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Dentin surface treatment using a non-thermal argon plasma brush for interfacial bonding improvement in composite restoration

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Abstract

The objective of this study is to investigate the treatment effects of non-thermal atmospheric gas plasmas on dentin surfaces for composite restoration. Extracted unerupted human third molars were used by removing the crowns and etching the exposed dentin surfaces with 35% phosphoric acid gel. The dentin surfaces were treated by using a non-thermal atmospheric argon plasma brush for various durations. The molecular changes of the dentin surfaces were analyzed using FTIR/ATR and an increase in carbonyl groups on dentin surfaces was detected with plasma treated dentin. Adper Single Bond Plus adhesive and Filtek Z250 dental composite were applied as directed. To evaluate the dentin/composite interfacial bonding, the teeth thus prepared were sectioned into micro-bars as the specimens for tensile test. Student Newman Keuls tests showed that the bonding strength of the composite restoration to peripheral dentin was significantly increased (by 64%) after 30 s plasma treatment. However, the bonding strength to plasma treated inner dentin did not show any improvement. It was found that plasma treatment of peripheral dentin surface up to 100 s gave an increase in interfacial bonding strength, while a prolong plasma treatment of dentin surfaces, e.g., 5 min treatments, showed a decrease in interfacial bonding strength.

Keywords

Plasma treatment; Composite restoration; Bonding strength

Composite restoration has become the preferred form of restorative material due to aesthetic requirements and elimination of the potential health risk of mercury release from dental amalgams. However, composite restorations generally underperform dental amalgam in longevity. There are various reasons for premature failures of composite restoration including polymer shrinkage, inadequate adhesive bonding to dentin, and formation of secondary caries. In fact one study has shown that the average life span for class II composite restoration is only 6-8 yr (1). These premature failures are particularly detrimental to patients because of the extensive loss of healthy dentin (1). When compared

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to amalgam, composite restorations could induce significantly more loss of tooth structure due to restoration failure and secondary decay (2). Therefore, it is even more important to decrease the large percentage of premature failures seen clinically. Many factors contribute to the inadequate adhesive bonding to dentin, which can be correlated with low bonding strength as reported with a wide range of literature values, 5-70 MPa (3-6). The preparation procedure is another factor that contributes to the interfacial bonding strength which makes it impossible to correlate laboratory results directly to the clinical data (6-9). However there has been an overall increase in clinical retention of class V composites restoration due to information uncovered by laboratory derived techniques (8).

Non-thermal plasma treatment provides a unique opportunity in modifying dentin surfaces in order to improve the interfacial bonding of the dental composite restoration. Non-thermal plasmas are partially ionized gases that contain highly reactive particles including electronically excited atoms, molecules, ionic and free radical species, 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, bond to various substrates, or combine to form a thin layer of plasma coating, and consequently alter the surface characteristics (10,11). Non-thermal plasmas combine exceptional chemical reactivity with relatively mild, non-destructive character due to cold gas phase. Surface treatment using non-thermal plasmas has led to an enormous success in surface engineering and processing of solid state materials, especially in plasma cleaning/etching, surface engineering, adhesion enhancement, and biomaterial development (10-13). When utilized correctly and efficiently, non-thermal plasma is a gentle method used to change the surface characteristics of the topmost layer of polymeric surfaces, such as collagen fibrils on dentin surfaces, and thus to enhance the surface for various types of adhesives used in composite restoration. Our previous results have demonstrated that the non-thermal atmospheric plasma brush that was developed in our plasma research center were very effective and efficient in bacterial disinfection (14), which is desired and required for dental restoration in prevention of secondary caries. If successful, plasma treatment of dentin surfaces will avoid contamination, actively fight bacterial infections, and prepare/engineer the dentin surface for strong and durable bonding to composite restorative materials.

In this study, a non-thermal atmospheric plasma brush was employed to study the plasma treatment effects on dentin surface changes and interface bonding strength of the subsequent composite restoration. It was hypothesized that the interactions of the non-thermal plasmas with dentin surfaces would improve interface bonding of the dental composite restorations.

Material and methods

Silicon carbide abrasive paper (600-grit; Buehler, Lake Bluff, IL, USA) was utilized for polishing the dentin surface prior to demineralization to mimic the clinical use of dental burs (15). Scotchbond phosphoric acid gel by 3M ESPE (Dental Products, St. Paul, MN, USA) was utilized for demineralizing the dentin surface, Adaper Single bond plus from 3M ESPE was utilized as an adhesive, and Filtek Z250 from 3M ESPE was utilized as the dental composite for the restoration. Composite and adhesive were light cured by visible light via Spectrum 800 from Dentsply (Milford, DE, USA). Compressed argon gas (4.7 grade and 99.997% purity) purchased from Praxair (Columbia, MO, USA) was used as plasma gas.

Non-thermal plasma brush

The non-thermal atmospheric plasma brush developed in our plasma research center was used in this study. Detailed information about this plasma source can be found elsewhere [14]. Operating parameters including argon flow rate and electrical power input for creating the non-thermal plasma brush were varied in order to determine adequate plasma conditions,

such as plasma volume and temperature. Plasma temperatures were characterized by a type K thermocouple and infrared imaging. Plasma flame lengths were measured with a metric ruler based on visual observation.

FTIR spectral analysis of plasma treated dentin surfaces

The molecular structure of the demineralized dentin surfaces before and after plasma treatments was monitored using a Perkin-Elmer (Waltham, MA, USA) Spectrum One Fourier transform infrared spectrophotometer (FTIR) with a resolution of 4 cm^{-1} in the attenuated total reflectance (ATR) sampling mode. The plasma treated dentin surfaces and untreated controls were placed on the horizontal face of the internal reflectance crystal where total internal reflection occurs. The ATR crystal was diamond with a transmission range between $650\text{--}4000\text{ cm}^{-1}$. The reflected radiation penetrates the specimen to a depth of a few micrometers.

Dentin/adhesive/composite specimen preparation

Extracted un-erupted human third molars stored at 4°C in phosphate buffered saline (PBS), containing 0.002% sodium azide, were used. These molars were collected after patient's informed consent under a protocol approved by the UMKC adult health sciences institutional review board (16). Molars were prepared using an Isomet 5000 diamond saw purchased from Buehler. Specimens were polished and etched for 15 s before rinsing with de-ionized (DI) water (16). The surface was dried by blotting the surface with a Kimwipes' dust-free tissue prior to cold plasma treatment. Plasma conditions were set at 5 W with 2500 sccm Ar at various application times as determined from the cold plasma torch analysis. Fig. 1 shows a pictorial view of the plasma brush applied to a demineralized dentin surface. Water was first applied to the surface of the plasma treated dentin via a water-soaked Kimwipes' dust-free tissue. 15 s later, the dental adhesive was applied and then light cured for 10 s. The dental composite was applied to the adhesive and light cured for 20 s per mm of composite applied.

Mechanical testing and SEM analysis

The specimens prepared were stored in water at 25°C for 24 h before sectioning into bar-shape test specimens with cross-section dimension of $\sim 1.0 \times 1.0\text{ mm}$ for tensile testing. Typically, 20 to 25 microbar test specimens were prepared from one tooth. Among these 20 to 25 microbars, about 4 – 6 microbars obtained from the tooth center position were designated as inner dentin and the rest 15 to 20 microbars were designated as peripheral dentin. Before tensile test, the cross sectional area of each bar specimen was measured by a digital caliper and recorded. The bars were adhered to a universal testing system TAHD Plus (Stable Micro System, Golalming, Surrey, UK) via cyanoacrylate resin (Zapit, Corona, CA, USA) and subjected to tensile testing with strain rate of 0.5 mm/min . Ultimate tensile strength and tensile modulus were acquired. Following the tensile strength measurement, the fractured bars were mounted on aluminum stubs with the fractured surfaces upward facing, sputter-coated with carbon, and examined with backscattered electron microscopy in Field-Emission Scanning Electron Microscopy (Philips XL30, FEI Company, Hillsboro, OR, USA).

Data analysis

Procedural techniques were primarily characterized by micro tensile testing for the effect of plasma on bonding. Mean separation was analyzed by the Student Newman Keuls (SNK) method. The power of each statistical test was analyzed. Estimates on effective application times and plasma parameters were also discussed.

Results

Characterization of plasmas and plasma treated dentin

Gas phase temperature of the plasma brush was characterized using a sheathed thermocouple and thermal IR imaging. The plasma temperatures measured using the thermocouple at various argon flow rates and power inputs are shown in Fig. 2. The thermal IR images of the plasma brush are shown in Fig. 3. It was noted that the plasma temperature profile measured using both methods showed a similar trend with varying power input and flow rate. Lengths of the plasma brush were also recorded with varying flow rate and power input and are shown in Fig. 4. Argon flow rates between 2000 and 4000 sccm had no significant effect on the plasma length. Increasing power increased the resulted plasma size to a certain extent. The plasma brush size peaked at around 10 W of power input. The temperatures are well below 37 °C at 5 W with 3000 sccm (Fig. 3). Plasma conditions were set at 5 W with 2500 sccm Ar at various dentin application times in this study.

FTIR spectra of plasma treated dentin surfaces and the untreated controls are shown in Fig. 5. FTIR surface analysis showed structural changes in the surface of the demineralized dentin after plasma treatments. It was shown that there were two major changes in the representative spectrum of dentin surface after plasma treatment. First, a new shoulder peak around 1760 cm^{-1} (in the oval) associated with carbonyl stretch was found. This new peak has been confirmed by subtraction line between the FTIR spectra of plasma treated and untreated dentin. Second, an amide II shift of $\sim 10 \text{ cm}^{-1}$ was observed (1543 cm^{-1} before to 1533 cm^{-1} after), which might indicate the secondary structural changes of dentin collagen after plasma treatment.

Effect of plasma treatment on interface bonding

The mean cross sectional areas of the test specimens between treatments were from 0.87 to 0.95 mm^2 and no difference was detected among the treatments of all groups by one-way ANOVA ($p = 0.38$). No specimens from the peripheral dentin failed prematurely before testing. Table 1 shows the mechanical testing data obtained with the specimens prepared from the plasma treated dentin and the untreated controls. Fig. 6 shows the statistical comparison of ultimate tensile strength data obtained with test specimens prepared from plasma treated dentin and the untreated controls. Statistically significant differences in tensile strength between all specimens using SNK method were observed. A significant difference was found between the peripheral dentin that was plasma treated for 30 s and all the other treatments.

As the plasma treatment time was increased beyond 30 s the tensile strength decreased. For the 100 s plasma treatment, the tensile strength was increased as compared to the controls, but not significantly. For the 300 s plasma treatment, specimens' strengths are similar to control specimens, with a larger variance. The modulus for the 300 s plasma treatment specimens was also reduced (Fig. 7). Modulus data showed a trend of lower modulus for inner dentin as compared to peripheral dentin. The 30 s plasma treatment increased the modulus of the interface bonding when compared to the controls; however increasing treatment time did not continue to increase the modulus. Inner dentin specimens for 100 s and 300 s plasma trials were not successfully tested. Plasma treatment of inner dentin for 30 s does not affect the mechanical properties as seen in Figs. 6 and 7.

SEM images of the fracture surface generally showed that more composite remained on plasma treated dentin surfaces when compared with controls. Fig. 8 shows some representative SEM images of the fracture surfaces from specimens prepared with 0 s (control), 30 s, 100 s, and 300 s plasma treatment. Fractured surfaces were identified as cohesive composite failure, adhesive or mixed failure, cohesive dentin failure, or Zapit resin

failure. A failure was attributed as an adhesive or mixed failure when at least two of the following were observed on the fracture surface: dentin, adhesive, and/or composite. Figs. 8a and b show specimens with mixed adhesive fracture, while Fig. 8c shows cohesive dentin failure. Fracture modes determined through SEM examination were summarized in Table 1. More specimens cohesively failed in the composite for plasma treated specimens compared to controls, except for the specimens prepared from 300 s plasma treated dentin specimens. Control specimens had adhesive or mixed failures more frequently than the plasma treated specimens.

Discussion

While trends in plasma temperature were the same with each measurement device, the magnitudes varied slightly. Each method had inherent flaws which prevented the actual temperature from being recognized. However, comparison and combining the data measured with each method provided a reasonably accurate range of the actual plasma temperatures. The thermocouple wire was shielded to reduce errors in temperature measurement, although certain errors could not be completely eliminated. These errors were due to the thermocouple acting as a floating electrode, taking an applied voltage from the plasma, and skewing the measurements. The thermal IR imaging did not pick up gaseous IR signals and a piece of white paper had to be used to determine the plasma temperature. Thermal IR imaging also had some artifacts due to increased IR radiation with brighter portions of the plasma near the plasma nozzle, reflecting off of solid surfaces, which made the plasma to appear to have a higher temperature. During the thermal IR image recording, the plasma conditions were adjusted and controlled to limit such artifacts of the IR imaging method, although such effects could not be completely eliminated.

Fig. 3 shows the thermal IR images of the plasma temperature profile under several operating conditions. In comparison with the plasma temperatures measured using a thermocouple shown in Fig. 2, it was noted that an average of 5°C higher temperature was recorded using IR imaging method. It is known that a prolonged exposure to 80°C can cause 1st degree burns and are not suitable for biological applications, although dehydrated demineralized dentin collagen is thermally stable at elevated temperatures due to interpeptide hydrogen bonding (17). Besides, the nerve system of human teeth is very sensitive to temperature differences. The results shown in Figs. 2 and 3 indicate that the plasma temperature of the plasma brush could be well controlled as being close to human body temperature. In addition, the dimension of the plasma brush has to meet the requirement when used in dental clinics. Our results shown in Fig. 4 indicate that plasma length could be adjusted and controlled by simply adjusting the operating parameters.

Plasma treatment can generally change surfaces in two ways: modification and etching. Each interaction competes with one another on the applied surface. Modification of the surface could change the surface chemistry by introducing new functionalities, such as new chemical structures. By lowering the temperature of the plasma and reducing the quantity of high energy ions, the plasma intensity decreases and limits the etching effect that can be seen in certain conditions. However, if a surface undergoes prolonged exposure to plasmas under even low temperature, the surface structure such as the collagen fibrils on dentin surfaces can be etched away by the plasmas.

FTIR results shown in Fig. 5 indicate that plasma treatment introduced more carbonyl groups on the dentin surfaces, which were more likely on the organic components of the dentin, in this case, the collagen fibrils. The plasma brush was used to deactivate *Escherichia coli* and *Micrococcus luteus* bacteria in our previous work, in which optical emission spectroscopy (OES) was utilized to analyze the reactive photon-emitting species

that could be involved in the bacterial deactivation of bacteria (14). OES results indicated that argon plasma brush showed photo emitting species from nitrogen, oxygen, and nitrous oxide due to the interactions between argon plasmas and ambient air. The surface interaction of the reactive oxygen species in the plasma could be incorporated into the type I collagen molecule. The addition of more carbonyl groups to the collagen fibrils was hypothesized to increase hydrogen bonding interactions of the collagen fibrils with the adhesive that was subsequently applied to the dentin surfaces for test specimen preparation. This is believed to alleviate some of the adhesive phase separation that can occur during adhesive application as well. Phase separation commonly occurs when too much water is on dentin surface prior to adhesive application, which is clinically difficult to control. Phase separation of adhesive provides a poor interface for dental bonding (18,19). Another possible benefit of the increased carbonyl groups is the electrical repulsive forces which could cause the collagen fiber to be partially separated into smaller fibril aggregates or even individual fibrils. This would significantly improve the adhesive penetration into collagen fibrils and increase the interface area between the adhesive and collagen, and consequently significantly enhance interface bonding strength.

The shift in the amide II peak from 1543 cm^{-1} to 1533 cm^{-1} observed in FTIR suggests some denaturing of the collagen fibrils and/or breaking of some intrafibrillar bonding. Limiting plasma treatment time should reduce any denaturing effect. If intrafibrillar bonding is reduced the adhesive could interact with more collagen surface area and increase micromechanical interlocking. A shift to lower wave-numbers in the amide II peak entailed collagen structural changes and reduced intermolecular interactions. In atmospheric plasmas, plasma species can lose energy much faster due to the high frequency of collisions with the oxygen and nitrogen molecules in the air (14). The reactive species induced by the plasma will also have a short life span for the same reason. This prevents the reactive species from unintentionally reacting with other parts of the surrounding environment. Fig. 9 is a schematic of the hypothesized interaction of the cold plasma with dried collagen fibrils. After rewetting, many of the modifications such as charge transfer will be reduced significantly, while covalent modifications of the collagen fibrils will endure for the adhesive application. The modification can also include a change of conformation of the collagen fibrils, and/or the opening of the collagen fibers revealing more fibrils for interaction.

Collagen fibers are natural polymer materials that often can have functional groups that fold in on themselves. This prevents these functional groups from interacting with the adhesive and reduces the possibility of covalent bonding formation. Plasma modification of the surface of the collagen can allow the functional groups to become uncovered temporarily, and allow the functional groups to interact with the adhesive. Plasma's ability to change the conformation of polymers is utilized frequently in plastics industry to increase wettability and adhesion of plastics (20,21). Certain plastics, which have large quantities of hydrophilic functional groups, are generally hydrophobic due to their physical conformation. After plasma modification, the hydrophilic groups can be temporarily uncovered which significantly increase their surface hydrophilicity and in most cases improve adhesion properties. One possible mode of modification of the collagen fibers could be to allow the collagen fibers to partially de-aggregate temporarily and allow the dental adhesive to interact with the underlying fibrils as illustrated in Fig. 9.

The data obtained from prolonged exposure to plasma showed that treatment of 300 s lowered the bonding modulus of the adhesive to peripheral dentin and the interface bonding strength was similar to untreated inner dentin. The low strength was believed to be due to the plasma etching discussed previously. A prolonged plasma exposure could degrade the collagen fibrils by an increased plasma etching effect, which would be more pronounced

over prolonged treatment. A plasma treatment of 100 s showed an increase in strength, but not a significant one.

Statistical significance was found between the peripheral dentin plasma treated for 30 s and all the other treatments. A significant increase in tensile modulus obtained with 30 s plasma treated dentin implied that a proper plasma treatment could enhance the mechanical properties of the interface. Increase in modulus was believed to be due to an increase in the crosslink density of the adhesive with the collagen fibers. Such an increase in bonding strength was believed to be due to the increased surface area of the collagen fibers provided by the plasma treatment and the increase in cross-linking density.

On the other hand, no improvement in bonding strength was observed with plasma treated inner dentin. This result was believed to be due to the regional composition variability of dentin. Tubule size, orientation, surface area, and the water content of dentin can vary from location to location (8). When removing the smear layer by acid etching, areas with larger tubules and/or less mineral content are usually demineralized deeper. Increase in demineralization depth and water content of the hybrid layer could possibly decrease the effectiveness of the plasma modification because increased percentage of water content could increase the phase separation of dental adhesives. In other words, the effectiveness of plasma treatment to enhance the interface between dentin and adhesive is also reliant on the dentin composition, which varies upon location.

SEM examination of the fractured cross sections shows that large amounts of composite/adhesive were observed on plasma treated dentin surfaces, which implies the dentin adhesive interface is stronger than the bulk composite. These trends were also observed with the test specimens that gave higher tensile strength. Plasma treated specimens cohesively failed within the composite more frequently than the control specimens which also implies a stronger interface.

Our experimental study showed the prospect of utilizing non-thermal plasma technology for dentin surface treatment to increase the chemical interactions of dentin surfaces with dental adhesives and thus to improve the interface bonding of composite restorations. A wide range dependence of the plasma temperatures on plasma operating conditions showed the capability of controlling the plasma temperature to ensure minimal negative thermal effects on the dentin surfaces. FTIR investigation indicated an increase in carbonyl groups on dentin surfaces induced upon plasma application, which could provide increased chemical interactions with adhesives. It was found that regional variability and plasma modification duration affected the interface bonding strength as measured using tensile test. It was demonstrated that, under proper plasma conditions, plasma treatment of dentin could increase the bonding strength of dental adhesives to dentin surfaces. An effective plasma treatment time was around 30 s as observed from the mechanical testing data. This short plasma treatment is desired in dental clinical applications because it will allow a quick dental composite restoration. On the other hands, a prolonged plasma treatment could cause collagen fiber to degrade and as a result lead to a weak interface as expressed with lower ultimate tensile strength and elastic modulus.

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Figure 1.
A pictorial view of the non-thermal atmospheric plasma brush applied to an extracted tooth with crown removed.

Figure 2.
Gas phase temperature of the non-thermal plasma brush measured using a type K thermocouple at various argon flow rates and electrical power inputs.

Figure 3.
IR images of the plasma brush operated under various plasma conditions.

Figure 4.
The flame length of the plasma brush operated at various argon flow rates and electrical power inputs.

Figure 5.
FTIR spectra of demineralized dentin before and after plasma treatment.

Figure 6.

Statistical comparison of ultimate tensile strength obtained with test specimens prepared from plasma treated dentin and the untreated controls (0s P and 0s I). P: Peripheral dentin, I: Inner dentin; Different letters in the plot indicate statistically significant differences ($\alpha = 0.05$).

Figure 7.

Comparison of tensile modulus obtained with test specimens prepared from plasma treated dentin and the untreated controls (0s P and 0s I). P: Peripheral dentin, I: Inner dentin; Different letters in the plot indicate statistically significant differences ($\alpha = 0.05$).

Figure 8.

Back-scattered SEM images of the fracture surfaces of the test specimens prepared from: (a) the untreated controls (0 s), (b) 30 s, and (c) 100 s plasma treated dentin.

Figure 9.
Schematic illustration of the plasma treatment effects on a demineralized dentin surface.

Micro tensile test data and fracture location of the specimens prepared from plasma treated dentin and the untreated controls (0 s treatment)

Table 1

Treatment Time	Peripheral Dentin				Inner Dentin	
	0s	30s	100s	300s	0s	30s
Average Stress (MPa)	38.80	60.38	46.00	34.07	27.11	18.11
Standard Deviation (MPa)	8.66	15.66	10.89	15.09	7.14	6.48
Average Modulus (GPa)	642.49	963.45	586.22	503.61	421.63	450.64
Standard Deviation (GPa)	64.48	98.05	82.25	117.58	140.31	89.17
Fracture Location (%)						
Interface or Mixed	84.62%	50.00%	80.00%	90.00%	83.33%	75.00%
Composite	15.38%	50.00%	10.00%	0.00%	8.33%	25.00%
Dentin	0.00%	0.00%	10.00%	0.00%	8.33%	0.00%
Zapit	0.00%	0.00%	0.00%	10.00%	0.00%	0.00%