# Enhanced biodegradation of polymers by ultrasonic surface treatment

Kalogirou C.[1,2], Sourkouni G. [2], Höfft O. [2], and Argirusis Chr. [1,2]

[1] School of Chemical Engineering, National Technical University of Athens (NTUA),
15773 Zografou-Athens, Greece
[3] Clausthal Centre of Materials Technology (CZM), Clausthal University of Technology,
38678 Clausthal Zellerfeld, Germany

Keywords: microplastics, degradation, recycling, upgrading, ultrasonication
Presenting author email: cogsa@tu-clausthal.de

Plastics are artificial synthetic organic polymers that have found use in every facet of daily life as well as in industries. Microplastics are plastic pieces that enter natural ecosystems from a number of sources. Plastic pollution is currently one of the most serious issues. However, the majority of the procedures used to date are inadequate. As a result, in recent years, the interest has switched to innovative, alternative ways of managing plastic garbage. The samples should be treated since enzymatic or bacterial attachment is not easily feasible if the plastic surface environment is not optimal.

We focus on the use of new technologies in order to modify the surfaces of various polymeric materials for their further biodegradation by subsequently attaching bacteria on the pre-treated surface. We achieve the surface activation using Sonochemistry, High-Frequency Ultrasounds (US) at 860 KHz and Low-Frequency US at 20 KHz. Experiments were performed on plastic foils of Polylactic Acid (PLA), Polyurethane (PU) and Polycaprolactone (PCL).

Following the treatments, in order to see how they affect the surface of plastics, the samples were analyzed by various characterization methods, such as Infrared Spectroscopy (IR), Drop Contact Angle (DCA), Confocal Laser Scanning Microscopy (CLSM) and X-ray Photoelectron Spectroscopy (XPS) (Figure 1).

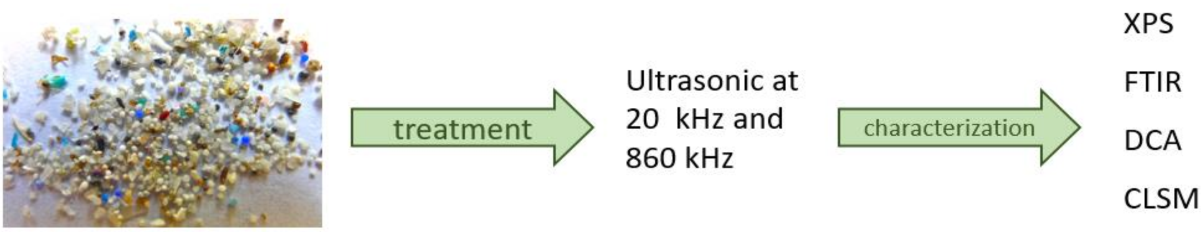


Figure 1: Schematic depiction of the experimental steps in this work.

Low-frequency Ultrasounds (20kHz) were applied through the ultrasonic processor UIP500hdT (20kHz, 500W) from Hielscher Ultrasound Technology, Germany. Power intensity was fixed at 100W/cm$^2$ through a 2.2cm diameter tip.

High-frequency ultrasound was achieved by the Ultrasound Multifrequency Generator equipped with the Ultrasound Transducer E805/T/M and an adapted glass reactor UST 02/500-03/1500 from Meinhardt® Ultrasonics, Germany, with a maximum output power of 400 W. The frequency was set to 860kHz and the power output to 40%.

**Materials and Methods**

Low-frequency Ultrasounds (20kHz) were applied through the ultrasonic processor UIP500hdT (20kHz, 500W) from Hielscher Ultrasound Technology, Germany. Power intensity was fixed at 100W/cm$^2$ through a 2.2cm diameter tip.

High-frequency ultrasound was achieved by the Ultrasound Multifrequency Generator equipped with the Ultrasound Transducer E805/T/M and an adapted glass reactor UST 02/500-03/1500 from Meinhardt® Ultrasonics, Germany, with a maximum output power of 400 W/cm$^2$. The frequency was set to 860kHz and the power amplitude to 40%.

For both low and high frequency an external Julabo recirculating cooler at 25ºC was used to help the plastics not overpass the glass transition temperature ($T_g$) which is low (around 55-60 ºC) and also protect the high-frequency equipment, which may be damaged at temperatures above 50 °C.

**Results**

Combining the results of each characterization method we scrutinize how each pre-treatment method affects the surface of treated samples, both chemically and morphologically.
The DCA results indicate whether the polymer surface is hydrophilic or hydrophobic. All treatments appear to increase the hydrophobicity of the polymer surface.

According to the XPS results, the surface of the treated samples is less oxidized than the reference sample, so either the US energy input is insufficient to significantly rearrange the surface, or the radicals created in the US are insufficiently reactive to further oxidize the surface.

Based on FTIR results, the difference in peak intensities suggests a concentration change of functional groups, which is also confirmed from the XPS results.

Based on the CLSM results, it is estimated that the high ultrasonic frequency of 860 kHz impacts the surface of the samples more, whilst the low frequency appears to generate just a modest change when compared to the non-treated sample. When compared to the reference sample, the CLSM findings reveal a flat surface with slightly increased root mean squared roughness. Treatment with US at 20 kHz appears to result in somewhat reduced surface activation compared to the other techniques, based on surface roughness.

**Acknowledgement**

This research received funding from the European Unions Horizon 2020 research and innovation program through the project BioICEP under grant agreement number 870292.