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Surface modification of several dental substrates by non-thermal, atmospheric plasma brush

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Abstract

Objective—The purpose of this study was to reveal the effectiveness of non-thermal atmospheric plasma brush in surface wettability and modification of four dental substrates.

Methods—Specimens of dental substrates including dentin, enamel, and two composites Filtek Z250, Filtek LS Silorane were prepared (~2 mm thick, ~10 mm diameter). The prepared surfaces were treated for 5–45 s with a non-thermal atmospheric plasma brush working at temperatures from 36 to 38 °C. The plasma-treatment effects on these surfaces were studied with contact-angle measurement, X-ray photoemission spectroscopy (XPS) and scanning electron microscopy (SEM).

Results—The non-thermal atmospheric argon plasma brush was very efficient in improving the surface hydrophilicity of four substrates studied. The results indicated that water contact angle values decreased considerably after only 5 s plasma treatment of all these substrates. After 30 s treatment, the values were further reduced to <5°, which was close to a value for super hydrophilic surfaces. XPS analysis indicated that the percent of elements associated with mineral in dentin/enamel or fillers in the composites increased. In addition, the percent of carbon (%C) decreased while %O increased for all four substrates. As a result, the O/C ratio increased dramatically, suggesting that new oxygen-containing polar moieties were formed on the surfaces after plasma treatment. SEM surface images indicated that no significant morphology change was induced on these dental substrates after exposure to plasmas.

Significance—Without affecting the bulk properties, a super-hydrophilic surface could be easily achieved by the plasma brush treatment regardless of original hydrophilicity/hydrophobicity of dental substrates tested.

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Keywords

non-thermal plasmas; contact angle; wettability; dental surfaces; composites

1. Introduction

In dentistry, most joints consist of two adherends (the term adherend refers to either an initial substrate or substrate being bonded to). For most of dental joints, one set of adherends could be any dental substrates such as enamel, dentin, cement, residual amalgam or composite from a previous restoration, or an implant; the other set of adherends could be restorative ones such as composite, amalgam, or ceramics. Generally, good adhesion is critical in effectively creating these dental joints between the substrates.

Good dental adhesion entails a supreme contact between the adhesive and the adherend surface [1]. To establish the adhesion, the adhesive material must spread impulsively across the entire adherend surface, or optimal wettability of the substrate is necessitated with reference to that adhesive [2]. However, the adhesive is not always well-matched to the wettability of the certain adherend surface. For example, a hydrophobic material generally does not provide intimate contact with a hydrophilic substrate. Enamel or wet dentin surfaces are commonly hydrophilic while most composites are comparatively hydrophobic. Offering satisfactory wettability for both of the distinct substrates certainly poses a big dilemma for dental adhesives. Surface modification or engineering for wettability enhancement is needed to improve adhesion between these substrates. For example, in an etch-and-rinse adhesive system, phosphoric acid is usually employed to improve the wettability, elevate the surface free energy, and increase the roughness of the dentin or enamel surface [3]. The acidic primers play a similar role in a self-etching system [4]. Other efforts have also been made to improve the dental surface wettability, such as application of the HEMA primer [5], irradiation of the laser [6], and treatment of sodium hypochlorite [7].

In the field of surface modification/engineering, many methods have been employed to alter the substrate to improve the surfaces properties such as adhesive ability, wettability, biocompatibility, permeability [8–13]. These conventional methods include mechanical abrasion, wet chemical treatment, exposure to flame and heating in oxidative environment. Although they have been widely used for years, there are always some adverse factors. For example, the abrasion method may greatly alter the surface morphology, or the wet chemical treatment may require a complicated procedure and leave a large amount of harmful wastes. Plasma surface treatment/modification has turned out to be a well-accepted method since it offers superior surface property enhancement than other chemical methods. Compared to these methods, the newly developed plasma surface engineering is “clean” and “effective”, while the bulk properties of the materials can be un-altered or well-maintained after the plasma treatment.

Plasmas are considered as “the 4th state” of matter and occur naturally in the sun, star, auroras and lightning bolts, containing a large amount of highly reactive species including ions, electrons, free radicals and electronically excited neutrals. Once being exposed to plasmas, the surface properties of the substrates would be modified as a result of the “bombing” of these excited species. The temperature of the plasmas can reach as high as 10,000 K (so called “thermal plasmas”), while that of “non-thermal plasmas” can be as low as 300 K [14]. Non-thermal gas plasmas are partially ionized gases that contain the above reactive particles, while the gas phase remains near room temperature. Depending on the plasma chemistry or gas composition, these highly reactive plasma species react with, clean, and etch surface materials, or otherwise modify the surface of plastic, metal, or ceramic

materials to improve their bonding capabilities or achieve totally new surface properties [15, 16]. This non-thermal feature has led to enormous successes of plasma techniques in surface engineering and modification of solid state materials, especially in plasma cleaning, plasma etching, surface engineering for adhesion enhancement, and biomaterial development [15–17].

Non-thermal atmospheric plasma technologies developed and improved over the past decade make it possible to investigate their applications for *in vivo* medical treatment. Because the gas phase can be controlled at or close to room temperature, plasma treatment of a biological system is not due to heat but the controllable plasma reactive species. The patented non-thermal atmospheric plasma brush, developed in our plasma research center, can be ignited and sustained in an ambient atmosphere, at very low power consumption (several watts), with temperatures close to that of the human body. Previous studies indicate that this brush was highly effective in oral bacterial disinfection [18], interfacial bonding improvement of composite restorations [19], and inducing dental adhesive polymerization [20]. In this study, the surfaces of human dentin, enamel, as well as two commercial dental composites were modified to alter wettability by the non-thermal argon plasma brush with different parameters. Good wettability of a dental surface is very important in adhesion improvement of dental restorations. With optimal wettability, the adhesives can easily spread on the dental substrates, enhance adhesion. Contact angle measurements, X-ray photoelectron spectroscopy (XPS or ESCA), and scanning electron microscopy (SEM) were employed to characterize the plasma-modified surfaces. The null hypothesis tested was that the wettability (reflected in contact angles) and surface chemistry of all four substrates would not be changed after short period (< 1 min) plasma treatment.

2. Materials and methods

2.1 Specimen preparation

Extracted non-carious human third molars were collected after the patients' informed consent was obtained under a protocol approved by the University of Missouri-Kansas City adult health sciences institutional review board. The teeth were stored in 0.9% w/v phosphate buffered saline (PBS) containing 0.002% sodium azide at 4°C, and the storage period was less than 1 month before use. The roots of molars were removed to 2–3 mm below the cemento-enamel junction (CEJ) using a water-cooled low-speed diamond saw (Isomet, Buehler Ltd, Lake Bluff, IL, USA). The teeth were then adhered to aluminum stubs using a cyanoacrylate adhesive (Zapit, Dental Ventures of America, Corona, CA). To make a dentin disc, the occlusal one-third to one-half was removed using the same water-cooled diamond saw until all enamel was removed from the resulting dentin surface (as determined by reflective light microscopy). The second cut was made perpendicular to the long axis to produce a slice with a thickness of ~2.0 mm and a diameter of ~10 mm. To make an enamel disc, two similar cuts were also performed; but for the first cut, the occlusal one-fourth to one-fifth was removed to make sure that only enamel was shown on the resulting surface. The dentin and enamel discs (~10 mm in diameter) were polished with 600-grit SiC sandpaper (Buehler Ltd) under water for 30 s, and then washed using ultrasonic cleaning for 5 min in deionized water to remove any possible debris. These discs were stored in ambient atmosphere (temperature ≈ 20°C, relative humidity ≈ 15%) for 24 hours to be naturally dried.

Two different commercial dental composites were employed in this study. The Filtek™ Z250 (Z250) was BIS-GMA based, and the Filtek™ LS (LS) was silorane-based (both were from 3M ESPE Dental Products, St Paul, MN, USA). The chemical composition of these two composites is shown in Table 1. Each composite was injected into a polytetrafluoroethylene mould of 10 mm in diameter and 2 mm in thickness, covered with a

Mylar film (Fisher Scientific, Pittsburg, PA, USA) and light cured by a conventional dental light polymerization unit (Spectrum Light, DENTSPLY, Milford, DE, USA) at an output power of 550 mW/cm² for a period of time according to its instructions (Z250: 20 s; LS: 40 s). After curing, the mould and the film were removed. The specimens were polished with 600-grit SiC sandpaper (Buehler Ltd) under water for 30 s, and then cleaned in deionized water using ultrasonic cleaning for 5 min to remove any possible debris. The composite discs were stored in ambient atmosphere accompanied with the dentin/enamel discs for 24 hours to be naturally dried.

2.2 Non-thermal atmospheric plasma brush

The non-thermal atmospheric plasma brush employed in this study was designed by the Plasma Research Center at University of Missouri and Los Alamos National Laboratory. The detailed information about this device can be found in previous publications [21, 22]. Compressed argon gas (ultra high purity) was used as the plasma gas supply. A MKS mass flow controller (MKS Instruments Inc., Andover, MA, USA) was introduced to adjust the argon gas flow rate. A glow discharge by the direct current power source (Model 1556C, Power designs Inc, Westbury, NY, USA) was ignited between the two electrodes in a walled, Teflon chamber (Fig. 1A). One of the electrodes was attached to a ballasted resistor which controls the discharge current. The other electrode was grounded for electrical safety. The formed plasma discharge could be blown out of the chamber to create a brush-shaped non-thermal plasma jet, which was generated in about 2 s after turning on the power. Fig. 1B shows a photograph of the plasma brush on a tooth in the atmospheric environment. Plasma temperatures were characterized by a type K thermocouple and infrared imaging.

The above dried dentin, enamel and composite discs were divided into different treatment groups, respectively, with 6 discs in each group. Every specimen was examined carefully under an optical microscope to avoid any micro fissure or defect on the surface before use. Each of the naturally dried discs was placed on a stage at a distance of 2 mm between plasma brush and specimen surface. The argon flow rate was fixed at 2000 sccm, at which the length of the brush was about 6–8 mm with plasma temperature at less than 38°C. The input power (5 and 10 W) and treatment time (5, 15, 30, 45 s) were varied.

2.3 Surface contact angle measurement

The wettability of the surfaces to water was determined with static contact angle measurements. Right after plasma treatment, the contact angles of the surfaces in each group (n=6) were measured by using a contact angle goniometer (A-100, Ramé-hart Inc., NJ, USA). Right above the specimen stage was the tip of a syringe that could be set to dispense a predetermined amount of water. Each time 0.5 µL deionized water droplet was dispensed on each surface. After the water was applied on the surface for 5 s, the droplet arc and the angle of contact (θ) at the interface were traced and recorded (Fig. 2). The contact angles of the discs were also tested and recorded before exposed to plasmas. The results were analyzed by one-way ANOVA and t-test ($\alpha=0.05$) by SPSS Version 11.0.

2.4 X-ray photoemission spectroscopy (XPS) measurement

The direct and instant chemical surface modification was measured using quantitative X-ray photoemission spectroscopy. The specimens were placed on graphite tape and XPS data were acquired using a Kratos AXIS HS electron spectrometer (Kratos Analytical Ltd., Manchester, UK) with an Al-K α X-ray source. All compositional measurements were acquired at surface normal with charge neutralization (binding energy shifts for charge compensation were unnecessary). For each specimen, a compositional survey scan was acquired using a pass energy of 80 eV and core level spectra with a pass energy of 20 eV. Two or more replicates of each specimen were analyzed and averaged to obtain the reported

atomic percent (at.%) values. Data analysis was performed with Vision Processing data reduction software (Kratos Analytical Ltd.) and CasaXPS (Casa Software Ltd, Teignmouth, UK). The concentration analysis was performed by integrating the cross-section-normalized Gaussian peaks of the relevant core levels both manually and by CasaXPS (Casa Software Ltd.), and the results were found to be within a maximum of 2% of each other; the CasaXPS values are reported.

2.5 Surface assessment using scanning electron microscope (SEM)

The un-treated and plasma-treated surfaces with different treatment times were observed in a Philips XL30 ESEM-FEG (Philips, Eindhoven, Netherlands). Specimens were sputter-coated (SCD050, Leica Microsystems GmbH, Wetzlar, Germany) with Au-Pd alloy and observed at a 5 or 15 kV accelerating voltage.

3. Results

The water contact angle changes on the dentin surfaces with different plasma treatment duration and input power are shown in Figure 3. The contact angle of a drop of water on un-treated dentin surface was $64.5 \pm 5.7^\circ$. After plasma treatment, the water contact angle values dropped dramatically. With a treatment time of only 5 s, the contact angles of water on dentin surfaces were decreased to $11.2 \pm 2.4^\circ$ (at 5 W) and $11.8 \pm 1.7^\circ$ (at 10 W), respectively. With a treatment time of 15 s, the values remained the same; but further decreased to $\sim 4^\circ$ after 30 s treatment. The values seemed to become relatively constant after 30 s of plasma treatment as there was no statistic difference between the 30 s and 45 s groups, regardless of an input power of 5 or 10 W ($P > 0.05$).

Since there was no difference in contact angles observed on the dentin surface as different input powers were applied, and longer treatment time (>30 s) was not necessary according to the contact angle values of dentin, the enamel and composite specimens were treated only at an input power of 5 W for 5 s and 30 s. The contact angle value of water dispensed on enamel and composite surfaces showed the same tendency as on dentin when being exposed to the plasma brush. Similarly, the values decreased considerably after only 5 s plasma treatment of these substrates. The water contact angle of enamel surface dropped from $24.0 \pm 5.5^\circ$ to $3.3 \pm 1.0^\circ$ after 30 s plasma treatment; For Z250 composite, it dropped from $46.0 \pm 1.3^\circ$ to $5.5 \pm 0.8^\circ$; and it dropped from $102.0 \pm 2.4^\circ$ to $4.0 \pm 1.3^\circ$ for LS composite after 30 s plasma treatment, respectively (Figure 4). These contact angles are close to values typical for super-hydrophilic surfaces.

XPS was carried out to analyze the atomic compositional changes of the surfaces before and after plasma brush modification. Representative XPS spectra of the Z250 composite surface before and after 30 s plasma treatment are shown in Figure 5. Before plasma treatment, the most dominant peak was associated with the C 1s peak located at 285 eV. After plasma treatment, this peak decreased, and the O 1s peak located at 533 eV became the foremost photoemission intensity. At the same time, the Si 2p spectral weight located at ~ 103 eV increased while the Zr 3d at 183.6 eV appeared. Quantitative atomic percent concentrations for all four substrates before and after plasma treatment are shown in Table 2. No Ar signal was detected after plasma treatment, indicating that no argon was integrated into the substrate surfaces. The atomic percent of carbon (at. %C) decreased in all plasma modified specimens: from 24.70% to 14.57% for dentin, 46.11% to 10.61% for enamel, 79.22% to 59.43% for Z250, and 78.89% to 46.96% for LS. The percent of nitrogen (at. %N) in both dentin and enamel also decreased after the plasma treatment. The atomic percent of the following elements increased after plasma treatment: Oxygen (O) in all 4 substrates; calcium (Ca) and phosphorus (P) in dentin and enamel; silicon (Si) and zirconium (Zr) in Z250; Si, yttrium (Y), and fluorine (F) in LS. The O/C ratio of all four substrates increased

dramatically according to the calculated results, suggesting that new oxygen-containing groups were formed on the surfaces after plasma treatment.

The surface morphology of the treated and untreated dental discs was observed by a scanning electron microscope. Representative SEM images of original and plasma-treated dentin surface are shown in Figure 6. No significant morphological difference can be seen among the surfaces with different times of exposure to the plasma brush, (Figure 6) although a little rougher surface was observed with a longer plasma treatment (e.g., 30 s). The results indicated that non-thermal plasma treatment did not induce much damage/etching to the surface under our experimental conditions.

4. Discussion

The results obtained by the non-thermal argon plasma treatment clearly showed that the excited argon neutrals were very efficient in the hydrophilicity modification of the dental surfaces. The results indicated that contact angle values decreased considerably after only 5 s plasma treatment of all these four substrates, further dropped after 30 s treatment. The argon-related species had a significant effect on the surface modification of the dental substrates without destructive effects. The null hypothesis that the surface wettability and chemistry of all four dental substrates would not be changed after short period (< 1 min) plasma treatment was rejected.

Contact angle evaluation has been widely used to measure surface wettability of different materials. Specifically, water contact angle is considered to be useful indication of the surface tension and to reflect the wetting of the substrate by water. High contact angles designate hydrophobic surface properties. The contact angle values rely on chemical composition of the substrates. Dentin is composed of 70 wt% inorganic material (mineral), 20 wt% organic material (collagen matrix), and 10 wt% oral fluids (mostly water). In contrast, enamel is a highly mineralized tissue composed of mostly hydroxyapatite mineral (~96 wt%), trace organic matrix (~1 wt%) and water (~3 wt%) [23]. Due to the difference in amount of organic material, the contact angle was dissimilar between dentin (~64.5°) and enamel (~24.0°), with dentin being more hydrophobic than enamel. Although wet dentin is considered to be hydrophilic, dry dentin is relatively hydrophobic. Similarly, the difference in hydrophobicity between the two composites was also attributable to compositional variance (Table 1). The silorane-based composite Filtek LS contains monomers combined of siloxane and oxirane moieties, which cure via cationic ring opening polymerization [24]. Due to the cyclosiloxane backbone, it is believed that siloranes may have much higher hydrophobicity as compared to conventional methacrylate-based composites [24]. The present result that Filtek LS demonstrated significantly higher contact angles (~102°) than Filtek Z250 (~46°) confirmed the assumption.

Although the baseline or original contact angle is reliant on chemical composition, the final contact angle after plasma brush treatment does not depend on the original composition. In our study, the water contact angles of all four dental substrates significantly dropped after only 5 s of exposure to plasmas. After 30 s treatment, the values were further reduced to <5°, which is close to a value for super hydrophilic surfaces. Based on the above results, such a super-hydrophilic surface could be easily achieved by the plasma brush treatment regardless of original hydrophilicity / hydrophobicity of dental substrates.

The reasons for capability of the non-thermal plasma brush to reduce contact angles in such a short time can be explained by the XPS results. The XPS analysis showed that after 30 s plasma treatment, the atomic percent of carbon (C) decreased for all four substrates, suggesting that the C-containing materials were removed by the treatment. It is known that

the plasmas are able to etch the surface and remove organic matter via breaking of C-C and C-H bonds. Polymeric matrix on the surface can be degraded into loosely-bonded oligomers, low-molecular-weight oxidized material, or even volatile species by plasmas [25]. Proteins can also be eliminated by plasmas through destruction and degradation [26]. However, low-pressure or thermal plasmas were used in those studies; our results indicated that the above phenomena could also occur under the non-thermal, atmospheric pressure plasmas within a very short time period. As a hybrid/composite material, dentin and enamel consist of inorganic mineral (mainly hydroxylapatite) and organic proteins. Carbon (C), oxygen (O), nitrogen (N), calcium (Ca) and phosphorus (P) could be detected in both dentin and enamel by XPS (Table 2). The plasma brush treatment broke-down and removed some of the proteins on these surfaces, indicated by decreases in the amounts of C and N (Table 2). As a result, more mineral containing elements were exposed and detected by the XPS, indicated by increases of Ca and P amounts (the main elements of hydroxyapatite). Similarly, for composites, the inorganic fillers were more impermeable to removal. After the plasma treatment, more filler-containing elements were left on the surfaces, indicated by increases of Si and Zr amounts for Z250, Y and F amounts for LS (Table 2). Since inorganic mineral or filler is relatively hydrophilic, it may contribute to the reduction of surface contact angles after plasma treatment.

Typically, a dramatic drop in the contact angle may be also due to the grafting of new polar functionalities onto the sample surface in addition to changes in the chemical composition. Besides the elemental changes mentioned above, the amount of O increased in all four substrates after plasma treatment. For example, O content of 17.2% in the original Z250 surface increased to O content of 31.9% for plasma-treated Z250. Plasma surface treatment generates reactive spots or species through bond splitting induced by the vigorous atom/ion bombardment. These reactive species can then bind to other available atom or functional groups. Since our non-thermal plasma brush was driven by high purity argon gas, the oxygen was likely from ambient air, which was excited to form highly reactive oxygen species [27], then reacted with the surfaces. It is reported that active peroxide radicals (R-O-O-) and functional groups (C-OH) can be produced when the treated surface is exposed to atmosphere [25, 27]. The increase in these oxygen-containing polar moieties on the surface enhanced the surface hydrophilicity. This explains the dramatic decrease in contact angle with plasma treatment as shown in Figs. 3 and 4.

As a indicator of surface wettability, the O/C ratio is usually used to designate the amount of oxygen-containing functional groups on the plasma-modified polymer surfaces [28–30]. Although increase of the ratio might be partly due to the decrease of %C, the %O did increase based on the results (Fig. 5 and Table 2). The XPS analysis showed that the O/C ratios of all 4 substrates increased a lot after 30 s plasma treatment. The most dominant change was in enamel surface, in which the ratio increased from 0.68 to 5.08. The increase in O/C ratio of other substrates was from 1.77 to 3.48 for dentin, 0.22 to 0.54 for Z250, and 0.17 to 0.82 for LS. The increase of O/C ratio is indicative of the wettability improvement of the plasma-modified surfaces.

The plasma treatment may also change the surface morphology [27, 29, 30]. SEM offers a clear-cut way for detecting the surface morphology changes of dental substrates after plasma treatment. In contrast to dramatic surface chemistry changes, there was no noticeable surface morphology modification identified by SEM on the plasma-treated surfaces. For example, SEM observation of the dentin surfaces showed no significant difference between treated and untreated specimen with the 5 s short-time plasma exposure (Figure 6). Although a bit rougher surface was observed with a longer plasma treatment (e.g., 30 s), no evident change was observed even at a magnification of 40,000 X. These results indicated that the non-thermal plasma treatment did not introduce much of etching or destruction to the dental

surfaces, which might be due to the following reasons. Firstly, the four dental substrates used are hybrid/composite materials, not pure polymers. Inorganic filler/mineral is much more resistant to plasma etching, so that the primary surface morphology was un-altered. Secondly, it may also have resulted from the short treatment time (<1 min) and less power input of only 5 W in this study as compared to 100 W used by others [31]. At such a short time exposure and low power output, there would be less reactive species, and quite limited amount of “etched” matter. Lastly, in our non-thermal plasmas, the major reactive species are excited argon neutrals that distinguish these plasmas from conventional plasmas in which ions and electrons play the vital role [32]. Since excited argon neutrals were less energetic than the high-energy electrons and ions, our non-thermal plasma brush offered more controllable surface treatments on dental substrates with minimal damage caused by the attack of energetic electrons and ions. Although with a low power and less energetic species, the plasma brush still proved to be very effective in the surface modification of dental substrates based on our results.

It is worth to mention that plasmas including both thermal and non-thermal ones can be used not only to improve surface hydrophilicity, but also to make the surface more hydrophobic. For example, surface modification with Ar, N₂, O₂ etc. directs to increase in the wettability / hydrophilicity [33]. On the other hand, surface fluorocarbon coating or fluorination guides to increase in hydrophobicity [34]. Barankin et al [11] produced hydrophobic coatings on glass and acrylic poly-methylmethacrylate surfaces by polymerizing liquid fluoroalkylsilane precursors on the surfaces using a low-temperature atmospheric plasma. It is well verified that fluoride-containing plasma is very effective in altering/decreasing surface hydrophilicity [35, 36]. By using CF₄, CHF₃, C₂F₆, and their mixtures in plasma surface modification of silk fibers, Li et al. [37] were able to increase the water contact angle to over 120° after only 1min treatment, which suggesting that the hydrophobicity has been enhanced remarkably. In dentistry, besides the above mentioned surface modification, fluoride-containing chemistry provides additional advantages such as dental caries prevention and bacteria killings. Fluorination using our non- thermal plasma brush for incorporation of fluoride into various dental surfaces is currently under way in our laboratory.

As shown in Fig 1, non-thermal atmospheric plasmas device is created and manipulated into brush shape and compact size that can be handheld and conveniently operated by dental practitioners in clinics. Because of its small volume and flat brush shape, the plasma brush has a large surface to volume ratio that promotes energy escape by thermal diffusion and limits gas heating in the plasma. The plasma temperature of the brush can be easily controlled between room temperature and human body temperature by simply adjusting plasma parameters [19, 38]. Previous study showed that, at a gas flow rate of 2.0 L/min and an input power of 5 W, the temperature of gas phase was <38 °C [19]. Because of its non-thermal nature, the plasmas can be touched by bare fingers without causing any heating or painful sensation. The results of this study indicate that the non-thermal plasma brush effectively modifies surface wettability of dental substrates under clinical settings, which could be used to enhance adhesion *in situ* during tooth or composite repair/restorations. For example, LS is one of the newest composites with new silorane chemistry and hydrophobic surface properties. Its non-sticky property is widely known. However, when adhesion to this composite is required for repair or for other applications, surface preparation has to be applied to improve its properties like surface hydrophilicity and roughness [39, 40]. It is speculated that the plasma brush could be used effectively for this purpose. Our results indicate that the wettability improvement by plasma brush treatment does not depend on the original composition/material. Especially, under *in vivo* condition, it is often hard to see what type of substrates to be bonded to. The substrate could be the mix of dentin, enamel and composites. The characteristic that final wettability after plasma treatment is irrelevant to initial chemical composition is particularly important in this application. As the plasma

brush can be hand-held and operated in atmosphere and at human body temperature, it can potentially be used to improve bonding to teeth or repair of composites in oral cavity.

5. Conclusion

Within the limitations imposed in the current study, the following conclusions may be made:

1. It was demonstrated that water contact angle values decreased considerably after only 5 s plasma treatment of all four substrates studied. After 30 s treatment, the values were further reduced to $<5^\circ$, which was close to a value for super hydrophilic surfaces. The non-thermal, atmospheric plasma brush could be used to effectively improve the surface hydrophilicity of these substrates under clinical settings.
2. The percent of elements associated with mineral in dentin/enamel (i.e., %P, %Ca) or fillers in the composites (i.e., %Si, %Ar, %Y, %F etc.) increased after plasma treatment.
3. The percent of carbon (%C) decreased while %O increased for all four substrates. As a result, the O/C ratio of the substrates increased dramatically, suggesting that new oxygen-containing polar moieties were formed on the surfaces after plasma treatment.
4. Although surface wettability and chemistry was effectively modified, SEM images indicated that no significant morphology change was induced on these dental substrates.

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Fig. 1.

A. The schematic diagram of the atmospheric argon plasma brush. B. Photographs of the plasma brush in atmospheric environment on a tooth, the side view was also inserted in the photo. Plasma conditions were 2000 sccm argon and 5 W direct current power input.

Fig. 2.
A schematic representation of plasma treatment of a dental substrate and water contact angle measurement.

Fig. 3. Water contact angle values of the dentin substrate as a function of exposure time to nonthermal argon plasmas. (A) with an input power of 5 W. (B) with an input power of 10 W. in each figure, means with different letters are significantly different ($p < 0.05$).

Fig. 4.

Water contact angle values of the enamel, composite Z250, composite LS substrates as a function of exposure time to non- thermal argon plasmas with an input power of 5 W. For each substrate, means with different letters are significantly different ($P < 0.05$).

Before plasma treatment

After plasma treatment

Fig. 5.

XPS survey scans for the composite Z250 before and after 30 s exposure to non-thermal plasmas with an input power of 5 W.

A. Untreated dentin

B. Plasma treated for 5 s

C. Plasma treated for 30 s

Fig. 6.

SEM micrographs of the dentin surfaces with different exposure times to non-thermal plasmas A. untreated dentin; B. plasma treated for 5 s; C. plasma treated for 30 s.

Table 1Composition of dentin, enamel, composites Filtek Z250^a and Filtek LS^a

Material	Organic/Resin Matrix	Content (wt)	Inorganic/Filler	Content (wt)
Dentin	Collagenous proteins	~20–23	Mineral apatite	~70–77
Enamel	Enamel proteins	~1	Mineral apatite	~96
Filtek Z250	BisGMA, BisEMA, UDMA, TEGDMA	~20	ZrO/SiO ₂	~80–82
Filtek LS	bis-3,4-epoxycyclohexylethyl-phenyl-methylsilane, 3,4-epoxycyclohexylcyclopolydimethylsiloxane	~24	Quartz, yttrium fluoride	~76

^aManufactures data. BisGMA: bisphenol A diglycidyl ether dimethacrylate, BisEMA: bisphenol A polyethylene glycol diether dimethacrylate, UDMA: urethane dimethacrylate, TEGDMA: triethylene glycol dimethacrylate

Table 2

Surface chemistry composition (in atomic percent of each element) of dentin, enamel, composites Filtek Z250 and Filtek LS before and after plasma treatment (30 s)

	Dentin		Enamel		Z250		LS	
	Before	After	Before	After	Before	After	Before	After
C	24.70 (0.31)	14.57 (0.53)	46.11 (0.44)	10.61 (0.44)	79.22 (0.27)	59.43 (0.39)	78.89 (0.35)	46.96 (0.43)
O	43.67 (0.25)	50.70 (0.45)	31.58 (0.34)	53.86 (0.35)	17.21 (0.20)	31.90 (0.31)	13.48 (0.21)	38.32 (0.35)
N	3.94 (0.16)	2.64 (0.30)	1.75 (0.29)	ND	2.50 (0.17)	2.52 (0.27)		
Ca	16.22 (0.13)	19.66 (0.23)	13.70 (0.19)	22.20 (0.20)				
P	10.80 (0.18)	12.43 (0.33)	6.86 (0.25)	12.64 (0.24)				
Si					1.08 (0.13)	5.58 (0.23)	6.20 (0.31)	11.84 (0.35)
Zr					ND	0.57 (0.04)		
Y							1.00 (0.06)	1.91 (0.07)
F							0.44 (0.08)	0.97 (0.12)
O/C	1.77	3.48	0.68	5.08	0.22	0.54	0.17	0.82

ND: not detected.