Monday, 12 June 2023

Reference Materials - Status and Needs

Chair: John Norman & Wendel Wohlleben

Talk B2C –O

Reliably Generating Microplastic Particles for Laboratory Testing *(online)*

Christie Sayes, Baylor University

Christie_Sayes@baylor.edu

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2023 ICCA MARII WORKSHOP

Alexis Royal Sonesta Hotel

Seattle, USA

#microplastics

Reliably Generating Microplastic Particles

INTRODUCTION

There is a need to generate microplastic particles less than 10 μm to perform systematic environmental health and safety studies that are reproducible across different laboratories worldwide.

The scientific community has found it difficult to produce reliable microplastic particle size populations that is scalable, free of contamination, narrow size distribution, and composed of different polymer types.

GOAL OF THIS RESEARCH

The goal of this proposed work is to produce a documented methodology that can generate microplastic particles that are < 10 μm in diameter in sufficient quantities necessary to create a microplastic reference material library.

Reliably Generating Microplastic Particles

EXPERIMENTAL DESIGN

The polymers relevant to this work include:

Polyethylene, Low-Density (PE-LD)
Polyethylene, High-Density (PE-HD)
PolyPropylene (PP)
PolyEthylene Terephthalate (PET)
Styrene AcryloNitrile (SAN),
    [Acrylonitrile Butadiene Styrene (ABS)]
PolyMethyl MethAcrylate (PMMA)
PolyAmide (PA6)
    [Nylon 6; Polycaprolactam]
PolyCarbonate (PC)
PolyUrethane (PU)

CONFIRMATION THROUGH CHARACTERIZATION

Each particle population is characterized:

Size and size distribution,

Shape and texture,

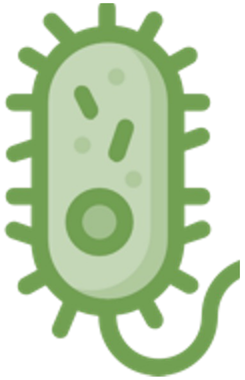
Surface characteristics, and

Composition.

Reliably Generating Microplastic Particles

Experiment 1.
Mechanical grinding

Experiment 2.
Chemical precipitation



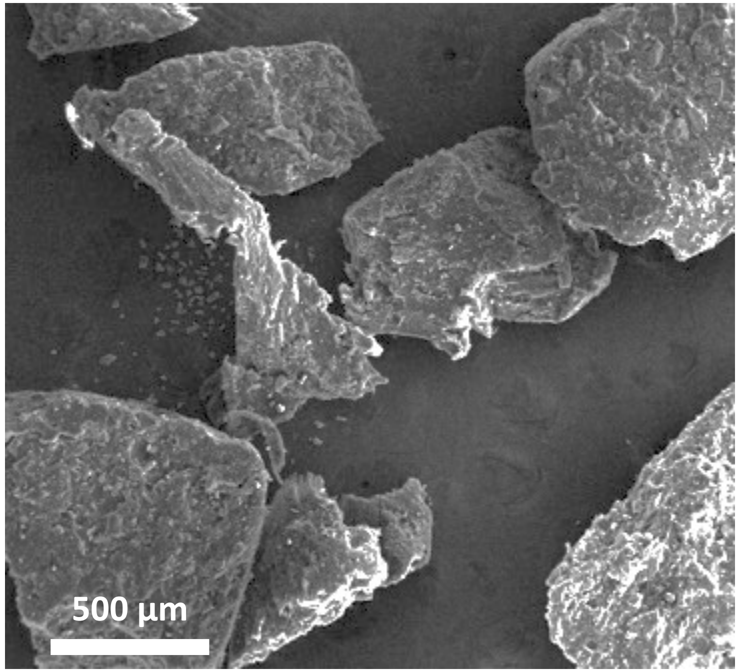
Experiment 3.
Bacterial breakdown

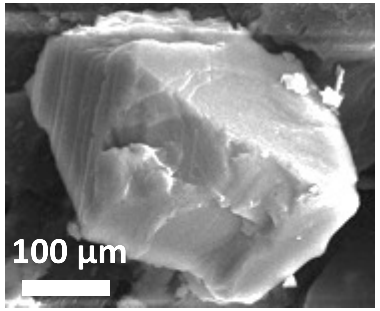
Experiment 4.
Enzymatic degradation

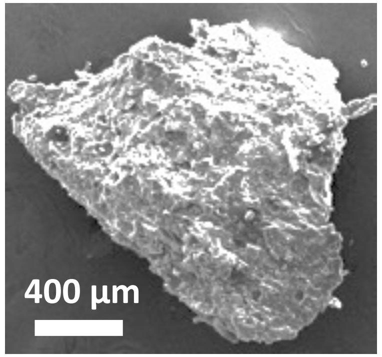
PRODUCING MICROPLASTIC PARTICLES VIA MECHANICAL GRINDING

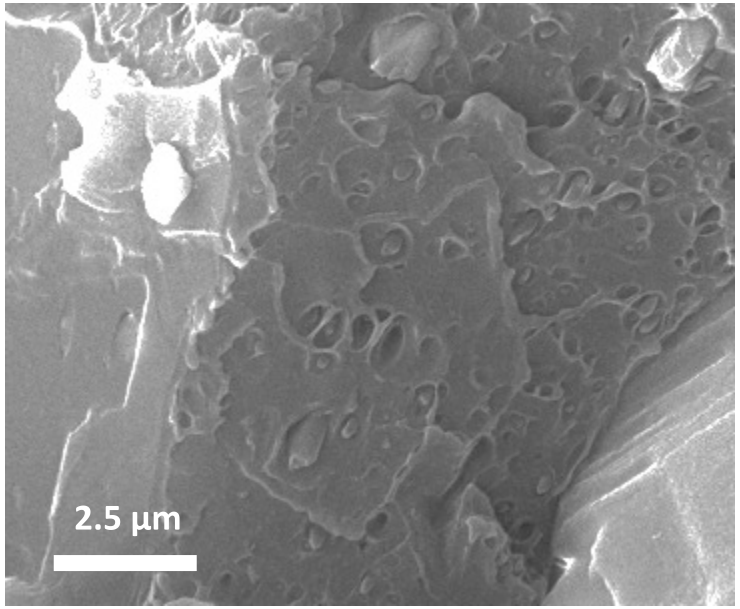
for lab-based experiments

- Heavy-duty food blender used to pulverize macro-sized plastics into **fine** and **ultrafine** powders
  - Macro-sized plastics include:
    - Polystyrene foam (<1 μm)
    - Nurdles (<1 μm)
    - Cutlery (1-5 μm)
    - Bottle (1-10 μm)
    - Straw (50-100 μm)
- Vary blending time
- Add **liquid nitrogen (LN_2)** to improve grinding performance









Polystyrene cutlery

LABORATORY GENERATED MICROPLASTIC PARTICLES

produced by grinding of commercial plastic cutlery

T. D. Ayorinde, P. Obiako, C. Collom, and C.M. Sayes. *Baylor University, Waco, TX.*

Simulation of Environmental Weathering of Laboratory-Generated Microplastic Particles (LG-MPP) for Defining Reference Materials

PRODUCING MICROPLASTIC PARTICLES VIA CHEMICAL DEGRADATION

for lab-based experiments

Advanced Oxidation Processes (AOPs)

A set of chemical treatment procedures designed to remove organic (and inorganic) materials in water by oxidation through reactions with radicals ($^{\bullet}OH$, $O_2^{\bullet-}$, $SO_4^{\bullet-}$)

The term refers to a subset of such chemical processes that employ O_3, H_2O_2, and UV

One such type of process is called ***In Situ*** **Chemical Oxidation** (ISCO)

Fenton

Ozonation

Persulfate

H_2O_2

Heat

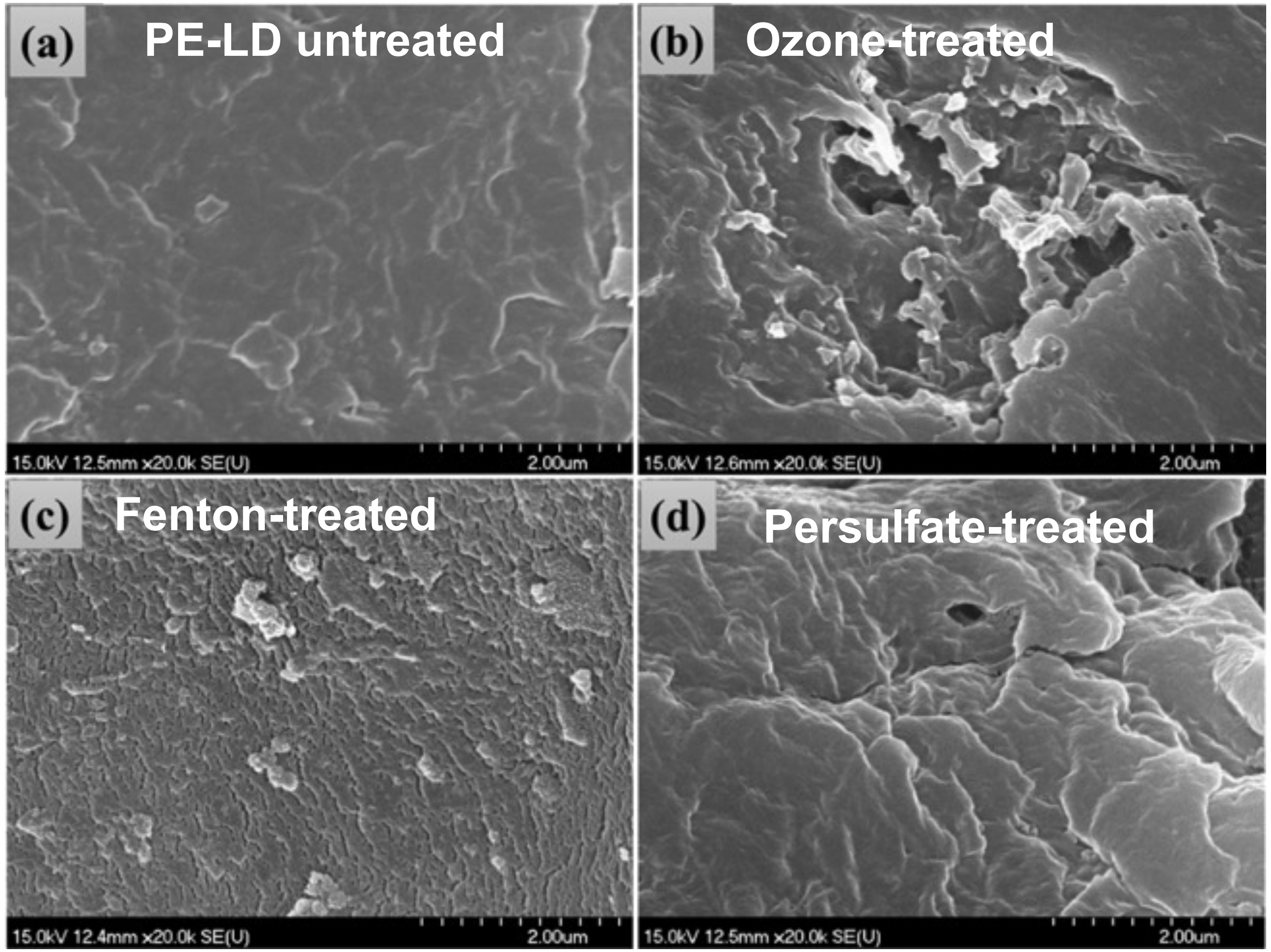
Ultraviolet

Mostly used in combination

Fenton, Ozonation, & Persulfate Treatment

Luo H, et al. (2021). JHM. 5(413):125342.

- The study's goal was to investigate the removal of pigment red from MPs
- **But the advantage was the degradation of MP's physical form**
- *The magnification of SEM micrographs is 20,000.*

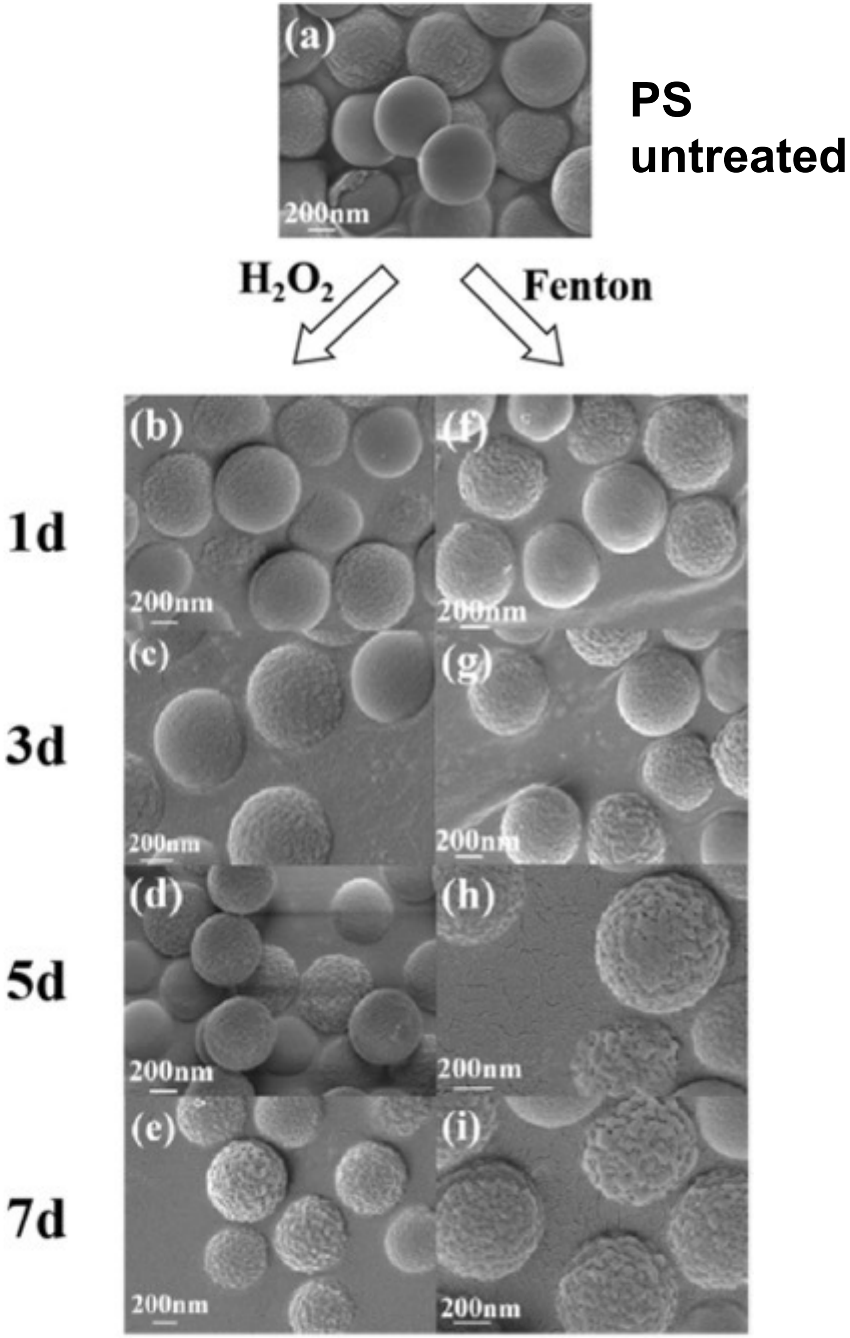


Ferrous sulfate ($FeSO_4 \cdot 7\ H_2O$)
Mohr's salt $(NH_4)_2Fe(SO_4)_2$

Lang M, et al. (2020). STOTEN 20(722):137762

Fenton vs. H_2O_2 Aging Treatments of Polystyrene Microplastics

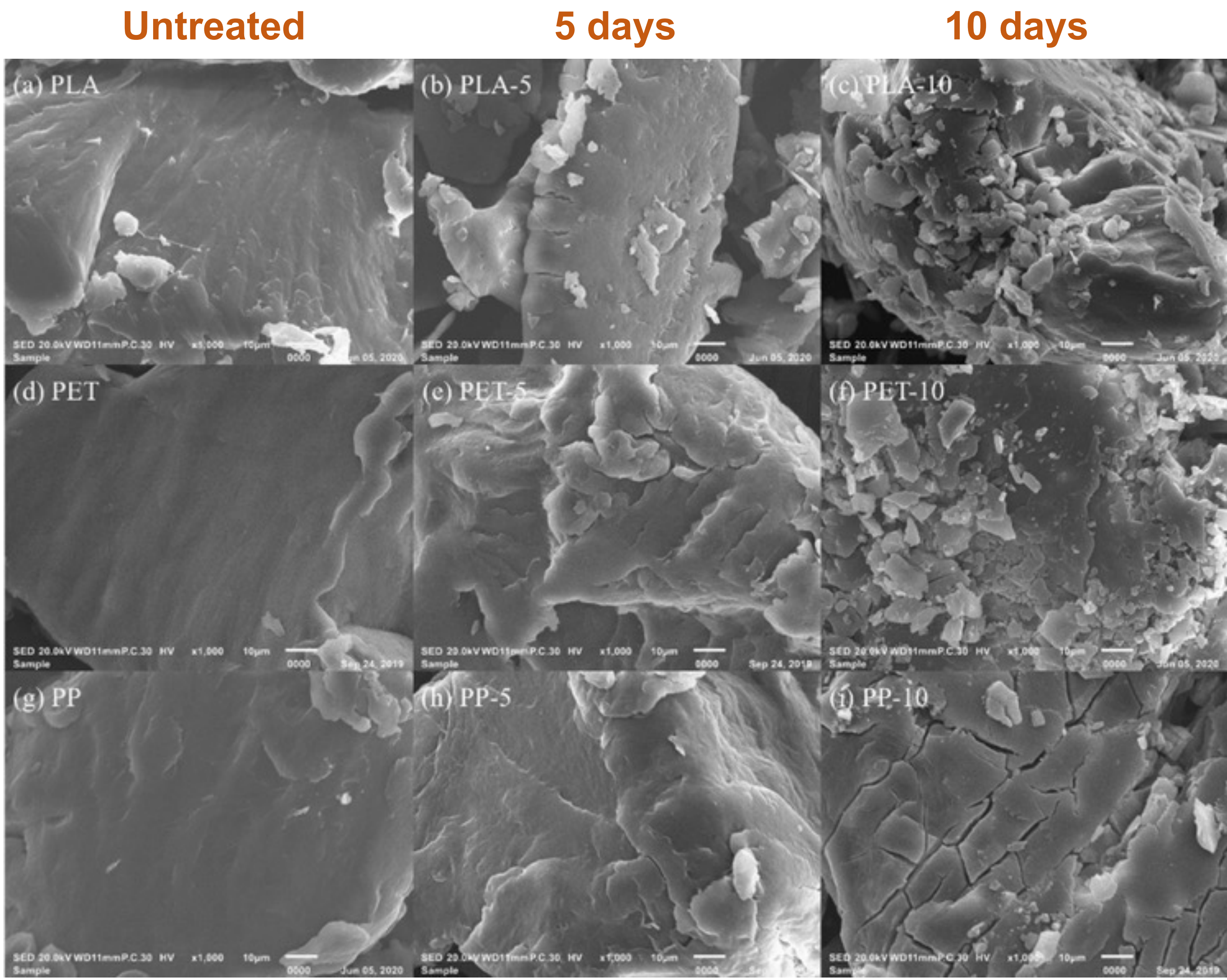
- The study's goal was to compare the properties of MP after 2 different treatment methods
- Polystyrene aging with Fenton reagent and H_2O_2 had similar effects
  - ***Increased surface roughness as time increased from 1 to 7 days***



Degradation of Microplastics by Thermal Activation using Persulfate Treatment

- Three aged microplastics as a function of aging time
- Used heat-activated potassium persulfate ($K_2S_2O_8$) to initiate the reaction
- Consequently, as the aging time increased, the adsorption capacity of the microplastics also increased significantly

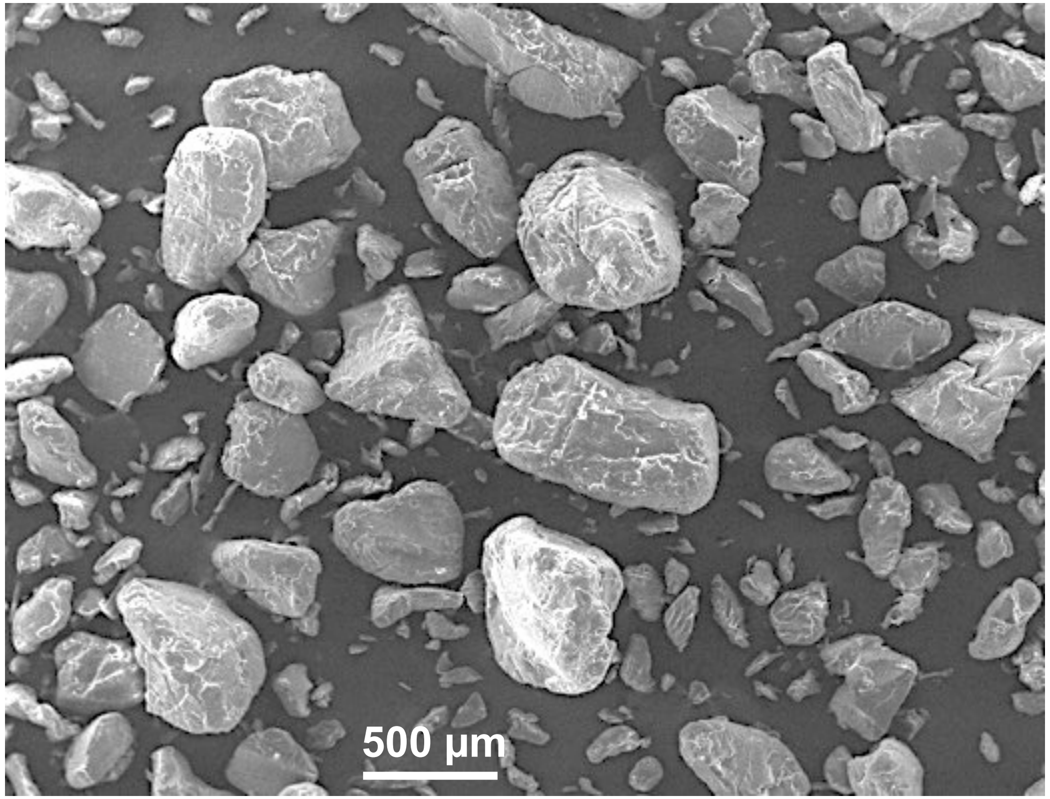
Kong F, et al (2021). AECT. 81(1):155-65.



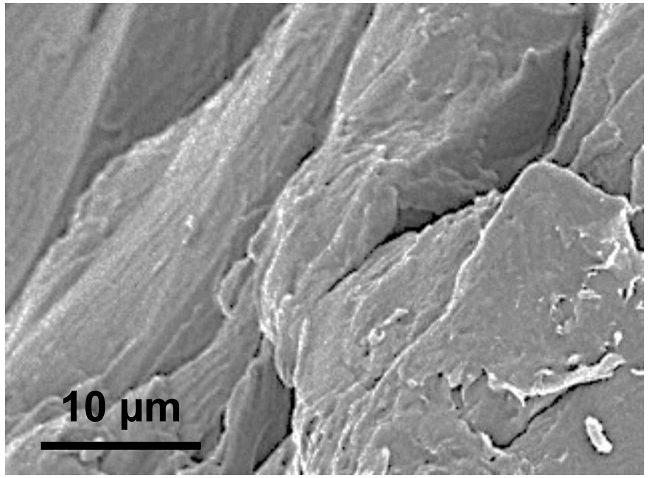
MORPHOLOGY OF POLYSTYRENE LAB-GENERATED MICROPLASTIC PARTICLES AFTER ADVANCED OXIDATION TREATMENTS

Efforts in Classification

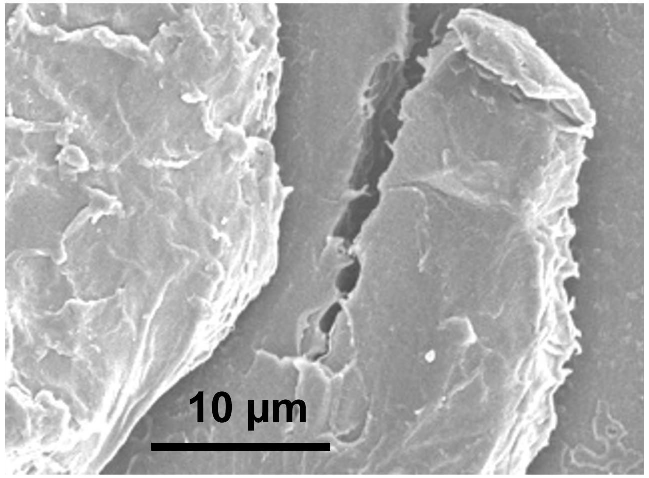
Pristine; immediately after grinding



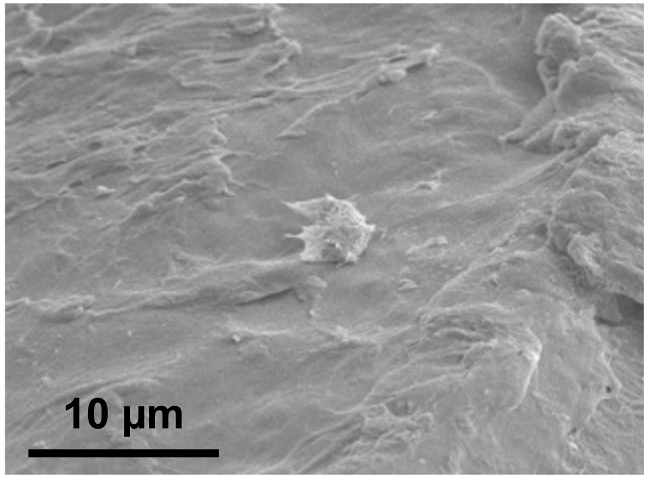
UV light; Crevices



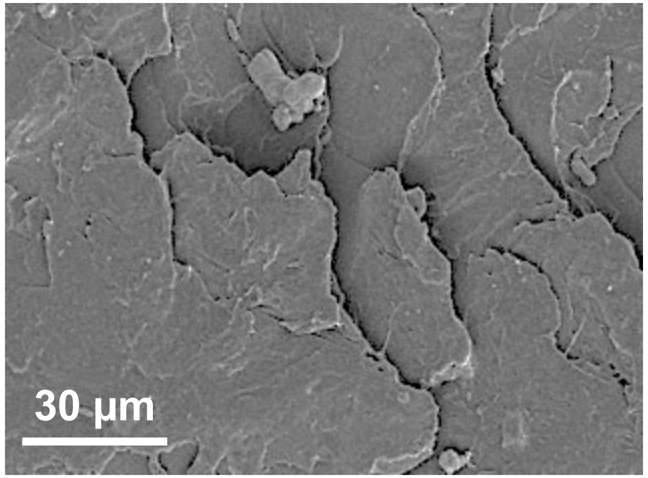
Thermal; Cracks



Salinity; Nanoparticles



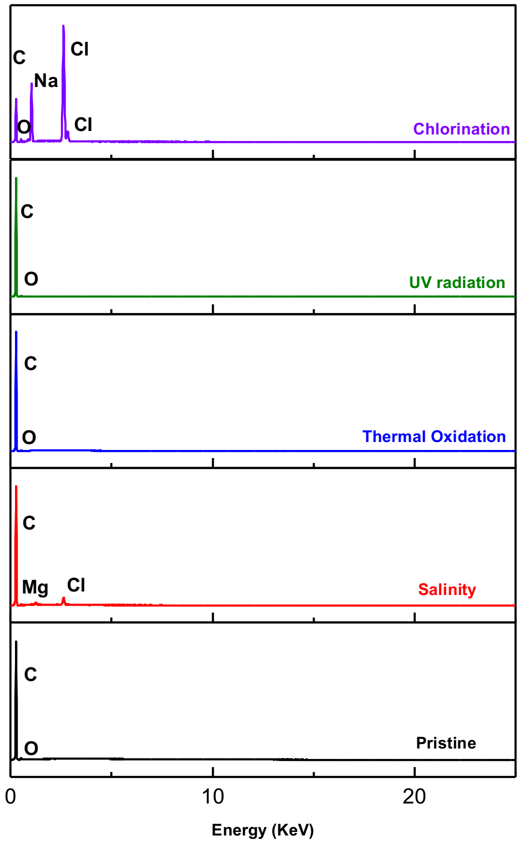
Chlorination; Flakes



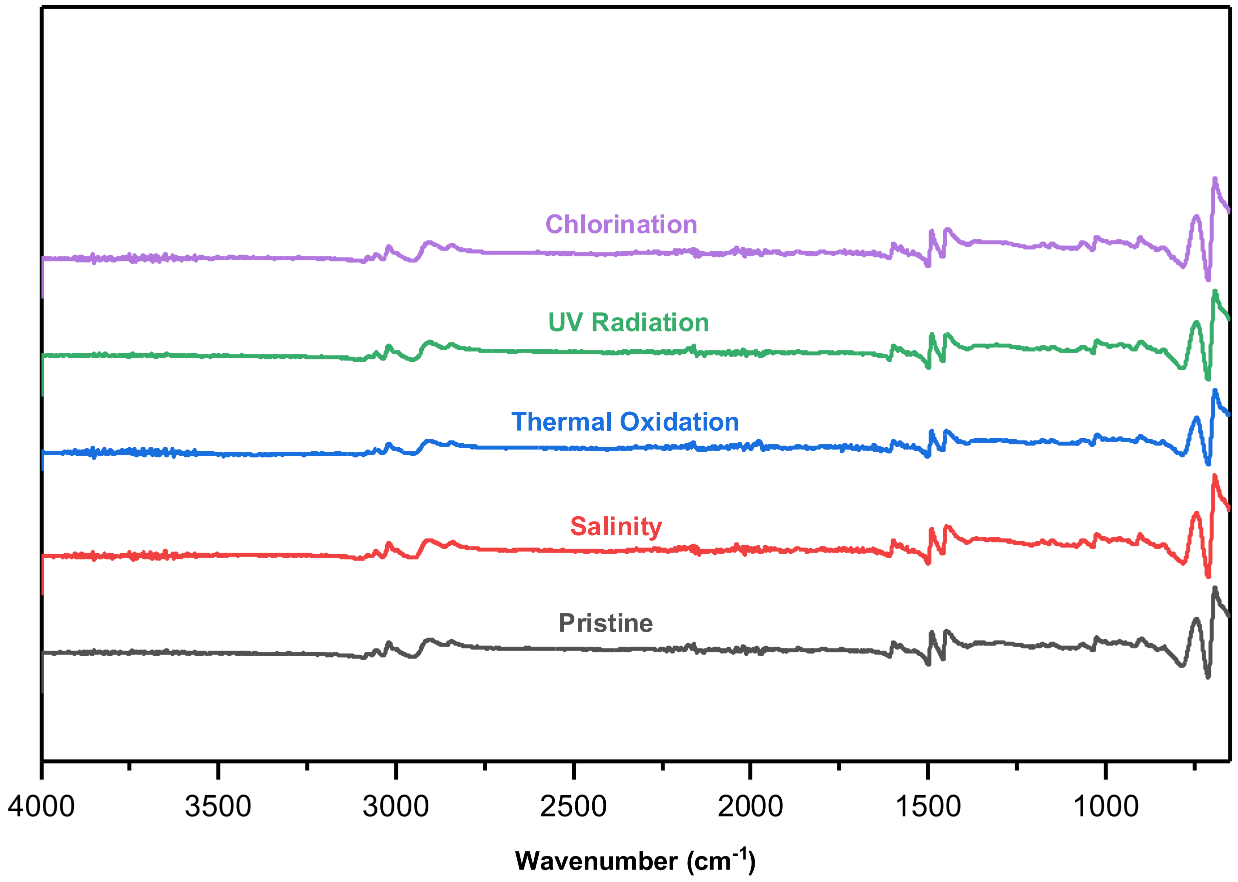
MEASUREMENTS OF POLYSTYRENE MICROPLASTIC PARTICLES

and additive identification

Energy Dispersive X-ray Spectroscopy

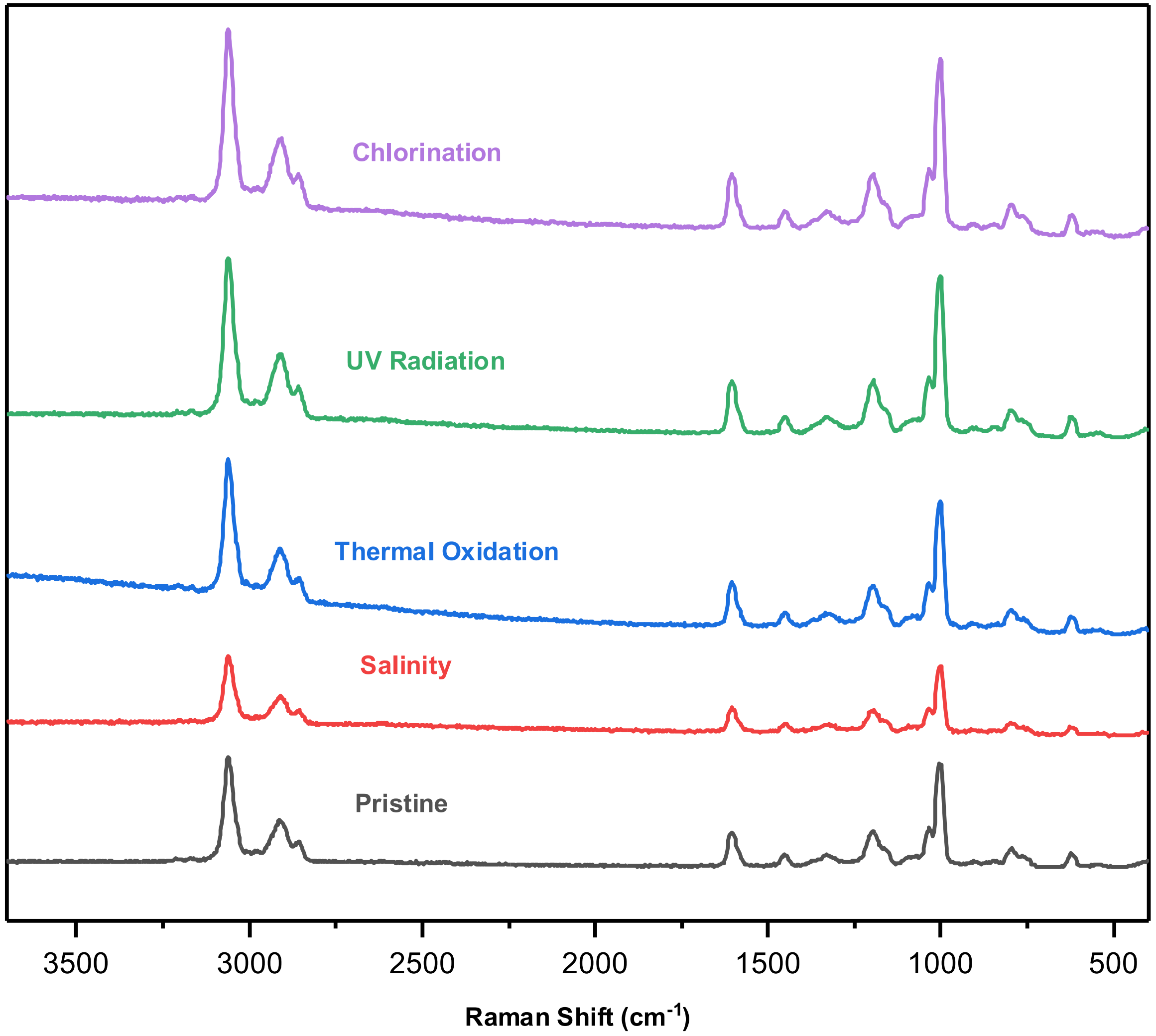


Fourier Transform Infrared Spectroscopy



RAMAN SPECTRA OF POLYSTYRENE MICROPLASTIC PARTICLES

as a measure of polymer and additive identification



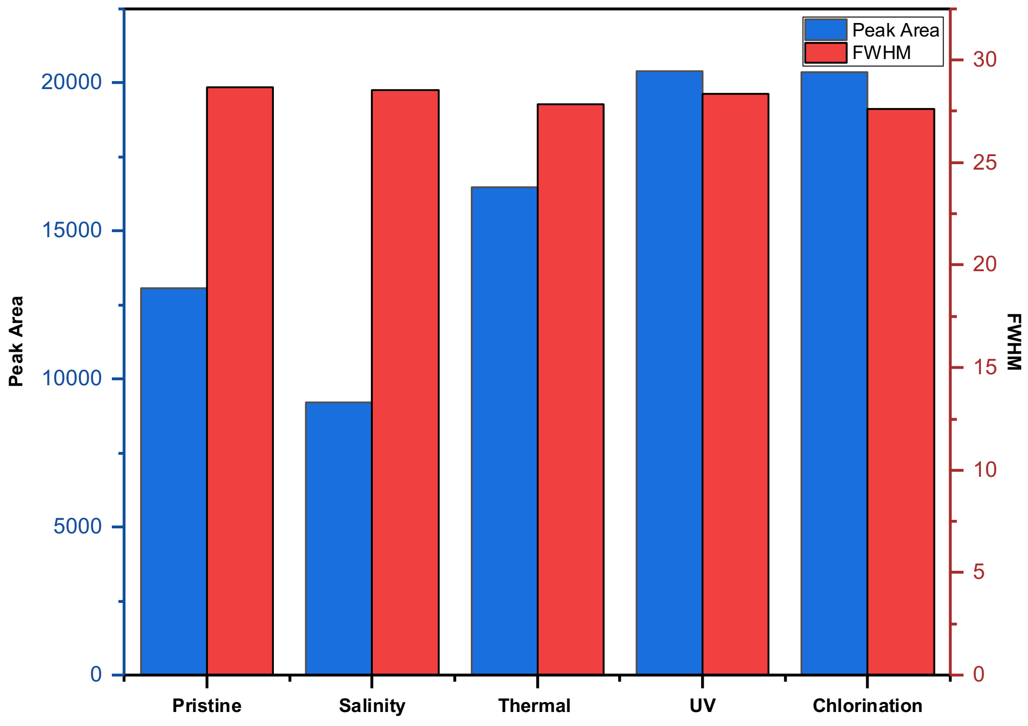
Oxidation Technique	Area Under Curve	Full Width at Half Maximum
Chlorination	3.72e+6	2,096
Ultraviolet	3.14e+6	2,096
Heat	3.69e+6	2,510
Salinity	2.73e+6	2,718
Pristine	2.45e+6	2,098

This will foster the use of the technique, which is becoming especially relevant in microplastic analysis.

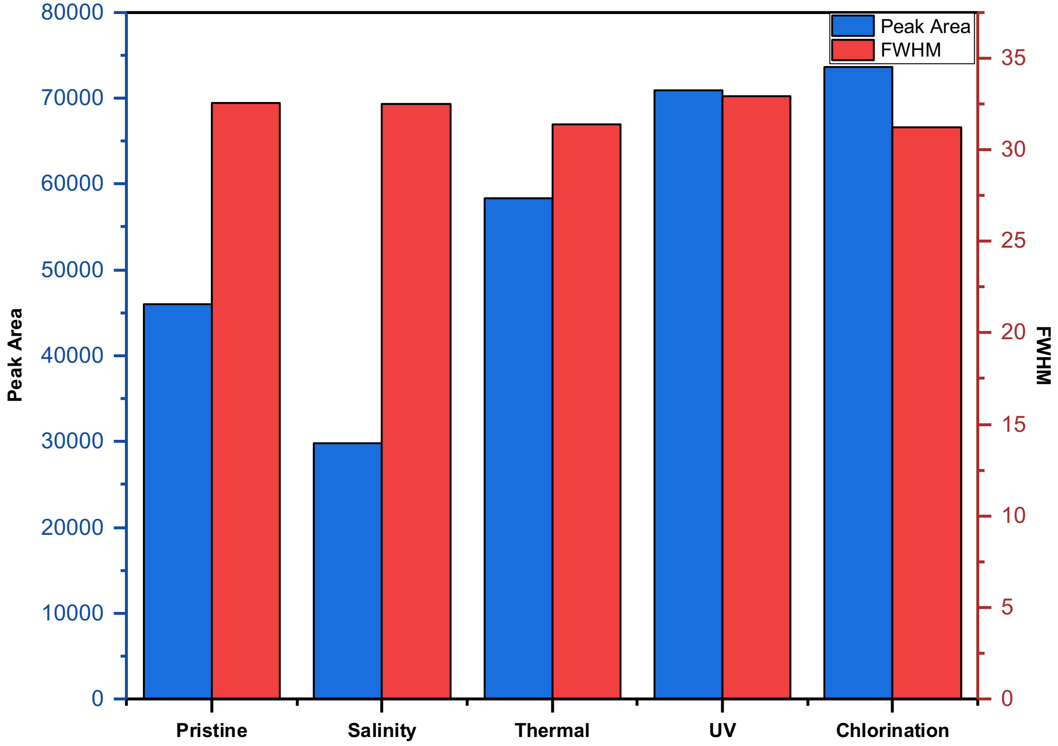
A DEEPER DIVE INTO THE RAMAN SPECTRA

as a measure of polymer and additive identification

The peak area and FWHM of the absorption band in the **carbonyl region** (1605 cm^{-1}) of the Raman spectra



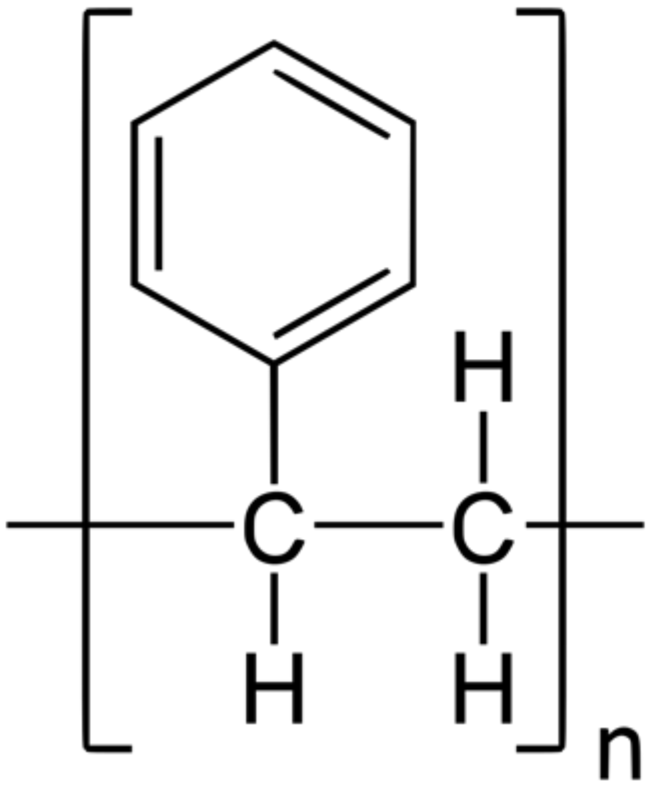
The peak area and FWHM of the absorption band in the **aromatic C-H stretch region** (3056 cm^{-1}) of the Raman spectra



OTHER REGIONS TO BE ANALYZED FROM RAMAN SPECTRA

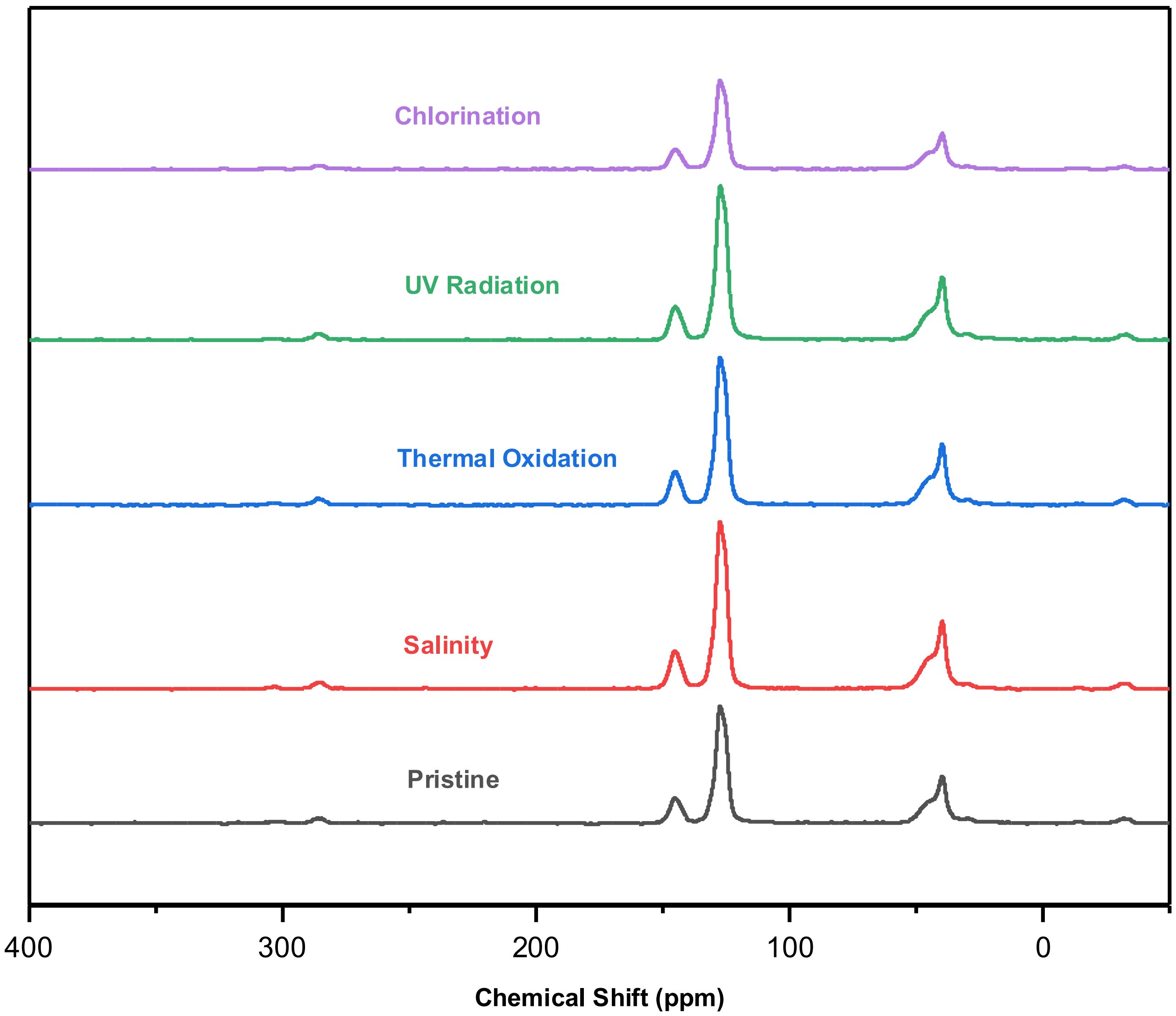
to reliably characterize microplastic particles

- The peaks in Raman spectra indicate the presence and abundance of:
  - Aromatic C-H stretches (3056 cm^{-1})
  - CH_2 asymmetric stretches (2911 cm^{-1})
  - Carbonyl groups (1605 cm^{-1})
  - CH_2 scissoring (1443 cm^{-1})
  - C-O stretch (1003 cm^{-1})
  - Ring deformation (620 cm^{-1})



^{13}C-NMR SPECTRA OF POLYSTYRENE LG-MPP

as a measure of polymer and additive identification



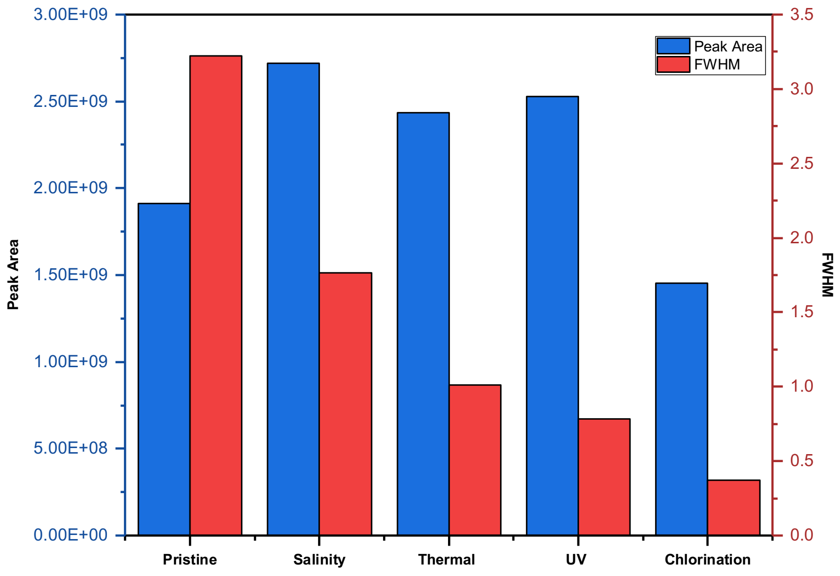
Oxidation Technique	Area Under Curve	Full Width at Half Maximum
Chlorination	3.23e+9	5.16
UV radiation	5.44e+9	5.13
Thermal oxidation	5.31e+9	5.16
Salinity	5.90e+9	5.14
Pristine	4.24e+9	5.14

This will foster the use of the technique, which is becoming especially relevant in microplastic analysis.

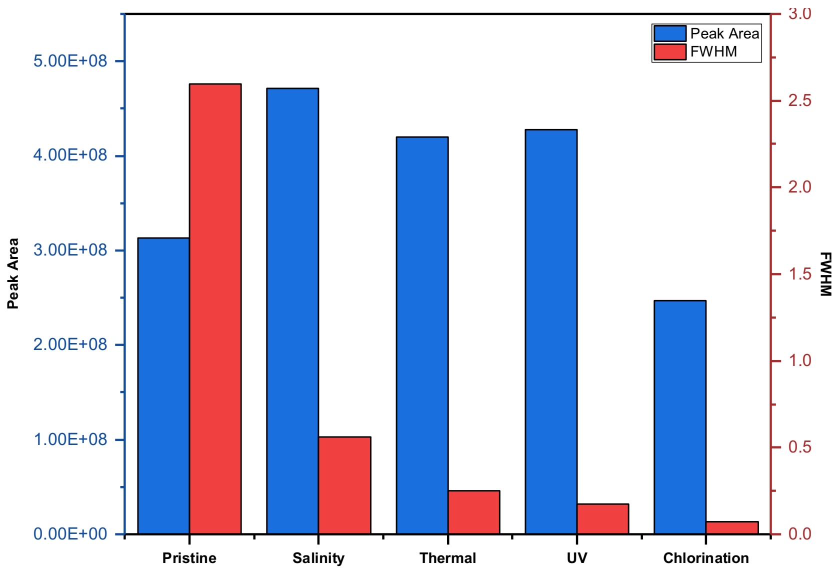
A DEEPER DIVE INTO ^{13}C-NMR SPECTRA

as a measure of polymer and additive identification

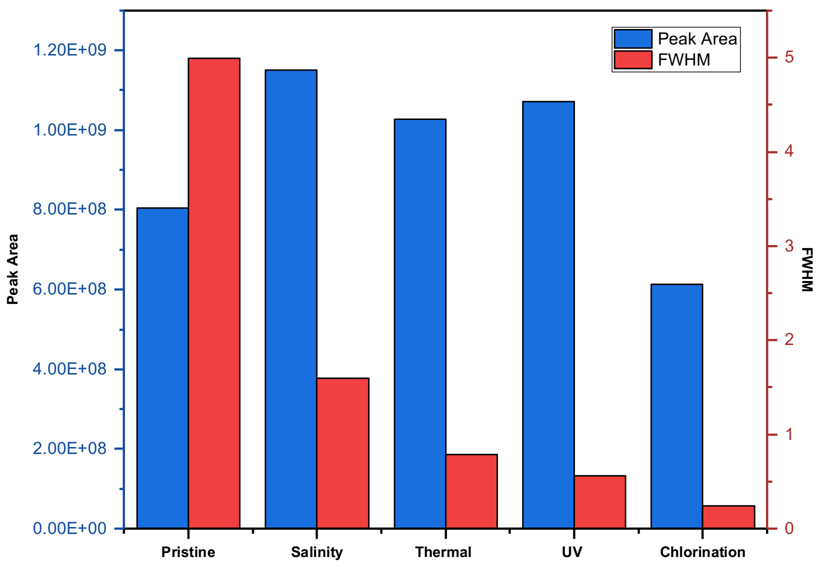
The peak area and FWHM of the absorption band in the **vinyl region** (127.62 ppm) of the NMR spectra



The peak area and FWHM of the absorption band in the **aromatic carbon region** (146.27 ppm) of the NMR spectra



The peak area and FWHM of the absorption band in the **saturated alkane region** (38.87 ppm) of the NMR spectra

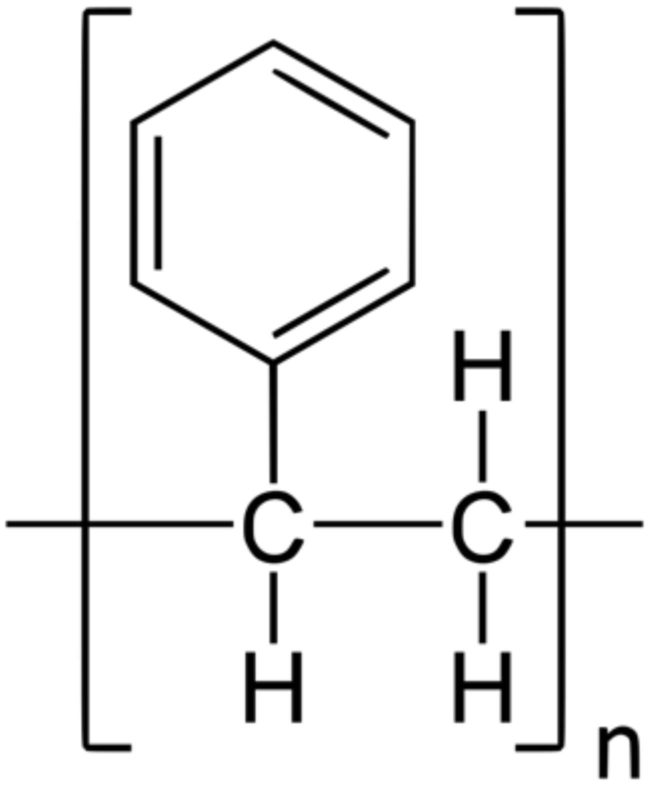


^{13}C-NMR SPECTRA OF POLYSTYRENE LG-MPP

as a measure of polymer and additive identification

- Solid-state Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance (CP/MAS 13C-NMR) is used to investigate the structure and interactions of microplastics

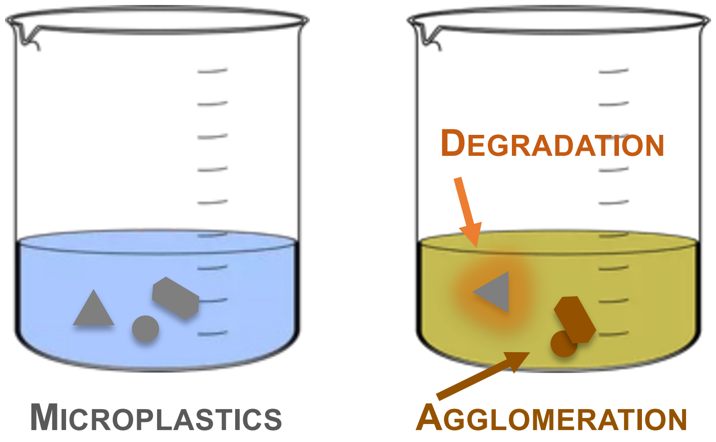
- The peaks indicate the presence of:
  - Saturated alkanes 38.87 ppm (10-60 ppm)
  - Non-aromatic alkenes 127.62 ppm (110-130 ppm)
  - Aromatic carbons 146.27 ppm (120-140 ppm)



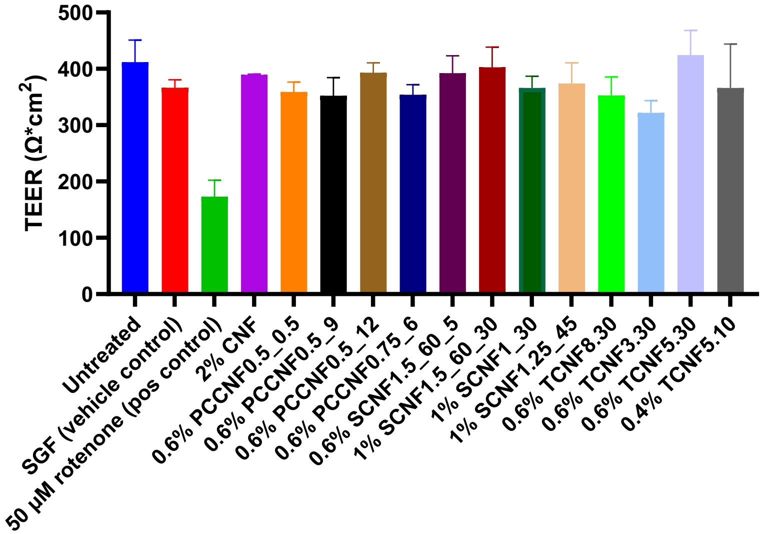
Other Characteristics Being Measured

The potential of **sorbed substances onto the surface of microplastic particles** combined with **exposure to changing environmental conditions** result in particle transformation producing “weathered” or “aged” microplastic particles

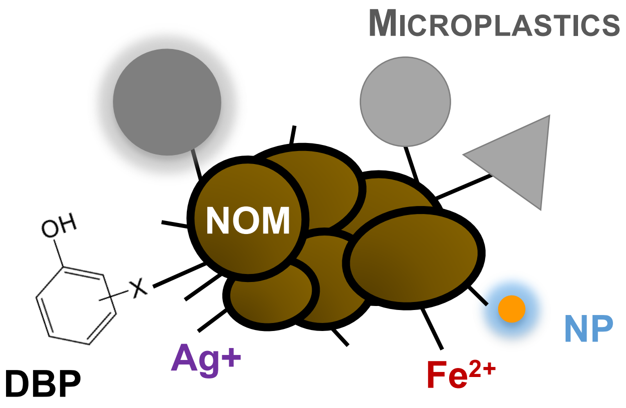
Assessing microplastic particle hazards can be performed using simulated real-world conditions



There is a need to develop methods for read-across relationships, correlations, and generalizations



This talk will present a case study weathering microplastic particles



The resultant data will provide critical information to inform public health and assess current and future risks

Particle-Chemical Interactions

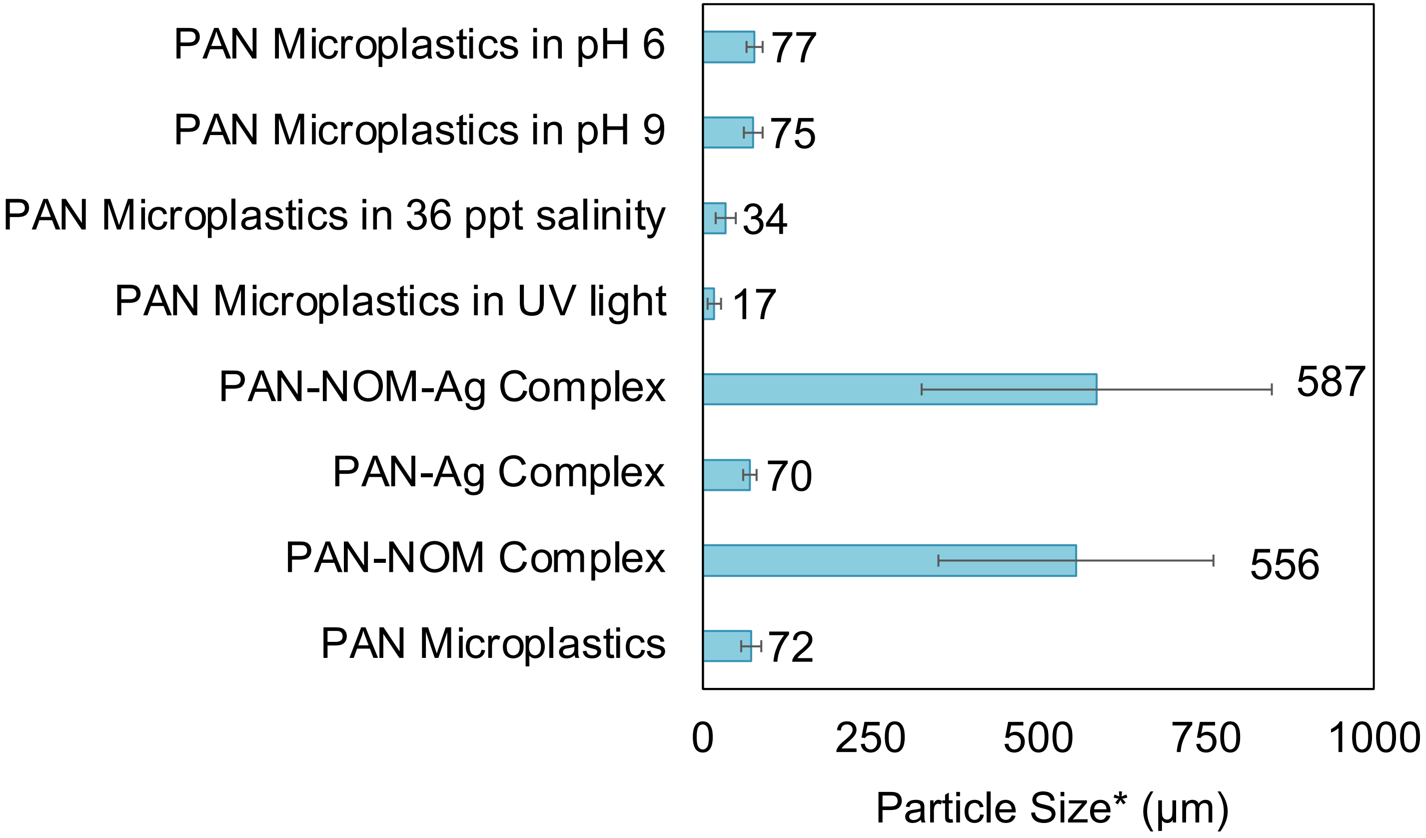
- Primary complexation of intact or degraded microplastics with natural/dissolved organic matter
- Secondary complexation of microplastics with other organic/inorganic matter (e.g., pesticides or metal ions)
- Hetero-aggregation with other plastic particles
- Reversible release of molecules or particles from aggregates

Exposure to microplastics is not to single particle types, but to a highly complex mixture

CHARACTERIZING PARTICLE INTERACTIONS

particles transform over time

- **Polyacrylonitrile (PAN) is a synthetic polymer with the linear formula $(C_3H_3N)_n$**
- The behavior of microplastics **depends** on the surrounding matrix
- Particles **aggregate…**
  - In the presence of NOM
  - UV light
  - Δ salinity
  - Δ pH



**microplastic component only*

(measurements taken from a series of microscopy images)

CONCLUSIONS

- It is possible to produce laboratory-generated microplastic particles that are representative of environmental microplastics using blenders, grinders, and other milling apparatuses
- Advanced oxidation processes and other environmental conditions can be simulated in the lab
- There is a measurable amount of oxidized groups on the surfaces of microplastics
- Aged microplastics are potential vectors for environmental contaminants and pathogens
- Microscopy should be a standard technique used to characterize microplastic surface features, while spectroscopy should be a complementary technique for identifying the presence and abundance of sorbed substances