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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 dentine.

Methods: Prepared dentine 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 dentine, adhesive/dentine interface, and adhesive layer at 1-μm spatial resolution. SEM was also employed to examine the adhesive/dentine 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/dentine 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/dentine 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 dentine 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.

1. Introduction

Contemporary dental restorative techniques usually include a dentine bonding step in order to create a stable bond/connection between composite resin and intact dentine. A fundamental principle of dentine bonding is related to the concept of hybridization of tooth tissue with primer/adhesive systems (to form the so-called hybrid

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layer).[1,2] Hybridization involves penetration of the primer/adhesive into the dentine substrate. In the systems where etching precedes the priming and bonding steps, the interfacial compatibility of the primer/adhesive formulation with the demineralized dentine 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 environment,[6–8] which will further contribute to hydrolytic degradation of the hybrid layer. Under *in vivo* conditions, the adhesive/dentine 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]

Dentine surface can be different in its structure, morphology, and chemical composition, which may affect the ability of dentine bonding systems in achieving good/durable adhesion .[14–16] Recently, efforts have been devoted to develop dentine 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 dentine. 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/dentine 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/dentine 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 dentine.

2. Materials and methods

2.1. *Adhesive/dentine 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 dentine surfaces with 600-grit silicon carbide sandpaper for 30 s. The prepared dentine 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 (Fig. 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