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Surface Characterisation of PEEK and Dentin, Treated with Atmospheric Non-Thermal PDD Plasma, Applicable for Dental Chair-Side Procedures

Marius Behnecke *, Vincent Steinert and Svea Petersen *

Faculty of Engineering and Computer Science, University of Applied Science Osnabrück, Albrechtstraße 30, 49076 Osnabrück, Germany; steinertvincent@gmx.de

* Correspondence: m.behnecke@hs-osnabrueck.de (M.B.); s.petersen@hs-osnabrueck.de (S.P.)

Abstract: This study investigates the suitability of Piezoelectric Direct Discharge Plasma as a tool for wetting behaviour modification of PEEK and dentin, and compares the results of this method with low-pressure plasma treatment and phosphoric acid etching. Static contact angle measurements were made, roughness was assessed using tactile measurement, and AFM and SEM images were taken. An optimum operating distance of ≤15 mm was determined for the plasma based on the water contact angle. Furthermore, it was demonstrated that despite only a fraction of the power, the PDD plasma also produces hydrophilic and nanostructured PEEK surfaces with a 38° water contact angle in the same plasma time. In contrast, the gold standard of dental surface modification of dentin—phosphoric acid etching—showed no measurable contact angle due to the exposed dentin tubules. Treatment with PDD plasma reduces the water contact angle of dentin from 65° to 43° and is not negative affected by water. Wet, PDD plasma-treated dentin samples show a water contact angle of only 26.5°. The dentin tubules exposed by chemical etching led to a significantly increased roughness. No comparable effect could be demonstrated for plasma treatment on dentin, but based on the contact angle measurements, a chemically strongly activated surface with strongly polar interaction behaviour can be assumed. The additional use of the PDD plasma technique to improve wetting could therefore have a positive effect on the adhesive bond between human dentin and polymeric dental restorative materials or, depending on the adhesive system, replace the etching process altogether.

Keywords: Piezoelectric Direct Discharge; plasma-treatment; dentin; etching; polyetheretherketone; contact angle measurement

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1. Introduction

Due to the improvement of living conditions and healthcare in our society, the incidence of edentulism is currently decreasing among older people. In the older generation, a shift away from mucosa-supported total dentures to periodontally supported fixed dentures is thus becoming apparent, due to the aforementioned decrease in toothlessness [1]. The long-term success of inserted fixed dentures depends on various factors, including the chemical and micromechanical properties of the surface of dental hard tissues and restorative materials. Improving the wettability of the surface and the associated bond strength at the interface between tooth structure or restorative material and dental adhesives has always been a major research focus. Especially attractive in this context is the modification by means of an atmospheric pressure plasma using a hand-held plasma device which is suitable for manual use in chair-side procedures. In the present study, the effectivity of Piezoelectric Direct Discharge (PDD) atmospheric pressure plasma is compared to that of conventional treatment with low-pressure plasma, with regard to the wetting behaviour of polyetheretherketone (PEEK) as one promising model dental material. PEEK is particularly challenging for bonding applications due to its inert character. This is reflected, for example,

in the lower fracture strengths of temporary crowns, the insufficient adhesion of veneers on PEEK abutments, or the cementing of premade PEEK posts. These applications might be improved via PEEK surface modification in the laboratory, but also chair-side or even in-mouth [2–4]. However, when plasma is applied within a patient's mouth, dental hard tissue might be also affected. In this context, this study focuses on the investigation of the PDD plasma treatment of dentin, which is the most important human dental hard tissue. To the best of our knowledge the treatment of dentin via PDD plasma has not been investigated before. We therefore aim to eliminate a negative alteration of dentin due to unintended plasma treatment, but also to provide general insights into the intentional plasma modification of dentin. On the one hand, the latter could be favourable for the wettability of dentin, which would be interesting in terms of optimization of the interface between dental adhesives and tooth structures, but also with regard to the prevention of possible gap formation in dental fillings. On the other hand, plasma exposition has been found to be toxic to microorganisms, which may lead to the removal of biofilms on tooth structures after cavity preparation [5]. The gold standard of dentin preparation for further bonding is acid etching by means of concentrated phosphoric acid [6]. In this process, an etching gel is applied to the tooth and then, after a defined exposure time, aspirated. This process produces a clean, chemically active, and rough dentin surface, which exhibits sufficient bond strength with dental adhesives. However, there are various risks of misapplication, which can have a negative effect on the bond and the patient's sensitivity [7–9]. In the course of the test series, we will discuss whether plasma treatment through Piezoelectric Direct Discharge atmospheric pressure plasma (PDD) is additionally suitable for dentin modification.

2. Materials and Methods

2.1. Materials

In the series of experiments carried out, differently modified surfaces of PEEK and human dental hard material (dentin) were investigated. A 100 µm thick "VESTAKEEP 4000G" PEEK foil made by "EVONIK Industries AG" (Essen, Germany) was used for the optimization of the working distance and comparative plasma process studies. The films were thoroughly cleaned with distilled water and cut into 55 × 25 mm^2 pieces. These samples were then rinsed with isopropanol and cleaned for 3 min in an ultrasonic bath with isopropanol. All examinations were performed on the smooth side of the pieces of foil, which were glued onto glass slides to provide a flat surface for contact angle measurements. The dentin examined, however, originated from a molar donor tooth. After extraction, it was cleaned with ethanol and water in an ultrasonic bath. To create a planar analysis surface, the tooth was horizontally embedded in polyester resin and sanded down to 1000 grit (Figure 1). Conventional etching of the surface was performed with a 37% phosphoric acid etching gel from "Henry Schein Services GmbH" (Gallin, Germany) for 30 s.

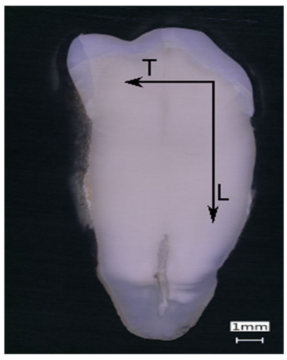

Figure 1. Representation of the prepared dentin surface on a human donor tooth indicating the two measuring directions for the transversal (T) and longitudinal (L) roughness measurement.

2.2. Methods

2.2.1. Plasma Treatment

Both atmospheric and low-pressure plasmas were used for surface modification. In the case of atmospheric plasma, the portable plasma source "Piezobrush® PZ3" manufactured by "relyon Plasma GmbH" (Regensburg, Germany) was utilized. For all comparative studies, the device was moved with a 10 mm distance over the surface. To allow relative comparability between the plasma processes, the surfaces were exposed to the plasma for 120 s in both processes, and air was used as the process gas in each case. All plasma treatments were carried out at the unit-dependent maximum power. The low-pressure plasma treatment was carried out using an "HPT-100" from the manufacturer "Henniker Plasma" (Runcorn, UK). A volume flow of 0.2 sccm was applied, which resulted in a pressure of 0.3 mbar.

2.2.2. Contact Angle Measurement

All contact angles were measured with an "OCA 20"-Goniometer manufactured by "DataPhysics Instruments GmbH" (Filderstadt, Germany). In addition, the manufacturer's "SCA20" software was used to perform drop contour analysis, define a baseline, and determine the resulting angles. The test liquids used were water, formamide, and diiodomethane. The sessile drop method was used to determine the contact angle. For this purpose, a droplet of 0.2 µL was dosed onto a sample surface and the contact angle at the three-phase point was measured. The method, developed by Owens, Wendt, Rabel, and Kaelble (OWRK), is widely used as a standard method for determining surface free energy and is based on the Young Equation (1).

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}{}^{*}\cos(\theta) \quad (1)$$

This equation establishes a relationship between the surface tension of the liquid (γ_{lv}), the interfacial tension between the solid and the liquid (γ_{s}), the surface free energy of the solid (γ_{sv}), and the resulting measurable contact angle (θ), and is fundamental to many approaches in surface free energy calculation. In the OWRK method, the solid-vapour and liquid-vapour-interactions are split into a polar ($\gamma_{sv}{}^{p}/\gamma_{lv}{}^{p}$) and a dispersive part ($\gamma_{sv}{}^{d}/\gamma_{lv}{}^{d}$) (2), and the interfacial tension is interpreted as a geometric mean of the disperse and polar part, as per (3).

$$\gamma_{sv} = \gamma_{sv}{}^{d} + \gamma_{sv}{}^{p} \text{ and } \gamma_{sv} = \gamma_{lv}{}^{d} + \gamma_{lv}{}^{p} \quad (2)$$

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{(\gamma_{sv}{}^{d}{}^{*}\gamma_{lv}{}^{d})} - 2\sqrt{(\gamma_{sv}{}^{p}{}^{*}\gamma_{lv}{}^{p})} \quad (3)$$

Thus, in addition to the calculation of the surface free energy, the division into polar interactions, including hydrogen-bonding, and disperse interactions is also possible by using a minimum of two different liquids [10]. A series of three test liquids was used in this study. Contact angle measurements were performed two hours after the treatment to obtain measurable, reproducible contact angles. For each liquid, the mean value of at least 10 contact angles was calculated. An ANOVA significance test was performed on some selected results. For this purpose, a Tukey test with a significance level of 0.05 was used to compare the mean values, while the homogeneity of the variance test was ensured at the same significance level using Levene's test. Significant differences in the results are indicated in the respective diagrams with an "*".

2.2.3. Surface Roughness Measurement

The roughness of the surfaces was determined by means of a tactile roughness measurement via the contact section method. The device used was a "MarSurf M 400" from the manufacturer "Mahr GmbH" (Göttingen, Germany). After determining the natural frequency correction value of the measuring system, the samples were measured both horizontally and vertically with a measuring distance of 4 mm. Following the measurement,

the surface was examined microscopically for its integrity, and Ra and Rz were determined mathematically from the roughness profiles. Additionally, atomic force microscopy was performed on the PEEK samples to analyse nanostructures. Therefore, an "Easyscan 2"-device manufactured by "Nanosurf AG" (Liestal, Switzerland) was used in contact mode to scan a 40 × 40 mm^2 area. The resolution was set to 512 × 512 pixels with a line-scan time of one second.

2.2.4. SEM Analysis

The scanning electron microscopic investigations were performed using an "Auriga Crossbeam" SEM system from the manufacturer "Carl Zeiss Microscopy Deutschland GmbH" (Oberkochen, Germany). It was operated at a 5 kV accelerating voltage using a SESI detector.

3. Results

To determine the optimal and maximal operating distance of the atmospheric PDD plasma device, the PEEK samples were modified with defined working distances and the water contact angle was determined. The contact angles shown in Figure 2 indicate that there is a clear correlation between operating distance and the resulting wetting improvement.

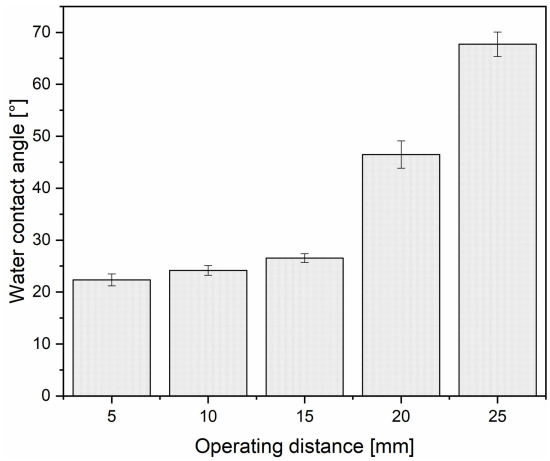

Figure 2. Water contact angle on PEEK depending on the working distance during PDD plasma treatment (18 W, 120 s, n = 10).

The lower the operating distance, the lower the water contact angle. However, the difference between 5 and 15 mm working distance is only 5°, whereas the resulting angles between 15 and 20 mm working distance already differ by 20°. For further investigations, the working distance was therefore defined as 10 mm. The comparison between the PEEK specimens modified by atmospheric PDD plasma and low-pressure plasma in terms of the resulting wettability with different liquids is pictured in Figure 3. Both methods led to significantly lower contact angles compared to untreated reference surfaces. The only exception was diiodomethane after low-pressure plasma treatment, where no considerable alteration of the contact angle was observed. A comparison of PDD plasma and low-pressure plasma-treated surfaces reveals that contact angle reduction was lower for PDD plasma treatment. The same applies to surface energy. Compared to the reference, surface energy was increased via both procedures, with the polar fraction increasing strongly and the disperse fraction decreasing. The disperse fractions of the plasma-modified surfaces differed only slightly, with 27.7 mN/m for PDD and 25.2 mN/m for low-pressure plasma. However, it was found that the low-pressure plasma generated a surface with a polar fraction that was 10 mN/m higher.

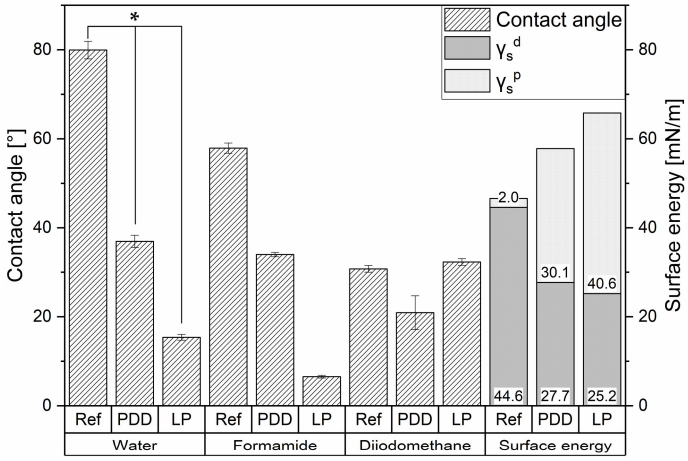

Figure 3. Comparative plot of the resulting contact angle of different test liquids (water (ANOVA tested, $p = 0.05$ indicated by *), formamide, diiodomethane) and surface energies on PEEK after surface modification using atmospheric (PDD, 18 W, 120 s, 10 mm,) and low-pressure plasma (LP, 100 W, 120 s, 2 sscm) ($n = 10$).

The determination of the surface roughness shows the influence of the plasma treatments on the surface topography of PEEK. The surfaces treated by low-pressure plasma showed lower roughness (R_z (L&T) ≈ 0.11 µm) than the reference (R_z (L) = 0.16 µm, R_z (T) = 0.12 µm), as indicated in Figure 4. The same applies to the atmospheric PDD plasma, where the effect was, however, less pronounced. Underlining this result, the SEM images show more textured surfaces, which is confirmed by the AFM images. The latter show that both plasma processes provoked a clear nanostructuring of the surface, which is not reflected in the results of the tactile measurement.

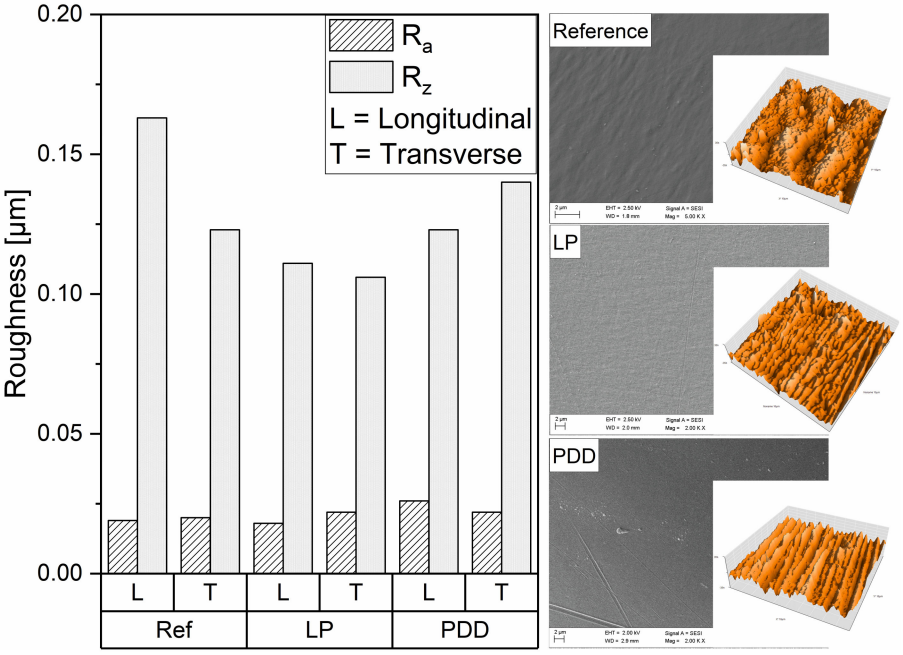

Figure 4. Longitudinal (L) and transverse (T) measured tactile surface roughness of PEEK surfaces modified by atmospheric (PDD, 18 W, 120 s, 10 mm) and low-pressure plasma (LP, 100 W, 120 s) compared to the reference ($n = 1$) with SEM and AFM images of the reference and the modified surfaces.

The plasma treatments carried out on dentin and moist dentin using atmospheric PDD plasma also showed a clear influence on its wetting behaviour (Figure 5). The water contact angle was reduced by 20°, the polar fraction of the surface energy increased from

19.7 mN/m to 45.7 mN/m, and the disperse fraction was only slightly reduced. Dentin immersed in water and dried before the measurement also showed an increased polar fraction, but with a likewise increasing disperse fraction. Plasma treatment of the wet dentin increased the polar fraction of the surface energy to as much as 35.2 mN/m, and at the same time, the sample was completely dried by the airflow in the course of the treatment. This specimen achieved the lowest water contact angle of all the specimens, at 26.5°.

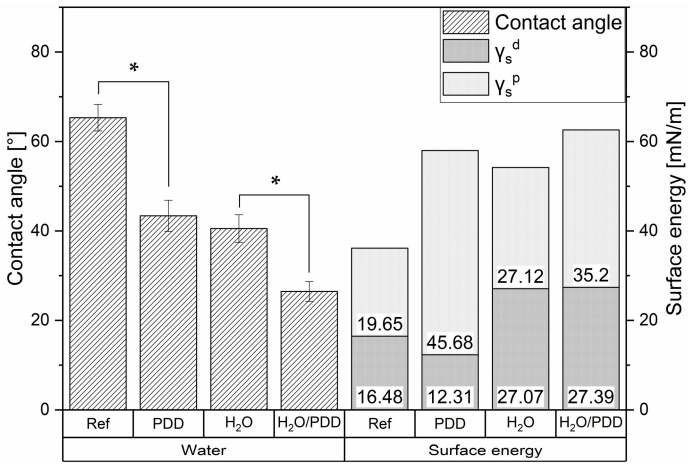

Figure 5. Comparative plot of the resulting contact angle of water ($n \geq 10$, ANOVA tested, $p = 0.05$ indicated by *) and calculated surface energies on dentin (Ref), wet dentin (H_2O), and after the surface modification via atmospheric PDD plasma (PDD & H_2O/PDD) (18 W, 120 s, 10 mm).

The results obtained by measuring the surface roughness (Figure 6) of the etched and plasma-treated dentin show that the etching of the surface produced significantly higher roughness in all characteristic values compared to the reference. The plasma treatment, on the other hand, showed no clear influence on the resulting roughness. The SEM images of the surfaces show that the surfaces also differ strongly topographically. While clear surface cavities can be identified after etching, traces of the grinding process can still be seen on the plasma-treated sample. The surface was thus not recognizably changed.

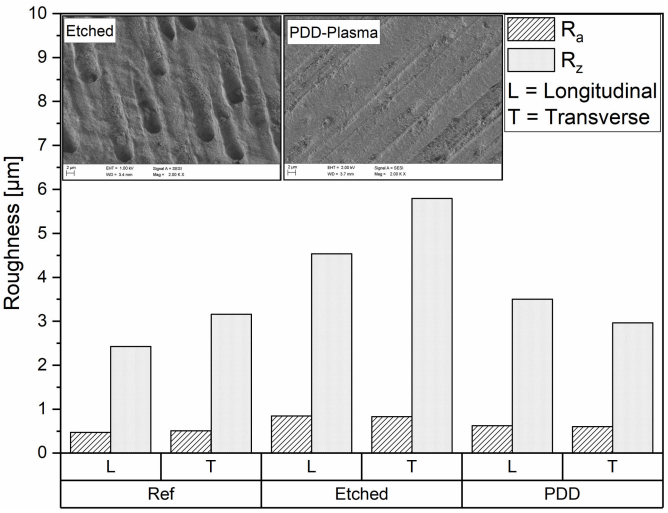

Figure 6. Longitudinal (L) and transverse (T) tactile measured surface roughness of dentin (Ref), of surfaces modified by acid etching (Etched), and of surfaces modified by atmospheric PDD plasma, with SEM images of the modified surfaces ($n = 1$).

4. Discussion

When preparing the dentin specimens, the focus was not only on creating a flat surface for the contact angle measurement, but also on the surface topography, which is realistic for dental applications. For this reason, the surface was deliberately not polished. Investigations of the working distance on PEEK show that the wetting improvement of the surface achieved by plasma treatment decreases significantly at distances of 20 and 25 mm. At a working distance of 15 mm, considerable wettability improvement is observed, which becomes only slightly more pronounced as the distance decreases. The fact that small changes in the distance, as they occur during manual guidance of the device, hardly alter the wettability effect, is very promising for chair-side application of the PDD plasma treatment. Moreover, the distance range of up to 15 mm is a realistic size that could be maintained during real-life dental interventions. Although this observation has been made for the treatment of PEEK here, it can be expected that the depicted relationship is similar on other substrates, since the critical size of the free path length of the energetic particles is independent of the treated material [11–13]. On PEEK, no contact angles comparable to the low-pressure plasma treatment were achieved after exposure to PDD plasma, but the wetting improvement is nonetheless remarkable. The water contact angle is more than halved, the surface energy is significantly increased and the polar fraction of the surface energy is increased by a factor of 15 [14,15]. At this point, it must be kept in mind that we are dealing with fundamentally different processes: Low-pressure plasma treatment is carried out at significantly higher power under optimal conditions, requires pumping and aeration times in addition to the treatment time, and cannot be used independently of location. The PDD plasma can be ignited immediately at atmospheric pressure and is not restricted by the limitations of a process chamber. Therefore, a complete treatment of the surface must be realized by manual movements of the nozzle, which entails the usual disadvantages. It can also be assumed that by using PDD plasma for a longer treatment time, the level of wetting improvement can be further approximated to that of low-pressure plasma, if necessary [11,13,16]. A treatment time of 120 s has been determined in previous studies as an optimal treatment time for PEEK in low-pressure plasma; at the same time, it is a realistic timeframe for a chair-side application. In order to allow some comparability, this treatment time was also selected for the PDD plasma. The contradictory results in the macroscopic, tactile-determined roughness could be clarified by AFM measurements. Both PDD and low-pressure plasma lead to nanostructuring of the PEEK surface with simultaneous degradation of raised areas on the surface, which reduces the macro-roughness. SEM images also show that the topography of the PEEK surface has been slightly smoothed, but larger defects or topographies remain, as can be seen in the PDD plasma image. In general, it can be seen that the performance of the PDD plasma is slightly lower than that of the low-pressure plasma. However, considering its low electrical power and extreme flexibility in application, it is still a promising modification method. The wetting enhancement on PEEK should be sufficient to successfully apply strong adhesive bonds or coatings/veneers after treatment. Nanostructuring of polymeric surfaces should also have a significant positive impact on these applications [17,18]. There might also be useful applications for the surface smoothing effect, for example, as supplement to the polishing of gingiva-near abutment areas, where the biocidal effect of the plasma could be additionally beneficial. But also on dentin, the PDD plasma results in a significant wetting improvement. The contact angle can be reduced by more than 20° using atmospheric PDD plasma, and the surface energy of the material is also increased considerably. Interestingly, similar results were obtained on moist dentin without plasma treatment. This is most likely due to the multiphase structure of dentin, which has—in addition to hydroxyapatite—a network of collagen fibres. It is assumed that part of the water seeps into this network, leads to swelling during moistening and thereby improved wettability. One difference between moist and plasma-treated dentin, however, becomes apparent in the surface energy. As in the case of PEEK, the plasma treatment of dentin reduces the disperse fraction while, at the same time, greatly increasing the polar fraction. This is more than doubled, from

19.7 mN/m to 45.7 mN/m. Comparing the results with those published in the literature suggests that longer treatment times and pure process gases could improve the wettability of dentin even further [17,19]. The wetted dentin, on the other hand, which was dried again directly before the measurement, showed both increased disperse and polar fractions, which were present in a 1:1 ratio. Plasma treatment of this surface with PDD plasma further increased the polar fraction, while the disperse fraction remained unchanged, resulting in the highest surface energy of 62.6 mN/m determined in the course of this series of tests. It must be assumed that the higher disperse fraction compared to the reference and PDD-plasma-modified samples is related to the prior wetting of the sample. The influence of stored water is unlikely since, in the course of the plasma treatment, the sample was dried and warmed up to lukewarm. Nevertheless, water seems to have an influence on the process of the plasma treatment and the resulting ionized particles probably lead to an altered surface chemistry. It is also plausible that evaporation residues, which interact with the activated plasma-treated surfaces, are responsible for the improved wettability [12]. It should be noted that the treatment of dry and wet dentin results in similar surface energies, which, however, differ in their polar and disperse fractions. The resulting water contact angle is also different. The positive effect of plasma-activated water (PAW) could also be responsible for the low contact angles and high surface energies of the wet plasma-treated dentin samples. The literature provides numerous examples showing that plasma treatment in water produces numerous reactive species [12,20–22]. These result in the water taking on an acidic character, which could result in an etching effect. A further targeted promotion of the effect might make it possible to expose the dentin channels even without phosphoric acid. Nevertheless, it must be emphasized that no clear negative influence was found, but the possibly deviating surface chemistry must be taken into account in further application tests [5,11,17]. Unfortunately, a comparison of the wetting behaviour with the status quo method of etching was not possible, since no graphically evaluable contact angles were available. However, the reason is not the extreme wetting improvement by etching, but the exposure of the dentin tubules in the material (see SEM images in Figure 5). This results in water interpenetration within the tubules during droplet deposition and thus falsified contact angle measurements. A direct comparison of etching and PDD plasma was therefore unfortunately not possible. The opened tubules are also partly responsible for the increased roughness on the etched dentin surfaces [13,19]. Plasma treatment, on the other hand, has only a very limited influence on the topography of the dentin. Due to the material characteristics, plasma-etching processes are less intense and thus the amount of material removed is also less compared to polymeric surfaces. Nanostructuring could not be detected here. The determined difference between the topography of reference dentin and PDD-modified material is negligible, especially considering the manual grinding process without subsequent polishing of the surface. Concerning mechanical interlocking with dental bonding systems, the importance of the exposed dentin tubules should not be underestimated [9,23]. Adhesive flowing into them leads to strong mechanical bonding relatively independently of the wetting behaviour. Due to the apparent absence of nanostructuring on dentin, it cannot be assumed that similar mechanically interlocked bonds can be achieved on plasma-treated dentin [13,16]. However, the modified surface chemistry and the resulting improvements in bond strength could possibly compensate for this disadvantage.

5. Conclusions

The investigations carried out indicated that the use of PDD plasma on dental materials such as PEEK and human dentin results, in all cases, in a definite improvement in wettability. The influence of the operating distance on the resulting wettability improvement is small enough to allow reproducible results even with manual guidance of the device during a chair-side application. The comparison with the superior low-pressure plasma treatment, however, shows less effectivity. Nevertheless, the improvement in wetting seems considerable enough, and longer treatment periods could bring it even closer

to the level of low-pressure treatment. That the results of the analyses on moist dentin evidenced no reduction of plasma efficiency with regard to improved wettability is particularly interesting, as this case represents a real-life situation during chair-side application. However, the measurements on dentin show that the alteration of surface topography, as a secondary effect of plasma treatment besides improving the wettability, is strongly substrate-dependent, resulting in a nanostructuring of the rather soft PEEK surface and no visible alteration of the harder dentin. This almost unchanged roughness of the dentin surface after plasma treatment appears to be a clear disadvantage of the process compared to etching, which is currently conveniently applied prior to bonding processes. Subsequent studies on the bonding strength of dental adhesive systems to etched versus plasma-treated dentin surfaces should follow, in order to further assess whether etching could possibly be replaced by the less harmful PDD plasma treatment. If it turns out that the majority of dental bonding systems fail without mechanical anchorage in the dentin tubules, the bonding strength and/or susceptibility to failure of the process could be further improved by an additional plasma treatment. Furthermore, parameter and device adjustments could be investigated to promote the etching effect the PDD plasma provides in order to reliably reveal the dentinal canals.

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