Enhanced biodegradation of polymers by ultrasonic surface treatment

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

[1] Clausthal Centre of Materials Technology (CZM), Clausthal University of Technology, 38678 Clausthal-Zellerfeld, Germany
[2] School of Chemical Engineering, National Technical University of Athens (NTUA), 15773 Zografou-Athens, Greece
*cogsa@tu-clausthal.de

Introduction

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, most of the procedures applied to date to tackle this issue are inadequate. As a result, in recent years, the interest has switched to innovative, alternative ways of managing plastic garbage. Enzymatic or bacterial attachment on the samples 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). X-ray photoelectron spectroscopy (XPS) measurements of the foils prior to and after the treatment proved the changes on the polymer surface. A short discussion of the possibilities the treatment opens is given.

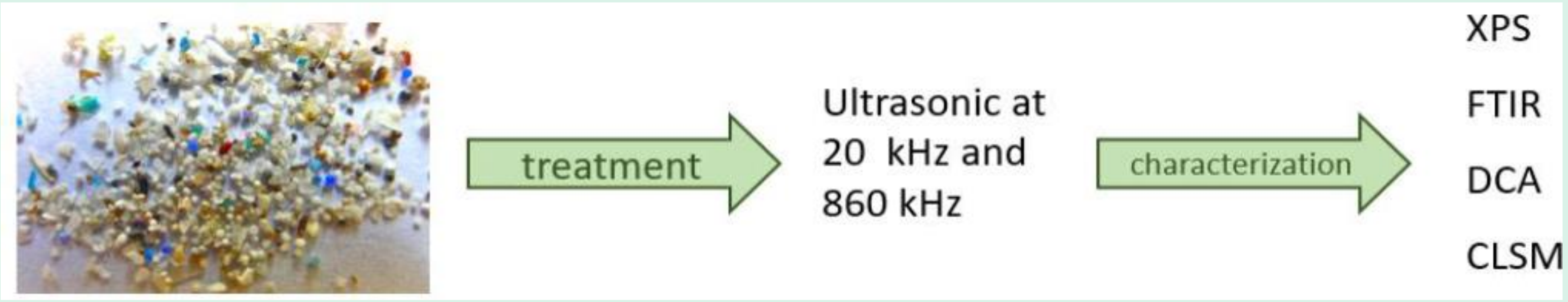

***Fig 1**: Schematic depiction of the experimental steps in this work.*

Experimental part

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/cm2. The frequency was set to 860kHz and the power amplitude to 40%.

***Fig. 2** : Double walled reactor for the US treatment of polymer foils*

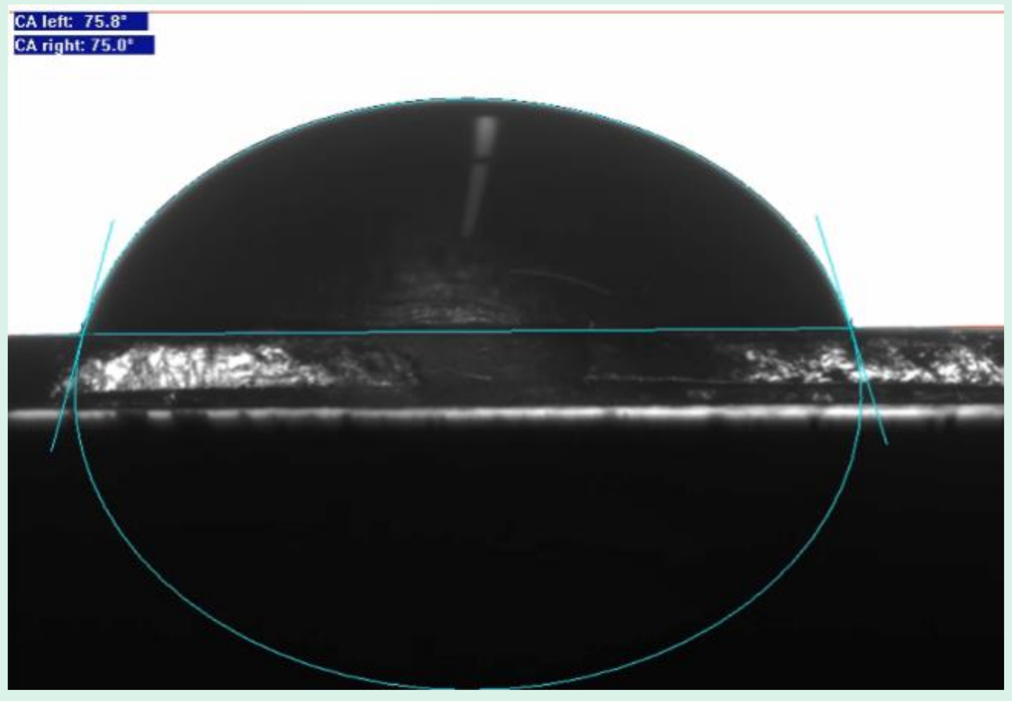

***Fig. 3** : Contact angle measurements of the activated PLA surface. A decreased contact angle means an increased surface hydrophilicity*

Results

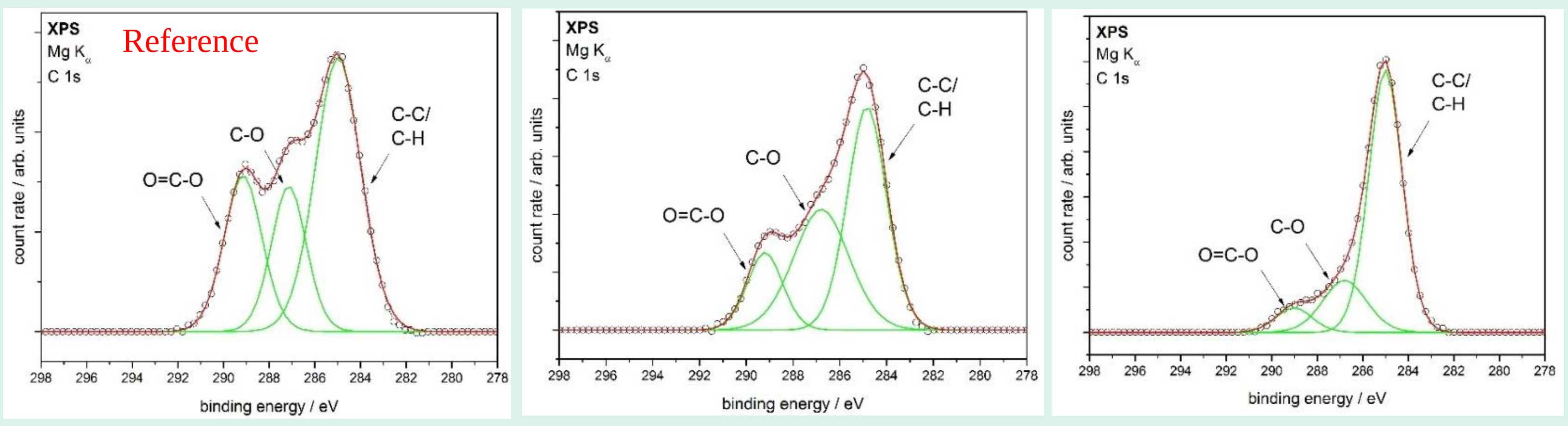

***Fig. 4** : XPS spectra of the pristine and US treated PLA samples*

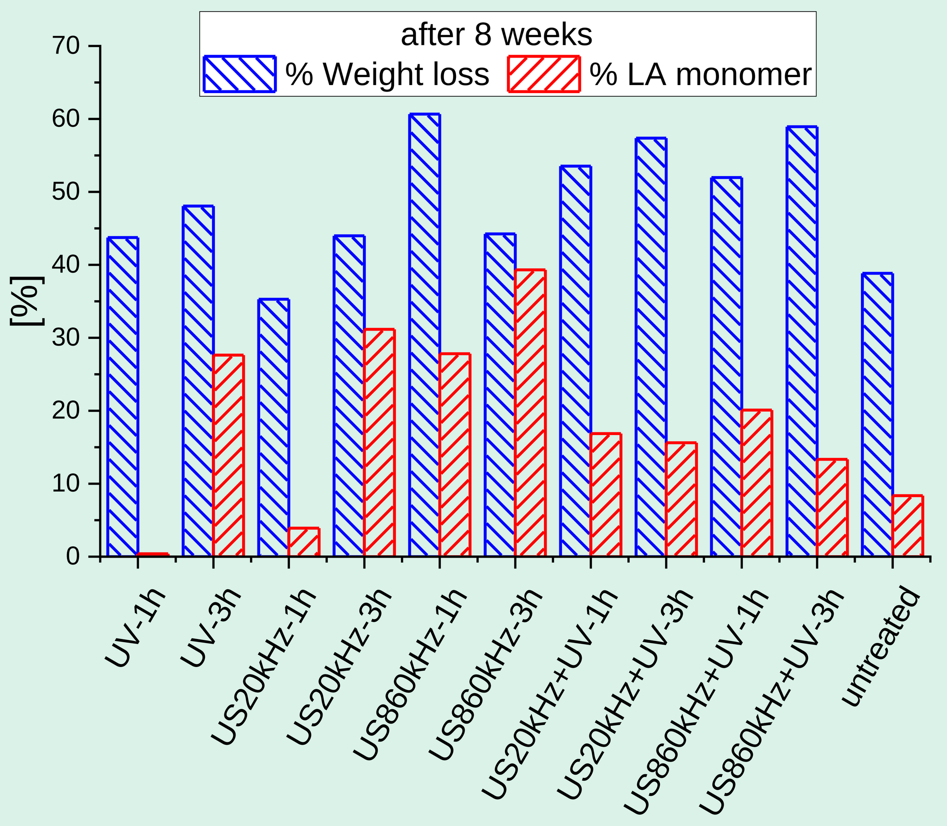

***Fig. 5**: Weight loss of the pre-treated PLA foils and monomer yield after 8 weeks.*

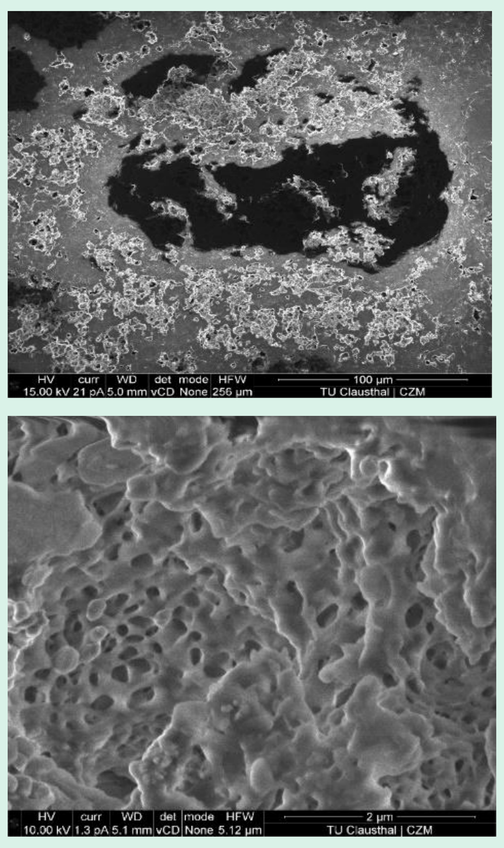

***Fig. 6**: Degradation of the pre-treated PLA foils.*

Conclusions

Advanced Oxidation Processes can improve the degradation of polymers. 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.

Recently we have shown the possibility of the valorization of enzymatic PLA degradation products to nanocellulose [1].

[1] Georgia Sourkouni, S. Jeremić, Ch. Kalogirou, O. Höfft, M. Nenadovic, V. Jankovic, D. Rajasekaran, P. Pandis, R. Padamati, J. Nikodinovic-Runic, Chr. Argirusis, "Study of PLA pre-treatment, enzymatic and model-compost degradation, and valorization of degradation products to bacterial nanocellulose", World Journal of Microbiology and Biotechnology (2023) 39:161 . https://doi.org/10.1007/s11274-023-03605-4

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