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

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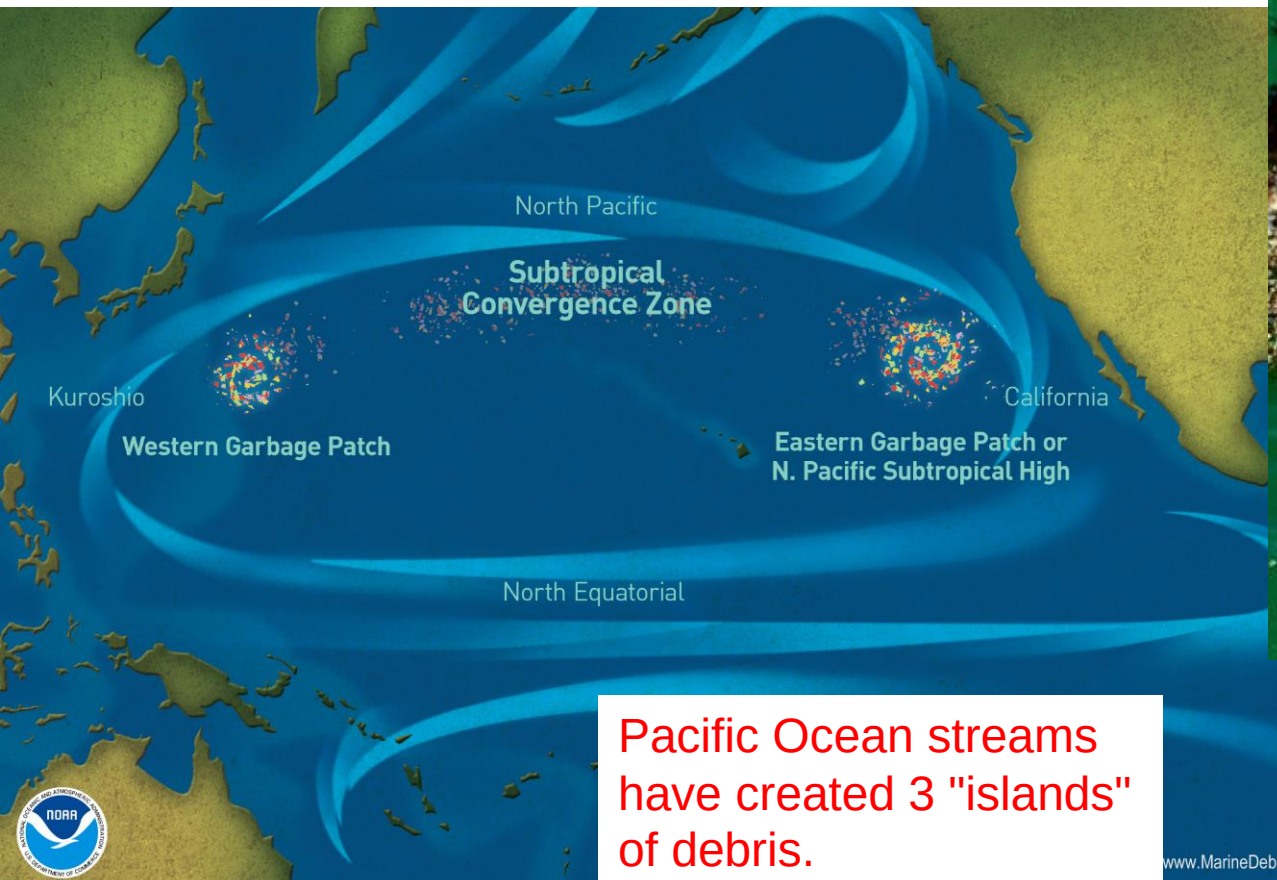
and Christos Argirusis

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

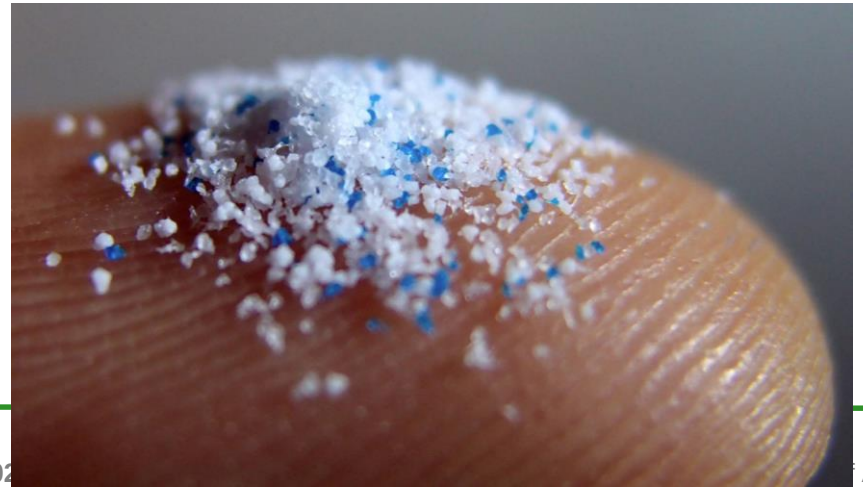
What are Microplastics ?

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)



Microplastics found in sea salt!

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**

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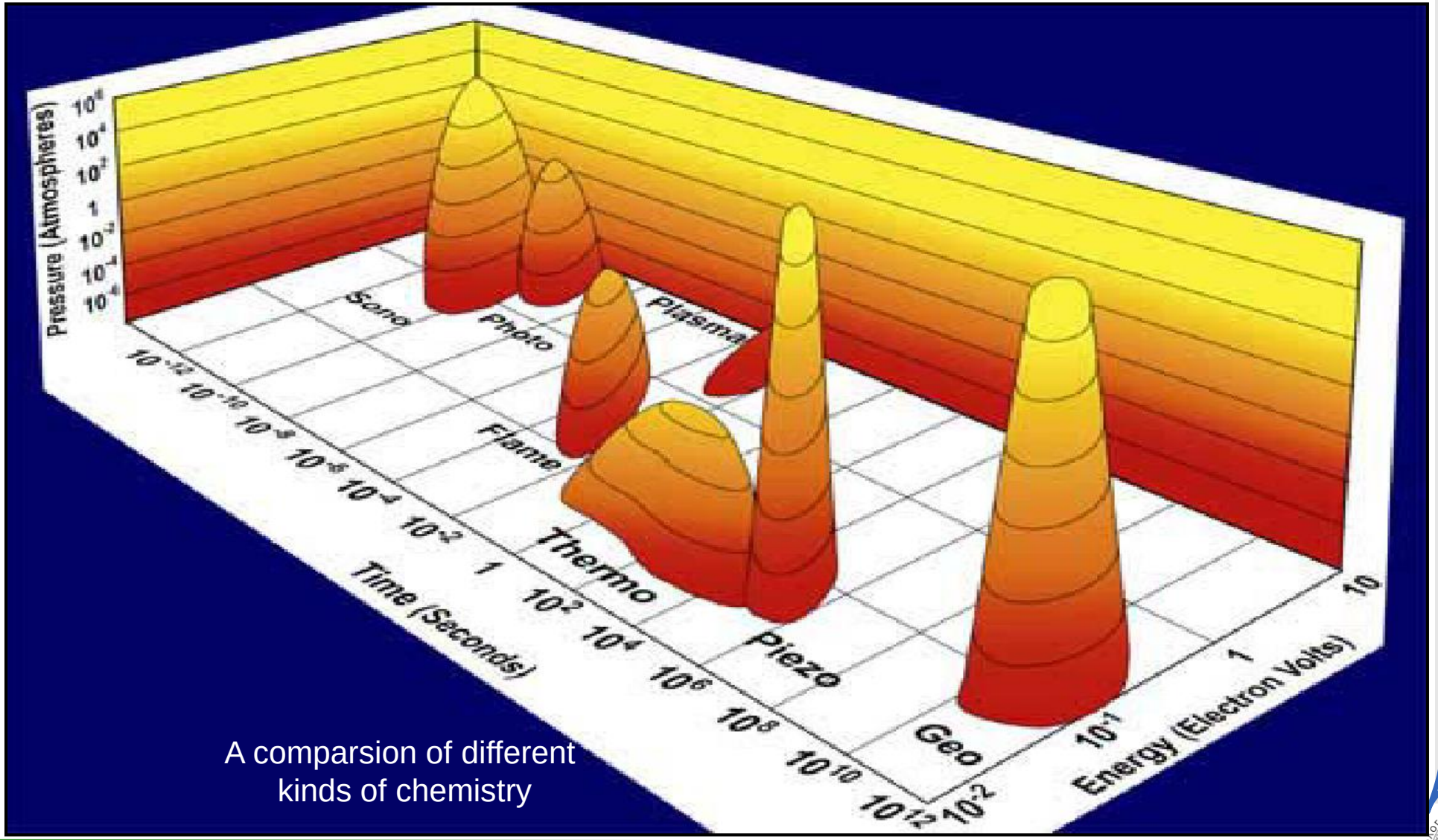
Sonochemistry

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 comparsion of different kinds of chemistry

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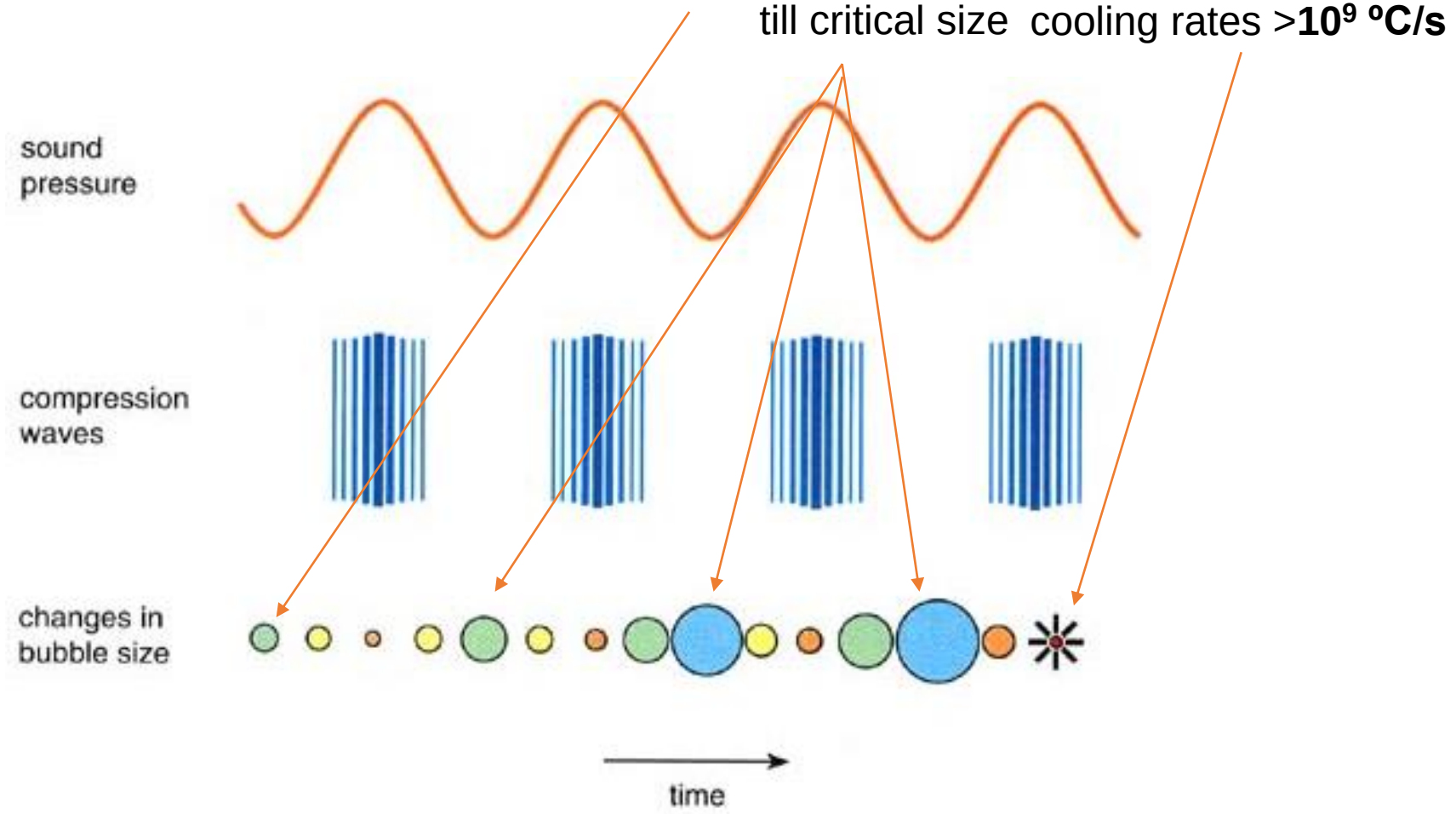
Acoustic cavitation

Physical phenomenon responsible for chemical effects caused by ultrasound !

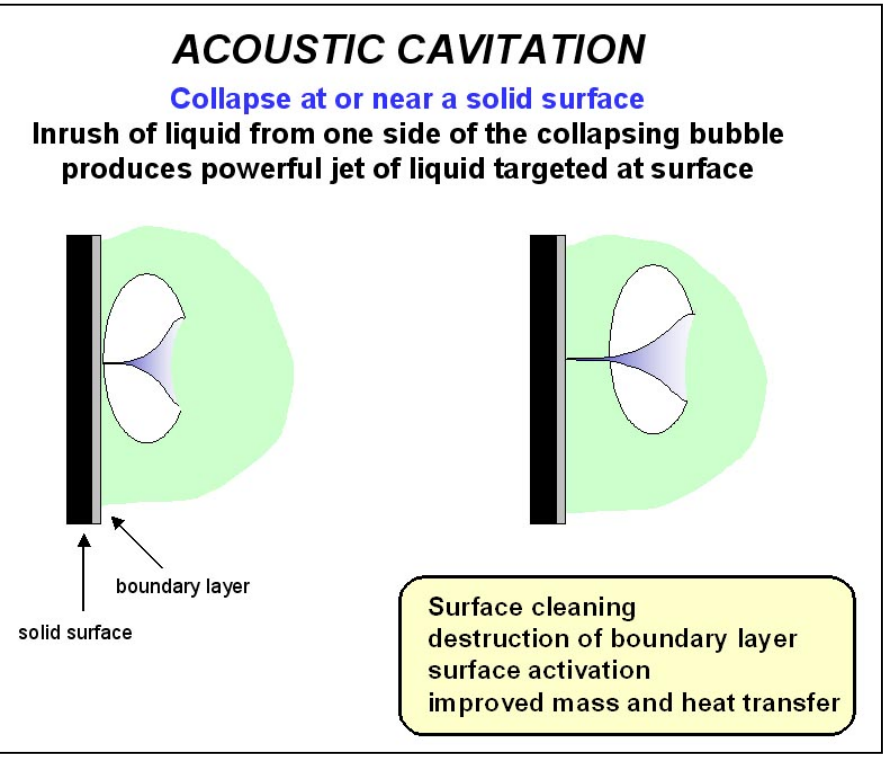
Occurs in 3 stages:

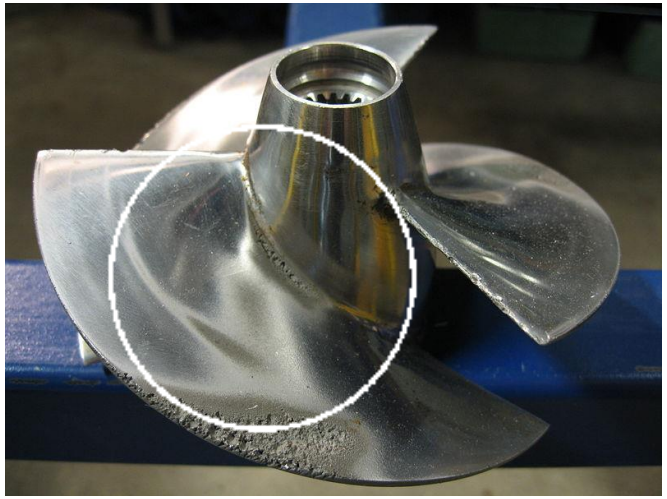
1. bubble formation
2. bubble growth during rarefaction period of a few cycles till critical size
3. bubble collapse acts as a localised „hotspot“:
   T~**5000ºC**
   p~**2000atm**
   lifetime<**us**
   heating and cooling rates >**10^9 ºC/s**

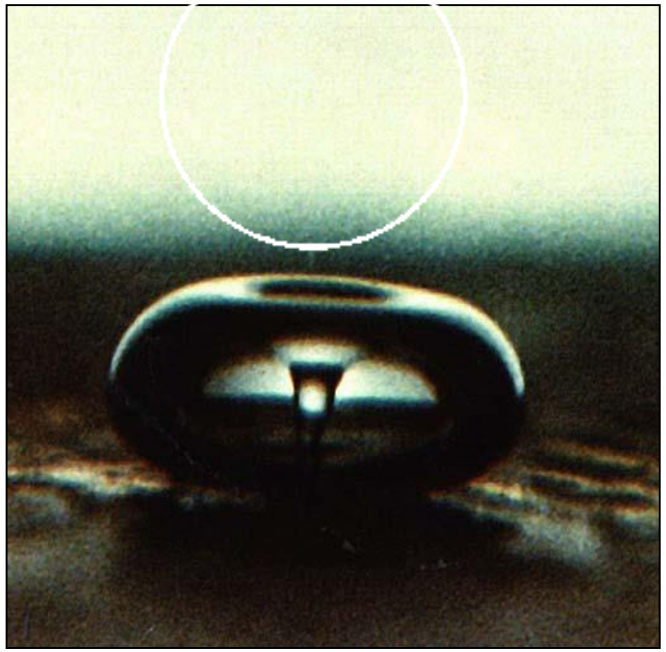


Acoustic cavitation in a liquid near a solid surface

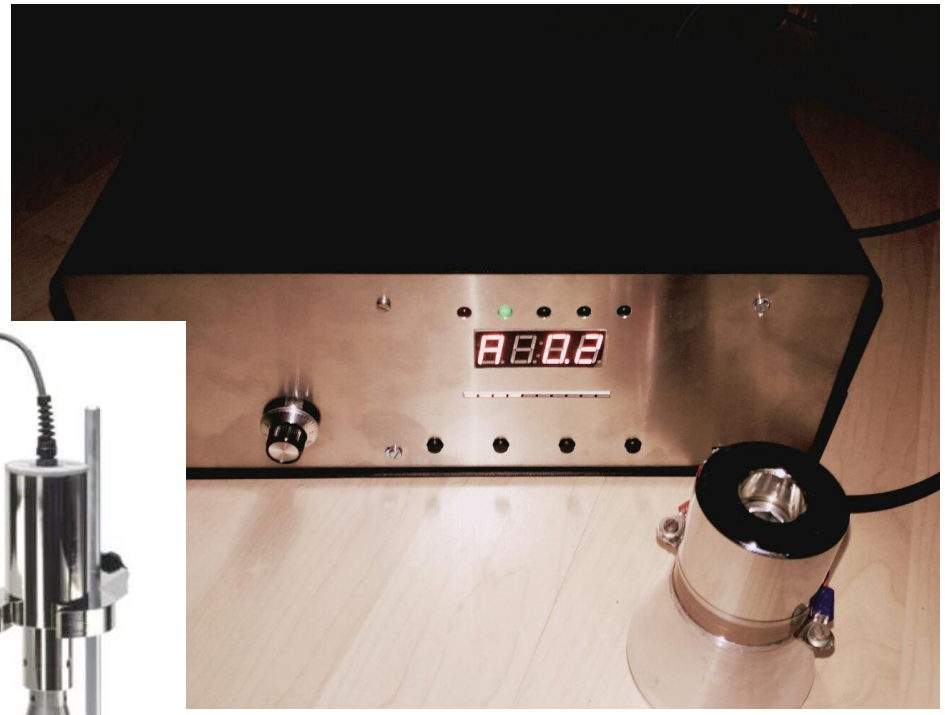
Mechanical „damage“ of the surface







Several commercial and self-made Ultrasound Work Benches using US with Frequences from 20 kHz up to 1150 kHz



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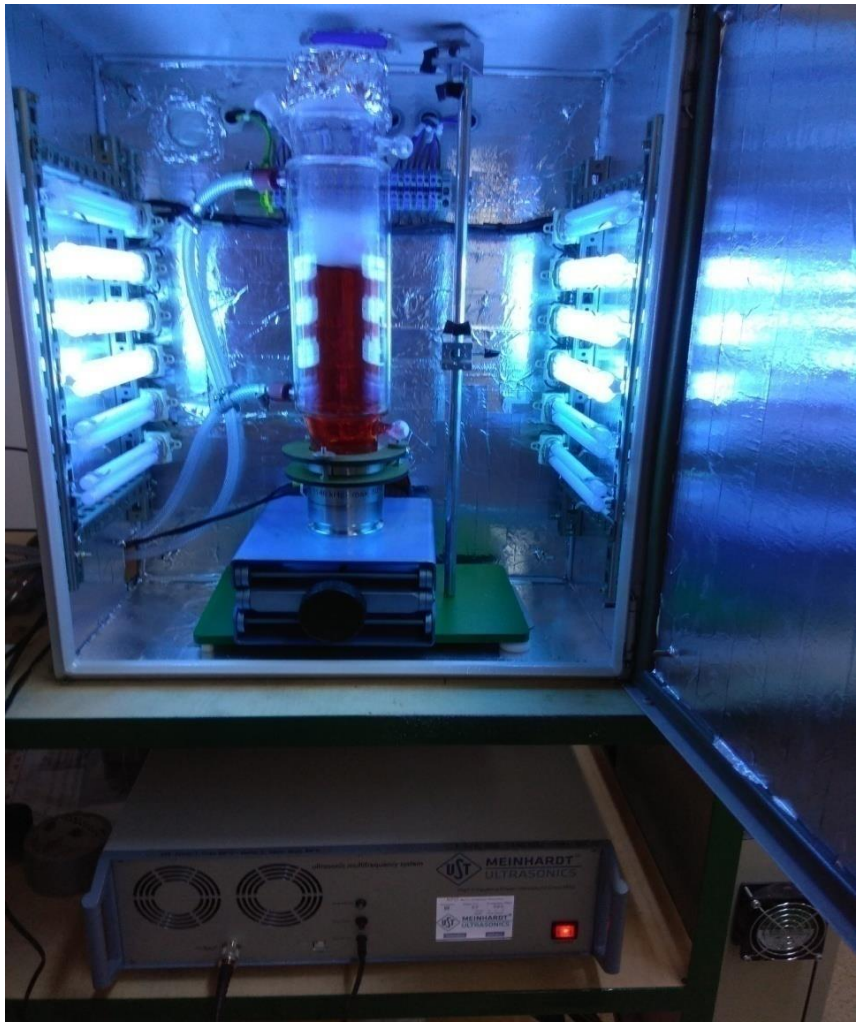
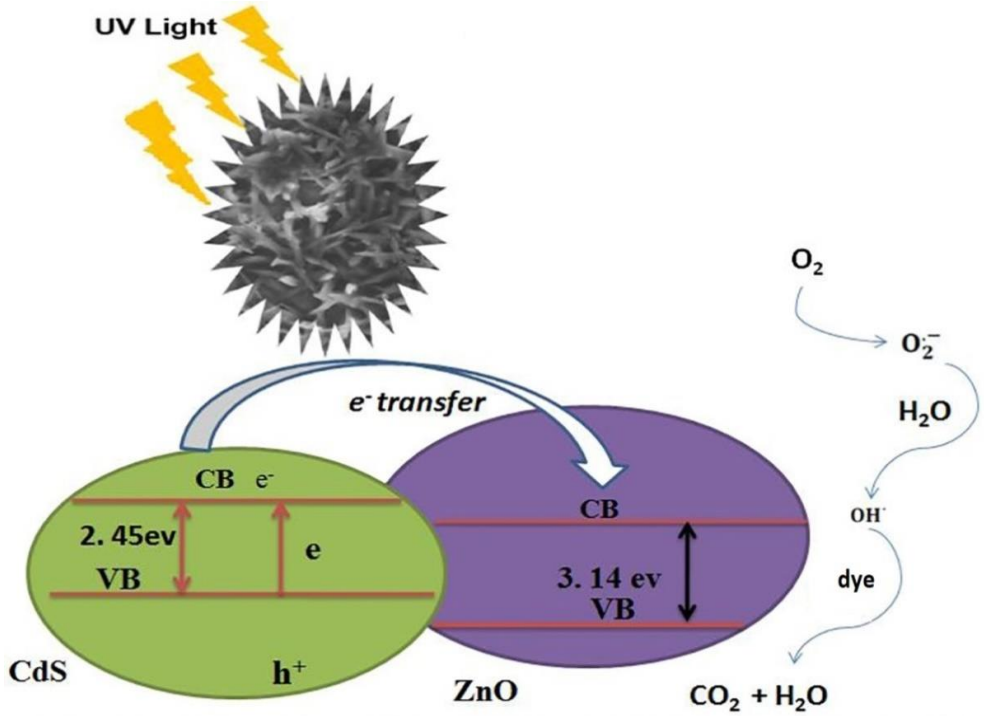
Combined experiments by putting the sonicator in the UVA reactor chamber!



Custom-made chamber for sono-photocatalytic experiments.



Schematic of the photodegradation process

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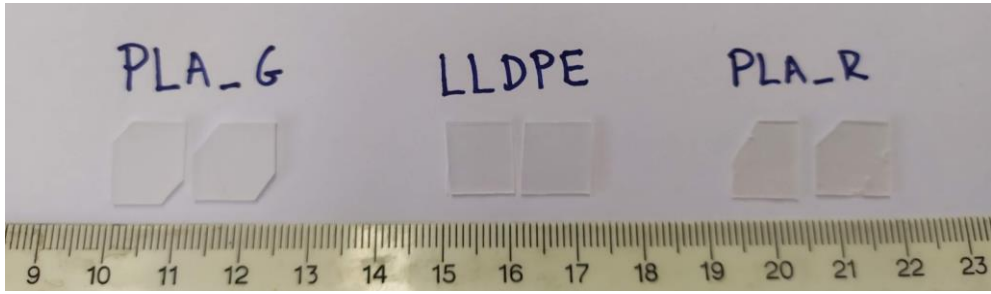
Experimental parameters

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

Sonication and UV irradiation time 6 h



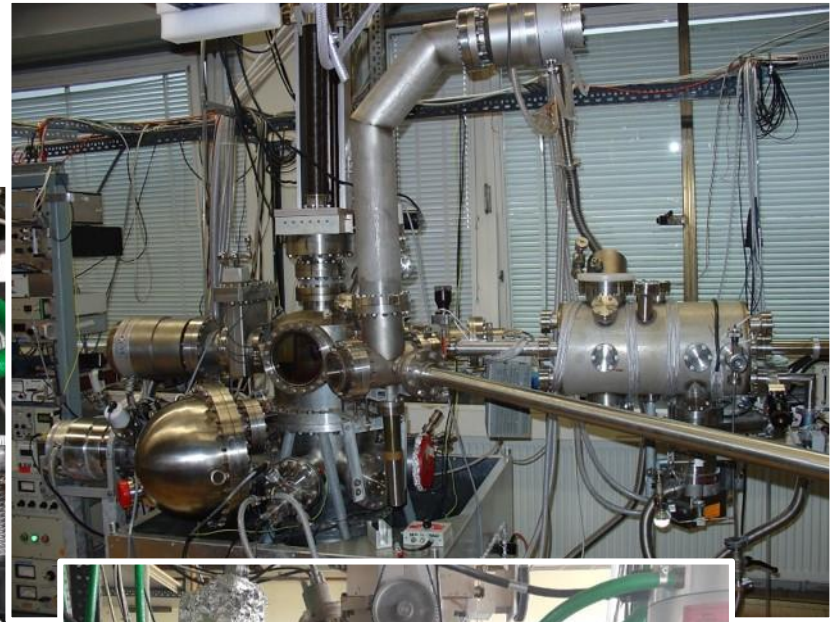
Sonication at 20 kHz with an energy input of 100 W/cm^2
Sonication at 860 kHZ with 40 % of the max. output
UV irradiation with 6x11 W lamps (66 W in total)

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)

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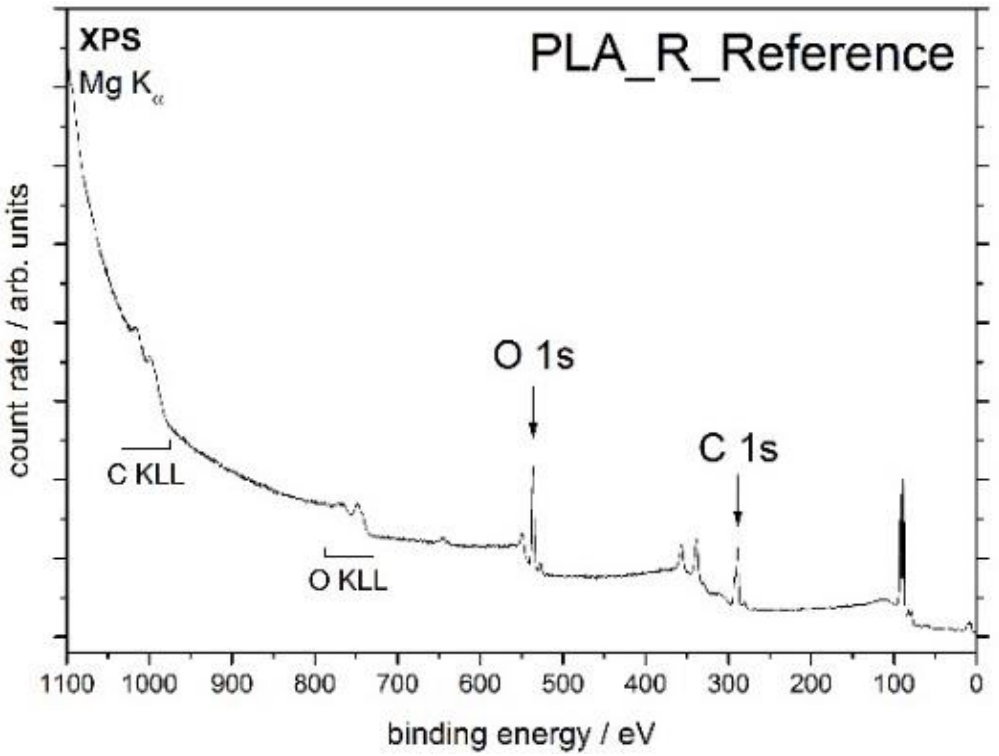
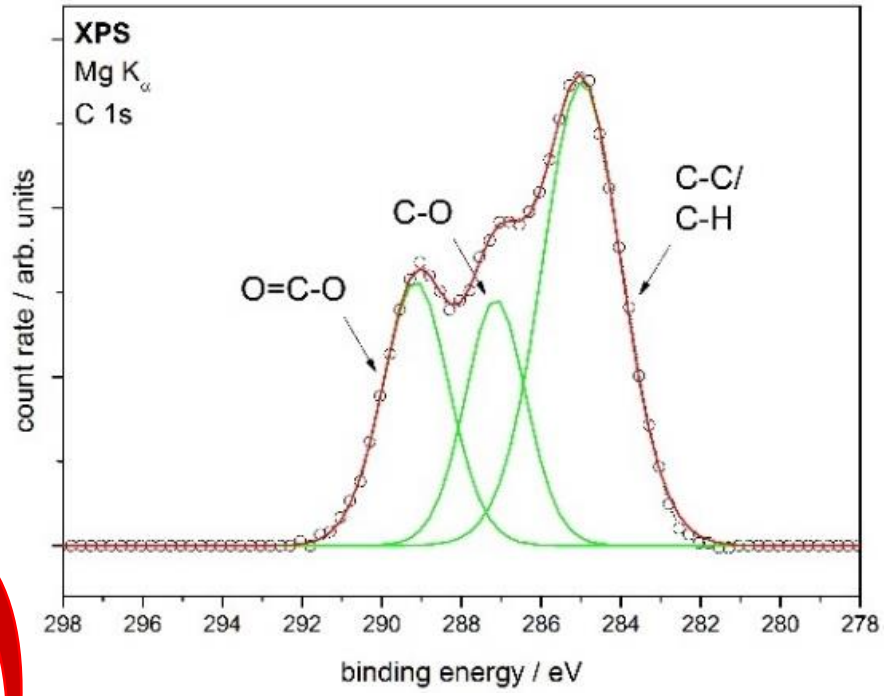
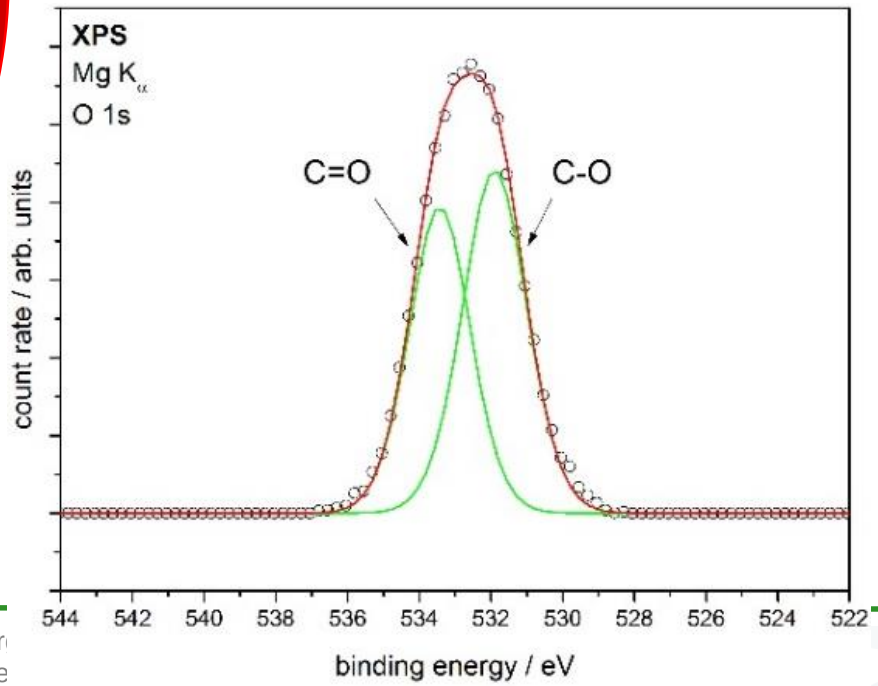
XPS reference spectra of the untreated PLA foil



Deconvoluted XPS spectra

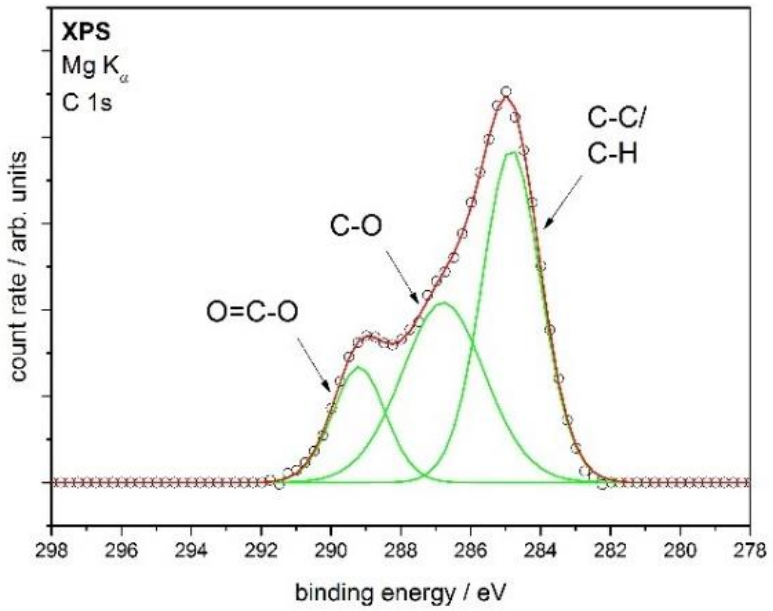




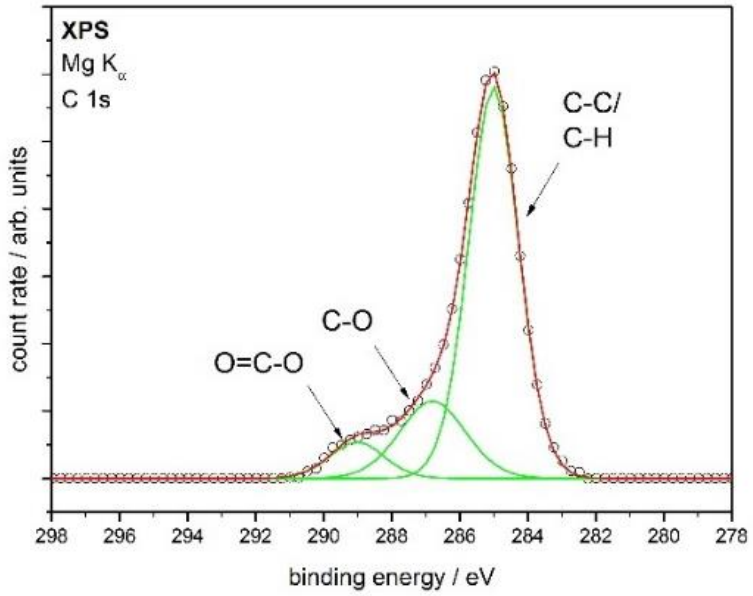
	Reference
Time [h]	0
Surface C [%]	67,56
Surface O [%]	32,44

XPS spectra of the treated PLA samples

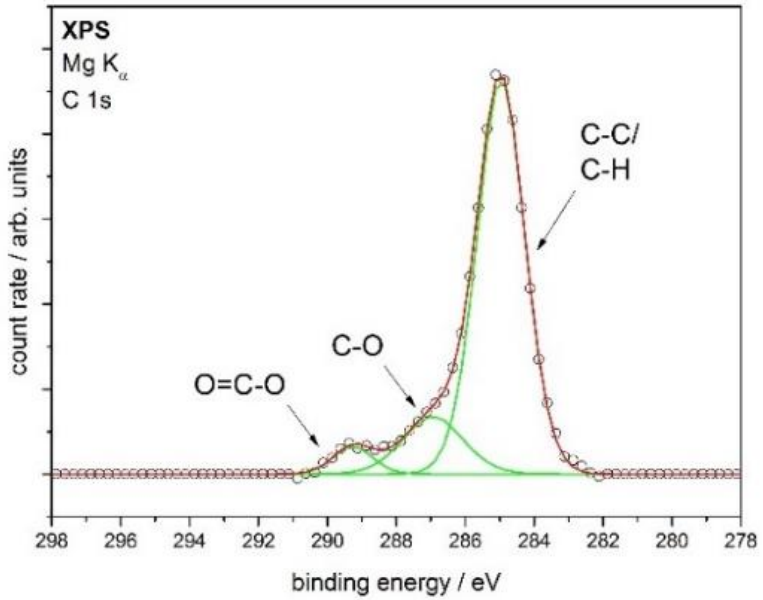
PLA 20 kHz US



PLA 860 kHz US



PLA UVA US



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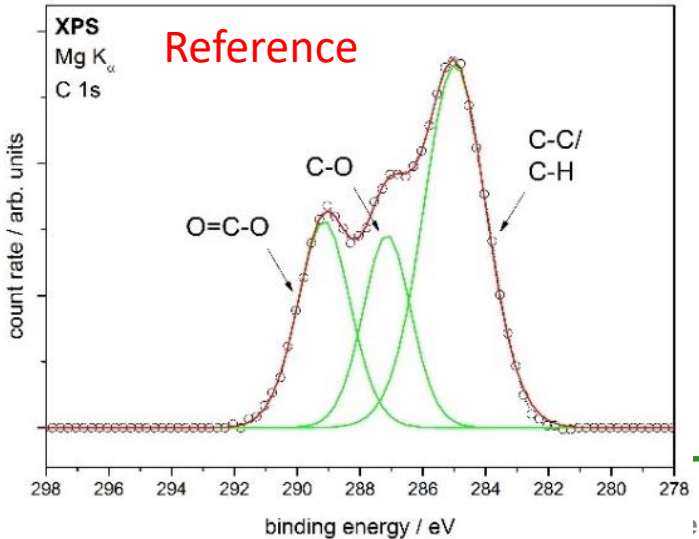

	Reference	US 20 kHz	US 860 kHz	UV
Time [h]	0	6	6	6
Surface C [%]	67,56	68,81	76,03	84,27
Surface O [%]	32,44	31,19	23,97	15,73

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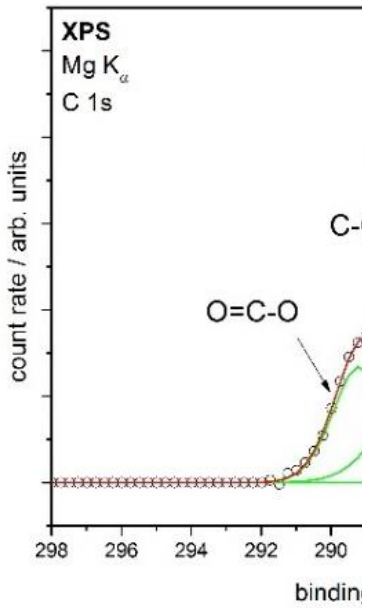
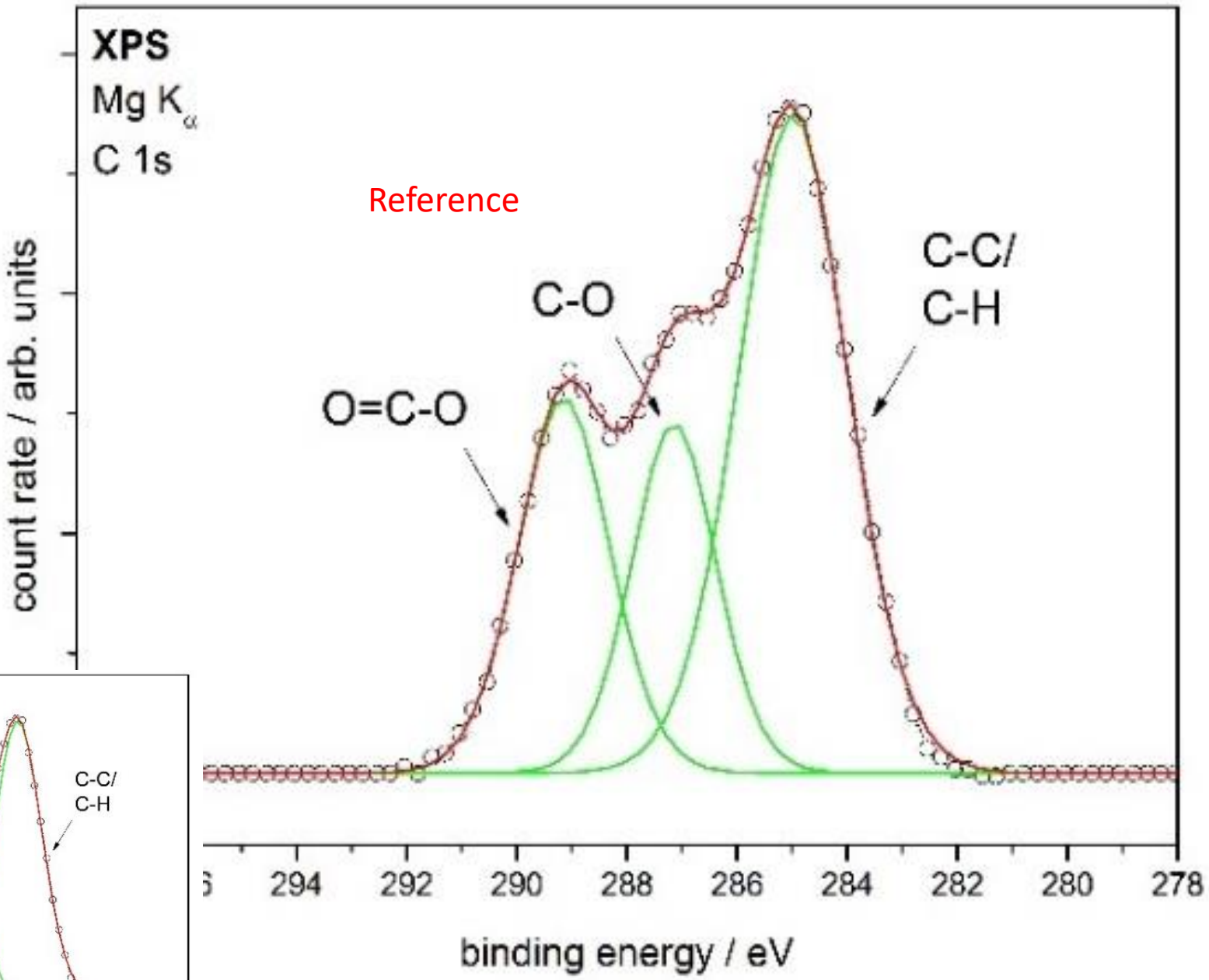
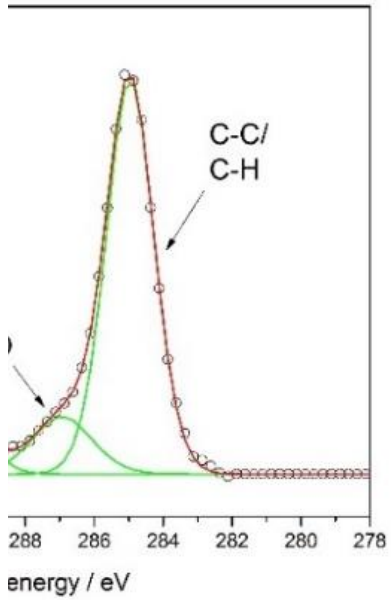
XPS spectra

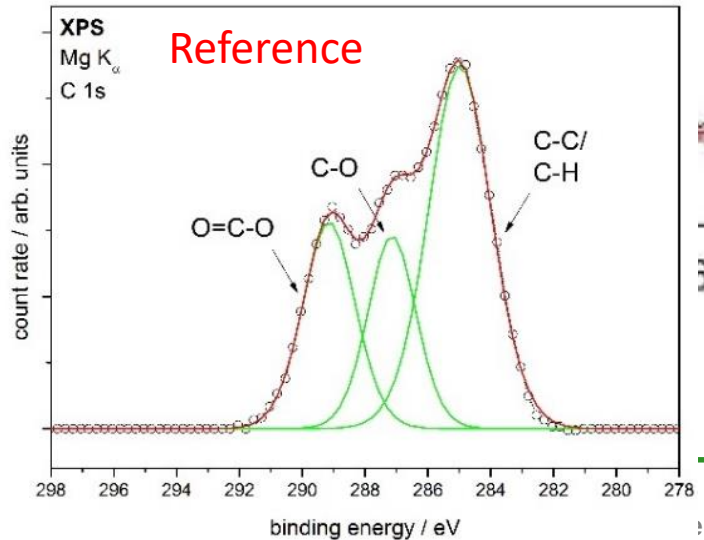
PLA 2(





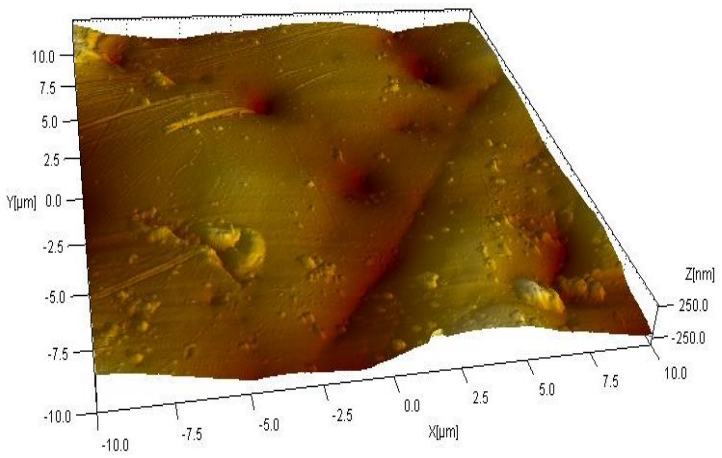
JVA US



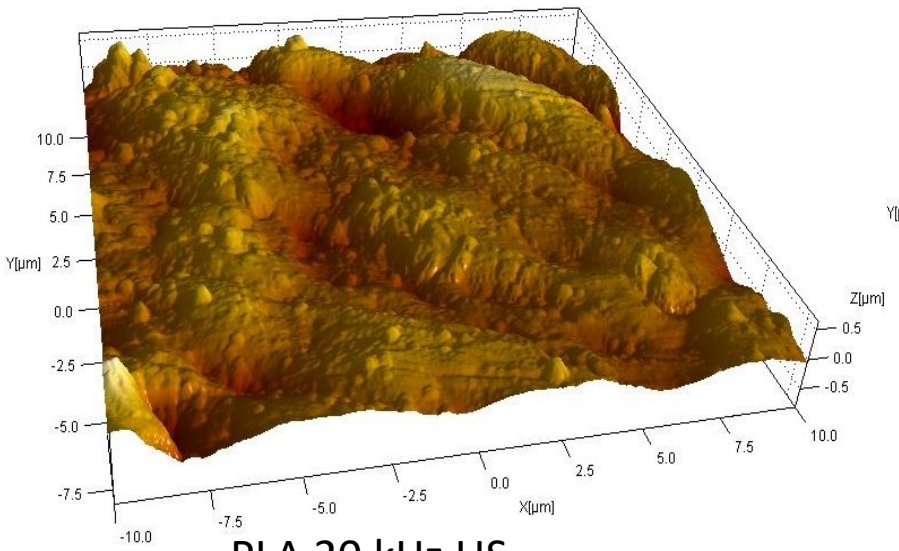


kHz	UV
	6
3	84,27
7	15,73

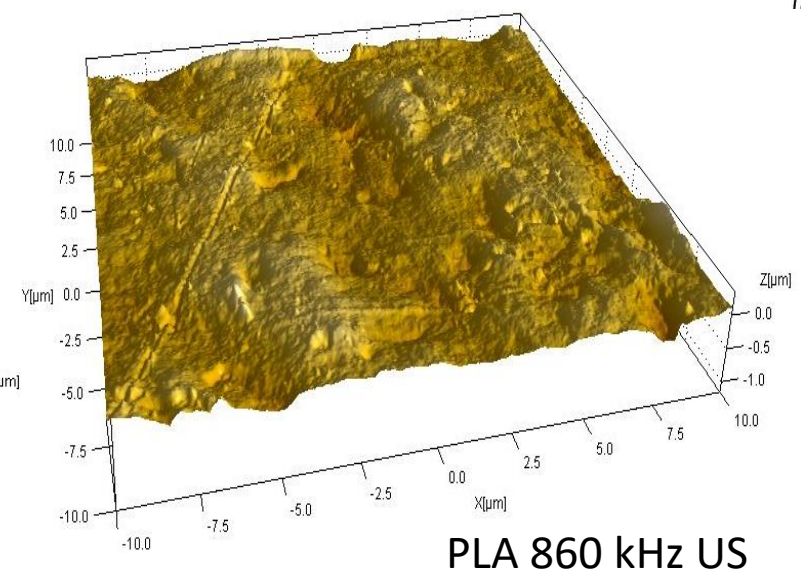
AFM images of the PLA samples



PLA reference

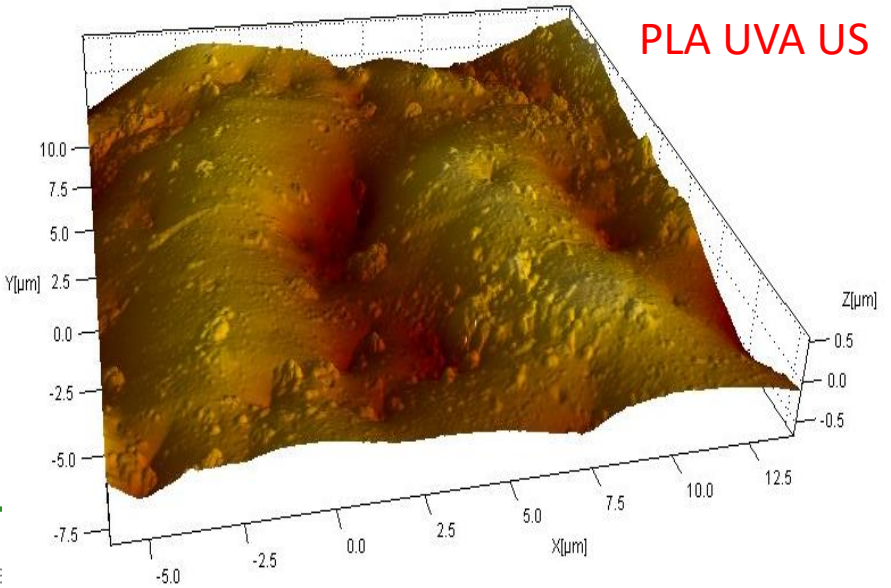


PLA 20 kHz US



PLA 860 kHz US

PLA UVA US



Surface roughness depending on the treatment method

	Reference	US 20 kHz	US 860 kHz	UV
Time [h]	0	6	6	6
R_a [nm]	61,13	64,42	123,15	135,10
R_q [nm]	77,04	83,85	160,72	169,58

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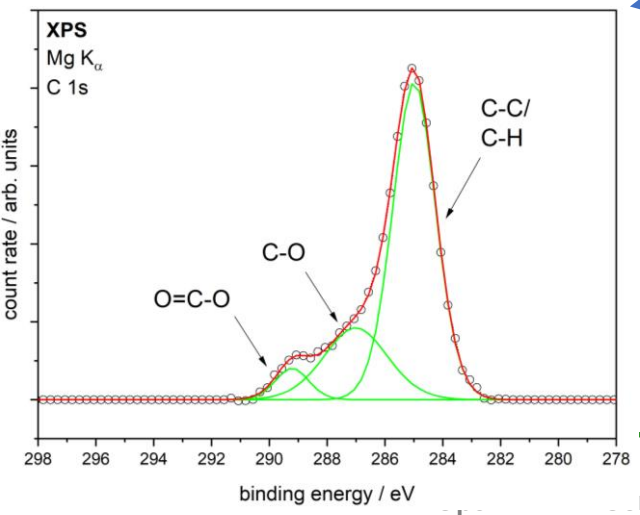
Combination of US and UVA

	Reference	UV/US 20 kHz	UV/US 860 kHz
Time [h]	0	6	6
Surface C [%]	67,56	79,99	72,95
Surface O [%]	32,44	20,01	27,05



	Reference	US 20 kHz	US 860 kHz	UV
Time [h]	0	6	6	6
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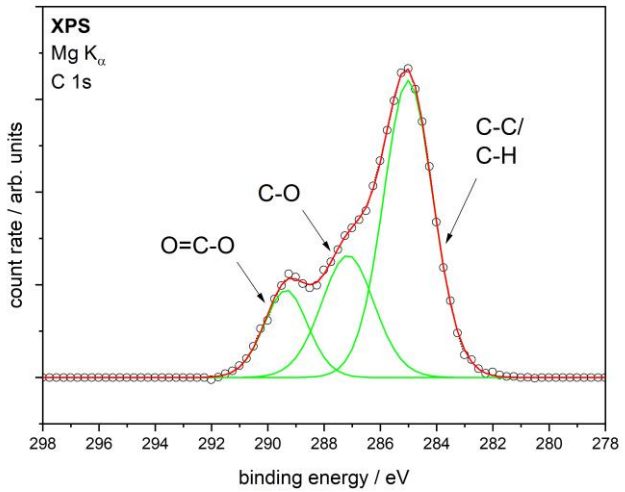

The question arising from this observation, is why the combination of US and UV irradiation does not lead to higher decomposition of the surface?

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.

European Commission

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BioICEP

Thank you!