Published in final edited form as:

J Dent. 2014 August ; 42(8): 1033–1042. doi:10.1016/j.jdent.2014.05.005.

Non-thermal atmospheric plasmas in dental restoration: improved resin adhesive penetration

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Abstract

Objective—To investigate the influence of non-thermal plasma treatment on the penetration of a model dental adhesive into the demineralized dentin.

Methods—Prepared dentin surfaces were conditioned with Scotchbond Universal etchant for 15 s and sectioned equally perpendicular to the etched surfaces. The separated halves were randomly selected for treatment with an argon plasma brush (input current 6 mA, treatment time 30 s) or gentle argon air blowing (treatment time 30 s, as control). The plasma-treated specimens and control specimens were applied with a model adhesive containing 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane (BisGMA) and 2-hydroxyethyl methacrylate (HEMA) (mass ratio of 30/70), gently air-dried for 5 s, and light-cured for 20 s. Cross-sectional specimens were characterized using micro-Raman spectral mapping across the dentin, adhesive/dentin interface, and adhesive layer at 1~micron spatial resolution. SEM was also employed to examine the adhesive/dentin interfacial morphology.

Results—The micro-Raman result disclosed that plasma treatment significantly improved the penetration of the adhesive, evidenced by the apparently higher content of the adhesive at the adhesive/dentin interface as compared to the control. Specifically, the improvement of the adhesive penetration using plasma technique was achieved by dramatically enhancing the penetration of hydrophilic monomer (HEMA), while maintaining the penetration of hydrophobic monomer (BisGMA). Morphological observation at the adhesive/dentin interface using SEM also confirmed the improved adhesive penetration. The results further suggested that plasma treatment could benefit polymerization of the adhesive, especially in the interface region.

Conclusion—The significant role of the non-thermal plasma brush in improving the adhesive penetration into demineralized dentin has been demonstrated. The results obtained may offer a better prospect of using plasma in dental restoration to optimize adhesion between tooth substrate and restorative materials.

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Keywords

non-thermal atmospheric plasmas; dental adhesive; resin penetration; dentin; micro-Raman

1. Introduction

Contemporary dental restorative techniques usually include a dentin bonding step in order to create a stable bond/connection between composite resin and intact dentin. A fundamental principle of dentin bonding is related to the concept of hybridization of tooth tissue with primer/adhesive systems (to form the so-called hybrid layer) ^{1, 2}. Hybridization involves penetration of the primer/adhesive into the dentin substrate. In the systems where etching precedes the priming and bonding steps, the interfacial compatibility of the primer/adhesive formulation with the demineralized dentin matrix to a great extent determines permeability of the resin monomers ³⁻⁵. The penetration and the subsequent polymerization of the monomers efficiently promote the bond strength and margin sealing. Incomplete penetration of adhesive monomers into the full depth of the demineralized layer may, however, lead to leakage and marginal gap in this region and leave the collagen fibrils exposed to harsh oral environment⁶⁻⁸, which will further contribute to hydrolytic degradation of the hybrid layer. Under *in vivo* conditions, the adhesive/dentin hybrid layer can be the first defense against the noxious, damaging substances. However, considerable evidences have suggested that the hybrid layer is in fact the weakest link in the dental interfaces ⁹⁻¹³.

Dentin surface can be different in its structure, morphology, and chemical composition, which may affect the ability of dentin bonding systems in achieving good/durable adhesion ¹⁴⁻¹⁶. Recently, efforts have been devoted to develop dentin surface modification techniques such as chemical or electric approaches that would facilitate the penetration and absorption of bonding reagents ¹⁷⁻¹⁹. As an “effective” and “clean” approach for material surface modifications, non-thermal atmospheric plasma technology has recently attracted considerable interest ²⁰⁻²³. Non-thermal plasma surface treatment is based on an ionized gas with an essential equal density of positive and negative charges that produce excited particles. These excited particles will decay and excite other particles, thus create interactions with the material surface in a dry chemical way, thereby forming a new modified surface layer ^{22, 24}. Surface treatment by plasmas is a potential option that represents a process of changing surface energy of different materials and leads to an improvement of surface bonding characteristics. Recently published studies ^{25, 26} have demonstrated that non-thermal plasma treatment could improve the bonding strength of restorative composites to dentin. Nevertheless, more detailed mechanism of the bonding improvement, especially with regard to the influence of plasmas on the hybrid layer region, has not been understood yet.

Micro-Raman spectroscopy has been shown to be a powerful spectroscopic tool for both qualitative and quantitative chemical characterization of the adhesive/dentin bond. It can provide detailed information about the chemical composition and the molecular/structural changes at a high spatial resolution that is comparable to the optical microscopy ^{4, 27, 28}. In this study, micro-Raman technique was employed to investigate the adhesive/dentin interface influenced by non-thermal atmospheric plasmas. The micro-Raman spectra

collected would enable us to evaluate the penetration of adhesive as well as its individual components as a function of position at the interface, so that a better understanding on the plasma effect could be acquired. Other determining factors for the interfacial bonding such as polymerization efficacy of the adhesive at the interface would be also obtained through micro-Raman spectral analysis. The present study also employed scanning electron microscopy (SEM) method to provide morphological observations at the interface. The null hypothesis tested was that non-thermal plasma treatment would not enhance the adhesive penetration and polymerization efficacy at the interface with dentin.

2. Materials and methods

2.1. Adhesive/dentin specimen preparation

The monomer mixtures used in this study were 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane (BisGMA, Polysciences, Washington, PA) and 2-hydroxyethyl methacrylate (HEMA, Acros Organics, Morris Plain, NJ) with a mass ratio of 30/70. The photoinitiator system (all from Aldrich, Milwaukee, WI) consisted of camphorquinone (CQ, 0.5 wt%) as photoinitiator and 2-(dimethylamino) ethyl methacrylate (DMAEMA, 0.5 wt%) as coinitiator, and diphenyliodonium hexafluorophosphate (DPIHP 1.0 wt%) as the third component. The concentration of each component of the photoinitiator system was calculated with respect to the total amount of monomers. Ethanol and water at the concentrations of 40 wt% and 5 wt%, respectively, were added to the above mixture to prepare the model adhesive. Shaking and sonication were required to yield a well-mixed solution.

The teeth (n=6) used in this study were extracted non-carious, unerupted human third molars, which were stored at 4°C in phosphate buffered saline (PBS) containing 0.002% sodium azide. The teeth were collected after the patients' informed consent under a protocol approved by the UMKC adult health sciences institutional review board. The occlusal one-third of the crown was removed by means of a water-cooled low-speed diamond saw (Buehler Ltd, Lake Bluff, IL, USA). Each prepared dentine surface was examined under a light microscope (Nikon Instruments Inc., Eclipse ME600P, Japan) to ensure it was free of enamel. Uniform smear layers were created by wet-sanding the dentin surfaces with 600-grit silicon carbide sandpaper for 30 s. The prepared dentin surfaces were conditioned with Scotchbond Universal etchant (35% phosphoric acid gel, 3M ESPE, Seefeld, Germany) for 15 s. Each prepared tooth was sectioned equally perpendicular to the etched surface, and the separated halves were randomly selected for treatment with/without non-thermal plasmas.

2.2. Non-thermal atmospheric plasma brush treatment

The non-thermal atmospheric plasma brush (Figure 1) employed in this study was designed by the Plasma Research Center at the University of Missouri and Los Alamos National Laboratory. The detailed information about this device can be found in the previous publications^{29, 30}. 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 (3000 sccm). 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. One of the electrodes was attached to a ballasted resistor which controlled 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. One half of an above prepared tooth specimen was placed under the plasma nozzle (5-6 mm from bottom of the nozzle) for treatment with input current of 6 mA (equivalent to a power level of 2-3 W) and treatment time of 30s. As control, another half of the prepared tooth specimen was only subjected to argon gas treatment (without igniting the plasmas, while keeping other conditions such as distance from plasma nozzle, treatment time same as those with plasma treatment). Immediately after the plasma or argon gas treatments, the dentin surfaces were applied with the prepared model adhesive, gently air-dried for 5 s, and light-cured for 20 s with a conventional dental light polymerization unit (Spectrum Light, DENTSPLY, Milford, DE, USA) emitting 550 mW/cm². All experiments were performed in sextuplicate following the above procedures. The prepared specimens were stored for at least 24 h in an environment avoiding moisture and light before further sectioning. Cross-sectional specimens of the adhesive/dentin interface, approximately 2 mm × 6 mm × 4 mm, were cut from the prepared specimens for micro-Raman and SEM studies.

2.3. Micro-Raman spectroscopy

To collect Raman spectra of the specimens, a LabRam HR 800 Raman spectrometer (Horiba Jobin Yvon, Edison, NJ) using monochromatic radiation emitted by a He-Ne laser (632.8 nm) and operating at excitation power of 20 mW was employed. The Raman spectrometer was focused through a 100× Olympus objective to a beam diameter of ~1 μm. Raman spectra were acquired starting from the dentin, across the adhesive/dentin interface and adhesive layer at 1-μm intervals. Spectra were obtained over the spectral region of 200-2000 cm⁻¹ and with an acquisition time of 60 s. The degrees of adhesive and BisGMA penetration into the demineralized dentin were determined based on the band ratios of 1454 cm⁻¹ (CH₂ of HEMA and BisGMA)/1667 cm⁻¹ (amide I of collagen) and 1609 cm⁻¹ (phenyl ring C=C of BisGMA)/1667 cm⁻¹, respectively. The relative content of BisGMA in the model adhesive was determined based on the band ratios of 1609 cm⁻¹/1454 cm⁻¹ and 1113 cm⁻¹ (C-O-C of BisGMA)/1454 cm⁻¹. The adhesive degree of conversion (DC) was calculated based on the band ratio of 1640 cm⁻¹ (C=C of HEMA and BisGMA) and 1454 cm⁻¹ (CH₂ of HEMA and BisGMA). The intensities of these two bands were integrated and the change of the band ratio profile with 1640 cm⁻¹/1454 cm⁻¹ was monitored. The DC was calculated by the following equation:

$$DC = \left(1 - \frac{Absorbance_{1640cm^{-1}}^{sample} / Absorbance_{1454cm^{-1}}^{sample}}{Absorbance_{1640cm^{-1}}^{monomer} / Absorbance_{1454cm^{-1}}^{monomer}} \right) \times 100\%$$

Two-point baseline and maximum peak height ratio protocol were used to measure the absorption intensity. Each band ratio or DC of polymerization was determined and averaged based on at least 6 Raman spectra. Data were analyzed using analysis of variance (ANOVA), together with the T test (p<0.05).

2.4. Scanning electron microscopy (SEM)

The specimens characterized by micro-Raman spectroscopy were subject to SEM examination subsequently. In order to evaluate the interfacial morphology, the specimens were treated by soaking in 5N HCl for 30 s, washed with water, followed by soaking in 5% NaOCl for 30 min and another water-wash and air-drying. The prepared specimens were mounted on aluminum stubs and sputter-coated with a 20 nm layer of gold-palladium. The adhesive/dentin interfaces were then examined at a variety of magnifications and tilt angles in the SEM (Philips XL 30, Eindhoven, Netherlands) at 5kV.

3. Results

Representative micro-Raman mapping spectra across the dentin, interface, and adhesive layer at 1- μm intervals for specimens without or with non-thermal plasma treatment are shown in Figure 2. The characteristic Raman bands associated with dentin collagen (1667 cm^{-1}), mineral (960 cm^{-1}), and model adhesive (1640 , 1609 , 1454 , and 1113 cm^{-1}) were identified from the mapping spectra. The middle five spectra in Figure 2 (A) and (B) contained notable Raman bands for both dentin collagen and adhesive, thus the related region was determined as the adhesive/dentin interface. The result indicated that the specimens without or with nonthermal plasma treatment showed a similar thickness of interface region. In order to evaluate the adhesive penetration into the demineralized dentin, relative intensity ratios of $1454\text{ cm}^{-1}/1667\text{ cm}^{-1}$ and $1609\text{ cm}^{-1}/1667\text{ cm}^{-1}$ were calculated. A spectral subtraction technique^{4, 31} was employed prior to the band ratio calculation using spectra from the interface region. The spectral subtraction eliminated the interference of Raman signals between adhesive and dentin collagen. As shown in Figure 3, after subtraction, we were able to obtain “pure” spectra associated with adhesive and dentin in the interface region, respectively.

Figure 4 (A) showed the calculated band ratios of $1454\text{ cm}^{-1}/1667\text{ cm}^{-1}$ in the interface region for specimens without and with non-thermal plasma treatment. The result indicated that the specimens with non-thermal plasma treatment had significantly higher ratios of $1454\text{ cm}^{-1}/1667\text{ cm}^{-1}$ as compared to the specimens without plasma treatment. However, the comparison of $1609\text{ cm}^{-1}/1667\text{ cm}^{-1}$ ratios between specimens without and with plasma treatment showed no apparent difference, as indicated in Figure 4 (B). Band ratios of $1609\text{ cm}^{-1}/1454\text{ cm}^{-1}$ and $1113\text{ cm}^{-1}/1454\text{ cm}^{-1}$ were also determined to understand the effect of plasma treatment on the relative content of individual component (BisGMA) in the overall model adhesive at different positions. The result shown in Figure 5 disclosed that both band ratios of $1609\text{ cm}^{-1}/1454\text{ cm}^{-1}$ and $1113\text{ cm}^{-1}/1454\text{ cm}^{-1}$ for specimens with plasma treatment showed lower values than those without plasma treatment.

The influence of non-thermal plasma treatment on the polymerization performances of the model adhesive was also investigated. Figure 6 (A) and (B) showed representative micro-Raman mapping spectra collected across the interface and adhesive layer at 2- μm intervals for specimens without and with plasma treatment (the spectral interference from dentin collagen was removed from the spectra of interface shown using the spectral subtraction technique). By integrating the band heights of 1640 cm^{-1} and 1454 cm^{-1} , and normalizing with respect to their band heights of spectra for monomer, the DC would be quantified.

Figure 6 (C) displayed the calculated DC for the model adhesive in both the adhesive layer and interface regions. The data indicated that in the adhesive layer region, the mean values of DC for specimens with plasma treatment were generally greater than those without plasma treatment. However, the difference was not statistically significant. Differences of DC for the two groups of specimens became more apparent as the location was closer to the interface region. At the interface, the obtained DCs for specimens with plasma treatment were significantly greater than those without plasma treatment.

Figure 7 showed representative SEM micrographs of the interfaces between model adhesive and dentin without (A and B) and with (C and D) non-thermal plasma treatment. SEM results depicted that a hybrid layer and adhesive resin tags were clearly observed in both interfaces. The hybrid layer thickness for two different groups of specimens was similar, which was about 3-4 μm . However, in specimens with plasma treatment the width of hybrid layer was more uniform, and slightly more than that in untreated specimens. In addition, as compared to the specimens without plasma treatment, the morphology of those with plasma treatment appeared much less gap and/or cracks between the hybrid layer and adhesive layer. In addition, the specimens with plasma treatment formed longer ($\sim 80 \mu\text{m}$) resin tags than their counterpart ($\sim 40 \mu\text{m}$) of without plasma treatment.

4. Discussion

A basic tenet of adhesion is that bonding solution must come into close contact with the substrate to facilitate molecular interaction and allow either surface micromechanical entanglement or chemical absorption^{16, 32}. Dentin bonding depends not only on the wetting ability of the adhesive system itself, but also on the corresponding capability of the dentinal surface to accommodate and promote wettability^{15, 33}. In the present study, using of nonthermal atmospheric plasmas was disclosed to be an effective approach to enhancing the penetration of adhesive at the interface with dentin. After non-thermal plasma treatment, the contents of the model adhesive at the adhesive/dentin interface regions were significantly higher than those without plasma treatment (Figure 4 A). The improvement of adhesive penetration with plasma treatment could also be confirmed by SEM observations at the adhesive/dentin interface (Figure 7). The present study further suggested that non-thermal plasma treatment could benefit polymerization of the model adhesive, especially in the interface region (Figure 6). The calculated DC of the adhesive clearly showed a higher level for the plasma-treated specimens as compared to the untreated ones. Therefore, the null hypothesis that non-thermal plasma treatment would not enhance the adhesive penetration and polymerization efficacy at the interface with dentin was rejected.

Non-thermal atmospheric plasmas contain charged species, radicals and energetic photons capable of specific surface modifications. Plasma treatment can lead to an increase of surface energy and produce hydrophilic characteristics on the solid surface, due to removal of hydrocarbon and introduction of hydroxyl groups^{21, 25, 26}. Our previous study²⁰ has revealed that the non-thermal atmospheric argon plasma brush was very efficient in improving hydrophilicity and wettability of dentin surface. 30 s of plasma treatment could decrease the water contact angle of dentin surface from 65° to 4° , which was close to a value of super hydrophilic surfaces. This feature of non-thermal atmospheric plasmas should have

played significant role in the observed better penetration of the model adhesive for the present study. Furthermore, it is disclosed that plasma treatment contributed differently to the penetration of individual components of the model adhesive due to their distinct hydrophilicity (BisGMA is more hydrophobic in comparison with HEMA). In this study, with the help of micro-Raman technique, we were able to identify penetration of a specific component (for example, BisGMA) of the model adhesive into the demineralized dentin, as well as its relative content. As shown in Figure 4, the penetration of the overall model adhesive was higher at the adhesive/dentin interface after plasma treatment as compared to untreated control (Figure 4A). However, the content of BisGMA in the same region/location showed no significant difference between plasma-treated and untreated specimens (Figure 4B). Analysis of the above information would enable us to conclude that the plasma treatment had led to a compositional change with the model adhesive in the interface region, inducing more adhesive (especially HEMA) penetration in the interface. This was further confirmed by the changes in the $1609\text{ cm}^{-1}/1454\text{ cm}^{-1}$ and $1113\text{ cm}^{-1}/1454\text{ cm}^{-1}$ ratios between the two groups shown in Figure 5. Such detailed information provided by micro-Raman technique would be critical to understand the role of plasma treatment in the interfacial bonding of the adhesive systems containing components with distinct hydrophilicity/hydrophobicity.

Another important reason for the enhanced adhesive penetration (particularly its hydrophilic component, HEMA) by plasma-treatment is associated with the produced chemical and/or physical interactions between adhesive and dentin. Non-thermal atmospheric plasmas can create highly reactive particles that cross-link or react rapidly to form various chemical functional groups on the substrate surfaces^{24, 34, 35}. This provides unique opportunity to enhance the affinity of dental adhesive components (such as HEMA) with dentin or its components such as collagen fibrils through specific binding approaches. A recent study³⁶ has demonstrated that non-thermal atmospheric plasmas could induce significant chemical bonding or grafting of HEMA onto dentin collagen. In addition, reactive oxygen species in the plasmas could be incorporated into the type I collagen molecules as carbonyl groups via surface interactions, which are believed to play a role in increasing hydrogen bonding³⁷ between the collagen fibrils and adhesive. Both strong chemical and physical bondings formed by plasma treatment would consequently promote HEMA to migrate into the demineralized dentin.

It is noted that treatment with non-thermal atmospheric plasmas could also improve polymerization of the model adhesive, especially at the interface. The plasma-treated specimens showed a DC level of $\sim 94\%$ at the interface, which was distinctly higher than that of $\sim 77\%$ for the untreated specimens (Figure 6C). The improvement of DC might be related to plasma-induced polymerization. Upon plasma treatment, the energy generated from collisions of excited particles (direct transfer) and the irradiation of photons (indirect transfer)^{38, 39} were transferred to the dentin surface. Since plasma-treated dentin substrate was immediately coated with the model adhesive, the energy transferred from plasmas would still remain active and induce cleavage of vinyl double bonds of the adhesive monomers to form di-radicals, thus initiating polymerization. The more the produced di-radicals, the higher the performance of plasma-induced polymerization. This explains observations that DC improvement was especially pronounced in the interface region and at

locations close to the interface (i.e., within the adhesive layer close to dentin surface). Moreover, plasma-induced polymerization also showed advantage in that it is less dependent on water content⁴⁰ as compared to free radical photopolymerization. This could be beneficial to achieve an optimal DC at a location with considerable water or dentinal fluids presence, such as in the interface region.

In consistent with the micro-Raman result, morphological evidence provided by SEM also demonstrated dramatic effect of plasma treatment on penetration of the model adhesive. Figure 7 clearly displayed more uniform hybrid layer, better interface integrity in plasma-treated specimens than untreated controls. Obtained morphological features of the interfacial areas generally correlate to their bonding capacity. Previous studies^{5, 15, 33} have illustrated a close relationship of adhesive penetration with the resulting bond strength. Therefore, the current result suggests that non-thermal plasmas might be able to increase bond strength through enhancing adhesive penetration. Additionally, the plasma-treated specimens exhibited much less morphological features of cracks and gaps in the interface region. This may imply higher resistance of plasma-treated specimens to interfacial microleakage, hydrolytic degradation, or bacterial attack^{6, 7}. Overall, morphological observation provided in this study suggests the potential of plasma treatment to improve the adhesive/dentin interfacial adhesion. Further efforts are needed to verify practical bonding performance of plasma-treated interfaces especially with regard to the long-term stability.

In summary, the present study has provided detailed information to understand the mechanism of plasma treatment for improving adhesive penetration and polymerization at bonding interface with dentin. The result obtained may offer better prospect of using plasmas in dental therapies to optimize adhesion between tooth substance and restorative materials.

Acknowledgments

This investigation was supported by Research Grant R01-DE021431 from the National Institute of Dental and Craniofacial Research, National Institutes of Health, Bethesda, MD 20892, USA.

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Figure 1.
Photograph of the non-thermal atmospheric plasma brush set-up.

Figure 2. Micro-Raman mapping spectra acquired at 1- μ m intervals across the dentin, adhesive/dentin interface, and adhesive layer for the specimens (A) without and (B) with plasma treatment.

Figure 3.

Illustration of the spectral subtraction technique with the purpose to eliminate the interference of Raman signals between adhesive and dentin collagen. Spectra in (A) and (B) represent those of the specimens without and with plasma treatment, respectively. Each of the spectra employed was the third spectrum collected from the adhesive/dentin interface. Raman spectra of pure dentin and adhesive were from the underlying dentin and adhesive layer of the same specimen, respectively. The following criteria was followed: the amide I at 1667 cm^{-1} peak needed to be removed after subtracting pure dentin, or the 1609 cm^{-1} peak from adhesive needed to be removed after subtracting pure adhesive. The negative peak at $950\text{--}980\text{ cm}^{-1}$ was due to the phosphate peak at 960 cm^{-1} of dentin after subtraction.

Figure 4.

Micro-Raman band ratios of (A) $1454\text{ cm}^{-1}/1667\text{ cm}^{-1}$ and (B) $1609\text{ cm}^{-1}/1667\text{ cm}^{-1}$ as a function of position in the adhesive/dentin interface region. There was a significant difference ($P < 0.05$) with the $1454\text{ cm}^{-1}/1667\text{ cm}^{-1}$ (A), while no significant difference ($P > 0.05$) with the $1609\text{ cm}^{-1}/1667\text{ cm}^{-1}$ (B) for the specimens without and with plasma treatment.

Figure 5. Micro-Raman band ratios of (A) $1609\text{ cm}^{-1}/1454\text{ cm}^{-1}$ and (B) $1113\text{ cm}^{-1}/1454\text{ cm}^{-1}$ as a function of position in the adhesive/dentin interface region. There was significant difference ($P<0.05$) with both the $1609\text{ cm}^{-1}/1454\text{ cm}^{-1}$ and $1113\text{ cm}^{-1}/1454\text{ cm}^{-1}$ for the specimens without and with plasma treatment.

Figure 6.

Micro-Raman mapping spectra acquired at 2-μm interval across the adhesive/dentin interface and adhesive layer for the specimens (A) without and (B) with plasma treatment, as well as the calculated degree of conversion (C) of the model adhesive in both regions. There was significant difference ($P < 0.05$) with calculated DCs in the interface region for the specimens without and with plasma treatment.

Figure 7. Representative SEM micrographs of the adhesive/dentin interface for the specimens (A, B) without and (C, D) with plasma treatment.