Pre-treatment processes for a bio-based circular economy for plastics

Georgia Sourkouni, Philipp Moritz, Pavlos K. Pandis, Oliver Höfft, Charalampia Kalogirou, Stamatina Vouyiouka, and Christos Argirusis
Plastics in the environment

- Since 1950 about 8300 million tonnes of plastics have been produced
- Generated globally around 6300 million tonnes of plastic waste
- Around 79% of this amount remains in the environment

Pacific Ocean streams have created 3 "islands" of debris.
Plastics problem in the marine environment

Based on that numbers, it is not surprising that plastics can be found almost everywhere in the environment!

Especially the marine environment, where large amounts of plastic waste accumulate with increased risks for humans and fauna

Plastics and Microplastic discovered in the bodies of every dolphin, whale and seal studied
What are Microplastics?

**Microplastics** are very small pieces of *plastic* that pollute the *environment*.

They enter natural ecosystems from a variety of sources, including *cosmetics*, *clothing*, and industrial processes.

Microplastics are not a specific kind of *plastic*, but rather any type of plastic fragment that is less than 5 mm in length.

*U.S. National Oceanic and Atmospheric Administration* (NOAA)
Bio-based depolymerisation technologies

The development of bio-based depolymerisation technologies and hence solutions to the world’s plastic crisis is hampered by three main challenges:

• recalcitrant nature of plastics
• non-biological degradability
• new technologies must sustainably manage the plastic waste crisis in a low carbon footprint fashion
Bio-based depolymerisation technologies

• Microbes have a natural propensity to evolve in order to degrade new materials and thus to maintain nature’s cycle of generation, degradation, and regeneration.

• However, several factors hinder the microbial and/or enzymatic degradation of plastics
  ✓ microbes did not have the time to adapt themselves to the degradation of the new materials
  ✓ plastic degradation bacteria with diverse metabolic capabilities are needed
  ✓ only a limited number of bacteria/enzyme strains discovered that exhibit any activity in the degradation of plastics
  ✓ complex mechanisms behind the degradation of the plastic → concerted efforts are necessary to improve the efficiency of the used strains
  ✓ The production of new enzymes, more active towards plastic degradation is difficult to scale-up for industrial use
Bio-based depolymerisation technologies

Different techniques to degrade polymers such as

• thermal degradation
• photolysis
• chemical methods
• high “energy input” methods like ultrasonication and microwaves
• ....

Also as pre-treatment methods for

• biodegradation with enzymes and bacteria
Sonochemistry

If chemistry is the interaction of energy and matter
Then we define Sonochemistry = Ultrasound + Chemistry

Short timescale along with high energy input and high pressure

A comparison of different kinds of chemistry
Acoustic cavitation

Physical phenomenon responsible for chemical effects caused by ultrasound!

1. Bubble formation during rarefaction cycle of wave
2. Bubble growth period of a few cycles till critical size
3. Bubble collapse acts as a localised "hotspot":
   \[ T \sim 5000^\circ C \]
   \[ p \sim 2000 \text{ atm} \]
   \[ \text{lifetime} < \mu s \]
   \[ \text{heating and cooling rates} > 10^9 ^\circ C/s \]

Occurs in 3 stages:
Acoustic cavitation in a liquid near a solid surface

Mechanical „damage“ of the surface

**ACOUSTIC CAVITATION**

**Collapse at or near a solid surface**

Inrush of liquid from one side of the collapsing bubble produces powerful jet of liquid targeted at surface

- **Boundary layer**
- **Solid surface**

**Surface cleaning**
- Destruction of boundary layer
- Surface activation
- Improved mass and heat transfer
Several commercial and self-made Ultrasound Work Benches using US with Frequences from 20 kHz up to 1150 kHz
Combined experiments by putting the sonicator in the UVA reactor chamber!

Custom-made chamber for sono-photocatalytic experiments.

Schematic of the photodegradation process
Experimental parameters

Suspensions of PLA samples with ca. 3 wt% in demineralized water

Sonication and UV irradiation time 6 h

Sonication at 20 kHz with an energy input of 100 W/cm$^2$
Sonication at 860 kHz with 40 % of the max. output
UV irradiation with 6x11 W lamps (66 W in total)

Samples dried at ambient air and kept dark until characterization

Characterization methods

X-ray Photoelectron Spectroscopy (XPS) → Information about the first 10 nm of the surface
Atomic Force Microscopy (AFM) → Information about macroscopic changes (roughness) of the surface
Ultra High Vacuum-Spectroscopy

» Methods:
  • XPS (X-Ray electron spectroscopy)
  • UPS (UV photoelectron spectroscopy)
  • MIES (Metastable He* impact electron spectroscopy)
  • AES
  • STM
  • AFM

» Preparation techniques:
  • Ion Etching/Sputtering
  • Thermal etching (up to 800 °C)
  • DBD
  • PVD

» Preparation and Measurements under Ultra High Vacuum Conditions (10^-10 mbar)
XPS reference spectra of the untreated PLA foil

<table>
<thead>
<tr>
<th>Reference</th>
<th>Time [h]</th>
<th>Surface C [%]</th>
<th>Surface O [%]</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0</td>
<td>67,56</td>
<td>32,44</td>
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XPS spectra of the treated PLA samples

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<tr>
<td><strong>Time [h]</strong></td>
<td>0</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td><strong>Surface C [%]</strong></td>
<td>67,56</td>
<td>68,81</td>
<td>76,03</td>
<td>84,27</td>
</tr>
<tr>
<td><strong>Surface O [%]</strong></td>
<td>32,44</td>
<td>31,19</td>
<td>23,97</td>
<td>15,73</td>
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XPS spectra of the treated PLA samples

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<tr>
<td>6</td>
<td>84,27</td>
</tr>
<tr>
<td>3</td>
<td>84,27</td>
</tr>
<tr>
<td>7</td>
<td>15,73</td>
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Reference
AFM images of the PLA samples

Surface roughness depending on the treatment method

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<tr>
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<td>0</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td><strong>R_a [nm]</strong></td>
<td>61,13</td>
<td>64,42</td>
<td>123,15</td>
<td>135,10</td>
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<tr>
<td><strong>R_q [nm]</strong></td>
<td>77,04</td>
<td>83,85</td>
<td>160,72</td>
<td>169,58</td>
</tr>
</tbody>
</table>
Combination of US and UVA

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<td><strong>Surface C [%]</strong></td>
<td>67,56</td>
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</tr>
<tr>
<td><strong>Surface O [%]</strong></td>
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<td>20,01</td>
<td>27,05</td>
</tr>
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**Graphs:**

- Left: XPS Mg Kα C 1s, showing C-C/H and C-O peaks.
- Right: XPS Mg Kα C 1s, showing C-C/H and C-O peaks.

**Table:**

- **Reference**
  - Time [h]: 0
  - Surface C [%]: 67.56
  - Surface O [%]: 32.44

- **UV/US 20 kHz**
  - Time [h]: 6
  - Surface C [%]: 79.99
  - Surface O [%]: 20.01

- **UV/US 860 kHz**
  - Time [h]: 6
  - Surface C [%]: 72.95
  - Surface O [%]: 27.05

**Reference Values:**

- **US 20 kHz**
  - Time [h]: 6
  - Surface C [%]: 68.81
  - Surface O [%]: 31.19

- **US 860 kHz**
  - Time [h]: 6
  - Surface C [%]: 76.03
  - Surface O [%]: 23.97

- **UV**
  - Time [h]: 6
  - Surface C [%]: 84.27
  - Surface O [%]: 15.73
The question arising from this observation, is why the combination of US and UV irradiation does not lead to higher decomposition of the surface?

1) The mechanical removal of parts of the surface is bringing continuously fresh PLA to the surface leading to an erroneously measured higher oxygen groups content

2) Hindrance of the UV irradiation to reach the samples due to the strong cavitation, i.e. the UV light is reflected on the bubble clouds and thus less UV irradiation reaches the surface of the PLA samples.
Conclusion

• Two different pre-treatment methods of plastics have been used to degrade PLA as a model polymer for micro-plastics.

• Ultrasonication affects the surface chemistry as well as the morphology by increasing the roughness of the sample especially when the high frequency of 860 kHz is used.

• The C/O ratio is increased in both sonication methods with higher impact at 860 kHz.

• UV photodegradation is more active than the two ultrasonication methods for PLA.

• A combination of both US and UV pre-treatment methods does not lead to the expected synergetic effects and the change in the C/O ratio is less as compared to the UV pre-treatment alone.
Thank you!