

Assessing the time dependence of AOPs on the surface properties of Polylactic Acid

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Abstract

Plastics are artificial synthetic organic polymers that have been used in every area of daily life. However, because of their slow degradation rate their use is contentious. The treatment of the surface of the sample is considered necessary as enzymatic or bacterial attach is not possible if the plastic surface environment is not ideal. The main topic of this work is the pre-treatment of samples of Polylactic acid (PLA) using different Advanced Oxidation Processes (AOPs) in order to modify their surface in such a way as to foster the adhesion of enzymes or bacteria for further biodegradation. The Advanced Oxidation Processes that have been used are Ultrasonication, UV photodegradation and Dielectric Barrier Discharge (DBD) plasma. After the treatments, the surfaces were characterized by Infrared Spectroscopy (IR), Drop Contact Angle (DCA), Confocal Laser Scanning Microscopy (CLSM) and X-ray Photoelectron Spectroscopy (XPS). Both Ultrasonication and UV have a significant impact on surface characteristics by removing the oxygen content of the polymer, although in distinct ways, whereas plasma uncovers the oxygen groups at the surface.

Introduction

Nowadays plastic pollution is one of the biggest problems due to the widespread use of plastics. Several efforts have been made to alleviate this global problem, however, the durability of plastics and their longevity led to huge waste that cannot be easily managed [1]. Strikingly, in 2015 the annual volume of plastics was equal to the volume of the total human weight of the planet [2]. Furthermore, scientists anticipate that up to 10% of all plastic waste produced will end up in the ocean, and that by 2050 plastics would outnumber fish [3]. Plastics, and especially microplastics, can become entangled in the ecosystem and be carried to the oceans by rivers and winds [4].

Despite significant progress in understanding the behavior of microplastics in the environment as a result of increasing awareness and research focus, much remains unknown, particularly in terms of the ability to accurately anticipate exposure situations and identify exposure hotspots. The fate of micro/nano-plastics in the environment is difficult to predict. This is because of the many sources and channels of entry into the environment, as well as the time required to identify their degradation mechanisms.

Plastics are artificial synthetic organic polymers that have found application in every aspect of everyday life as well as in industries due to their properties, including their stability and durability. However, because of their slow breakdown rate, the use of biodegradable plastics in solid waste management is rather unclear [5]. Plastics are resistant to microbial processing and in addition there are no enzyme structures in nature capable of degrading synthetic polymers in reasonable time. For this reason, recent attempts for biodegradation of polymers focuses mainly on changing their surface, enabling and enhancing microbial adhesion. Therefore, pre-treatments of the polymer surfaces are considered necessary for an effective microbial adhesion. These pre-treatments result in the formation of functional groups of carbonyls, carboxyls and esters [6], [7].

Aside from physical modification, polymers may be degraded using a variety of processes, including thermal degradation, photolysis, chemical procedures, microwaves, atmospheric DBD plasma and biodegradation using enzymes and bacteria [8], [9]. The majority of these reactions occur at random and produce unwanted mono- and oligomers as well as changes in the chemical microstructure of the side groups. On the other hand, it has also been reported that ultrasound is an ideal approach when reduced molecular weight products are needed [10].

Sonochemistry can be used to bring molecules of a compound to reaction, due to the application of high-power ultrasound (20 kHz-10 MHz) [11]. The chemicals resulting from ultrasonication have been studied for more than 60 years. Compared with the rest of the traditional techniques, ultrasonic radiation provides unusual reaction conditions, such as very high temperatures and pressures which cannot be achieved by other methods [12]. Several theories have been developed to explain how chemical bonds are broken, against the effect of 20 kHz ultrasound radiation. In the scientific field it has been established that the main event that takes place in sonochemistry is the creation, development and final collapse of a bubble formed in a liquid. The diffusion of its vapours with the dissolved substance in the volume of the bubble, leads to its growth, while the collapse of the bubble occurs when its size reaches a critical value. To determine the location at which the sonochemical reaction takes place, the rates of volatile metal carbonyl substitution reactions have been studied turning out that there are two areas: one corresponding to the gas phase inside of the collapsing bubble, and one corresponding to a thin layer surrounding the cavity. Also, after the determination of the above positions, it became possible finding the effective temperature in each reaction zone. It turned out that the belts of liquid and gaseous phase reactions, have effective temperatures of 1900 K and 5200 K, respectively. The phenomenon of the creation, growth and eventual collapse of the bubble, can be explained based on the hot spot mechanism. Based on this theory, when the bubble collapses, very high temperatures are obtained, (5,000–25,000 K), and since this collapse occurs in less than 1 ns, very high cooling rates, higher than 10^{11} K / s are achieved [13], [14], [15].

Photochemistry studies the chemical effects of light on matter. It is known that classical chemical reactions may happen due to the influence of visible (Vis) and ultraviolet light (UV). UV is a non-mechanical energy input technique that could destroy organic compounds including water-soluble contaminants as well as solid organics and plastics. Light has the ability to decompose organic materials and is one of the primary drivers of plastic deterioration in ambient conditions, while especially the impact of ultraviolet (UVA) radiation (400 – 290 nm) and visible light can partly degrade the majority of synthetic polymers. This is because UVA radiation has energy ranging from 3.1 to 4.3 eV, corresponding to 72–97 kcal/mol. This implies that it has enough energy to disrupt most chemical bonds, and therefore light can function similarly to heat deterioration [16], [17].

In recent years, Dielectric Barrier Discharge (DBD) Plasma has shown to be a viable technique for modifying the surface characteristics of polymers. The dielectric performs two important purposes in the discharge operation: first, it restricts the amount of charge that can be transferred from one electrode surface to another by a single micro-discharge, and second, it spreads these micro-discharges across the

whole electrode region. Voltages of a few kV and frequencies ranging from 5 to 500 kHz are commonly utilized. The average electron energy in DBD plasma is in the 0–10 eV range, meeting the chemical binding energy of plastics which is no more than 10 eV. Plasma modification techniques provide advantages over other treatments, such as the capacity to modify the surface evenly without affecting bulk characteristics. This approach has been demonstrated to be a potential method for performing surface treatments on polymers without altering their bulk properties. Another advantage of DBD is the ability to alter the surface characteristics of polymers without the need for a costly vacuum equipment [18], [19].

Materials And Methods

Materials

In this work polymeric samples of polylactic acid (PLA) were used, which has been the subject of research for over a century. In the beginning, PLA films (20x20 cm) with a thickness of around 1 mm were produced. The samples were created as the film was initially engraved on the marked points and then by applying pressure on the edges it breaks into smaller pieces. More information about how the PLA film were prepared can be found in our previously published paper [20].

Treatment Methods

Our main focus was to see how the time that the samples were under treatment affects their surface properties. Therefore, the samples have been treated separately via UVA irradiation and ultrasonication of High (860 kHz) and Low Frequency (20 kHz) for 1, 3 and 6 hours. Initially, 6 PLA samples are immersed in demineralized water. After 1 hour, the experiment was stopped and 2 samples were taken out, dried under ambient conditions, and kept in dark environment. Similarly, we took samples at 3 and 6 hours of the experiment. In another experiment, samples have been treated with atmospheric DBD plasma for 5, 10, 20 and 60 seconds.

UVA treatments

The PLA samples were treated with UVA irradiation by immersing them in demineralized water in a UVA transparent baker and placing them on a stirring plate in the self-made UV reactor. The reactor includes three 11 W UVA lamps on each side, resulting to 66 W UVA irradiation while being stirred continuously. In the UV treatments, no photocatalytically active materials were included.

Sonication Treatments

The ultrasonic processor UIP500hdT (20 kHz, 500 W) from Hielscher Ultrasound Technology, Germany, was used to generate low-frequency ultrasounds (20 kHz). The power intensity was set at 100 W/cm² and delivered through a 2.2 cm diameter tip. The Ultrasound Multifrequency Generator fitted with the Ultrasound Transducer E805/T/M and an adapted glass reactor UST 02/500-03/1500 from Meinhardt®

Ultrasonics, Germany, produced high-frequency ultrasound with a maximum output power of 400 W. The frequency was set to 860 kHz, and the power amplitude was set at 40%. An external Julabo recirculating cooler set to 20 °C was used for both low and high frequency to prevent the polymers from exceeding the glass transition temperature (T_g), which is low (about 55-60 °C) and to shield the high-frequency equipment, which can be destroyed at temperatures over 50 °C. Temperature was kept at 25 ± 1 °C for ultrasonication treatments.

DBD plasma treatment

The dielectric barrier discharge (DBD) reactor, which was used for the experiments, consists of two parallel stainless-steel electrodes with 30×50 mm² dimensions and a 7 mm thick alumina ceramic plate as dielectric. For the experiments the DBD plasma settings at ambient air were 16 KV at a frequency of 7 kHz with a spacing of 9 mm between the electrodes and the samples (including the 7 mm thick dielectric).

Characterization Methods

After the treatments and in order to see how they affect the surface of the PLA, the samples were analyzed using various characterization methods. Using X-Ray photoelectron spectroscopy (XPS) we can observe the change of the elemental surface composition, while with FTIR the concentration of the active surface groups can be estimated. Drop Contour Analysis (DCA) is used to characterize the wettability of the surface and Confocal Laser Scanning Microscopy (CLSM) to measure the surface roughness and observe the morphology of the surface, as CLSM provides 3-dimensional surface profiles, by capturing multiple two-dimensional images at various depths. Combining the results of each characterization method we are able to scrutinize how each pre-treatment method affects the surface of PLA samples, both chemically and morphologically.

X-Ray photoelectron spectroscopy (XPS)

XPS spectroscopy is used for chemical analysis and identification of the chemical state of the elements on the surface of a solid. In XPS spectroscopy the sample is exposed, under ultra-high vacuum conditions, to a monochromatic or non-monochromatic X-ray beam with defined energy (energy $h\nu$) that causes photionization and emission of photoelectrons. The XPS spectrum reflects the energy spectrum of the emitted photoelectrons and consists of a series of distinct responsive bands in the characteristic layers of the electronic structure of the atom [21].

The experimental investigations of the untreated and treated PLA samples were performed in an UHV chamber with a base pressure of below 5×10^{-10} mbar. The films were characterized by core level spectroscopy (XPS) using Al K radiation with 1486.6 eV photon energy of a non-monochromatic X-ray source (Omicron DAR 400). Emitted electrons were detected by a hemispherical analyzer (Omicron EA125) under an angle of 45° to the surface normal. The analyzer was operated with a constant pass energy of 50 eV for survey spectra and 20 eV for detail spectra. Since degradation of polymer films, that

are exposed to non-monochromatic X-ray radiation, was observed before [22, 23] the XPS analysis was performed as fast detail scan of the C 1s, O 1s, regions and the survey spectra with a total exposure time of about 1 h. All spectra were displayed as a function of the binding energy with respect to the Fermi level. The XPS spectra have been charge-corrected by fixing the C 1s component of the aliphatic C-C/C-H group to 285.0 eV. For quantitative XPS analysis, a Shirley-background-subtraction was employed. Photoelectron peak areas were calculated by fitting Gauss-type profiles optimized by the Levenberg-Marquard algorithm with the CasaXPS software. Photoelectric cross-sections calculated by Scofield [24] and asymmetry factors calculated by Yeh and Lindau [25] as well as the transmission function of the hemispherical analyzer have been considered for stoichiometric calculations.

Confocal Laser Scanning Microscopy (CLSM)

CLSM is an optical imaging technique widely used in the field of Materials Science. The principal of CLSM is quite similar to fluorescence microscopy however it can provide better vertical and lateral optical resolution and observation precision by combining the colour and laser intensity information from the camera and from the laser light photoreceptor, respectively. In the case of Confocal Laser Scanning Microscopy (CLSM) a laser beam is focussed on the surface of the sample. The reflected light is detected behind a pinhole aperture. This technique enables a lateral resolution that is one third better in comparison to a classic wide field microscope.

The measurements were performed using the microscope VK-X200K from KEYENCE. The good lateral resolution (approx. 160 nm) enables the accurate mapping of many samples. On the software side, several images can be combined to produce one large image, meaning that even when significantly enlarged, wide areas of the sample can be mapped. Because the topography of the sample is recorded, it is possible to conduct roughness analyses or profile sections. A wide field microscopic image is also captured at the same time [26], [27].

Drop Contour Analysis (DCA)

Drop contour analysis enables contact angle measurement in case of configurable pressures and temperatures. The contact angle θ is the most important value in order to characterise the wetting of surfaces with a liquid (Fig. 1). In accordance with the Young equation, it is directly dependent on the involved surface tensions between the solid and the drop, the solid and the atmosphere, and the drop and the atmosphere. The greater the surface tension between the solid and the atmosphere, the greater surface energy of the solid. The drop will attempt to spread out, which results in a small contact angle. The DCA measurements were performed using the Dataphysics OCA. The Dataphysics OCA enables contact angle measurements and the determination of associated material parameters under various conditions. Different atmospheres, such as nitrogen or vacuum conditions ($p_{\min} = 1 \text{ mbar}$) can be configured. The temperature can vary between room temperature and 1800°C. The video recording enables the recording of changes in the contact angle over time and the determination of the melt

temperature. Due to the geometry of the furnace, the size of the drop is limited to a diameter of approximately 2 cm [28], [29].

Infrared Spectroscopy (IR)

Infrared spectroscopy (IR) is one of the basic spectroscopic techniques. Molecules can absorb electromagnetic radiation of the infrared range, resulting in molecular vibrations. Infrared spectroscopy is based on this principle. Vibrational modes of chemical bonds can be assigned to specific absorption energies. Each spectrum of infrared radiation is characteristic of each sample and is its fingerprint with absorption peaks which result respectively from the frequencies of vibrations between the bonds of the atoms that make up the material.

The characterization of the treated PLA samples by IR spectroscopy was carried out using the Bruker ATR-FTIR-spectrometer ALPHA-T FTIR, which is coupled with an Attenuated Total Reflexion (ATR) accessory. A diamond crystal serves as the internal reflection element. The measurements were performed by pressing the sample onto the ATR-crystal. In a spectral range from 4000 to 400 cm^{-1} , 16 scans with a spectral resolution of 2 cm^{-1} were recorded for each sample [30].

Results And Discussion

XPS Results

The XP survey spectrum of the reference sample (Fig. 2) shows the main photoelectron peaks of carbon (C 1s) around 285 eV and oxygen (O 1s) around 530 eV. In some samples we could detect fluorine (F 1s) peak around 690 eV) in the surface, most probably due to the production process of the PLA film samples. The spectra of the ultrasonically treated samples additionally showed nitrogen in a small percentage (< 2.5%). The C 1s and O 1s detail spectra (Fig. 3a-3b) of the reference sample show the binding species (C-C/C-H, C-O, O = C-O) typical for PLA, whose binding energies correspond well with the literature after charge correction [23].

The respective peak areas for the individual carbon bonds do not correspond to the theoretical values for PLA of 33% per bond [21], [29], [30]. The excessive amount of C-C bonds is often observed for untreated PLA [31], [32], [33] and is likely due to unknown additives or atmospheric contaminations. Figure 4 shows the C 1s spectra at the 20 kHz Ultrasound treatment comparing the samples that have been treated to the reference sample. The percentages of the respective bonding types (C-C/C-H, C-O, O = C-O) were evaluated for each spectrum (presented in Fig. S1, S2 and S3 in Supporting Information File). When the samples are treated with 20 kHz, there is a slight increase in the C-C bonds and a reduction of C-O or O = C = O bonds in the PLA. However, a clear trend in time dependence cannot be identified. It looks as if the C-C content increases up to the 3-hour treatment and then falls again slightly. It should be noted, however, that nitrogen is only found in the samples after a period of 3 hours. In contrast to the low frequency US, the samples treated with 860 kHz show clear changes. In this case, there is a clear increase in the C-C bonds

and a strong reduction in the C-O bonds, whereby the O-C = O bonds are stronger reduced. This behaviour is also seen in the interaction of UVA radiation with the samples. There is also a strong increase in the C-C bonds and reduction of C-O bonds in the PLA. Similar to 20 kHz, the proportion of C-C bonds varies with time without following a clear trend. However, the 6 hour treatment resulted in the strongest decrease in C = O bonds. Again, nitrogen could only be observed after 3 hours.

The interaction with the DBD plasma shows a different picture. The C-C bonds first increase in the first 5 s of treatment period and then decrease with further treatment time. The O-C = O- and C-O-bonds also decrease at first and then increase again, whereas the proportion of C-O-bonds after 60 s rather corresponds to the initial value (Fig. 5). However, the O-C = O bonds increase due to the plasma treatment compared to the reference. The proportions of the bonds almost correspond after 60 s to those that would be expected for a clean PLA surface [23], [31]. In this respect, the changes due to plasma treatment are reinterpreted in contrast to our previous publication [20]. As already mentioned above, many XP spectra of untreated PLA show a higher fraction of C-C bonds. Different types of air plasma treatments reduce this fraction as observed here [32], [33], [34]. This change is mostly associated with an increase in the fraction of oxygen bonds and is interpreted as an oxidation of the surface [32], [33], [34]. However, since all proportions are close to the theoretical values of pure PLA after the interaction, the observed changes could also be interpreted as a cleaning effect. To clarify this, further investigations would have to be carried out with, for example, longer treatment times and other gas atmospheres. Furthermore, the time after the plasma treatment has to be considered. For example, Song et al. observed an increase in C-C and C = O bonds after microwave plasma treatment in O₂ [35]. Their data suggest the formation of carboxylic acid and ethyl groups at the surface.

The comparison with results for UV treatment of PLA shows an opposite picture. The PLA that was treated here in water with UV shows a significant increase in C-C bonds. This increase also does not change with treatment time. The values differ only marginally. In contrast to the ultrasound samples, no nitrogen was observed. Ikada observed an increase in C = C and carboxylic acid groups with IR spectroscopy for PLA treated with UV light in air [36]. He attributed this to the Norrish II type photo cleavage process, where cleavage occurs at the C-O bond in PLA [37]. This scission of the C-O bond is also the basis for the explanations of the plasma results of Song et al. and Laput et al. [34], [35]. The cleavage leads to the formation of radicals, which leads to the formation of carboxylic acids and ethyl groups with cleavage of CO₂, C₂H₄, and H₂O [34], [35]. This clearly shows that the environment plays a major role in the interaction. However, it could be that the water dissolves compounds, like carboxylic acids, formed on the PLA surface, leaving behind a higher proportion of C-C bonds. To our best knowledge, ultrasound assisted degradation of PLA has not yet been studied by other groups.

Comparing the 20 kHz and 860 kHz data, it appears that the 860 kHz treatment has a much stronger influence on the PLA structure and leads to similar results as the interaction with UVA radiation due to the higher energy input. At first glance, the treatment time has little influence on the chemical composition. The strong changes could be observed already after a treatment of 1 hour. To what extent or whether compounds are transferred into the water cannot yet be said.

IR Results

The characterization of the treated PLA-samples with ATR-FTIR-spectroscopy enables the obtaining of chemical information in a range of 0,5 to 5 μm . The relevant peaks, which were assigned to corresponding chemical bonds, show different intensities, depending on the treatment.

For the samples that were treated with 20 kHz ultrasound, a basically increasing tendency of the intensities with an increase of duration of the treatment can be recognized [Fig. 6a].

An exception is the intensities of the C = O, CH₃ and CO bands of the three-hour treated sample. These are higher than those of the other samples for the first two cases, but the CO peak is less pronounced than the peaks of the one- and three-hour treated samples.

The sample series treated with 860 kHz ultrasound shows only slight deviations of the intensities from the reference for both C-H-bonds [Fig. 6b]. These only marginal differences are also present for the six-hour treated sample. In contrast, the intensities of the C-O, CH₃, C = O, COC bands of the one-hour treated sample are up to 39% higher than those of the reference.

With the exception of the sample irradiated for three hours, the samples treated with UV radiation show a decreasing trend in intensities [Fig. 6c]. An irradiation for three hours has led to a strong increase in the intensity of all bands.

Figure 6a: Absorbance of surface groups derived from FT-IR spectra for samples treated with 20kHz Ultrasounds. The treatment time, where R is the non-treated sample, is indicated on the X-axis.

Structural differences are shown only in the IR spectra of the samples treated for three hours with 20 kHz, for one hour with 860 kHz, and for one hour with UV radiation. The latter shows the formation of two small peaks at 1554 and 1509 cm^{-1} . The first two show the formation of a new band at 1540 and 1542 cm^{-1} , respectively. The formation of a peak in this range was already observed by Lambert and Wagner for microplastic PLA that had been naturally aged for 112 days [38]. The range between 1500 and 1600 cm^{-1} is typically where the peaks of nitrogen compounds are found [39].

Because of the greater depth of penetration of the infrared radiation into the material, a different region of the material is imaged than, for example, in XPS spectroscopy. Accordingly, the IR spectra provide information from deeper layers of the PLA.

Drop Contour Analysis Results

The drop contour analysis findings indicate whether the polymer surface is hydrophilic or hydrophobic. The non-treated sample of PLA appears to have a hydrophilic surface and the values of the left and the right angles are 71.8 ° and 71.2 °, respectively, as shown at Fig. 7. After the samples were treated either with Ultrasounds or with UVA irradiation their surfaces, even though they are still hydrophilic, in general they turned to be more hydrophobic than the reference, as shown at Table 1. These results seem to agree

with the results obtained from the XPS characterization method, as it is explained above, when the samples are treated with ultrasonication there is an increase in the C-C bonds and a reduction of C-O or O-C = O bonds in the PLA. On the other hand, samples that have been treated with DBD plasma appear to be more hydrophilic, as shown at Table 2. Once again, the results of DCA match the XPS results for the plasma treatment as the C-C bonds decrease and the O-C = O bonds increase. Therefore, the results of one treatment method cross the results of the other giving us the opportunity to adapt the surface chemical properties to different bacteria and enzymes.

Table 1

Contact angle values from the drop contour analysis of the samples treated at different times and different methods.

Treatment	Reference	UVA Irradiation			Ultrasounds at 20kHz			Ultrasounds at 860kHz		
		1h	3h	6h	1h	3h	6h	1h	3h	6h
Time		1h	3h	6h	1h	3h	6h	1h	3h	6h
Angle 1 (°)	71.8	87.9	80.8	97.8	75.8	65.7	78.8	90.9	79.2	72.4
Angle 2 (°)	71.2	87.2	80.5	98.1	75.0	65.4	77.0	92.4	80.4	73.3

Table 2

Contact angle values from the drop contour analysis of the samples treated with DBD plasma.

Treatment	Reference	Plasma			
Time		5 sec.	10 sec.	20 sec.	60 sec.
Angle 1 (°)	69.2	53.4	50.8	49.7	53.6
Angle 2 (°)	70.2	52.9	50.1	53.8	53.7

CLSM Results

This particular characterization method focuses more on the roughness and in general on the morphology of the surface. We, therefore, used it to collect more information about how the surface of our samples is changing morphologically, given by the values R_a and R_q . R_a expresses, as an absolute value, the difference in height of each point compared to the arithmetical mean of the surface and this parameter is used generally to evaluate surface roughness, R_q represents the root mean square value of ordinate values within the definition area and it is equivalent to the standard deviation of heights. Based on the results of CLSM we observe that the samples treated for 6 hours at 20kHz of Ultrasounds have a

smoother surface than the Reference sample, but also from the samples treated for 1 or 3 hours. The R_a value is decreased from 9.102 to 6.082 nm. Therefore, the smoother the surface gets one would expect that the surface is turning more hydrophobic. This theory agrees also with the DCA results showing that the surface is more hydrophobic as the contact angle is increased from 71.8° to 78.8° . Additionally, for the 860kHz Ultrasound treatment it is observed a decrease of the R_a value for the samples treated for 3 hours at 7.463 nm. Then the value is increased again at 8.628 nm when the samples are treated for 6 hours, which is really close to the Reference. The DCA results also match this changes. However, during a measurement the roughness is calculated only for a small part (in nm) of the whole surface of the sample, and although the values are the average of at least two measurements per sample, we do not consider that they represent the general aspect of the samples. More information about the CLSM results exist in the Supporting Information File.

Conclusion

Considering all results of the methods together, it can be concluded that the changes of the PLA take place rather in the near-surface region. As can be seen from the XPS and IR results, the time, at first glance, in which the samples are processed, does not play an important role. Large differences are observed after only 1 hour of treatment. Therefore, we could assume that at time zero we have a "clean" untreated sample surface. Whereas the XPS investigations show that, the surface does not correspond to pure PLA but it is slightly contaminated. Then we start treating the samples for one hour, during which changes are observed. Then the results of the three-hour analyses show that the sample surfaces again show significant differences from the reference but little difference from the sample after one hour. This is also true for samples treated for six hours. Especially the UVA treated samples show no major changes after 1 hour. So it seems that at least the ultrasonic treatments during the experiments cause the ablation of the top layer of the surface, resulting in a new modified PLA surface all the time. The IR results show, with two exceptions, that the PLA scaffold inside initially remains intact. It is not possible to say how much material can be removed with the respective treatment method now. However, the XPS results show that the changes start at the surface, and this is where the differences in treatment type become apparent. The strongest changes were observed during treatment with 860 kHz and UV light. Here, we observe a strong increase in the C-C bonds on the surface. In contrast, treatment with 20 kHz leads to only marginal changes. Thus, the interaction of 20 kHz ultrasound with PLA in water seems to be less effective than that with 860 kHz.

Comparing the UV data from the literature with the UV results presented here, a strong influence of the treatment environment is also evident. Significant differences are therefore observed between the samples where the treatment method was applied either in a wet environment either or in air. Perhaps free radicals of the PLA surfaces are generated during hydrolysis and then water may transport the hydrolysis products away. This theory comes in agreement with literature [40] when PLA samples were treated via laser ablation in water.

In the plasma experiments it is also observed that the treatment has an effect on the surface over time, but after a certain point, of approximately 20 seconds of treatment, the surface properties are very similar to the untreated surface. The plasma treatment, which took place in air, shows at first glance to have an opposite effect on the PLA. In this case, one could speak of an oxidation of the surface, which is associated with the relative increase in oxygen bonds compared to the C-C bonds. At second glance, however, only the C-C bonds are reduced and the relative proportions approach the ratio of a pure PLA surface. This is also in good agreement with the literature [32]. Thus, one could speak of a cleaning effect. Drop Contour Analysis measurements support the XPS results. The samples with an increased amount of C-C bonds become more hydrophobic and the plasma treated samples with a lower amount of C-C bonds turn more hydrophilic.

Declarations

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Competing Interests

The authors declare that they have no known competing interests.

Author Contributions

Charalampia Kalogirou, Georgia Sourkouni and Christos Argirusis contributed to the study conception and design. Material preparation, data collection and analysis were performed by Charalampia Kalogirou, Georgia Sourkouni, Oliver Höfft, Anna Gödde and Pavlos Pandis. Quality control of the data and analyses were performed by Georgia Sourkouni, Charalampia Kalogirou and Christos Argirusis. The first draft of the manuscript was written by Charalampia Kalogirou and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Figures

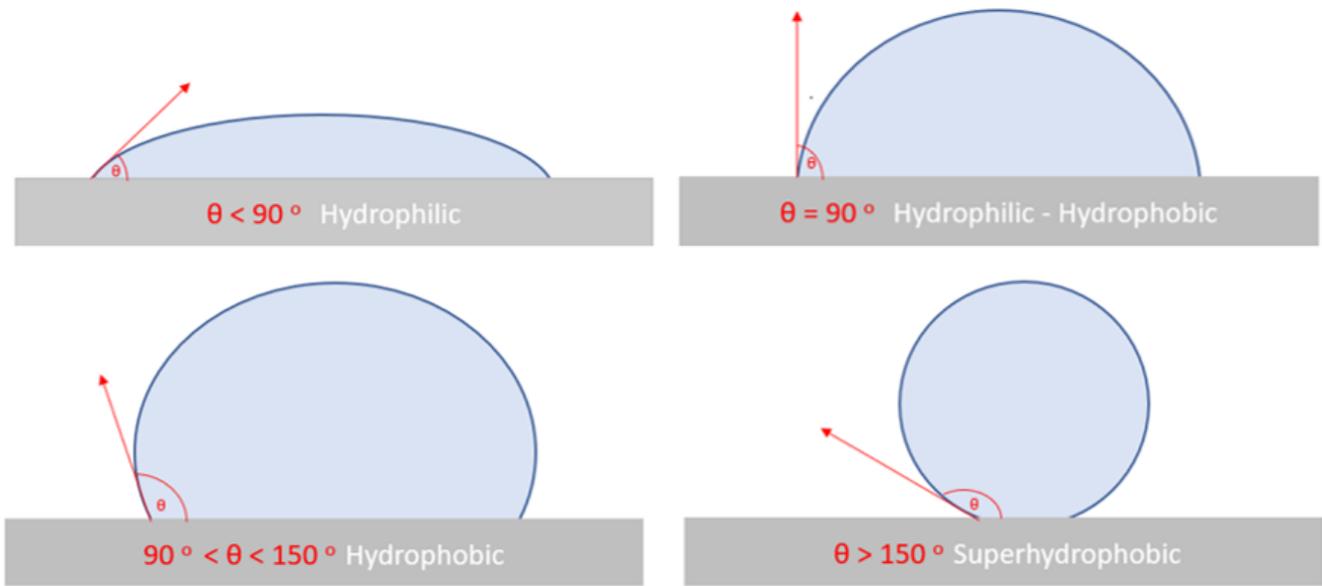


Figure 1

Surface wetting characterization by the values of contact angle.

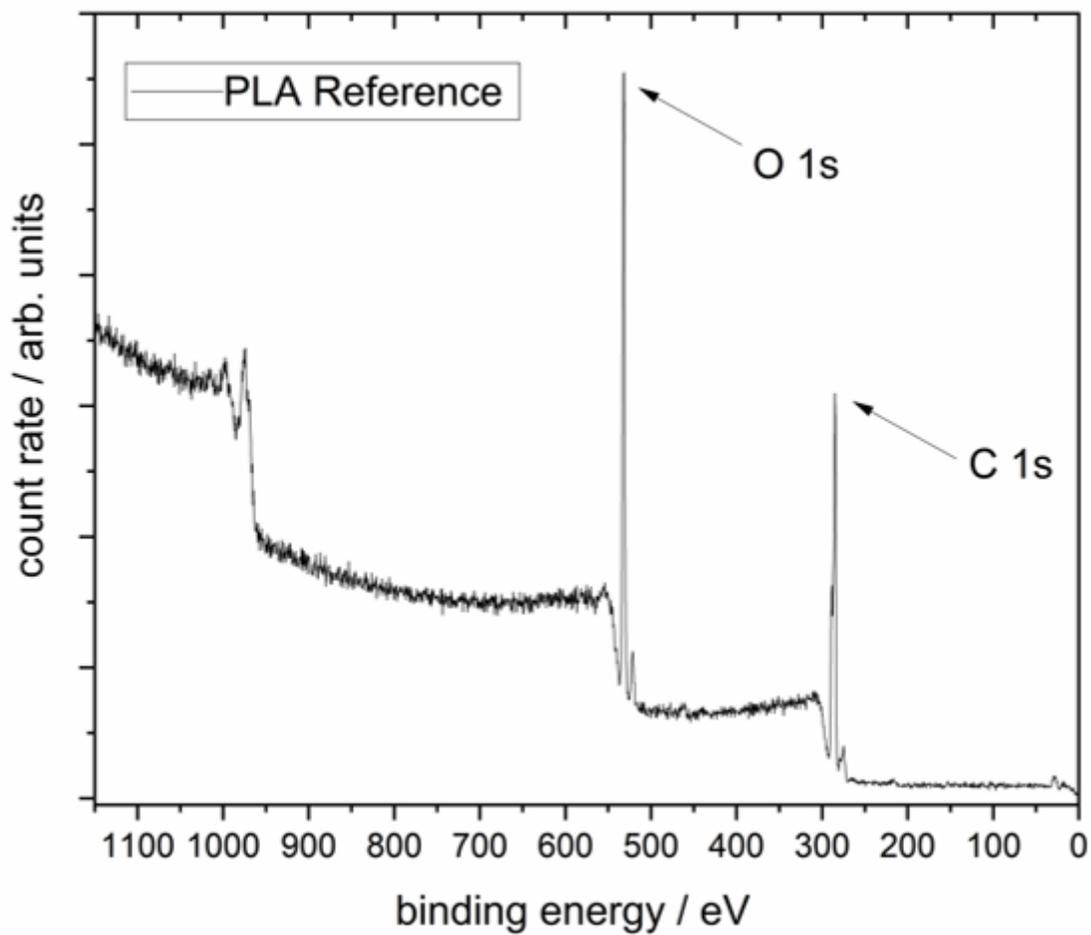


Figure 2

XPS survey spectra of the Reference PLA sample, showing the characteristic peaks for Carbon and Oxygen.

Figure 3

a: XPS Carbon peaks Spectra of PLA Reference sample.

b: XPS Oxygen peaks Spectra of PLA Reference sample.

Figure 4

C1s spectra at the 20kHz Ultrasound treatment comparison between the samples that have been treated and the non-treated sample.

Figure 5

The different ratios of functional groups and elements for each sample treated with plasma at different times.

Figure 6

a: Absorbance of surface groups derived from FT-IR spectra for samples treated with 20kHz Ultrasounds. The treatment time, where R is the non-treated sample, is indicated on the X-axis.

b: Absorbance of surface groups derived from FT-IR spectra for samples treated with 860kHz Ultrasounds. The treatment time, where R is the non-treated sample, is indicated on the X-axis.

c: Absorbance of surface groups derived from FT-IR spectra for samples treated with UV. The treatment time, where R is the non-treated sample, is indicated on the X-axis.

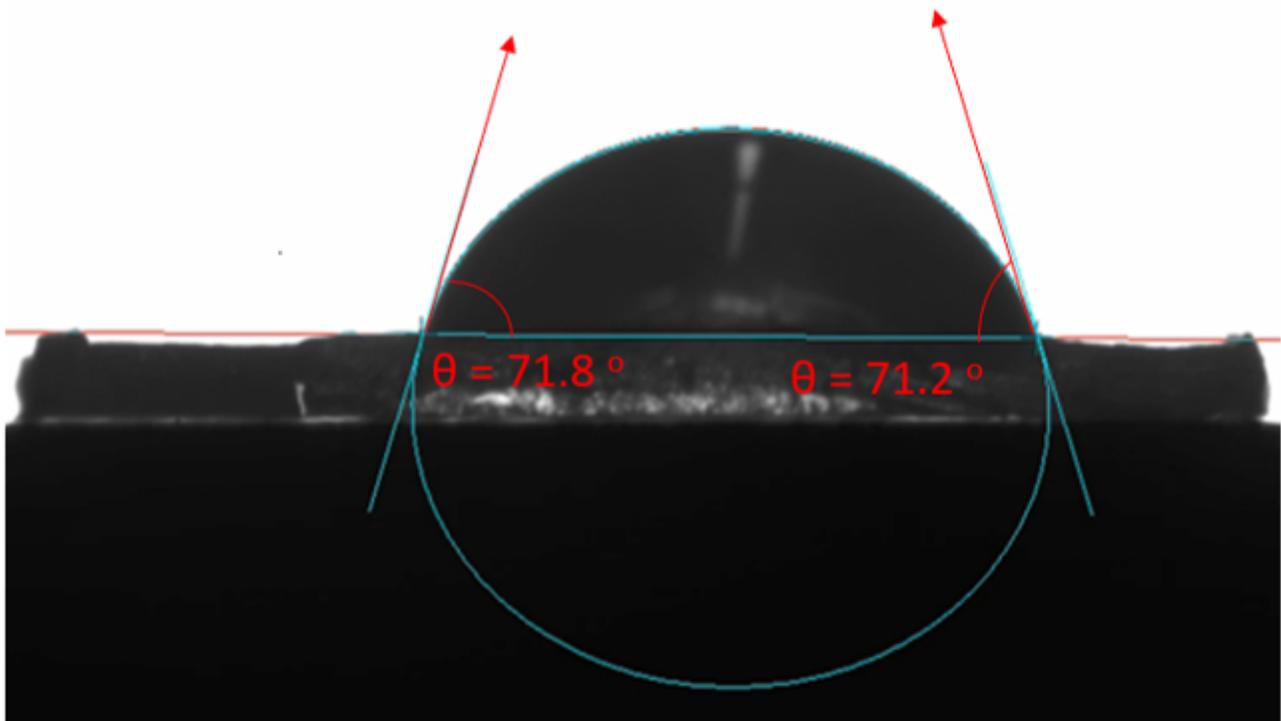


Figure 7

The non-treated (Reference) sample of PLA measured by DCA.

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