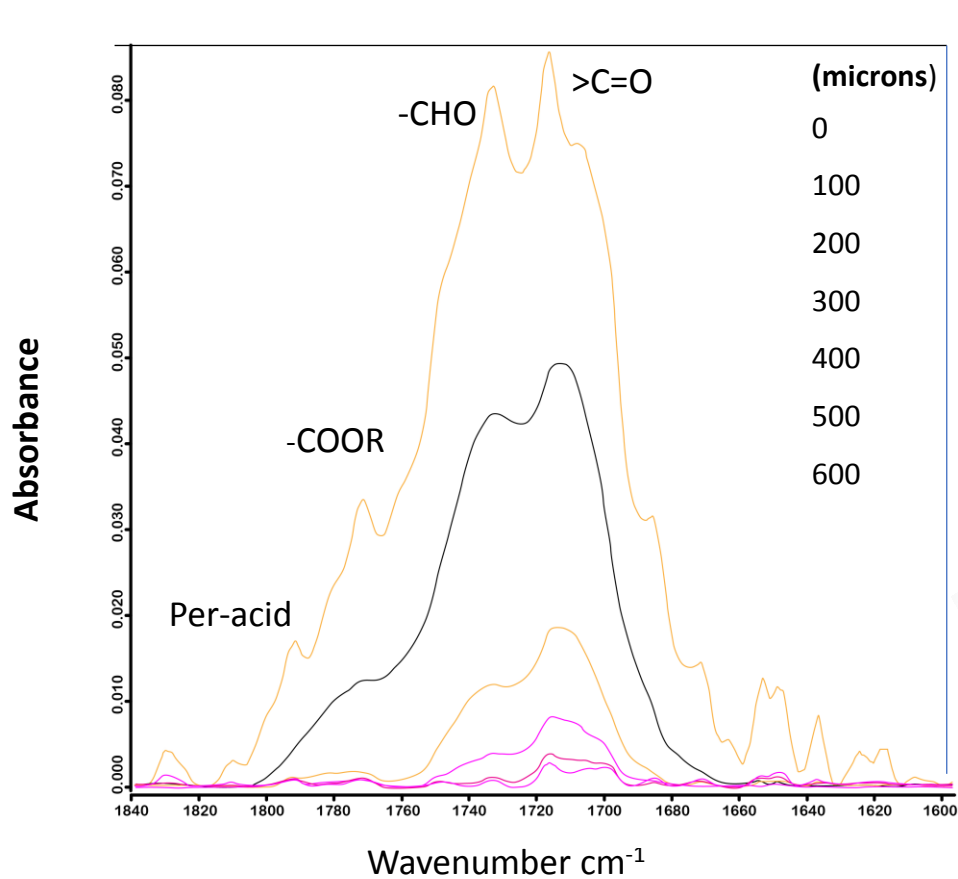
1. $>\text{C}=\text{O}$ absorbance around 1700 cm^{-1}
2. Vinyl absorbance at 909 cm^{-1}
3. $-\text{O}-\text{C}-\text{O}-$ absorbance at 1176 cm^{-1}
4. Splitting of peak at 1467 cm^{-1}



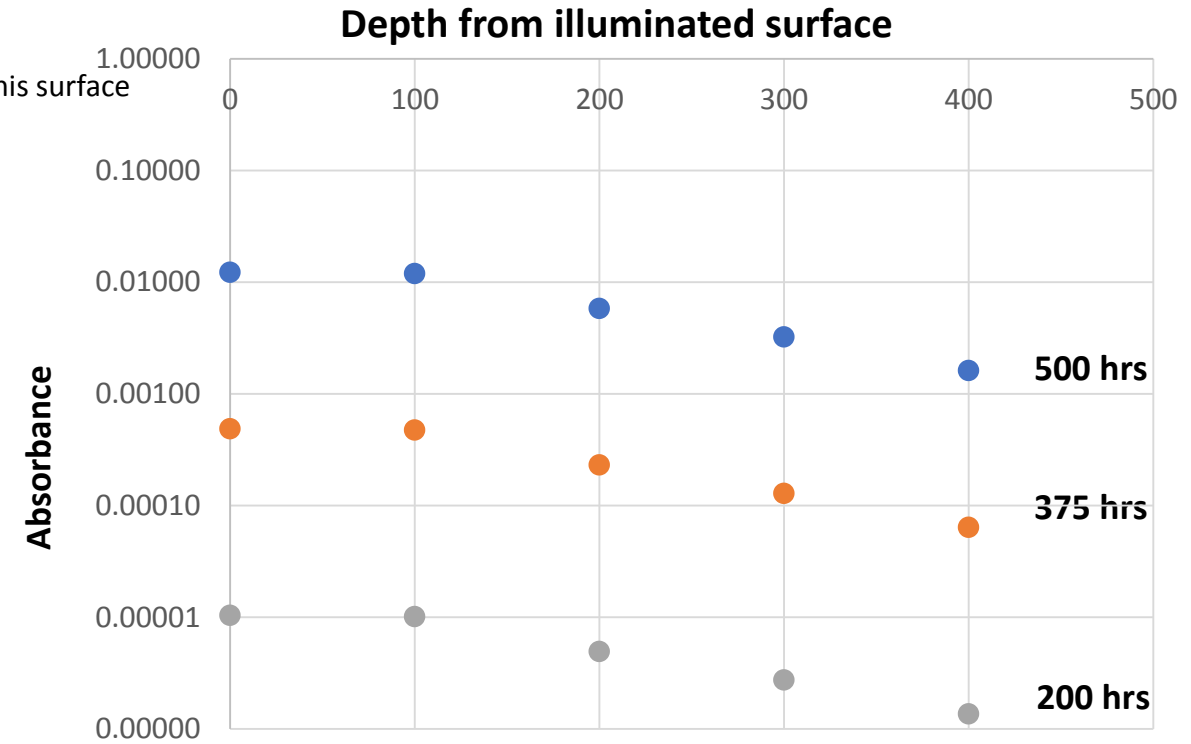
500 to 5000 micron depth



FTIR: Carbonyl Absorbance



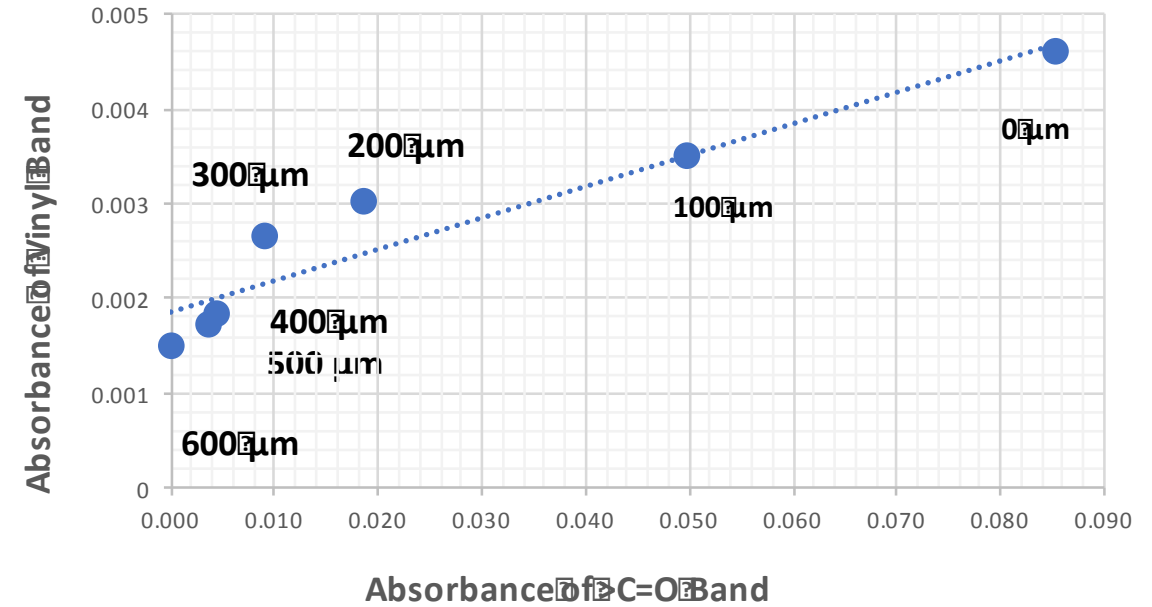
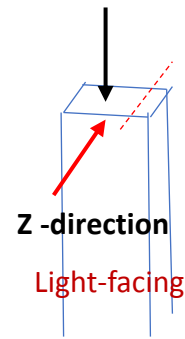
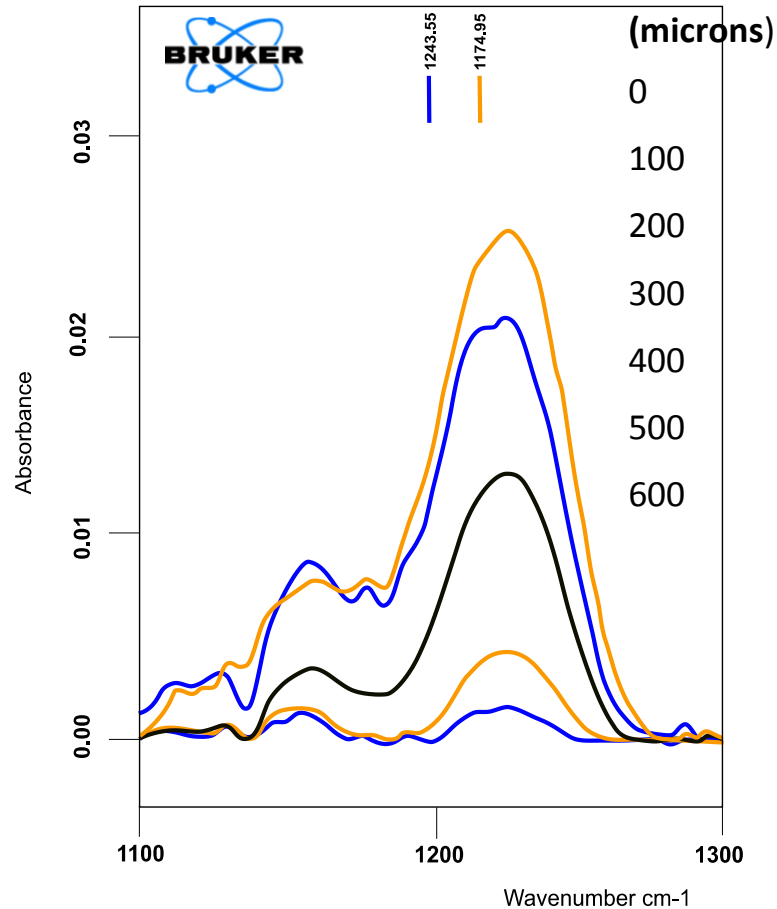
Carbonyl Absorption Region LDPE 500 hrs. Air



Peak absorbance of >C=O group drops with depth and is undetectable after about 600 microns.

In field-collected weathered polyethylene mesoplastics the layer is closer to 400-450 microns.

Layer with Spectral Signature ~700 nm



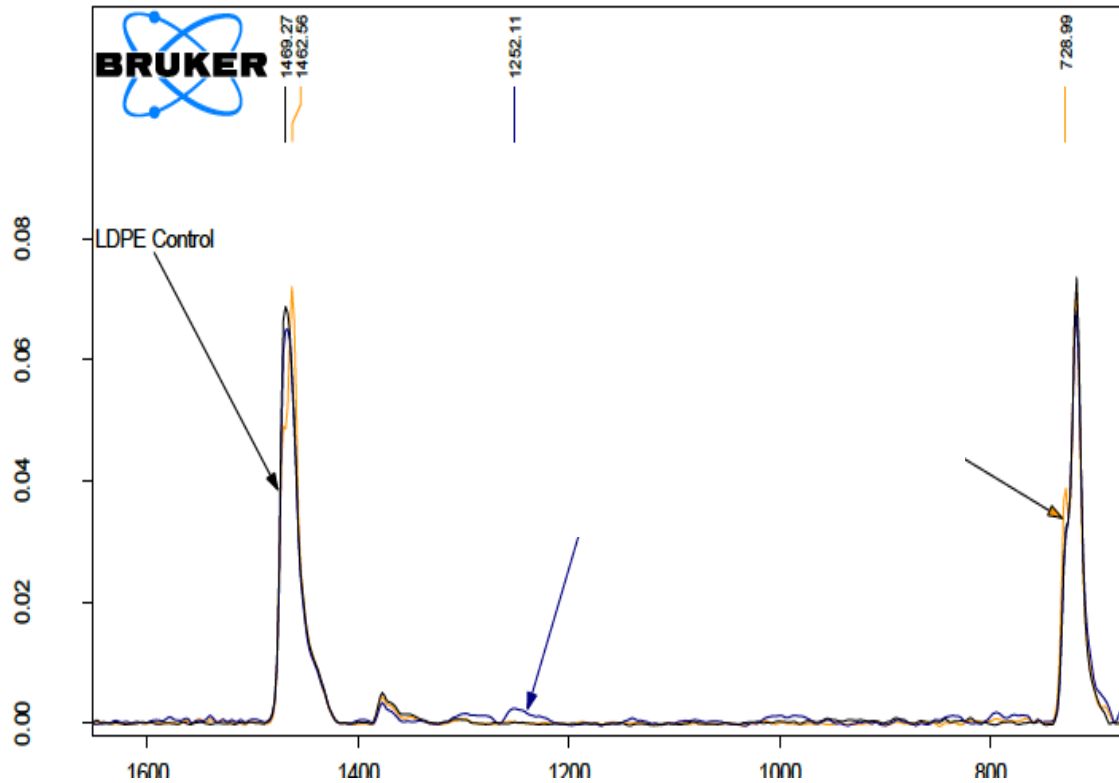
Increase in intensity of $>C=O$ band and $-C=C-$ with depth from surface correlate well

Absorbance at $\sim 1170 \text{ cm}^{-1}$ due to $-C-O-$ stretching in ethers and esters. Correlates very well with $>C=O$ band. $[r^2 = 1.00]$

At a depth of $\sim 700 \text{ nm}$ the spectral signature is unobservable.

Change in $-O-C-$ absorbance at 1176 cm^{-1}

Exposures in Seawater



Weathered in seawater for 375 hrs

Air

Seawater

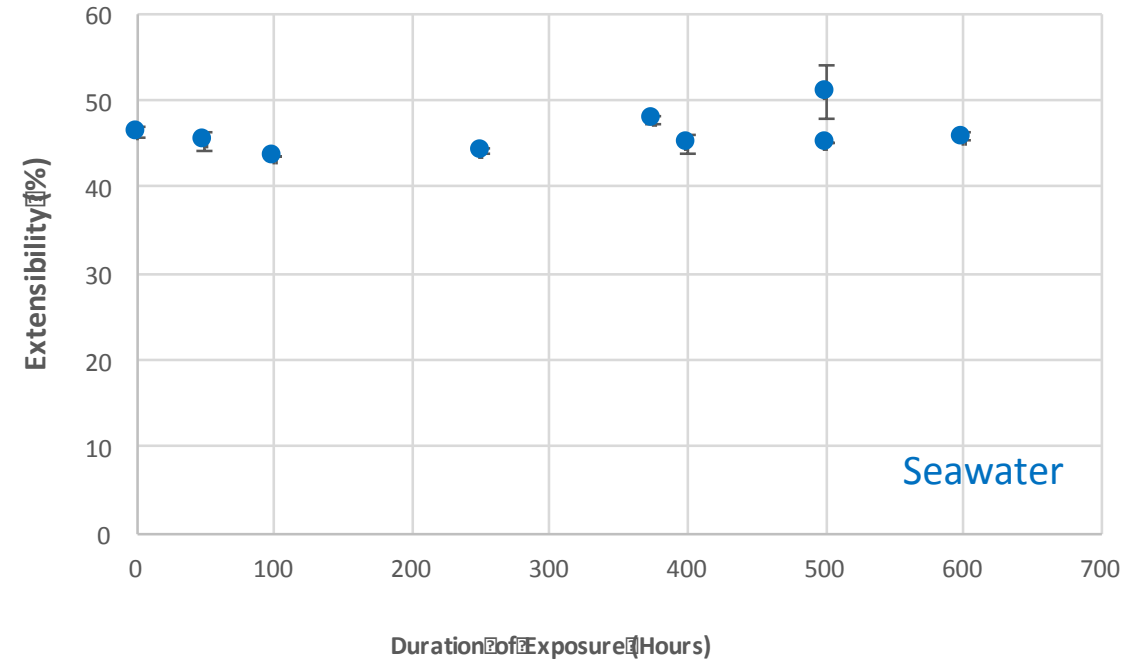
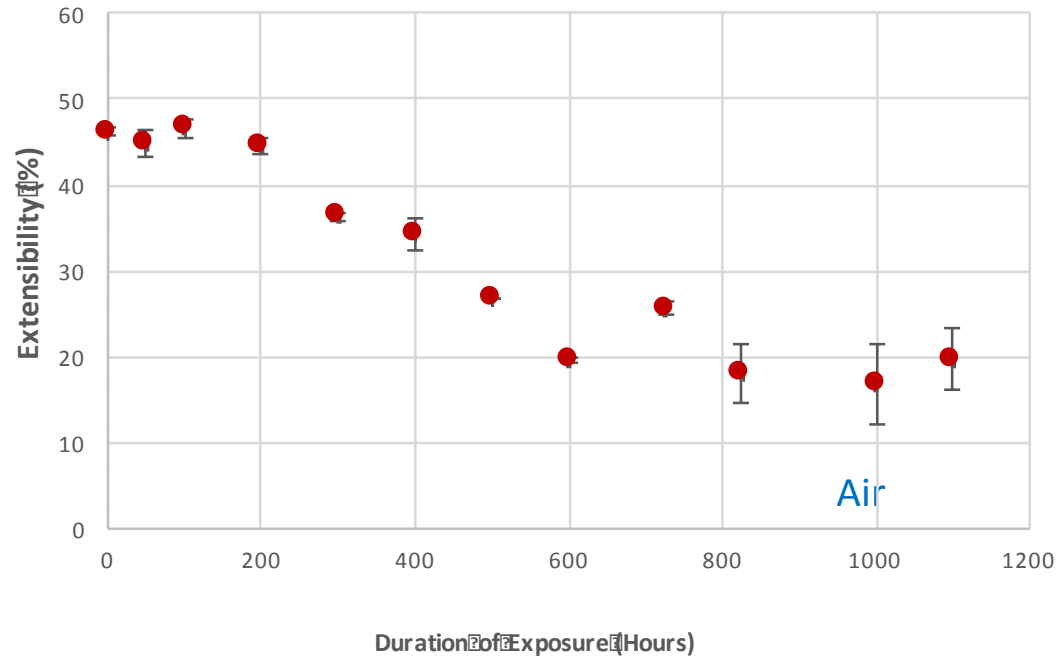


1 mm

1. Even the small changes limited to 100 microns!
2. No marked $>C=O$ band observed.
3. Extensive surface cracking not observed

Since $>C=O$ is not present anticipate no chain-scission
No surface cracking in seawater sample.

Tensile Extensibility of samples



- Extensibility does not change significantly with duration
- Slow decrease in Tensile strength (MPa) with durations – slower than for air exposure.
- Energy to break and the tensile modulus both show no change with duration.

Question: In Seawater degradation did not occur. But did oxidation take place?

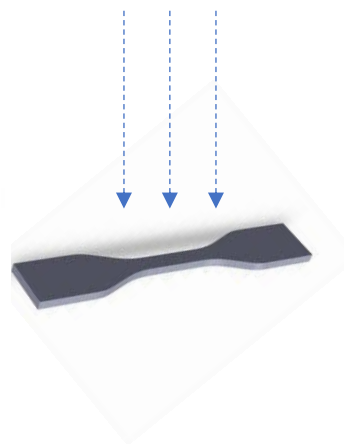
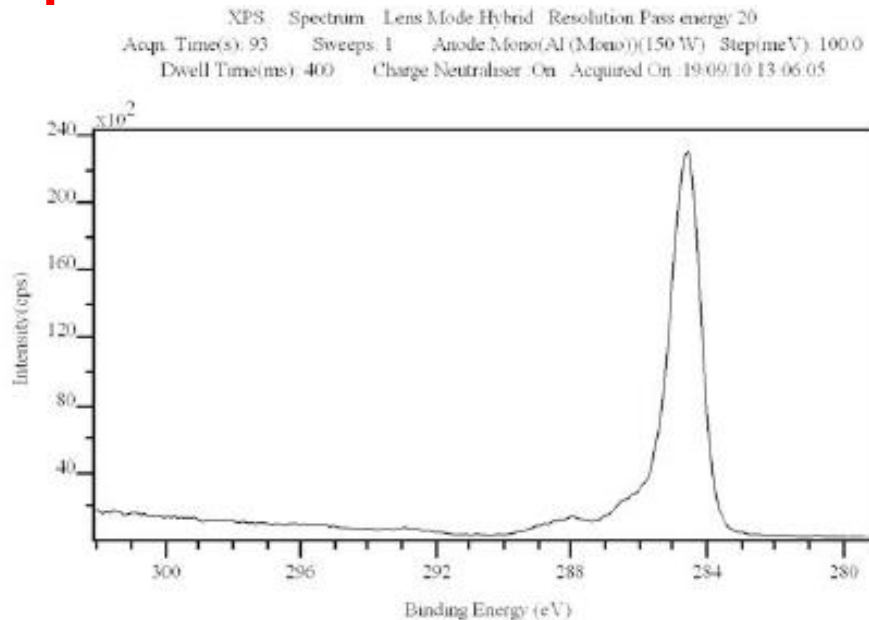
Surface Oxidation in Seawater Exposures



XPS {X-ray Photoelectron Spectroscopy} **1-10 nm**

EDX {Energy Dispersive X-ray} **500 – 1000 nm**

FTIR-ATR Spectroscopy **500 -5000 microns**



EDX Results: Percent Oxygen

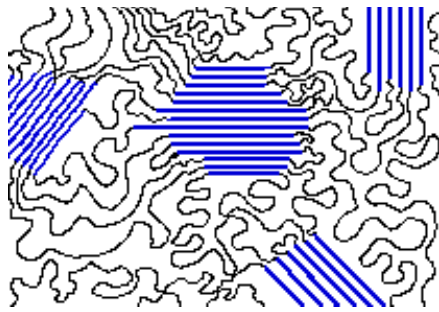
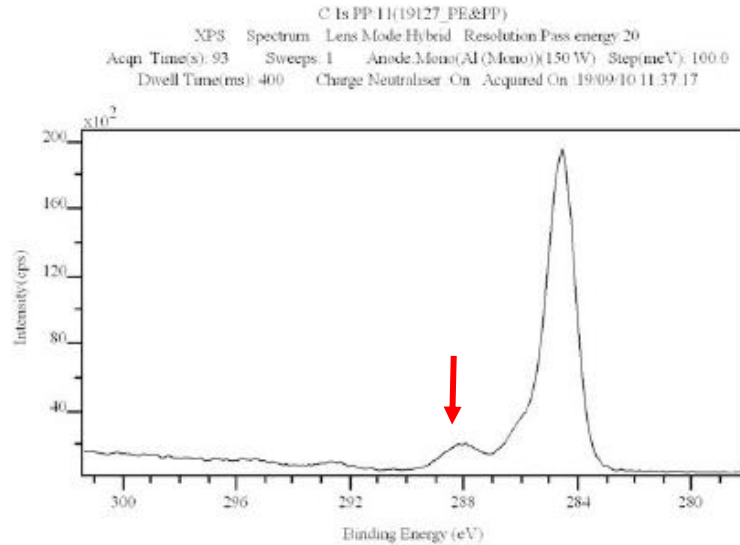
- Control LDPE Surface: 1.9 [0.25]
- 375 hr. exposure in seawater: 3.5 [0.70]

XPS Results : C/O atomic Ratio

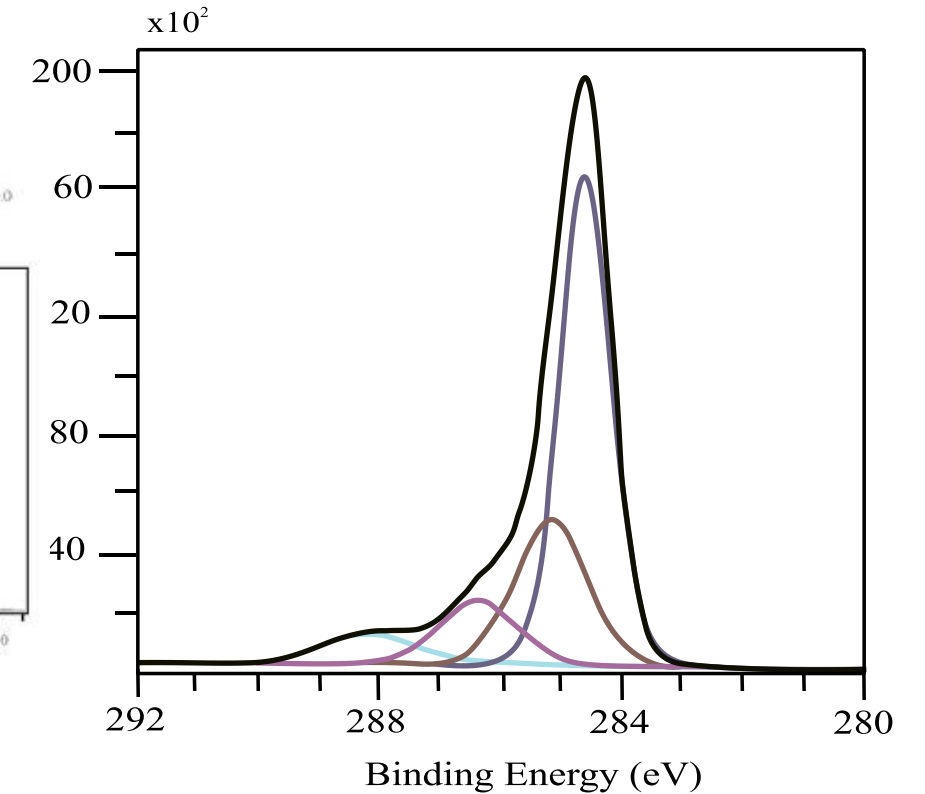
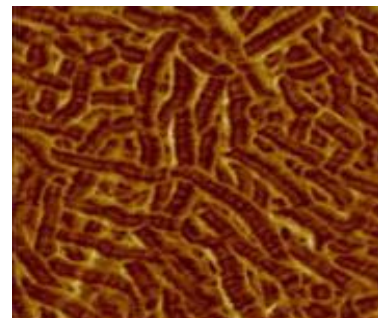
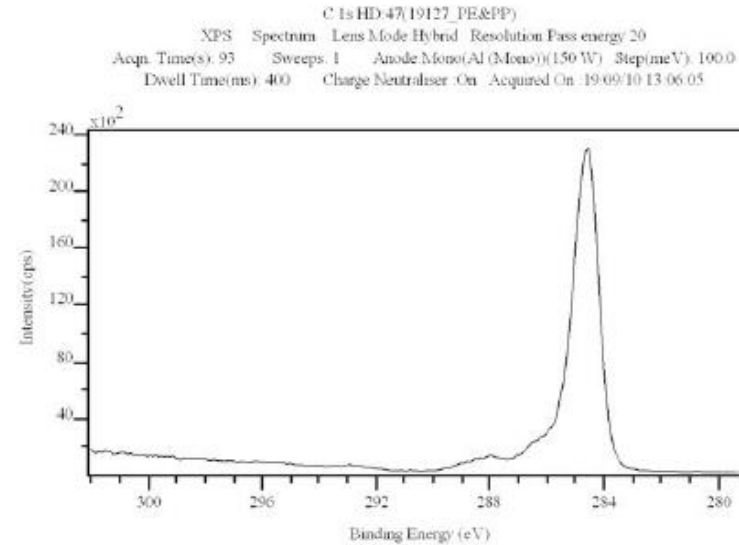
- Control LDPE Surface: 64.34
- 375 hr. exposure in seawater: 6.99

Surface Oxidation with Different Chemistry

Expose 375 hr. in seawater



Control



- Oxidation takes place in seawater exposures
- But no accompanying scission is apparent
- Negligible amounts of $>\text{C}=\text{O}$ groups produced

A Different Chemistry?

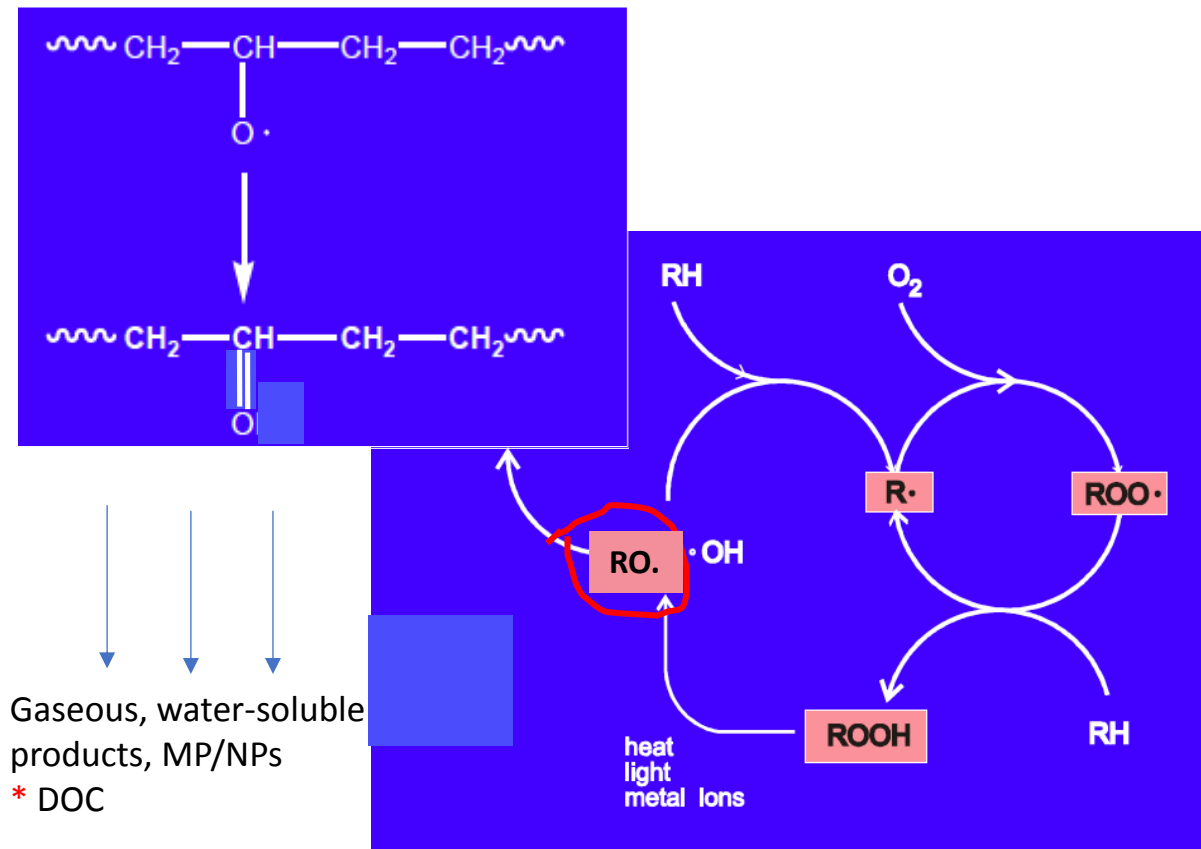
Seawater + UV + DOM \Rightarrow **[.OH]** Br. Cl. oxidant radicals

1. Quenching effectiveness

F. > .OH > Cl. > CH₃. > Br. > ROO.

2. Macro-radicals do not translate and cannot freely orient in solid state. OH radicals are **mobile** and react **faster** relative to macro-radicals. [LDPE water sorption ~ 0.01 wt.%]

3. **[.OH]** is the most efficient oxidant in the system and is mobile. Chain-bound -CHO, >C=O, -C-OH will be oxidized by preferentially by **[.OH]** corresponding acids.



Presence of UV-initiated oxidant radical species in seawater exposures promote oxidation by pathways that avoid chain-scission.

Thank You



Kara Lavender-Law & Jessica Donohue (SEA, MA);

Giora Proskurowsky (University of Washington, WA)