Plasma treatment of polymers to optimize the adhesion of coatings*

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Abstract— **In the present work, polyetheretherketone (PEEK) was pretreated with oxygen plasma to investigate the influence on the contact angle and surface energy. For this purpose, PEEK samples were fabricated over several manufacturing steps, which were used as substrates for later investigations. A series of measurements was performed at a power of 300 W for different treatment durations and the contact angle of H_2O on the PEEK surface was determined. The results show that plasma pretreatment significantly affects the surface modification of PEEK disks. The best hydrophilic properties of the PEEK surfaces were measured at a treatment time of 540 s and a power of 300 W. A much longer treatment time caused the correlated values of contact angle and surface energy to increase and in this case an excessive treatment time did not contribute to a further increase in hydrophilicity.**

I. Introduction

Polyetheretherketone (PEEK) is a linear and biocompatible polymer that offers significant advantages over metallic materials due to its bone-like mechanical properties, so it is often used in joint and bone implants. While the use of titanium in orthopedic implants creates a self-passivating layer with good corrosion resistance and bone strength, there is still the disadvantage of a high elastic modulus that can lead to implant loosening. By depositing TiO_2 on the PEEK surface, the osseointegrative properties can be improved [1].

Atomic layer deposition (ALD) is one method for coating PEEK with titanium. This is a multi-stage process in which the coating is applied to a substrate step by step in monolayers in a cycling process. This allows precise control of the coating thickness at the monolayer level and very conformal deposition. ALD is a method based on self-limiting surface reactions, which can deposit layers with very high aspect ratios and is particularly well suited for the coating of large areas [2].

Functionalization of the PEEK surface by plasma pretreatment with oxygen can improve film adhesion. In this process, chemical oxygen groups are introduced into the PEEK surface, which realize improved adhesion of the titanium coating. In addition, the polar component of the surface energy is greatly increased by plasma treatment, which means that plasma pretreatment with oxygen also affects the contact angle of water [3].

In this work, plasma pretreatments with oxygen were performed on PEEK substrates at different treatment durations and a power of 300 W. The contact angle of water on the substrates was determined and used as an indicator for the surface energy. In addition, the surface energy was specified with the aid of the polar and disperse fractions of the test liquids used. By means of these investigations, a statement can be made on the extent to which different treatment durations influence the hydrophilicity of the PEEK surface and how these affect the surface energy.

II. Materials and Methods

A. *Specimen preparation and purification*

The specimens required for contact angle measurement were made from PEEK rod material (Invibio PEEK-OPTIMA NATURAL) with a diameter of 19 mm. For this purpose, the specimens were first sawn, ground and then polished (using a diamond suspension with a grain size of 1 µm (Struers NapR1)), so that a uniform and smooth micrograph was produced. The reason for this is that the surface roughness influences the contact angle and the measurements were therefore carried out on polished PEEK samples [1]. Subsequently, the specimens were cleaned in an ultrasonic bath for 15 minutes each in acetone (purity ≥ 99.5 %), isopropanol (purity ≥ 99.5 %) and distilled water. The remaining liquid on the surface of the samples was then evaporated in an oven at 100 °C for 30 minutes. This ensured that excess liquid residues were removed, which could have influenced the contact angle measurement.

Figure 1: PEEK specimens for the determination of contact angles and surface energy.

B. *Plasma activation*

The series of experiments was carried out with plasma treatment at 300 W for different treatment durations. Plasma activation of the PEEK samples was done in a MyPlas2014 III ALD (Plasma Electronic GmbH). After the ventilation process of the machine, the samples were each placed individually on a preheated plate in the center of the chamber, which was evacuated to a pressure of about 1 Pa. With a constant gas supply of 35 sccm oxygen and a chamber pressure of approximately 5.5 Pa, a high-frequency plasma was ignited at 13.56 MHz and a power of 300 W in remote mode. If this caused the pressure to rise above 6 Pa, the oxygen supply was reduced accordingly to 34 sccm. The sample was then removed from the chamber and was ready for the measurement of the contact angle.

C. *Contact angle measurement*

A DataPhysics OCA 200 was used to measure the contact

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angles of the individual liquids. The measurement of the contact angle is used to determine the surface energy. Before starting each measurement, the surface tension of the corresponding liquids was checked and determined using the pendant drop method. For the determination of the contact angle and surface energy of the PEEK samples, the three liquids used in this research were H_2O, diiodomethane and ethylene glycol. For this purpose, one drop of each liquid with a volume of 4 µL was deposited on the sample surface and the contact angle was measured using the sessile drop method. In this case, the contact angle was determined with the images of the droplets taken with a CCD camera of the DataPhysics OCA 200. The machine table was then moved so that a new drop could be deposited at a non-overlapping position. Special care had to be taken to ensure that the remains of previous drops did not have any optical influence on the contact angle and thus falsify the result. Contact angles of drops that formed too close to the edge of the surface or the position of the previous drop were discarded.

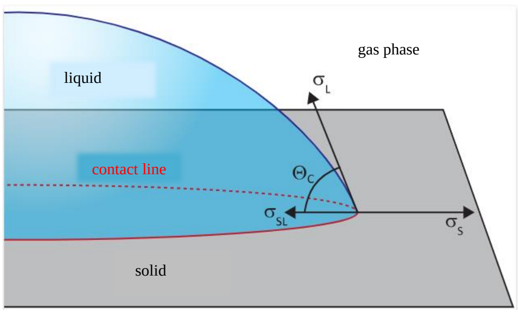

Figure 2: Contact angle measurement on a solid-liquid-gas contact line [4].

D. *Surface energy*

For the calculation of the surface energy, an average of five drops of each liquid were examined and the contact angle determined. Using the arithmetic mean values of the measured contact angles, as well as the disperse and polar fractions of the surface tension of the three different test liquids, the surface energy was calculated using the method according to OWENS, WENDT, RABEL and KAELBLE (OWRK method). The surface energy is decisive for the incorporation of functional groups on the PEEK surface.

III. RESULTS

A. *Contact angle measurement*

The results of the contact angle measurement are shown in Figure 3. Samples with a treatment duration of 0 s - 960 s were measured. The contact angle at 960 s should be used to estimate the effect of a significantly longer treatment time. The lowest mean value of the series of measurements performed at 300 W is 15.9° ± 1.3° for a treatment duration of 540 s. Looking at the series of measurements at 300 W, it is noticeable that the maximum hydrophilicity can be significantly increased with increasing treatment time up to a certain level.

While the untreated PEEK samples have a contact angle of 81.7° ± 2.8°, even a short treatment duration of 180 s leads to a considerable decrease in the contact angle of water on the PEEK sample. From this point on, a continuous decrease of the contact angle can be observed up to a treatment duration of 540 s. A longer treatment duration leads again to an increase of the contact angle, as it was observed in the case for 660 s with a contact angle of 21.4° ± 3.5° and at an even longer treatment duration of 960 s with a contact angle of 29.7° ± 1.7°.

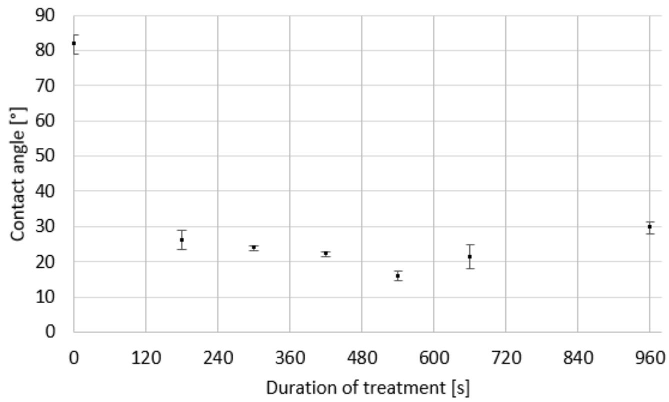

Figure 3: Mean values and standard deviation of contact angle measurements of H_2O on PEEK for an oxygen plasma pretreatment time of 300 W.

B. *Surface Energy*

Figure 4 shows the results of the surface energy for the different treatment durations for the 300 W measurement series. In order to be able to make a precise statement about the polar and disperse components of the surface energy, the two components are marked by the color grey (disperse) and black (polar).

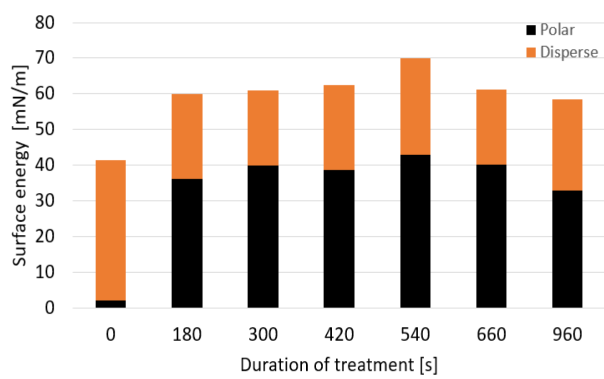

Figure 4: Summary of the surface energy for different treatment durations at a power of 300 W. The surface energy is divided into polar (black) and disperse (orange) components.

Looking at the series of measurements, the untreated PEEK sample, with a polar value of only 2.1 mN/m, has a very small share of the total surface energy of 41.5 mN/m. A short plasma pretreatment of 180 s already causes the surface energy to increase to a total value of 60 mN/m. It can also be seen that the polar fraction has risen to a value of 36.2 mN/m because of the plasma pretreatment. A longer treatment time causes the surface energy to increase steadily, so that at a treatment time of 540 s, the highest surface energy of 70.1 mN/m could be calculated. Here, the results of the contact angle measurement correlate with the results of the surface energy. With the largest possible polar fraction at a treatment duration of 540 s with 43 mN/m, the smallest contact angle could be measured. A longer treatment time beyond the 540 s, makes both the polar fraction and the total surface energy decrease again. To be able to make a statement about the surface energy at a significantly longer treatment duration, a surface energy of 58.4 mN/m with a polar fraction of 32.9 mN/m could be determined at a treatment duration of 960 s.

At a treatment duration of 420 s, the surface energy has increased, but the polar value has decreased from 40 mN/m to 38.8 mN/m compared to the previous treatment duration of 300 s. This may be due to a measurement error, which should be considered for further investigation. No correlation for the individual disperse fractions with the treatment duration of the surface energy could be observed.

The surface energy was calculated based on the OWRK method using the contact angle determination of the three test liquids H_2O, diiodomethane and ethylene glycol on the PEEK samples. For the untreated PEEK specimen, the contact angle measurement of the three liquids did not pose a problem. However, in the case of ethylene glycol, it turned out that a contact angle had to be assumed for the determination of the surface energy from a treatment time of 180 s, since it led to an extreme spreading of the droplet or the droplet placement to a complete wetting of the surface, so that a contact angle measurement was no longer possible. In this case, an angle of < 3° was assumed for the calculations.

IV. DISCUSSION

As can be seen from the results of the contact angle measurements and the surface energy, the plasma pretreatment has a significant influence on the properties of the PEEK surface. A short plasma treatment of the PEEK substrate already leads to an increased hydrophilicity, so that the maximum hydrophilicity, in this case, the lowest contact angle of H_2O on PEEK, could be measured at a treatment time of 540 s. At the same time, the highest surface energy with the largest possible polar fraction was measured at this treatment duration. The results correlate with each other at this point.

As already shown by Comyn et al. in their investigations, pretreatment of the PEEK substrate with oxygen plasma results in the formation of oxygen functional groups on the PEEK surface. They observed that oxygen- and air-plasmas increase the amount of oxygen on the surface by the same amount and ---COO--- groups are formed by this plasma treatment [3]. A short oxygen pretreatment of the PEEK surface of 60 s with a power of 300 W and a pressure of 40 Pa already decreased the contact angle of water by 46° to 25° compared to the untreated sample. By introducing polar groups, the water can form a better bond with the PEEK surface, which finally makes the contact angle decrease [3]. Furthermore, it was demonstrated that the surface energy could be greatly increased due to the plasma treatment.

Likewise, Blendinger et al. demonstrated in their studies on the determination of the contact angle on plasma-treated PEEK substrates with TiO_2 coating, that the contact angle of water of TiO_2 coating is significantly lower after a plasma treatment time of 5 minutes compared to uncoated PEEK samples. This indicates that the hydrophilicity can be improved by the coating. Moreover, the PEEK substrates were treated with plasma before coating to achieve better adhesion to TiO_2, which needs to be verified in further studies [1].

If a too long treatment time is applied to the plasma pretreatment of the PEEK samples, both the contact angle of water on the PEEK samples and the total surface energy increase. Inagaki et al. have shown that the surface modification and degradation in remote oxygen plasma treatment of PEEK, which was used in the present work, are in a competitive state. Thus, excessive treatment of the PEEK surface could result in degradation products remaining on the surface, preventing the PEEK surface from being further modified to a hydrophilic surface. In addition, it was observed that PEEK is susceptible to plasma effects while degradation products and the introduction of oxygen functionalities occur on the PEEK surface. If the case occurs that degradation predominates and the PEEK surface is thus covered with degradation products, the degradation interferes with further hydrophilic modification of the PEEK surface [5].

This could explain why a longer treatment time of 660 s and 960 s of the PEEK substrates in the present work does not contribute to further improved hydrophilicity and surface energy, but on the contrary increases both the contact angles and surface energy as the PEEK surface is disturbed by the degradation products.

According to Inagaki et al., remote oxygen plasma treatment is more suitable for hydrophilic surface modification of the PEEK surface than direct oxygen plasma treatment, but degradation also occurs on the PEEK surface, which disturbs the hydrophilic properties.

V. CONCLUSION & OUTLOOK

PEEK specimens treated with oxygen were subjected to different treatment durations in a series of measurements at a power of 300 W. In summary, this research has shown that plasma pretreatment of PEEK samples by oxygen influences the surface modification at different parameters. The best hydrophilic properties of the PEEK samples were obtained at a treatment duration of 540 s and a power of 300 W. The results of the contact angle measurements and the determination of the surface energy correlate with each other. To be able to make a further statement of the plasma treatment of polymers for optimizing the adhesion of coatings, further plasma parameters of different gases or pretreatment properties must be considered.

In the next step, TiO_2 thin films must be deposited on the biocompatible implant material PEEK by atomic layer deposition (ALD) to characterize them with respect to their ability to improve osseointegrative properties. The use of the ALD process allows the deposition of homogeneous and defect-free layers on complex surfaces. The layer adhesion will then be determined by pull-off tests and peel tests. In general, it can be assumed that a high surface energy promotes cell adhesion. In addition, hydrophilic surfaces are more suitable for cell adhesion [1]. Accordingly, with a treatment time of 540 s at 300 W and the highest measured surface energy of 70.1 mN/m, the best adhesion would be expected in an adhesion test of this series of measurements. For further investigations, it must therefore be verified by means of the adhesion tests whether and to what extent an adhesion value of 22 MPa, which is specified by the Food and Drug Administration (FDA) as the minimum tensile strength for coatings on orthopedic implants, can be realized.

VI. REFERENCES

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