Plasma Sci. Technol. **20** (2018) 044010 (8pp) https://doi.org/10.1088/2058-6272/aaa6be

Influences of the cold atmospheric plasma jet treatment on the properties of the demineralized dentin surfaces

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Received 2 November 2017, revised 9 January 2018
Accepted for publication 9 January 2018
Published 1 March 2018

Abstract

Improvement of the bonding strength and durability between the dentin surface and the composite resin is a challenging job in dentistry. In this paper, a radio-frequency atmospheric-pressure glow discharge (RF-APGD) plasma jet is employed for the treatment of the acid-etched dentin surfaces used for the composite restoration. The properties of the plasma treated dentin surfaces and the resin–dentin interfaces are analyzed using the x-ray photoemission spectroscopy, contact angle goniometer, scanning electron microscope and microtensile tester. The experimental results show that, due to the abundant chemically reactive species existing in the RF-APGD plasma jet under a stable and low energy input operating mode, the contact angle of the plasma-treated dentin surfaces decreases to a stable level with the increase of the atomic percentage of oxygen in the specimens; the formation of the long resin tags in the scattered clusters and the hybrid layers at the resin–dentin interfaces significantly improve the bonding strength and durability. These results indicate that the RF-APGD plasma jet is an effective tool for modifying the chemical properties of the dentin surfaces, and for improving the immediate bonding strength and the durability of the resin-dentin bonding in dentistry.

Keywords: high-frequency and RF discharges, plasma-material interactions, plasma dentistry

(Some figures may appear in colour only in the online journal)

1. Introduction

Cold atmospheric plasmas (CAPs) have attracted much attention from researchers due to their unique features, such as low gas temperatures, abundant chemically reactive species and flexible operations with the removal of vacuum system, and have bright application prospects in the fields of bio-medicine, advanced materials synthesis and modifications, energy saving and environmental protection, etc. Among the preceding CAP applications, biological and medical applications of the CAPs have become one of the research focuses in the interdisciplinary fields of plasma physics and chemistry, biochemical engineering, medical science and clinical operations [1–3]. As one of the most three promising application fields in plasma medicine at the present time, i.e., cancer therapy, dermatology and stomatology, study of the CAPs in dentistry can also be regarded as a miniature of the plasma medicine, including indirect applications of CAPs for the surface modifications of biomedical materials, and direct applications of CAPs for the medical therapy [2, 3]. Recent studies have shown that the CAP treatment can be regarded as an effective and clean method for producing the micro- or nano-scale structures on the biomaterials or implants [4, 5].

In dentistry, because of its good aesthetic property and biocompatibility, composite resin is gradually replacing dental

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amalgam and becoming the preferred form of the restorative materials. However, the effect of composite restorations is not satisfactory in longevity [6]. How to improve the bonding strength between the dentin surface and the composite resin is still a challenging job for the resin–dentin bonding [7]. As is known, it is the fundamental principle of the dentin bonding to form a uniform hybrid layer [8]. Therefore, it would be very helpful to achieve a better resin-tooth hybridization by improving the dentin surface properties and employing the high hydrophilic dental adhesives.

CAP, as a partially ionized gas operating at an open environment, has various chemically reactive species including atoms, molecules, ions, electrons and free radicals, and can act on the surface of the biological materials leading to surface modifications, e.g., etching, deposition, or grafting, etc [9, 10]. Recently, the CAPs have been used for the treatment of the dental-composite restoration [11, 12]. Current studies showed that a short CAP treatment could change the chemical structures of the exposed collagen fibrils and increase the hydrophilicity of the dentin surface [13, 14]. Several studies have also reported that the cold plasma treatment of demineralized dentin surfaces could improve the resin–dentin bonding [11, 15]. However, since the dentin collagen fiber is very sensitive to temperature, degeneration and degradation may occur on the surface of the collagen fibers when the heat is accumulated inside the collagen fiber to a certain threshold level. For example, the plasma treatment time was limited to a very short time (e.g., less than 30 s) and with a scanning operation mode in [16]. Therefore, it is of great importance to select an appropriate CAP source to control effectively the gas temperature of the plasmas so as to meet the requirements for the treatment of the temperature-sensitive biological materials, e.g., the collagen fiber studied in this paper. To our knowledge, AP-DBD plasma is one of the most popular plasma sources used for modifications of the dentin surfaces [17, 18]. However, a filamentary discharge may occur which would cause thermal damages due to the local high gas temperature inside the filaments [19]. Chen *et al* [13, 20] employed a non-thermal argon discharge plasma jet driven by a direct-current power supply for the plasma dentistry applications. However, the gas temperature in the plasma jet region was higher than the room temperature, e.g., 38 °C in [20], which might lead to heat accumulation inside the samples during plasma treatment. In our previous studies, a radio-frequency, atmospheric-pressure glow discharge (RF-APGD) plasma jet using a water-cooled, bare-metallic electrode configuration has been developed for the genome mutation of micro-organisms [1, 21]. Our studies showed that the RF-APGD was a uniform glow discharge with no filaments, and the gas temperatures were low and controllable by adjusting the operating conditions appropriately [21–24]. In this study, by adjusting the RF power input and the temperature of the plasma working gas at the inlet of the plasma generator, the gas temperature of the plasma jet can be controlled at a little bit lower level than the room temperature, which means that the heat accumulation inside the treated samples can be avoided during the plasma treatment process. Based on this, the major purpose of this study is to investigate the influences of the RF-APGD plasma jet treatment on the surface modifications of the temperature-sensitive collagen fibers under the specific operating conditions of the discharges, including the discharge features of the RF-APGDs, the adhesion of the resin composite to the dentin and the durability of the bonds.

2. Methods and materials

The teeth used in this study are extracted non-carious, unerupted human third molars, which are stored at 4 °C in the phosphate buffered saline containing 0.02% sodium azide. The storage period is less than one month before use. These molars are collected after obtaining the patients' informed consent under a protocol approved by the Peking University School of Stomatology Institutional Review Board (PKUSSIRB-201522043).

2.1. Dentin specimen preparation

The occlusal one-third of the crown is removed by means of a water-cooled low-speed Isomet saw (Buehler Ltd, Lake Bluff, IL, USA). Each prepared mid-crown dentin surface is examined under a microscope (SMZ 1500, Nikon, Japan) to make sure that it is free of enamel. Then, the uniform smear layers are created by wet-sanding the dentin surfaces with a 600-grit silicon carbide sandpaper for 1 min. And then, the prepared dentin surfaces are acid-etched with 32% H_3PO_4 gel for 15 s (Uni-etch BAC 32%, Bisco Inc., Schaumburg, IL, USA), rinsed with water for 15 s and kept wet until the plasma treatment.

2.2. Plasma jet treatment

In this study, the RF-APGD plasma jet is used for the treatment of the dentin samples, as shown in figure 1. The detailed descriptions on the experimental setup can be referred to [21]. The operating parameters for producing the uniform, low temperature plasma jet are as follows: the driving frequency of the power supply $f = 13.56$ MHz, the RF power input $P_{in} = 15$ W, helium flow rate $Q = 4$ slpm. With the control of the temperature of the plasma working gas at the inlet of the plasma generator, the gas temperature at the plasma jet region can be kept at a little bit lower level than the room temperature, e.g., ~20 °C, in this study. Thus, under such operating conditions, the low temperature plasma jet action on the collagen fiber surfaces will not lead to thermal damages to the samples during the plasma treatment process.

2.3. Scanning electron microscopy (SEM)

The untreated (negative control) surfaces and the surfaces after plasma jet treatment are observed in a field emission SEM (FEI, Helios Nanolab 600i, USA). The specimens are sputter-coated (Gatan, Model 681, USA) with a 7 nm-in-thickness of the Au–Pd alloy and observed at 15 mA for 85 s.

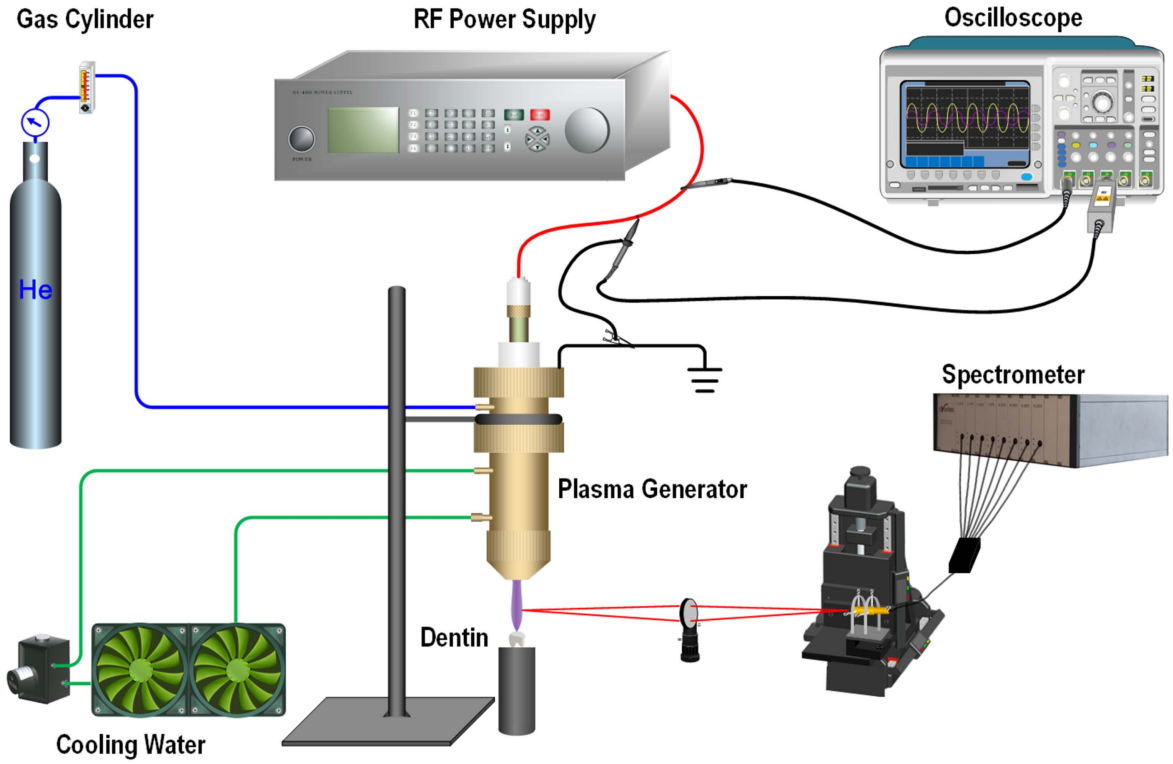

Figure 1. Experimental setup of the helium RF-APGD plasma jet for the treatment of the dentin surfaces.

2.4. Surface contact angle measurement

The wettability of surface to water is determined with the static contact angle measurements. The thickness and diameter of the prepared dentin discs are ~1.0 mm and ~10.0 mm, respectively. After the same procedure already described for the dentin specimen preparation, the etched dentin disks ($n = 30$) are randomly divided into five groups as described for the microtensile bond strength (MTBS) test groups in section 2.6. The contact angles of the surfaces in each group ($n = 6$) are measured immediately after plasma treatment using a contact angle goniometer (SL 200, USA Kino Industry, Norcross, GA, USA). All the measurements are conducted at three different locations on each disc with a 0.5 μl deionized water droplet dispensed on the sample surface each time. After dispensing the water droplet on the sample surface for 5 s, the droplet arc and the contact angle at the interface are traced and recorded.

2.5. X-ray photoemission spectroscopy (XPS) measurement

The chemical status of the surfaces is analyzed using the XPS (Quanten SXM ULVAC-PHI, Japan) with a monochromatic x-ray source for Al Ka producing photons with a 200 μm-in-diameter electron beam as an excitation source and a hybrid electron lens system. The spot checks are made and the sensitivity is at 3 M CPS. The wide scans are conducted for the measurements of the basic elements of tooth, including calcium, phosphorus, oxygen, nitrogen, carbon, silicon and sodium. In particular, The C 1s peak is adjusted to 284.6 eV with an energy resolution of 0.5 eV.

2.6. MTBS test

The teeth ($n = 20$) are randomly divided into five groups according to the plasma treatment parameters: (i) no plasma treatment (control), (ii) plasma jet treatment for 15, 30, 45, and 60 s. The specimens of the negative control group are blot-dried with the tissue paper (Kimberly-Clark, Roswell, GA, USA) after the acid-etching. The specimens with the plasma jet treatment are blot-dried with a moistened Kim-wipes tissue, and the acid-etched surfaces are then exposed to the RF-APGD plasma jet for different treatment times. After plasma treatment, the specimens are re-wetted with the deionized water before conducting the bonding procedures. The extra water is gently air-dried from the acid-etched dentin surfaces for 5 s. Subsequently, the dental adhesive (Adper Single Bond Plus, 3M ESPE, St. Paul, MN, USA) is applied, spread thinly with moisture-free air, and light-cured for 15 s using a visible light with an intensity of 800 mW cm^{-2} (Elipar FreeLight 2, 3 M ESPE). The resin composite (Clearfil AP-X, A2 shade; Kuraray, Japan) is then placed on top of the adhesive three or four times, and light-cured for 20 s after each operation. The tooth-composite bonded samples are stored in the distilled water at 37 °C for 24 h before being cut into microbar specimens for the MTBS testing. The prepared teeth are sectioned using a water-cooled diamond saw to produce the microbar specimens with the approximate cross-section dimensions of 0.7 × 0.7 mm^2. The specimens of each group are further divided into two subgroups according to the MTBS testing time: one subgroup is immediately submitted to the MTBS test ($n = 32$), whereas another subgroup is stored for 1 year in 0.5% chloramine solution at 37 °C. The

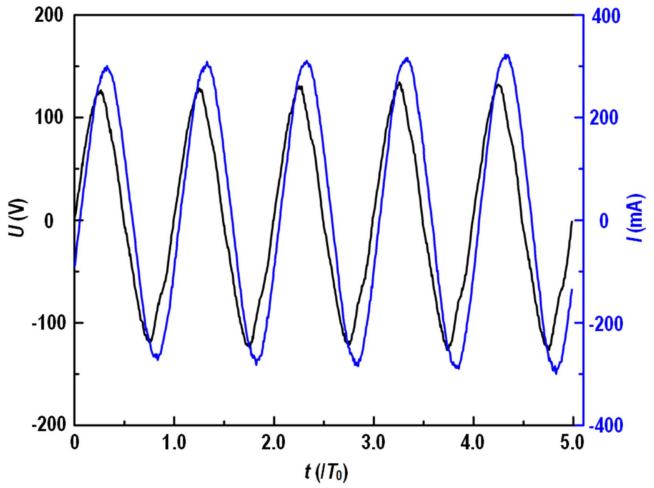

Figure 2. Waveforms of the discharge voltage and current of the helium RF-APGD plasmas ($Q = 4$ slpm, $P_{in} = 15$ W).

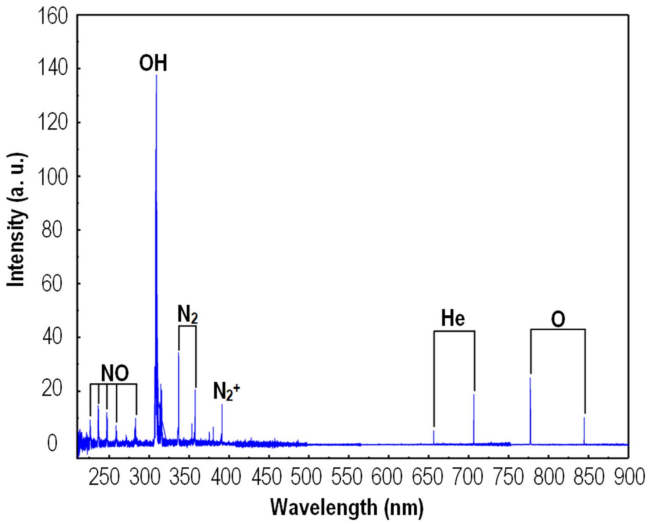

Figure 3. Optical emission spectrum of the helium RF-APGD plasmas ($Q = 4$ slpm, $P_{in} = 15$ W).

microbar specimens are examined using an optical microscope (SMZ 1500, Nikon, Japan) to screen for possible defects at the adhesive-dentin interface. The specimens which pass the screening are adhered to a microtensile tester (Shimadzu, EZ-L, Japan) using a cyanoacrylate adhesive (RITE-Lok, SF600) and are tested at a strain rate of 0.5 mm min^{-1}.

2.7. Statistical analysis

The surface contact angles and the MTBS data are analyzed using a statistical software—SPSS (Version 21.0, IBM, Armonk, NY, USA). The values of MTBS obtained from the beams derived from each of the 4 teeth in every group (5 groups) are pooled together to obtain a mean bond strength value with each treated tooth as a statistical unit. The one-way ANOVA is used for the MTBS within different groups (before and after aging). The relative decrement of the MTBS before and after the artificial aging by thermocycling within the factor of plasma treatment is also analyzed using the one-way ANOVA. Multiple comparisons are analyzed using the Bonferroni method. The analyses are performed at a significant level of $\alpha = 0.05$.

3. Results and discussions

3.1. Characteristics of the RF-APGD plasma jet

The waveforms of the discharge voltage and current of the helium RF-APGD are shown in figure 2 using the high-purity helium (99.9995%) as the plasma working gas, where T_0 is the period of the RF power supply. The root-mean-square (rms) values of the discharge voltage and current are $V_{rms} = 93.0$ V and $I_{rms} = 237$ mA, respectively. It is seen from figure 2 that: (i) the waveforms of the discharge voltage and current are very close to the sinusoidal from with a current–voltage phase difference of 35.6° which shows a capacitive nature of the discharge. (ii) There are no obvious sharp peaks for the current waveforms in a cycle which, to some extent, indicates that the discharges are uniform glow discharges with no micro filaments. This has also been verified by the iCCD images [25].

Figure 3 presents the optical emission spectrum of the helium RF-APGD plasma under the same operating parameters as those in figure 2. It shows that a great number of ions and radicals are produced during discharges. Since the discharges operate in an open environment as illustrated in figure 1, not only the helium species exist in the plasma region, but also the chemically reactive species containing the OH, O and N elements, such as the hydroxyl (·OH) band at 300–310 nm, the atomic oxygen at 777 and 844 nm, and NO at 200–300 nm, and the nitrogen emission lines between 330 and 420 nm [3, 26] due to the back-diffusion effect of the surrounding air into the discharge region [27]. The interactions between the plasma main stream and the entrained cold gas produce the reactive oxygen species (ROS) and reactive nitrogen species (RNS) [28, 29]. It is anticipated that these chemically reactive species would play an important role during the interaction processes between the plasma jet and the treated biomaterials. As a preliminary study, here we just use the optical emission spectrum to identify the kinds of the chemically reactive species in the plasmas. It is indispensable to measure the concentrations of the chemically reactive species, especially those of ROS and RNS, in future studies.

3.2. Dental surface modifications

The changes in water contact angles for the dentin surfaces with different plasma treatment times are shown in figure 4. It is seen that the contact angle of a drop of water on the untreated etched dentin surface is 57.0° ± 4.8°. Treatments with the RF-APGD plasma jet for 15, 30, 45, and 60 s lead to a decrease of the water contact angles on the dentin surfaces to 44.8° ± 3.5°, 39.0° ± 3.8°, 41.8° ± 3.4° and 42.1° ± 3.9°, respectively. These differences are statistically significant compared to the control value ($P < 0.05$). Furthermore, extension of the plasma treatment time to 45 and 60 s does not result in a continuously

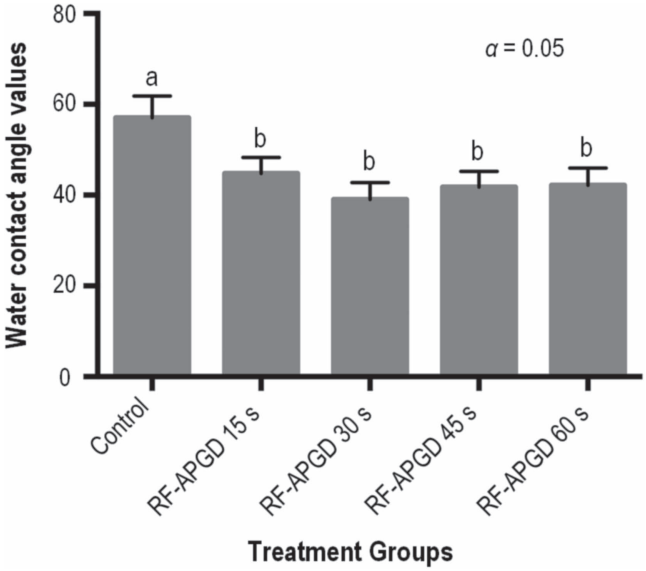

Figure 4. Averaged water contact angles on the slices for the untreated and plasma jet treated groups. The different letters in this figure indicate the statistically significant differences ($\alpha = 0.05$).

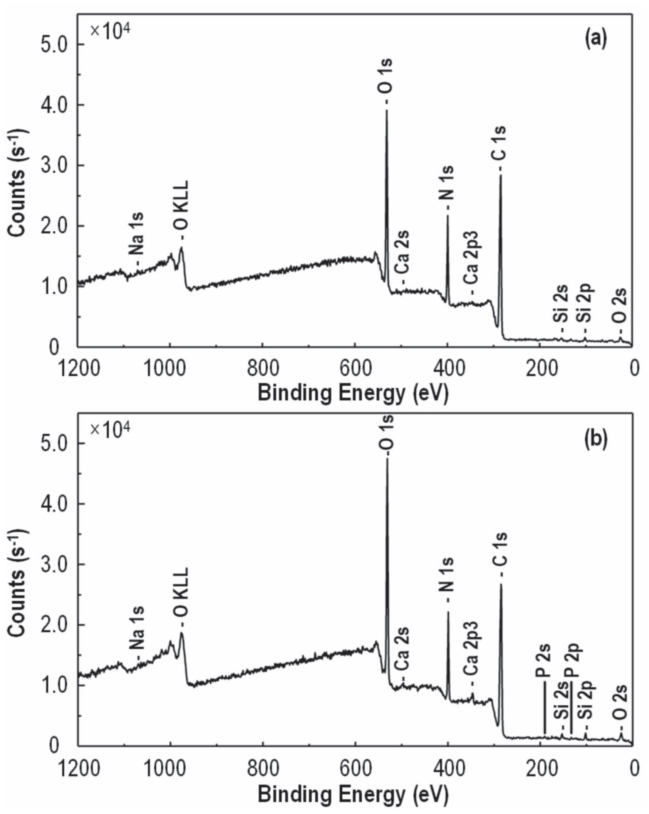

Figure 5. X-ray photoelectron spectra (XPS) of the demineralized dentins without (a) and with (b) 30-s RF-APGD plasma jet treatment.

Table 1. Chemical compositions (in atomic percentage of each element, %) in the demineralized dentin surfaces with and without plasma treatments.

Condition	Control (0 s)	Plasma treatment (30 s)
C (%)	62.96 (0.47)	58.77 (0.40)
O (%)	22.81 (0.79)	27.05 (1.01)
N (%)	13.12 (0.64)	12.23 (0.67)
O/C	0.36 (0.02)	0.46 (0.02)

Note. Values are given in the form of mean (SD).

significant decrease in the water contact angles compared with the cases of 15- and 30-s treatments. This is very different from the results reported in [16]. It was pointed out that the very high hydrophilicity might lead to the separation of different adhesive-phases, which affected the resin polymerization, and consequently, might lead to a poor adhesive durability [30]. In the present study, the hydrophilicity of the demineralized dentin surface is stabilized at about 40° with the extension of the plasma treatment time. The possible reasons may be explained as follows: on one hand, the free radicals or peroxide groups delivered to the exposed collagen fibrils during the plasma treatment process result in the improved hydrophilicity of the demineralized dentin surfaces [31]; while on the other hand, the low energy density levels of the RF APGDs slow down the grafting process of the functional groups.

The contact angle values rely on the chemical compositions of the substrates. The reasons for the increase in the hydrophilicity of the etched dentin surfaces after plasma treatment can be explained by the XPS results. Figure 5 provides the XPS wide-scan spectra for the specimens with and without the plasma jet treatments. It is seen that: (i) both groups show a common carbon contamination at 284.6 eV which is corrected by the program; (ii) after 30-s plasma treatment (figure 5(b)), the peak of C 1s (284.6 eV) decreases, while that of O 1s (533 eV) increases compared with their counterparts of the control (figure 5(a)). The quantitative atomic percentage concentrations for the demineralized dentin discs before and after the plasma jet treatments are listed in table 1. Averagely, the atomic percentage of carbon (C) decreases from 62.96% to 58.77%, while that of oxygen (O) increases from 22.81% to 27.05% after the plasma treatment; Correspondingly, the O/C ratio increases from 0.36 to 0.46. The XPS analysis suggests that the C-containing materials are removed, and simultaneously, the O-containing materials are introduced after the plasma treatment, which is qualitatively consistent with the results in [20, 32].

Dentin is composed of approximately 50% mineral in the form of a carbonate-rich calcium-deficient apatite, 30% organic matter mostly with the Type-I collagen, and approximately 20% water. Generally, the mineral is dissolved and replaced with water after the treatment with etchant. This means that water fills the inter-fibrillar space of the collagen network. It is known that plasmas can etch the surface and remove the organic substances by breaking the C–C and C–H bonds [33], especially with the presence of oxygen in the discharges [34]. Since the RF-APGD plasma operates in an open environment, there exist helium atom, hydroxyl (OH) and oxygenic groups in the plasma jet region (figure 3) due to the back-diffusion effect of the surrounding air into the discharge region [27]. The XPS narrow-scans of the C 1s spectra of the demineralized dentin surfaces are presented in figure 6

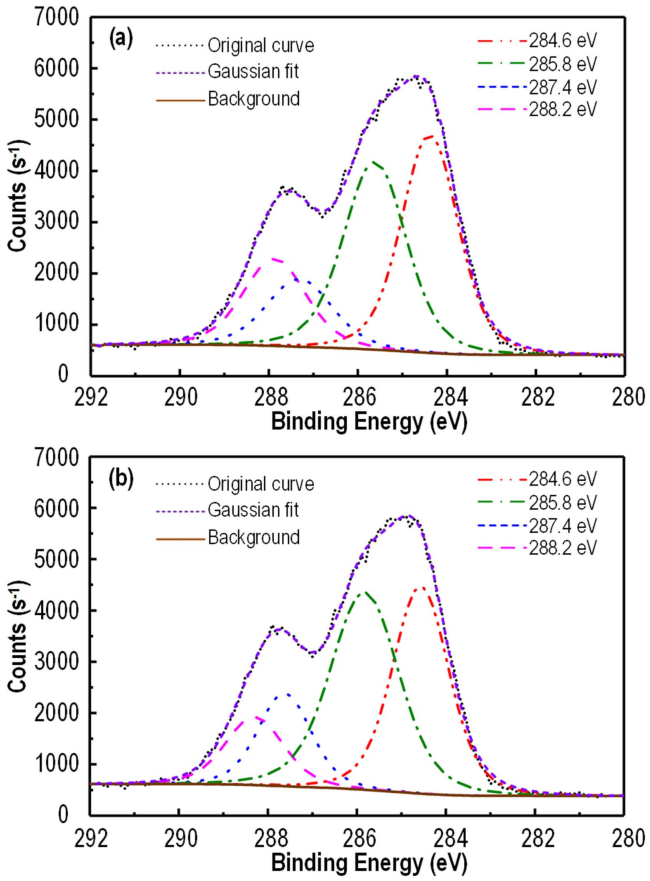

Figure 6. XPS narrow-scan spectra for the C 1s region of the demineralized dentin surfaces without (a) and with (b) 30-s RF-APGD plasma jet treatment. The black line represents the original line of the narrow-scan spectrum of the C 1s region, while the purple and brown lines represent the corresponding Gaussian fit curves and the background spectra after deconvolution. The four peaks stand for the C–C peak (284.6 eV, red line), C–O peak (285.8 eV, green line), C=O peak (287.4 eV, blue line), and the carbonate group (O–C=O) peak (288.2 eV, pink line).

for the cases with and without plasma jet treatment. As shown in figure 6, the C 1s peaks can be divided into four component peaks, which correspond to four carbon-containing groups: C–C (284.6 eV), C–O (285.8 eV), C=O (287.4 eV), and O–C=O (288.2 eV). It is shown in table 2 that after 30-s plasma treatment, the C–C content decreases from 29.70% to 26.07%. At the same time, the content of C–O increases from 27.13% to 30.88%; while for the other oxygen-containing components, C=O and O–C=O, the variations of their contents are not obvious after the plasma jet treatment. This phenomenon may be explained as follows: the OH and oxygenic groups in the plasma jet region mainly react with the carbon-containing group of C–C in the plasma-treated matrix, leading to an obvious increase of the C–O group as the oxidized carbon after plasma treatment. Simultaneously, the ROS introduced the polar functionality to the substrates, which may explain the increase of the hydrophilicity of the demineralized dentin after plasma treatment.

Table 2. Peak assignment (eV) and envelope composition (%) of various C 1s core level spectra of the demineralized dentin surfaces before and after the RF-APGD plasma treatments.

	C 1s peak assignment (eV)			
Sample	284.6 C–C	285.8 C–O	287.4 C=O	288.2 O–C=O
	Envelope composition (%)			
Before	29.70	27.13	21.08	22.09
After	26.07	30.88	21.48	21.57

3.3. Morphology of the resin–dentin bonding interface

The penetration of the adhesive into the demineralized dentin is observed using the SEM as shown in figure 7. The morphologies of the specimens after 30-s plasma treatment indicate the well-formed resin tags with a maximum length of ~50 μm in the scattered clusters (figures 7(b) and (d)), which is much longer than those of the untreated specimens, i.e., ~20 μm as shown in figures 7(a) and (c). These resin tags form the anchors penetrating deeply below the demineralized dentin surfaces. Thus, to some extent, it improves the mechanical properties of the bonding interface. Furthermore, the hybrid layer plays a pivotal role in maintaining the longevity of the resin and dentin bonding. Pashley *et al* [35] reported that the dentin permeability influenced the quality of the resin–dentin bonds, e.g., the strength and durability. In this study, the hybrid layer in the specimens treated by the RF-APGD plasma jet for 30 s is about 5.5–6.5 μm as shown in figure 7(d), which is much thicker than that in the control specimens (2.0 μm) (figure 7(c)). In addition, Armstrong *et al* [36] and Spencer *et al* [37] have shown that the well-infiltrated adhesive resin tags decreased the occurrence of the nanoleakage and the resist bacterial attacks, which could improve the bonding strength. Therefore, the current results suggest that the RF-APGD plasma jet treatment might be able to increase the resin–dentin bond strength and durability through enhancing the adhesive penetration. This is verified by the MTBS data presented in table 3 to be discussed in the next sub-section.

3.4. Durability of the resin–dentin bonding

Table 3 shows a statistical comparison of the MTBS values for all the tested groups at 24 h after plasma jet treatment and after aging storage for 1 year. It shows that: (i) the bond strength is higher for all the RF-APGD plasma jet treatment groups than that of the controls before or after storage for 1 year ($P < 0.05$). (ii) After aging, the mean bond strength of the 15- and 30-s plasma treatment groups show the lower decreases (9.7% and 9.5%, respectively) from their corresponding original values; while the control group has a significant decrease of 35.8% compared with its original mean bond strength with the lowest bond strength of 30.4 ± 2.0 MPa after the 1-year aging ($P < 0.05$).

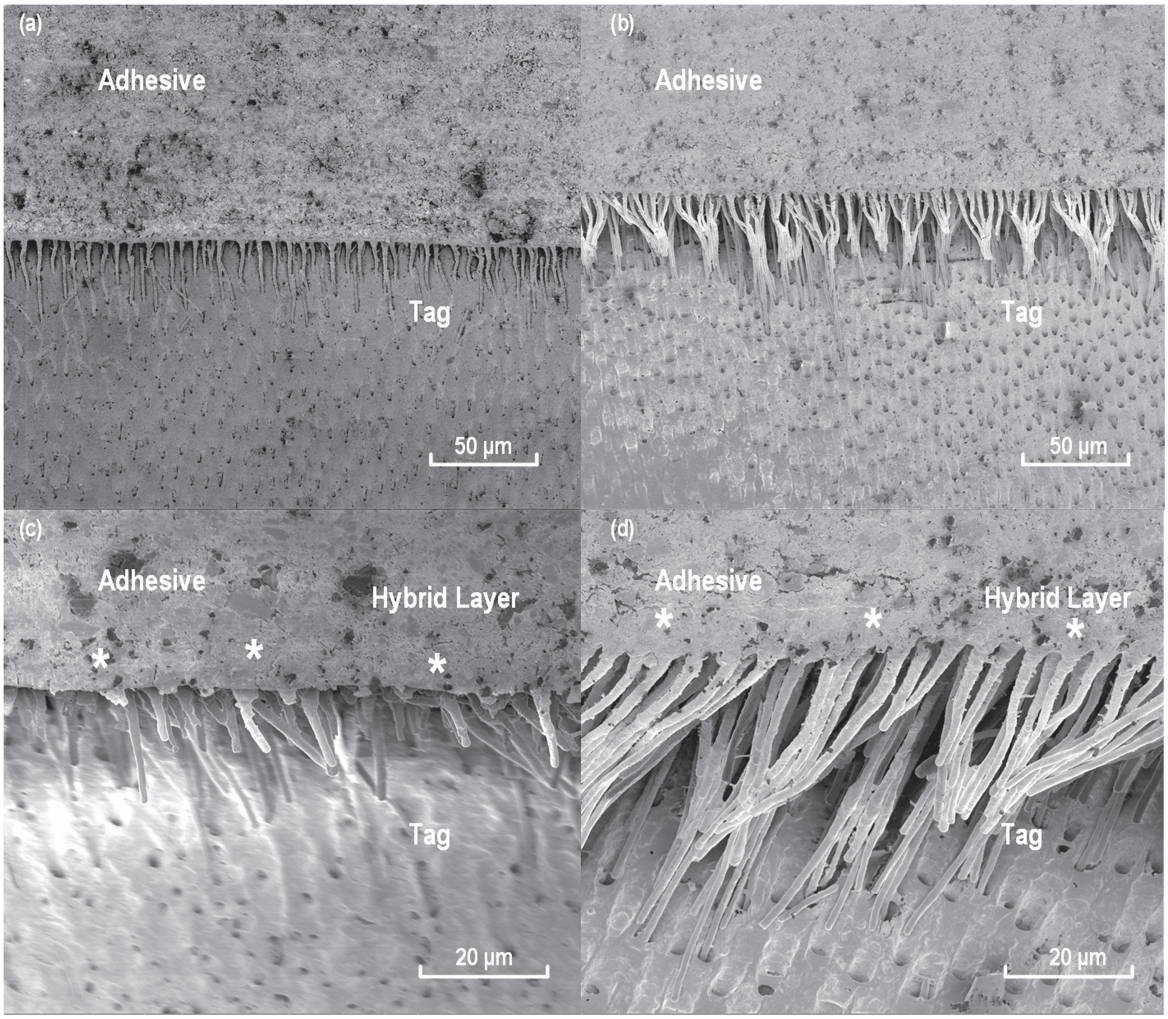

Figure 7. Typical SEM micrographs of the adhesive-dentin interface for the specimens without (a), (c) and with (b), (d) the 30-s RF-APGD plasma jet treatment. The asterisks designate the hybrid layer.

Table 3. MTBS data (in MPa) of the resin composite to the dentin surfaces measured at 24 h after plasma treatment and after 1-year water storage.

Groups		At 24 h ($n = 32$)	After 1 year (water storage, $n = 32$)
Control		47.4 (1.9)^{A}	30.4 (2.0)^{A}
RF-APGD plasma	15 s	53.7 (1.4)^{B}	48.5 (1.6)^{B}
	30 s	61.9 (1.5)^{C}	56.0 (1.8)^{C}
	45 s	61.0 (1.8)^{C}	54.6 (1.8)^{C}
	60 s	57.7 (1.4)^{D}	51.1 (2.3)^{D}

Notes. Values are given in the form of mean (SD). The mean values with the same superscript letter indicate no significant differences within the same column.

4. Conclusions

In this study, the RF-APGD plasma jet is employed for the treatment of the acid-etched dentin surfaces used for the composite restoration. The experimental results indicate that the RF-APGD plasma jet provides an effective opportunity to modify the chemical properties of the etched dentin surfaces and to improve the mechanical properties of the resin–dentin bonding. The major conclusions are as follows:

(1) The uniform RF glow discharge plasma jet with low energy input and abundant chemically reactive species, e.g., OH free radicals, ROS and RNS, is an appropriate tool for enhancing the resin–dentin bonding strength and durability in dentistry.
(2) The contact angle of the plasma-treated dentin surfaces decreases due to the variations of the chemical compositions in the dentin surfaces with plasma treatment, and approaches a stable level possibly resulting from the appropriate energy density levels of the RF APGDs. This is helpful for lengthening the resin–dentin adhesive durability.
(3) The RF-APGD plasma jet treatment provides one of the major prerequisites for improving the resin–dentin bonding strength, i.e., formation of the uniform and thick hybrid layers and long resin tags into the collagen layers.

Acknowledgments

This work has been supported by National Natural Science Foundation of China (Nos. 11475103 and 81200805) and Beijing Natural Science Foundation (No. 7162204).

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