Plasma assisted bio-degradation of poly-lactic acid (PLA)

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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 on 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 because 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 .

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 without the need for costly vacuum equipment [5,6].

In the plasma experiments despite the very short treatment times necessary, 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

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surface. This is also in good agreement with the literature [7]. 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 turn more hydrophilic.

The interaction with the DBD plasma shows a picture in which 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 (Figure 1). 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 [7]. With plasma we observe an oxidation of the surface, which, however, lies more on the reduction of the C-C bonds relative to the C-O and C=O bonds. 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 [8]. This change is mostly associated with an increase in the fraction of oxygen bonds and is interpreted as an oxidation of the surface [9]. 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.

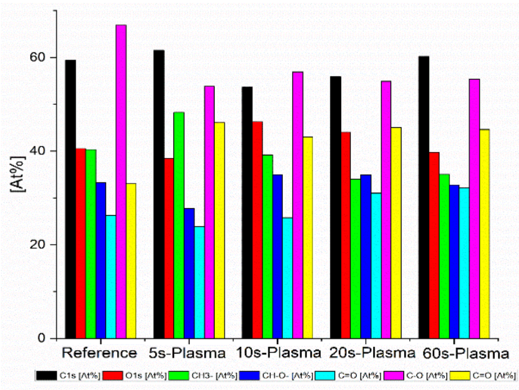

Figure 1: The different ratios of functional groups and elements for each sample treated with plasma at different times.

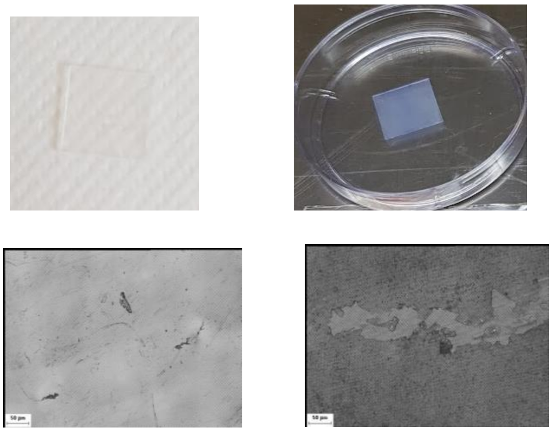

Figure 2: Pictures of the plasma treated PLA samples (right) after exposure to Pseudomonas Knackmussii showing the improved adhesion as compared to the non-treated (Reference, left) sample of PLA.

The drop contour analysis findings indicate whether the polymer surface is hydrophilic or hydrophobic. Samples that have been treated with DBD plasma appear to be more hydrophilic, as shown at Table 1. 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.

Table 1: Contact angle values from the drop contour analysis of the samples treated with DBD plasma.

	Reference	**Plasma treated samples**			
Treatment Time	*0 [s]*	*5 [s]*	*10 [s]*	*20 [s]*	*60 [s]*
Angle 1 [°]	69.2	53.4	50.8	49.7	53.6
Angle 2 [°]	70.2	52.9	50.1	53.8	53.7

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