Title
Bond strength of etch-and-rinse and self-etch adhesive systems to enamel and dentin irradiated with a novel CO2 9.3 µm short-pulsed laser for dental restorative procedures

Author
Bartolome, Nicole Ong

Publication Date
2017

Peer reviewed|Thesis/dissertation

Bond strength of etch-and-rinse and self-etch adhesive systems to enamel and dentin irradiated with a novel CO_2 9.3 μm short-pulsed laser for dental restorative procedures

by

Nicole Ong Bartolome, DDS

THESIS

Submitted in partial satisfaction of the requirements for the degree of

MASTER OF SCIENCE

in

Oral and Craniofacial Sciences

in the

GRADUATE DIVISION

of the

UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

DEDICATION

This project could not be completed without the guidance and support of my loving family: my parents, Constante and Evelyn Bartolome; my sister, Desiree Lapira; and my fiancé, Jason Le. I dedicate my work and accomplishments not only to them, but also to all friends and family who have encouraged me along the way.

SPECIAL ACHNOWLEDGEMENT

I would like to express my deepest gratitude to a team of people, whom without their help this project would not have been possible:

My greatest appreciation goes to my mentor, Dr. Peter Rechmann for his constant guidance, support and dedication to this project. Thank you to Mrs. Beate Rechmann for your assistance and encouragement throughout the process. To my thesis committee members, Dr. John Featherstone and Dr. Ignatius Nate Gerodias, thank you for your critique and advice. Thank you, Charles Le for your assistance in the laboratory, and UCSF pre-doctoral students, Brian Lee and Khanh Ngyuen for your hard work and contribution to the project. Lastly, thank you Dr. Krunal Sherathiya for your collaboration and guidance. It truly has been an honor to work with such an amazing team.

CONFLICTS OF INTEREST DISCLOSURES

This study is a Principle Investigator Initiated Study and was funded by Convergent Dental, Inc. through University of California, San Francisco's Contracts & Grants Division.

ABSTRACT

Bond strength of etch-and-rinse and self-etch adhesive systems to enamel and dentin irradiated with a novel CO_2 9.3 µm short-pulsed laser for dental restorative procedures

By

Nicole Ong Bartolome, DDS

BACKGROUND:

The bonding protocol of the dental substrate is essential for successful adhesive restorations. Dental adhesive systems can be classified into two categories: etch-and-rinse (total-etch) and self-etch systems. Highly absorbed 9.6µm CO_2 short-pulsed laser prototype irradiation has successfully shown enhancement of enamel caries resistance in laboratory and prospective, randomized controlled clinical studies. Recently, a 9.3µm microsecond short-pulsed CO_2-laser was introduced to the dental profession. In addition to caries preventive procedure, this laser can be used for tooth preparation and osseous surgery.

OBJECTIVES:

The objective of this study was to evaluate the CO_2 9.3µm short-pulsed laser irradiation influence on shear bond strength of composite to enamel and dentin.

METHODS:

200 enamel and 210 dentin samples were irradiated with a 9.3μm carbon-dioxide laser (Solea, Convergent Dental; Needham, MA) with energies enhancing caries resistance for ablation of enamel and dentin. A 5th generation etch-and-rinse bonding agent OptiBond Solo Plus [OptiBondTE] (Kerr Corporation; Orange, CA) and Peak Universal Bond light-cured adhesive [PeakTE] (Ultradent Products) were used on both ablated enamel and dentin. A 6th generation self-etch system Scotchbond Universal [ScotchbondSE] (3M ESPE, St. Paul, MN) and Peak SE self-etching primer with Peak Universal Bond light-cured adhesive [PeakSE] were used on both ablated enamel and dentin. Clearfil APX (Kuraray, New York, NY) composite was bonded to the samples, and after 24 hours storage at 37°C, a single plane shear bond test was performed to determine enamel and dentin bond strengths.

RESULTS:

Using the caries preventive setting on enamel resulted in increased shear bond strength values for all bonding agents except for self-etch PeakSE with a slight, statistically non-significant 16.3% decrease. The highest overall bond strength to caries preventive-treated enamel was seen with PeakTE (41.29±6.04MPa), presenting a 6.6% increase over the not laser treated control.

To ablated enamel, etch-and-rinse systems achieved higher bond strength values than the self-etch systems. PeakTE showed the highest shear bond strength with 35.22±4.40MPa (90.9% of the not laser treated control). OptiBondTE reached 93.8% of the control bond strength values. The self-etch system PeakSE presented significantly lower bond strength

(41.7 to 53.9% of control value), ScotchbondSE showed a non-significant increase of the bond strength after enamel ablation.

After ablation of dentin the shear bond strength values ranged between 19.15±3.49MPa for OptiBondTE and 43.94±6.47MPa for PeakSE. The shear bond strength was significantly lower (57.2 and 75.4% of the not laser treated control values) for all bonding systems.

CONCLUSION:

Etch-and-rinse systems achieve consistently high bond strengths to short-pulsed CO_2 9.3μm laser-ablated enamel. After irradiation with the highest recommended energy for laser dentin removal, PeakSE reached 43.9±6.5MPa bond strength followed by 36.0±7.4MPa for PeakTE and 25.3±3.8MPa for ScotchbondSE. Following dentin ablation, all bonding agents reached higher shear bond strength values than the reported required minimum value.

KEYWORDS:

CO_2 9.3μm laser, microsecond short-pulsed, human enamel, human dentin, laboratory study, shear bond strength, etch-and-rinse, self-etch, scanning electron microscopy

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The bonding protocol of the dental substrate is essential for successful adhesive restorations. Dental adhesive systems can be classified into two categories: etch-and-rinse (total-etch) and self-etch systems (1,2). The etch-and-rinse protocol involves the prior application of phosphoric acid, which produces deep etch-pits in the hydroxyapatite (HAp)-rich substrate of enamel. This facilitates penetration of the bonding agents to form resin tags that enhances micromechanical retention (3,4). Etch-and-rinse as well as self-etching agents demineralizes up to a depth of a few micrometers to expose a HAp-deprived collagen mesh in dentin (1). Consequently, a hybrid layer is created with the exposed collagen fibrils, which are infiltrated by hydrophilic monomers (5,2). Etch-and-rinse adhesives are available for use in three steps (acid etching, primer, adhesive) or two steps (acid etching with primer and adhesive in a single formulation). Self etch systems do not use phosphoric acid but instead utilize a weaker acidic monomer that does not remove the smear layer. This weak acidic monomer is not rinsed away and along with the primer and bonding agent is applied all-in-one and then light cured to form a hybrid layer.

The Erbium laser has been considered as an alternate technique to etch enamel for restorative and orthodontic bonding (6-9). A number of studies demonstrated that the Er:YAG laser can etch enamel with negligible thermal damage (10-13). Other studies have indicated that Erbium laser-etched enamel surfaces bond less effectively than conventional phosphoric acid etched surfaces (14-16).

The 9.3 and 9.6μm carbon dioxide laser wavelengths are strongly absorbed by dental enamel (17). The enamel absorption coefficient at these specific wavelengths is ten times higher than the absorption coefficient of the traditional 10.6μm CO_2 surgical laser

(18). The highly absorbed 9.6μm CO_2 short-pulsed laser prototype irradiation has shown enhancement of enamel caries resistance in laboratory studies (17,19-21) and in prospective, randomized controlled clinical studies (22,23).

Recently, a 9.3μm microsecond short-pulsed CO_2-laser was introduced to the dental profession. In addition to caries preventive procedure, this laser can be used for tooth preparation and osseous surgery. The objective of this present in vitro study was to evaluate whether CO_2 9.3μm short-pulsed laser irradiation for cutting enamel or dentin enhances or reduces the shear bond strength of composites to the irradiated enamel and dentin surfaces.

OBJECTIVE

The objective of this present in vitro study was to evaluate whether CO_2 9.3μm short-pulsed laser irradiation for cutting enamel or dentin enhances or reduces the shear bond strength of composites to the irradiated enamel and dentin surfaces.

HYPOTHESIS

The use of CO_2-9.3 μm, short-pulsed laser irradiation (Solea, Convergent Dental Inc., Natick, MA) on sound human enamel and dentin produces superior bond strength in comparison to conventionally prepared enamel and dentin surfaces using different adhesive systems (self-etch and etch-and-rinse) as indicated by bond strength measurements in a laboratory study.

RESEARCH AIMS

Aim 1: To test shear bond strength to human enamel and dentin after 9.3 μm short-pulsed CO_2 laser irradiation with different fluences followed by etch-and-rinse bonding (Peak Universal Bond and Optibond Solo Plus).

Aim 2: To test shear bond strength to human enamel and dentin after 9.3 μm short-pulsed CO_2 laser irradiation with different fluences followed by self-etch bonding (Peak Universal Bond and Scotchbond Universal).

MATERIALS & METHODS

Human enamel and dentin samples were irradiated with a CO_2 9.3μm short-pulsed laser using up to six different laser energies and two irradiation patterns. Composite resin bonding was accomplished with two etch-and-rinse and two self-etch bonding systems. Shear bond strength was tested after 24 hours of storage.

Test samples

After sterilization with gamma irradiation (Cs 137) at a dose above 173 krad for 12 hours, freshly extracted, erupted human molars were kept in 0.1% thymol solution in deionized water. The teeth were collected under University of California at San Francisco Institutional Review Board exempt approval for collecting extracted teeth for research purposes.

At the cemento-enamel junction the roots were removed and the remaining dental crowns were sectioned into distal and mesial halves. The proximal surface of each half of the molar crown provided sufficient enamel or dentin surface for the bonding of only one

sample. Cylindrical blocks with the proximal surfaces on one side were created with acrylic resin (Blue Clear Acrylic, Great Lakes Orthodontics, NY). The whole dentin surface was polished with 600 silicon carbide papers; enamel was polished with 600 silicon carbide papers until 3mm of surface area was exposed. To remove polishing remnants, the samples were sonicated for 5 minutes and then transferred to a 0.1% thymol solution at room temperature until bonding. A total of 200 enamel and 210 dentin samples were used for bonding and shear bond strength testing. Each testing group comprised of 10 samples.

Laser settings and irradiation mode

A CO_2 laser emitting a wavelength of 9.3μm was used (Solea, Convergent Dental, Inc., Natick, MA). Pulse durations were set to 3, 7, 23, 43, 63 and 83μs, respectively, delivering pulse energies between 1.6mJ/pulse and up to 118.4mJ/pulse. The resulting fluences were between 3.3J/cm^2 and 241.6J/cm^2 at pulse repetition rates of 12.5 and 41.3Hz (at the single beam level). With a BeamTrack - Power/Position/Size Thermal Sensor 50(150)A-BB-26-PPS (Ophir-Spiricon, LLC, North Logan, UT) the pulse energy was measured before and after irradiation of 15 samples.

The beam diameter was 0.25mm, the laser focus length was 4 to 15 millimeter. The laser emitted a square pulse shape with a sharp initial peak. An Ophir-Spiricon Pyrocam III pyroelectric camera with BeamGage V5.11 Software was used to determine the beam profile and the beam was Gaussian.

Computer controlled galvos located inside the delivery handpiece managed the beam control by directing the original 0.25mm diameter beam. Two beam diameters were

subsequently used: the original 0.25mm diameter and a spiral beam pattern resulting in a 1mm irradiated surface area.

Table 1 for enamel and table 2 for dentin list the different laser settings - laser "speed" (set on the Graphic User Interface), pulse repetition rate, engaged beam pattern, and power and fluence at the basic 0.25mm single irradiation spot. To cover the sample area, the laser beam was moved in a sweeping motion by hand at a working distance of approximately 10 to 15mm. Enamel ablative energies were applied with 100% air-water mist (12ml water/min). One setting known to enhance caries resistance of enamel was used without air-water mist. Caries preventive irradiation resulted in no or only minor surface melting (3µs pulse duration) (23,21), while irradiation with 43 or 83µs pulses ablated enamel. When using ablative energies, only brief irradiation times (10 sec or less) were employed to prevent major substance loss with deepening of the surface.

Table 1: Laser parameters, energy settings and intended clinical effect on enamel

Enamel Clinical Effect	Pulse duration (µs)	"Speed" (%)	Repetition Rate (Hz)	Beam Pattern (mm)	Irradiation time (sec)	Power (mW)	Fluence / Pulse (J/cm^2)
Ablation/ Cutting	83	100	12.5	1 (spiral)	10	4,831	56.4
Ablation / Cutting	83	100	41.3	0.25	10	4,890	241.6
Ablation/ Cutting	43	100	12.5	1 (spiral)	10	2,604	30.4
Ablation / Cutting	43	100	41.3	0.25	10	655	75.1
Caries prevention	3	30	41.3	0.25	60	66	3.3

Irradiation of dentin occurred with three ablative energies (23, 43, 63µs pulse duration) and one low energy (7µs pulse duration, which was the lowest energy to show by observation with a stereomicroscope at 10x magnification a first small effect on dentin while 100% air-water mist was applied). The dentin irradiation was performed with 100% air-water mist (12ml water/min). An additional dentin group, using 0.25mm beam diameter and 7µs pulse duration with air-water mist reduced to 1% (8ml water/min), was studied to determine the influence of low (insufficient) water application during irradiation on bonding.

Table 2: Laser parameters, energy settings and intended clinical effect on dentin

Dentin Clinical Effect	Pulse duration (µs)	"Speed" (%)	Repetition Rate (Hz)	Beam Pattern (mm)	Irradiation time (sec)	Power (mW)	Fluence / Pulse (J/cm²)
Ablation/ Cutting	63	30	41.3	0.25	10	966	47.7
Ablation / Cutting	43	30	41.3	0.25	10	655	32.4
Ablation/ Cutting	23	30	41.3	0.25	10	352	17.4
"first visible effect"	7	30	41.3	0.25	10	122	6.0

Enamel irradiation occurred with 0.25 and 1.00mm beam patterns, but dentin was irradiated only with the 0.25mm irradiation pattern to reduce potential dentin overheating. At the 0.25mm beam pattern single laser pulses are emitted. The 1mm spiral pattern used "double pulses" (two pulses immediately after each other) before the galvos directed the beam to the next irradiation spot (software V2.6; software release V3.0 allows only a single

pulse at each spot of each pattern). Double-pulses result in a higher surface temperature at the irradiated spot because the second pulse hits before sufficient cooling occurs (thermal relaxation time is longer than the time in between the double pulses).

Adhesive composite system

Two 5th generation etch-and-rinse (OptiBond Solo Plus after Kerr Gel Etchant application [OptiBondTE] (Kerr Corporation, Orange, CA) and Peak Self-Limiting Etchant Ultra-Etch with Peak Universal Bond light-cured Adhesive [PeakTE] (Ultradent Products, Inc., South Jordan, UT) and two 6th generation self-etch bonding systems (Scotchbond Universal [ScotchbondSE] (3M ESPE, St. Paul, MN) and Peak SE self-etching primer with Peak Universal Bond light-cured Adhesive [PeakSE] (Ultradent Products, Inc., South Jordan, UT) were used. The composite resin employed in this study was Clearfil APX, a micro-hybrid composite (Kuraray America, New York, NY). Etching and bonding were done per manufacturer's instructions (table 3 details the bonding instructions). For each bonding system 10 samples served as control and were not laser treated before bonding.

After the bonding agent was applied and light-cured, the samples were positioned in a bonding clamp underneath a bonding mold insert (Ultradent Products, Inc., South Jordan, UT). A 2.38mm diameter x 3mm in height composite cylinder was bonded on top of the sample surface using the hollow tube of the bonding mold. The composite cylinder was built in one increment and light cured (Satelec® Mini LED curing light, Acteon North America, Mount Laurel, NJ) according to manufacturer's instruction (40 sec). The curing light output was confirmed with a curing radiometer; the curing light had a consistent >1250 mW cm^{-2} output during the study. After removing the samples from the mold, they

were stored in clear water in an incubator at 37°C temperature for 24 hours to allow curing of uncured composite.

Table 3: Manufacturers' bonding instructions

Etch-and-Rinse Agent	
OptiBond Solo Plus	Enamel and dentin is etched with 37.5% phosphoric acid for 15 seconds. The surface is then dried lightly, but not desiccated. The adhesive is applied to the enamel/dentin surface with an applicator tip for 15 seconds, using light brushing motions. The adhesive is air thinned for 3 seconds and light cured for 20 seconds.
Peak Universal Bond	Ultra-Etch is applied with a 'Blue Micro tip' to the prepared tooth surfaces for 20 seconds, followed by a thorough rinse for 5 seconds, and then by a light air drying, leaving the preparation slightly damp. A puddle coat of the bonding agent is applied with the 'Inspiral Brush Tip' and gently agitated for 10 seconds, followed by thinning/drying for 10 seconds using 1/4 to 1/2 air pressure and then by light curing for 10 seconds.
Self-Etch Agent	
Scotchbond Universal	The dentin surface is lightly air dried with only 2-3 airbursts until the surface has a slightly glossy appearance. The enamel is air-dried. Using a disposable applicator, the adhesive is applied to the entire tooth structure and rubbed in for 20 seconds. Subsequently, a gentle stream of air is directed over the liquid for about 5 seconds until it no longer moves and the solvent has evaporated completely. This is followed by light curing for 10 seconds.
Peak SE self-etching primer and Peak Universal Bond	The preparation is rinsed and left damp. The self-etching primer is applied with a 'Black Mini Brush tip' for 20 seconds with continuous scrubbing on dentin and no scrubbing on enamel. Then the primer is thinned/dried for 3 seconds using air and a puddle coat of the Peak Universal Bond is applied with the 'Inspiral Brush tip' and gently agitate for 10 seconds. After thinning/drying for 10 seconds using 1/4 to 1/2 air pressure, the agent is light cured for 10 seconds.

Shear bond strength testing

The adhesive bonding strength of Clearfil APX composite to the enamel or dentin surface was tested with a single plane shear bond test using the UltraTester testing machine (Ultradent Products, Inc., South Jordan, UT). The shear bond strength device was calibrated according to manufacturer's instructions.

The composite cylinder was placed under a 2.38mm notched crosshead assembly. Debonding was performed with a load shell of 1000lbs. (453.6kg) at a constant rate of 1mm/min. At the shear off moment, the peak shear bond strength was recorded automatically.

Statistical methods

Means and standard deviations were calculated for each group. The groups were compared statistically by one-way ANOVA, followed by a Bonferroni's Multiple Comparison Test for significance at $P<0.05$ (Prism, GraphPad software Inc., La Jolla, CA).

Stereomicroscope observations and Scanning Electron Microscopy [SEM]

A stereomicroscope (Fisher Scientific Stereomaster, Fisher Scientific LLC, PA) at 10x magnification was used to observe the debonding failure pattern - adhesive, cohesive with structural failure in enamel and/or composite, or mixed (adhesive and cohesive failure at the same surface). For the SEM investigation, twelve dentin samples were prepared as described above. A set of three samples was irradiated with each of the four dentin-applied energies followed by etch-and-rinse with phosphoric acid on half of the sample. Examination samples were fixed with formalin, desiccated in ascending alcohol solutions,

mounted and examined with the SEM (Sigma 500 VP FE-SEM, Carl Zeiss Microscopy Ltd, United Kingdom) at different magnifications.

RESULTS

Tables 4 and 5 present the shear bond strength values of Clearfil APX to enamel and dentin for controls and CO_2 9.3µm irradiated surfaces using OptiBondTE, PeakTE, ScotchbondSE, and PeakSE. Shown are the average values and standard deviations for different treatments with 0.25 and 1mm beam pattern and for the controls.

Table 4: Shear-Bond strength testing results for human enamel and PeakSE, PeakTE, ScotchbondSE and OptiBondTE as bonding agent with Clearfil APX composite; controls and laser parameters; results in MPa (Mean ± Standard Deviation); "blue" % numbers indicate achieved percent value of control bond strength. Statistically significant differences to the control are marked with asterisks; asterisks indicate significance level (**** P ≤ 0.0001).

Bonding Agent / Laser conditions / Human **Enamel**		Control Mean/SD (MPa)	3 µs/ 0.25mm Mean/SD (MPa)	43 µs/ 0.25mm Mean/SD (MPa)	43 µs/ 1mm Mean/SD (MPa)	83 µs/ 0.25mm Mean/SD (MPa)	83 µs/ 1mm Mean/SD (MPa)
			3.3 J/cm²	75.1 J/cm²	30.4 J/cm²	241.6 J/cm²	56.4 J/cm²
Etch-and-rinse	Peak TE	38.74 6.44 % control	41.29 6.04 106.6%	33.75 4.46 87.1%	33.56 3.57 86.6%	31.83 2.8 82.2%	35.22 4.40 90.9%
	Optibond TE	27.43 4.45 % control	30.73 4.56 112.0%		24.6 2.57 89.7%		25.72 3.08 93.8%
Self-etch	Peak SE	31.46 6.12 % control	26.34 5.95 83.7%	14.08 3.7 **** 44.8%	16.09 3.88 **** 51.1%	13.12 3.08 **** 41.7%	16.95 2.93 **** 53.9%
	Scotchbond SE	15.6 3.92 % control	16.5 3.25 105.8%		17.06 3.4 109.4%		18.75 2.76 120.2%

Table 5: Shear-Bond strength testing results for human dentin and PeakSE, PeakTE, ScotchbondSE and OptiBondTE as bonding agent with Clearfil APX composite; controls and laser parameters; results in MPa (Mean ± Standard Deviation); "blue" % numbers indicate achieved percent value of control bond strength. Statistically significant differences to the control are marked with asterisks; asterisks indicate significance level (** P ≤ 0.01; *** P ≤ 0.001; **** P ≤ 0.0001).

Bonding Agent/ Laser conditions / Human **Dentin**		Control Mean/SD (MPa)	7 µs/ 0.25mm Mean/SD (MPa)	23 µs/ 0.25mm Mean/SD (MPa)	43 µs/ 0.25mm Mean/SD (MPa)	63 µs/ 0.25mm Mean/SD (MPa)
			6.0 J/cm²	17.4 J/cm²	32.4 J/cm²	47.7 J/cm²
Etch-and-rinse	Peak TE	63.02 7.56 % control	40.97 7.78 **** 65.0%	36.85 8.82 **** 58.0%	36.02 9.11 **** 57.2%	36.02 7.44 **** 57.2%
	Optibond TE	31.58 6.02 % control	18.91 3.32 **** 59.9%	19.15 3.49 **** 60.6%	19.98 5.25 **** 63.3%	20.11 3.87 **** 63.7%
Self-etch	Peak SE	58.79 10.94 % control	57.07 7.20 97.0%	38.15 5.44 **** 64.9%	43.90 5.71 *** 74.7%	43.94 6.47 *** 74.7%
	Scotchbond SE	33.15 3.55 % control	28.46 4.65 85.0%	20.82 5.98 *** 62.8%	21.54 5.70 *** 65.0%	25.27 3.80 ** 75.4%

Shear bond strength to enamel

Table 4 shows the shear bond strength results for the control and for the laser test samples on enamel. The laser treatment using the caries preventive setting resulted in increased shear bond strength values for all test groups except for the self-etch system PeakSE, which showed a slight, non-significant 16.3% decrease. The etch-and-rinse PeakTE achieved the highest overall bond strength with a 6.6% increase of bond strength (41.29±6.04MPa) (Mean±Standard Deviation [SD]) over the control value (38.74±6.44MPa). OptiBondTE showed the highest percentage increase in bond strength

over the control value with a 12% gain. The differences in the shear bond strength values between the control and test groups for the caries preventive treated enamel samples were not statistically significant.

After applying laser energies for cutting enamel, most bond strength values were slightly but not significantly reduced. Enamel etch-and-rinse bonding systems to ablated enamel achieved higher shear bond strength values than the self-etch systems. Peak TE showed the highest shear bond strength (35.22±4.40MPa), which was 90.9% of the control value (statistically not significant different). OptiBondTE reached 93.8% of the control bond strength value (25.72±3.08MPa).

The self-etch system PeakSE showed significantly lower shear bond strength values to enamel after applying ablative laser energies, showing only 41.7 to 53.9% of the control bond strength depending on the applied laser energy (control 31.46±6.12MPa; laser 13.12±3.08 to 16.95±2.93MPa; $P \leq 0.0001$). ScotchbondSE, with a low control value of 15.6±3.92MPa, achieved slightly but not statistically significant higher bond strength values at the laser treated surfaces under all treatment conditions. The bond strength increased between 5.8% and 20.2% after ablative energy was applied and was slightly higher than the values of PeakSE. For all bonding systems, no significant differences in shear bond strength values between irradiation with the 0.25 mm and the 1 mm pattern were noted.

Shear bond strength to dentin

Shear bond strength to dentin irradiated with laser energies recommended to cut dentin ranged between 19.15±3.49MPa (OptiBondTE) and 43.94±6.47MPa (PeakSE) (Mean ± SD) (table 5). The shear bond strength reached 57.2 to 75.4% of the non-laser treated

control values. All bond strength reductions were statistically significant with significance levels between P≤0.05 and P≤0.0001. There were no significant differences in the bond strength values between the three different applied ablative energies.

Applying non-ablative energies (7μs pulse duration) for the etch-and-rinse bonding systems resulted in significant decrease of the bond strength values. The etch-and-rinse systems were at 59.9% to 65% of the control values, while the self-etch bonding systems reached 85% to 97%. The values were not significantly different from the controls.

The additional dentin samples (7 μs pulse duration, 0.25 mm beam diameter) irradiated while applying only 1% air-water mist reached only 53.1% of the control bond strength using self-etch PeakSE. In contrast, applying 100% air-water mist lead to 97% bond strength in comparison to the control. The difference was highly significant (P ≤ 0.0001) (Figure 1).

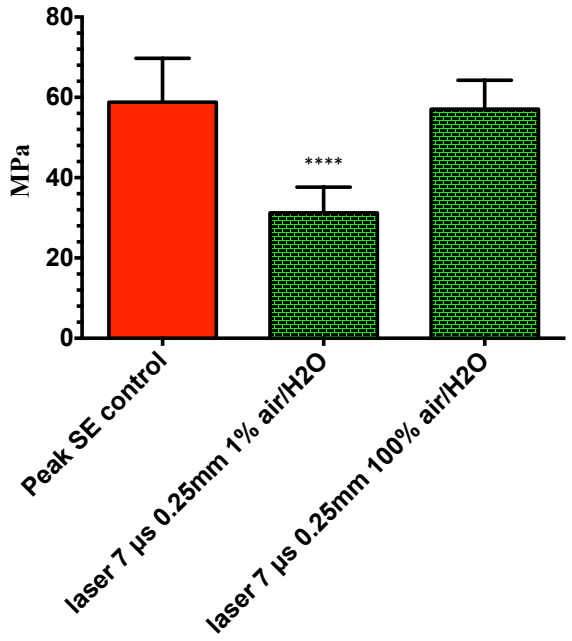

Figure 1: Human dentin – shear bond strength PeakSE, (Mean ± Standard Deviation), control versus laser irradiation with 1% and 100% air/water mist; statistically significant differences to the controls are marked (**** P ≤ 0.0001)

Stereomicroscope and Scanning Electron Microscopical observations

The failure mode incident calculations for composite resin debonding using etch-and-rinse and self-etch bonding systems for enamel and dentin are shown in figures 2 and 3. Adhesive, cohesive, and mixed failures are presented in percentage of observed failure. The enamel and dentin failure mode results are shown separately for controls, test samples irradiated with the low energy (3μs or 7μs pulse duration) and the ablative laser energies combined in one group (figure 2 for enamel and 3 for dentin).

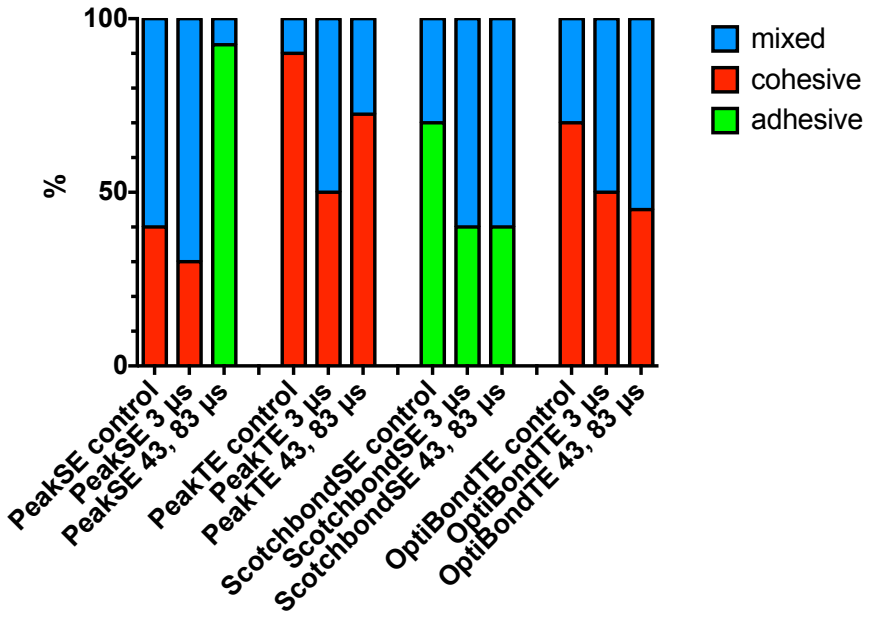

Figure 2: Failure mode for human enamel after shear bond strength testing of PeakSE, PeakTE, ScotchbondSE and OptiBondTE as bonding agents with Clearfil APX composite; adhesive, cohesive, and mixed failure in %; results separated in control, 3μs laser irradiation, and 43 and 83μs pulse duration irradiation combined, respectively.

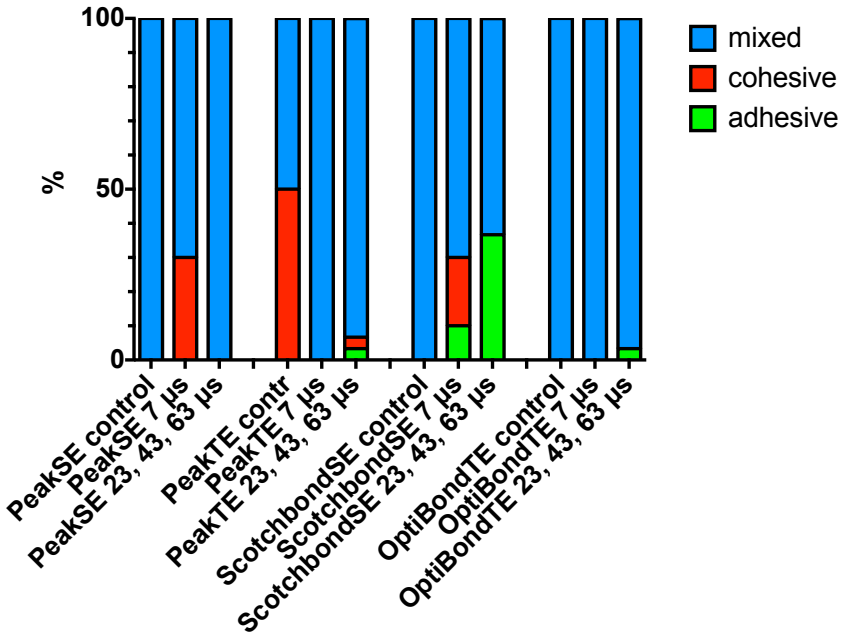

Figure 3: Failure mode for human dentin after shear bond strength testing of PeakSE, PeakTE, ScotchbondSE and OptiBondTE as bonding agent with Clearfil APX composite; adhesive, cohesive, and mixed failure in %; results separated in control, 7µs laser irradiation, and 23, 43 and 63µs pulse duration irradiation combined, respectively.

For enamel, using the caries preventive irradiation, the etch-and-rinse systems or self-etch PeakSE resulted in slightly reduced cohesive failures and increased mixed failures compared to the controls. For ScotchbondSE, this irradiation setting lead to a reduction of adhesive failures and an increase of mixed failures. After application of ablative energies, the etch-and-rinse systems showed slight reductions of cohesive failures in favor of increased mixed failures.

For dentin bonding, the self-etch systems showed 100% mixed failures for the controls. After 7µs energy application, the occurrence of mixed failures was reduced (by 30%) and more cohesive and adhesive/mixed failures were registered. For PeakTE, a 50%

mixed and 50% cohesive failure rate for the controls changed into a 100% mixed failure mode.

When using ablative energies on dentin, PeakSE and OptiBondTE showed no change in failure mode presenting 100% mixed failures. ScotchbondSE changed from 100% mixed failure for the controls to roughly 30% adhesive failures. The failure mode of PeakTE increased from originally 50% cohesive / 50% mixed to more than 90% mixed failure.

Figures 4 through 6 represent the SEM observations of dentin surfaces after laser irradiation with low laser energy and higher ablative energies. After irradiation with 7μs pulses, the CO_2 9.3μm laser irradiated areas showed minimal roughness of the non-etched surface (figure 4, left column). At higher magnifications, no melting was visible and peritubular dentin was visible. After acid etching (figure 4, right column), the laser treated areas presented minor unevenness of the dentin where the roughness was seen before. However, the acid etched non-laser irradiated and the acid etched laser irradiated surfaces showed no differences with open dentin tubules and at high magnifications exposed collagen fibers.

Figure 5 shows human dentin after irradiation with low ablative energies of 20μs pulse duration. The non-etched areas showed slight roughness of the irradiated surface with small islands of melting. After acid etching, the laser-treated areas showed some dentin loss due to the laser ablation but no differences to the non-irradiated areas. Open dentin tubules and exposed collagen fibers were visible at high magnifications. After 40μs pulse duration irradiation, a similar picture with more melting areas than after irradiation with 20μs pulses became visible.

Human dentin irradiated with 60μs pulse duration is demonstrated in figure 6. The non-etched surfaces showed some distinct roughness of the irradiated areas with bigger and more islands of melting than seen after 20μs and 40μs pulses. At higher magnifications, peritubular dentin is visible with molten islands with openings in the areas of dentin tubules. After acid etching, the laser treated and the control areas showed no significant differences. Compared to 20μs and 40μs pulses, the laser ablated more dentin, and again, open dentin tubules and exposed collagen fibers were visible.

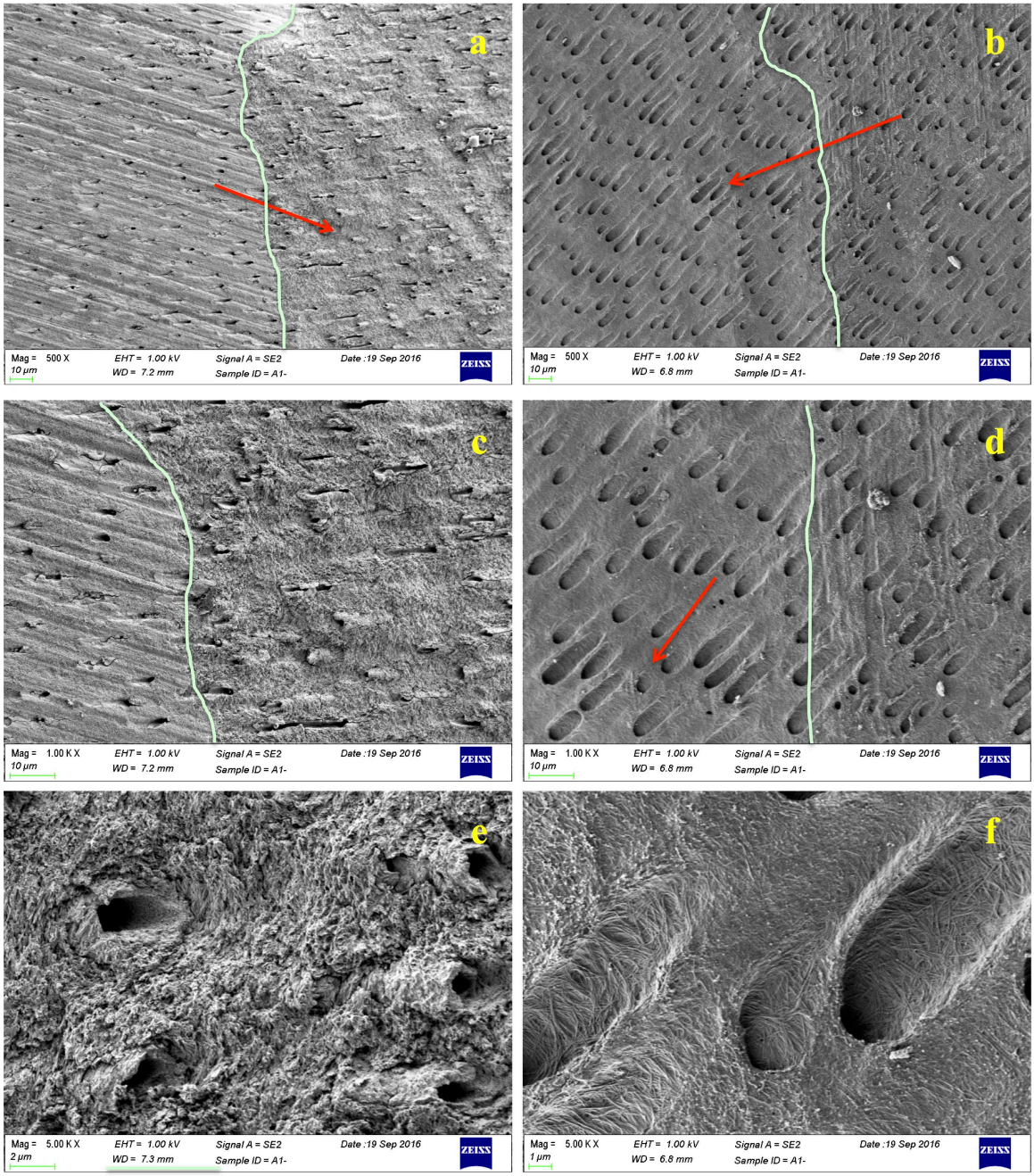

Figure 4: SEM pictures of human dentin after irradiation with 7µs pulse duration. Left column shows control areas and laser irradiated areas with no acid etching. Right column shows laser irradiated areas and non-irradiated areas after acid etching. A very slight roughness of the irradiated non-etched surfaces is visible (a, c). At higher magnifications melting is not visible and, peritubular dentin is evident (e). After acid etching, the laser treated areas show, besides minor dentin unevenness, no differences to the non-irradiated surface (b, d), with open dentin tubules and at high magnifications exposed collagen fibers (f) (red arrows point at area showed at the next higher magnification, green lines demarcate between irradiated and non irradiated surface; left columns non-irradiated area on the left, right columns non-irradiated area on the right).

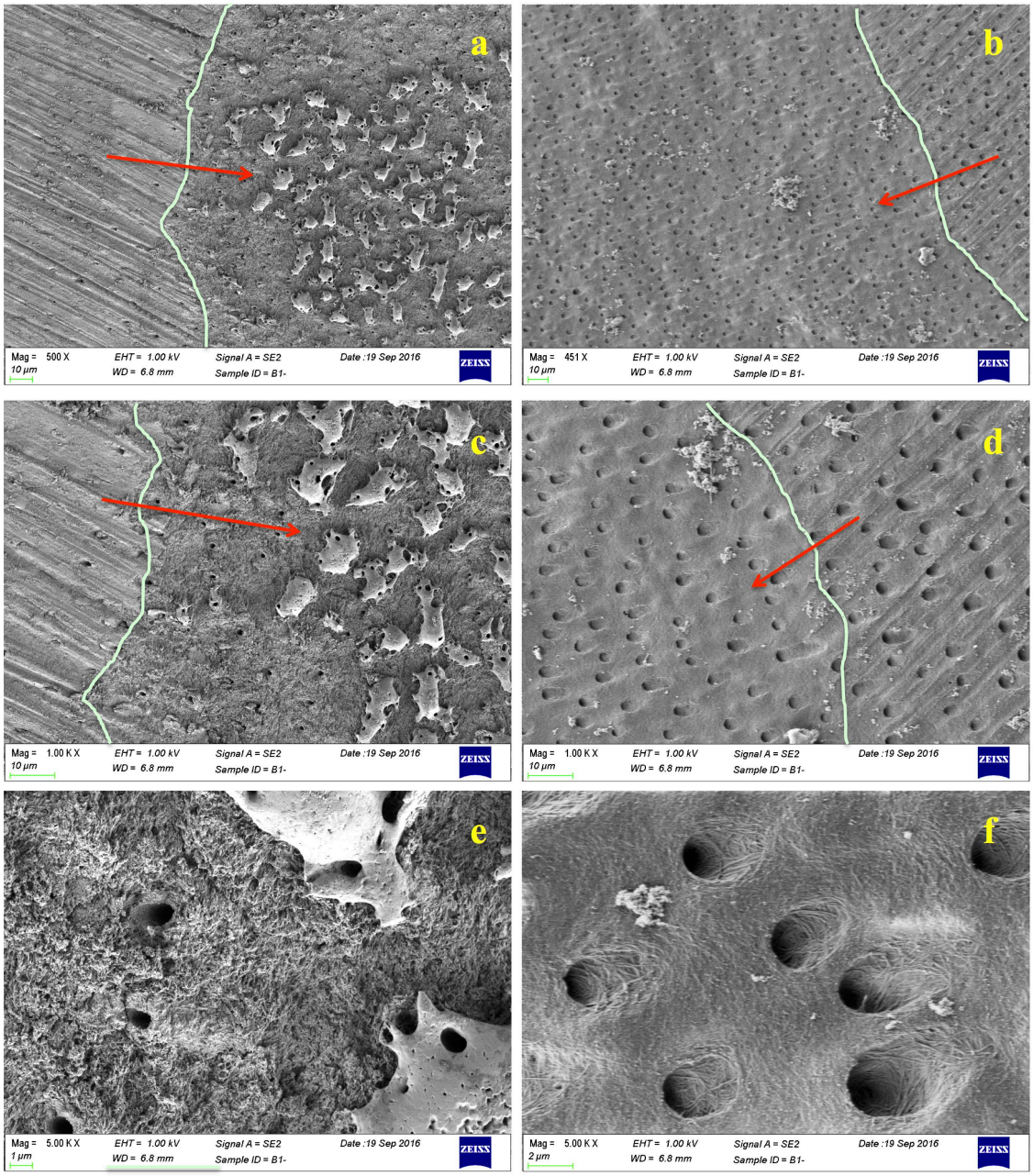

Figure 5: SEM pictures of human dentin after irradiation with 20µs pulse duration. Left column shows control areas and laser irradiated areas with no acid etching, right column shows laser irradiated areas and non-irradiated areas after acid etching. The non-etched areas showed slight roughness of the irradiated surface with small islands of melting (a, c). At higher magnifications peritubular dentin is visible (e). After acid etching laser treated areas show besides slightly enhanced dentin loss no differences to the non-irradiated areas (b, d), with open dentin tubules and exposed collagen fibers at high magnification (f) (red arrows point at area showed at the next higher magnification, green lines demarcate between irradiated and non irradiated surface; left columns non-irradiated area on the left, right columns non-irradiated area on the right).

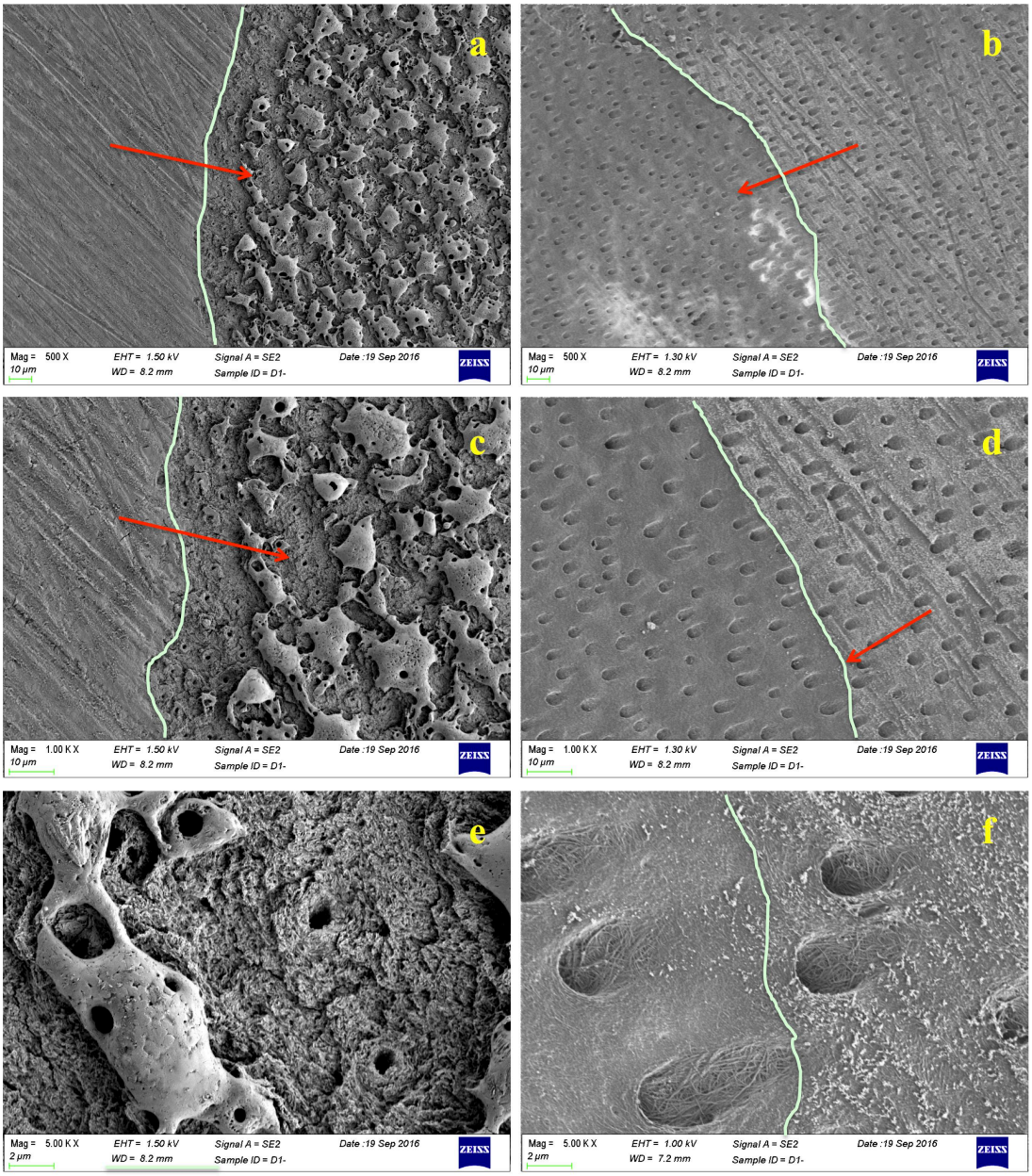

Figure 6: SEM pictures of human dentin after irradiation with 60µs pulse duration. Left column shows control areas and laser irradiated areas with no acid etching, right column shows laser irradiated areas and non-irradiated areas after acid etching. The non-etched surfaces showed some roughness of the irradiated areas with bigger and more islands of melting with openings in the areas of dentin tubules (a, c) (compared to figure 5). At higher magnifications peritubular dentin is visible (e). After acid etching laser treated areas show, besides more pronounced dentin loss, no differences to the non-irradiated surfaces, with open dentin tubules (b, d) and at high magnifications, exposed collagen fibers (f) (red arrows point at area showed at the next higher magnification, green lines demarcate between irradiated and non irradiated surface; left columns non-irradiated area on the left, right columns non-irradiated area on the right).

DISCUSSION

Irradiation with low laser energies - enamel

The use of CO_2 microsecond short-pulsed lasers at 9.6 or 9.3 micrometer wavelength has been reported to enhance caries resistance in laboratory (25,20,19) and clinical studies (23,22). As previously reported, enamel treated with a CO_2 9.3μm laser irradiation using settings known to enhance caries resistance showed significantly increased bond strength to a sealant composite (24). In that study, only one etch-and-rinse bonding system and one sealant composite that was bonded only to enamel surface was tested.

In this present study, both etch-and-rinse systems and the self-etch system ScotchbondSE showed up to 12% enhanced shear bond strength over the controls. Only the self-etch system PeakSE showed a slight but not significant reduction in bond strength to enamel, which was made more acid resistant without visibly modifying the enamel surface (21).

Irradiation with ablative laser energies - enamel

For the bonded enamel controls, the shear bond strength values found in this study were consistent with the literature with the following stated ranges: etch-and-rinse systems OptiBondTE 21.01 to 35.2MPa (26-29) and PeakTE 14.6 to 40.7MPa (30,31), self-etch systems PeakSE 17.8 to 38.3MPa (30,31) and ScotchbondSE 22.9 and 27.7MPa (32-35). In this present study, only ScotchbondSE's bond strength was 30% lower in bond strength than reported in the literature.

In this present study, bonding to cut enamel after CO_2 9.3µm laser ablation using etch-and-rinse systems showed only slightly but not significantly reduced shear bond strength values. This confirmed the findings of Nguyen et al in 2011 (36), who irradiated enamel with a laboratory 9.3µm CO_2 laser using a fast scanned computerized motor-driven stage to move the samples. Fluences of up to 20J/cm^2 were used with the etch-and-rinse system 3M ESPE Single Bond and Z250 composite, which achieved bond strengths of 31.2±2.5MPa (36).

The Nguyen et al results were comparable to values found in this present study for the etch-and-rinse systems. In addition, a clinically more relevant "free-hand" irradiation was used in contrast to a computer-controlled motor-driven stage. Nevertheless, the difference between irradiation modes does not have a major influence on bond strength values (24).

The bonding results for enamel were also independent of the applied laser pattern. The irradiated surface area is a function of the computer-controlled galvos-movement of the original beam with a width of 0.25 mm. Therefore, the beam pattern itself should not influence the bond strength. The study presented here also showed that within the limits of the irradiation energy levels utilized in this study, the applied wide range of fluences between 30.4 J/cm^2 and up to 241.6 J/cm^2 did not result in energy level-dependent significantly different shear bond strength values.

In contrast to the etch-and-rinse systems, the self-etch systems revealed very different results for bonding to enamel after laser ablation. For PeakSE the shear bond strength values were significantly decreased and reached on average only 47.9% of the control values. Unlike the more acidic etch-and-rinse systems, the less acidic nature of 6th

generation bonding agents (pH 1.2) as in the Peak self-etching primer, when applied to the laser treated enamel surface were not as successful in transforming this laser treated molten surface (21) into a strong bonding surface. Scanning electron microscopical pictures had revealed that the strong phosphoric acid was capable of breaking up molten surfaces, showing additional pores for retention (21) while the weaker acidic monomer of the self-etch system obviously was not able to make those transformations. Contrary to PeakSE, ScotchbondSE, another 6th generation product, displayed lower bond values but after laser irradiation the values were slightly enhanced but statistically not significant.

Suzuki et al in 2016 found that the enamel-bonding performance of universal adhesives was dependent on the adhesive material, and etch-and-rinse mode effectively increased the enamel bond strength and durability (35). Soderholm and others also concluded that an enamel etch-and-rinse protocol resulted in higher bond strengths than self-etching adhesives (37). With respect to long-term clinical outcomes, Heintze et al in 2012 stated "if the enamel was etched with phosphoric acid, the mean number of restorations with stained margins was only about 10% after 3 years, increasing to about 20% after 10 years. Composite restorations that are placed with self-etching adhesive systems showed a somewhat higher frequency of stained margins compared to those that were placed with enamel etching" (38). In addition, Sarrett et al specified, "practitioners should try to reduce the risk of marginal staining. This can only be achieved by etching the enamel with 37% phosphoric acid. This operative procedure contributes to less premature replacement of restorations, as general practitioners often associate marginal staining with caries at the margins" (39).

Irradiation with low laser energies - dentin

To prevent charring of the dentin surface even at very low laser energies, air-water mist has to be applied. The CO_2 9.3μm laser is strongly absorbed in water, therefore a 7μs pulse was required to penetrate the water layer and achieve a visible effect on dentin. When this low energy was applied the etch-and-rinse bonding systems showed significant loss in bond strength to dentin while the self-etch systems exhibited only slightly reduced bond strength.

Testing the influence of applied water amount during dentin irradiation revealed that applying air-water mist of 1% instead of 100% reduced the bond strength of Peak SE by more than 45%. Thus, adequate air-water mist cooling is critical during CO_2 9.3μm laser dentin ablation to reduce heat damage to the dentin surface and achieve sufficient bond strength.

Irradiation with high laser energies - dentin

For all four bonding systems used in this study for dentin bonding, the shear bond strength values reported in the literature were confirmed: etch-and-rinse systems PeakTE 35.5 to 51.7MPa (31,40) and OptiBondTE 26.9 to 46.2MPa (41,42,47), self-etch systems PeakSE 35.7 to 39.9MPa (31,43) and ScotchbondSE 32.4 to 42.6MPa (34,44). All shear bond values of the non-irradiated controls were above the lower limits described in the literature. Two systems (PeakTE and PeakSE) exceeded the reported maximum values by roughly 21% and 45%, respectively.

In this present study, the bond strength values for all bonding systems dropped significantly after laser irradiation, independent of the applied energies. For the 5th

generation etch-and-rinse systems, the bond strength values dropped significantly to roughly 60% of the control values. In contrast, the self-etch systems produced the highest bond strength of all bonding systems to dentin after laser use with up to 75% of their control bond strength. Obviously, the self-etch systems overcome changes of the dentin due to the laser dentin irradiation better than the rinse-and-etch systems do. Depending on their capability of removing or retaining a smear layer, it is also likely that the self-etch systems create superior hybrid layers in dentin even after laser irradiation.

As the composite resin polymerizes and shrinks (45), the bond between the dentin bonding system and the tooth should be strong enough to prevent the resin from pulling away from the tooth substrate (46,47). Munksgaard and Asmussen were the first to state a correlation between shear bond strength and marginal gap width of dentin fillings. They concluded that "this correlation predicts that a system must promote a shear bond strength of about 17MPa if gap-free fillings in dentin cavities are to be achieved" (48). All bonding systems used in this present study reached at least the required stated value in shear bond strength after dentin was cut with CO_2 9.3μm laser irradiation. Both the self-etch system PeakSE and the etch-and-rinse PeakTE achieved more than double the minimum required bond strength value (36.0±7.4MPA and 43.9±6.5MPa, respectively).

The scanning electron microscope pictures of dentin after irradiation with a low energy of 7μs pulses showed a very slight roughness and no obvious melting. Obvious melting was observed with increasing the laser energy. When more laser energy was applied to the dentin, the more surface and volume of molten dentin increased. Etch-and-rinse removed the smear layer on the non-laser treated surfaces and the molten dentin on

the irradiated surfaces. Open dentin tubules and exposed collagen inside the tubules as well as in the intertubular dentin areas were visible.

Further research should address the unexpected result that laser-treated dentin surfaces after acid etching appeared similar in SEM level to the acid etched control surfaces but exhibited very different bond strength values. There may be differences in the micro-mechanical interlocking (resin tags) or chemical interactions. Also changes in collagen that were not visible in the SEM may explain the reduced shear bond strength to laser irradiated dentin surfaces.

Limitations of this study

Limitations of this laboratory study are that the shear bond strength tests were performed on healthy teeth and not on teeth after excavation of carious lesions. Bonding to those surfaces might be different. The applied laser settings were within the recommended treatment energy levels and not above. Finally, only one hybrid composite was used and only one bond strength testing method was performed.

CONCLUSION

With regard to enamel rendered caries resistant after irradiation with low laser energies, we accept the hypothesis that laser irradiation produces superior bond strength in comparison to conventionally prepared enamel with both etch-and-rinse and self-etch systems, with exception to PeakSE. However, for higher laser energies used for enamel ablation, we reject the hypothesis for both etch-and-rinse and self-etch adhesive systems as bond strengths were slightly lower for both etch-and-rinse adhesive systems and

significantly lower for PeakSE. ScotchbondSE showed increased bond strength, but not statistically significant.

For dentin irradiated with low laser energies, we reject the hypothesis for etch-and-rinse adhesive systems as bond strengths were significantly lower. However, self-etch systems produced 85-97% of the controls. For high ablative energies, we reject the hypothesis for both etch-and-rinse and self-etch adhesive systems. Etch-and-rinse systems produced significantly lower bond strengths, while self-etch systems produced up to 75% of their control bond strength.

In summary, to obtain high bond strength values after CO_2 9.3μm laser use on enamel, etch-and-rinse bonding agents to bond a composite to the laser treated enamel is advisable. In contrast, with the exception of the etch-and-rinse system PeakTE, self-etch bonding agents achieve higher bond strength values than etch-and-rinse bonding systems to CO_2 9.3μm laser-treated dentin. Following dentin ablation, all bonding agents reached higher shear bond strength values than the reported required minimum value.

REFERENCES

1. Van Meerbeek B, Yoshihara K, Yoshida Y, Mine A, De Munck J, Van Landuyt KL (2011) State of the art of self-etch adhesives. Dent Mater 27 (1):17-28. doi:10.1016/j.dental.2010.10.023

2. Pashley DH, Tay FR, Breschi L, Tjaderhane L, Carvalho RM, Carrilho M, Tezvergil-Mutluay A (2011) State of the art etch-and-rinse adhesives. Dent Mater 27 (1):1-16. doi:10.1016/j.dental.2010.10.016

3. Perdigao J, Frankenberger R, Rosa BT, Breschi L (2000) New trends in dentin/enamel adhesion. Am J Dent 13 (Spec No):25D-30D

4. Voss JE, Charbeneau GT (1979) A scanning electron microscope comparison of three methods of bonding resin to enamel rod ends and longitudinally cut enamel. J Am Dent Assoc 98 (3):384-389

5. Reis A, Zander-Grande C, Kossatz S, Stanislawczuk R, Manso A, de Carvalho RM, Loguercio AD (2010) Effect of mode of application on the microtensile bond strength of a self-etch and etch-and-rinse adhesive system. Oper Dent 35 (4):428-435. doi:10.2341/09-319-L

6. Staninec M, Gardner AK, Le CQ, Sarma AV, Fried D (2006) Adhesion of composite to enamel and dentin surfaces irradiated by IR laser pulses of 0.5-35 micros duration. J Biomed Mater Res B Appl Biomater 79 (1):193-201. doi:10.1002/jbm.b.30530

7. Hossain M, Yamada Y, Nakamura Y, Murakami Y, Tamaki Y, Matsumoto K (2003) A study on surface roughness and microleakage test in cavities prepared by Er:YAG laser irradiation and etched bur cavities. Lasers Med Sci 18 (1):25-31. doi:10.1007/s10103-002-0235-5

8. Staninec M, Xie J, Le CQ, Fried D (2003) Influence of an optically thick water layer on the bond-strength of composite resin to dental enamel after IR laser ablation. Lasers Surg Med 33 (4):264-269. doi:10.1002/lsm.10229

9. Ozer T, Basaran G, Berk N (2008) Laser etching of enamel for orthodontic bonding. Am J Orthod Dentofacial Orthop 134 (2):193-197. doi:10.1016/j.ajodo.2006.04.055

10. Wigdor H, Abt E, Ashrafi S, Walsh JTJ (1993) The effect of lasers on dental hard tissues. J Am Dent Assoc 124:65- 70

11. Takamori K (2000) A histopathological and immunohistochemical study of dental pulp and pulpal nerve fibers in rats after the cavity preparation using Er:YAG laser. J Endod 26 (2):95-99. doi:10.1097/00004770-200002000-00009

12. Freitas PM, Navarro RS, Barros JA, de Paula Eduardo C (2007) The use of Er:YAG laser for cavity preparation: an SEM evaluation. Microsc Res Tech 70 (9):803-808. doi:10.1002/jemt.20470

13. Delme KI, De Moor RJ (2007) Scanning electron microscopic evaluation of enamel and dentin surfaces after Er:YAG laser preparation and laser conditioning. Photomed Laser Surg 25 (5):393-401. doi:10.1089/pho.2006.2069

14. De Munck J, Van Meerbeek B, Yudhira R, Lambrechts P, Vanherle G (2002) Micro-tensile bond strength of two adhesives to Erbium:YAG-lased vs. bur-cut enamel and dentin. Eur J Oral Sci 110 (4):322-329

15. Martinez-Insua A, Da Silva Dominguez L, Rivera FG, Santana-Penin UA (2000) Differences in bonding to acid- etched or Er:YAG-laser-treated enamel and dentin surfaces. J Prosthet Dent 84 (3):280-288. doi:10.1067/mpr.2000.108600

16. Chimello-Sousa DT, de Souza AE, Chinelatti MA, Pecora JD, Palma-Dibb RG, Milori Corona SA (2006) Influence of Er:YAG laser irradiation distance on the bond strength of a restorative system to enamel. J Dent 34 (3):245-251. doi:10.1016/j.jdent.2005.06.009

17. Fried D, Zuerlein MJ, Le CQ, Featherstone JD (2002) Thermal and chemical modification of dentin by 9-11-microm CO2 laser pulses of 5-100-micros duration. Lasers Surg Med 31 (4):275-282

18. Zuerlein MJ, Fried D, Featherstone JDB, Seka W (1999) Optical properties of dental enamel in the mid-IR determined by pulsed photothermal radiometry. Ieee J Sel Top Quant 5 (4):1083-1089. doi:Doi 10.1109/2944.796333

19. Featherstone JD, Barrett-Vespone NA, Fried D, Kantorowitz Z, Seka W (1998) CO2 laser inhibitor of artificial caries-like lesion progression in dental enamel. J Dent Res 77 (6):1397-1403

20. Kantorowitz Z, Featherstone JD, Fried D (1998) Caries prevention by CO2 laser treatment: dependency on the number of pulses used. J Am Dent Assoc 129 (5):585-591

21. Rechmann P, Rechmann BM, Groves WH, Jr., Le CQ, Rapozo-Hilo ML, Kinsel R, Featherstone JD (2016) Caries inhibition with a CO2 9.3 μm laser: An in vitro study. Lasers Surg Med 48 (5):546-554. doi:10.1002/lsm.22497

22. Rechmann P, Charland DA, Rechmann BM, Le CQ, Featherstone JD (2013) In-vivo occlusal caries prevention by pulsed CO2-laser and fluoride varnish treatment - a clinical pilot study. Lasers Surg Med 45 (5):302-310. doi:10.1002/lsm.22141

23. Rechmann P, Fried D, Le CQ, Nelson G, Rapozo-Hilo M, Rechmann BM, Featherstone JD (2011) Caries inhibition in vital teeth using 9.6-μm CO2-laser irradiation. J Biomed Opt 16 (7):071405. doi:10.1117/1.3564908

24. Rechmann, P., Sherathiya, K., Kinsel, R. et al. (2017) Influence of irradiation by a novel CO2 9.3 μm short-pulsed Laser on sealant bond strength. Lasers Med Sci (accepted)

25. Featherstone JD, Nelson DG (1987) Laser effects on dental hard tissues. Adv Dent Res 1

(1):21-26

26. Mortazavi V, Fathi M, Ataei E, Khodaeian N, Askari N (2012) Shear bond strengths and morphological evaluation of filled and unfilled adhesive interfaces to enamel and dentine. Int J Dent 2012:858459. doi:10.1155/2012/858459

27. Kimmes NS, Barkmeier WW, Erickson RL, Latta MA (2010) Adhesive bond strengths to enamel and dentin using recommended and extended treatment times. Oper Dent 35 (1):112-119. doi:10.2341/09-081-L

28. Pivetta MR, Moura SK, Barroso LP, Lascala AC, Reis A, Loguercio AD, Grande RH (2008) Bond strength and etching pattern of adhesive systems to enamel: effects of conditioning time and enamel preparation. J Esthet Restor Dent 20 (5):322-335; discussion 336. doi:10.1111/j.1708-8240.2008.00202.x

29. Khoroushi M, Aghelinejad S (2011) Effect of postbleaching application of an antioxidant on enamel bond strength of three different adhesives. Med Oral Patol Oral Cir Bucal 16 (7):e990-996

30. Ertugrul F, Turkun M, Turkun LS, Toman M, Cal E (2009) Bond strength of different dentin bonding systems to fluorotic enamel. J Adhes Dent 11 (4):299-303

31. Price R, McLeod M, Felix CM (2008) Bond Strengths of Self-Etching Bonding Systems to Dentin and Enamel. J Dent Res 87 (Spec Iss A:0825)

32. Michaud PL, MacKenzie A (2016) Compatibility between dental adhesive systems and dual-polymerizing composite resins. J Prosthet Dent. doi:10.1016/j.prosdent.2016.04.001

33. Isolan CP, Valente LL, Münchow EA, Basso GR, Pimentel AH, Schwantz JK, da Silva AV, Moraes RR (2014) Bond strength of a universal bonding agent and other contemporary dental adhesives applied on enamel, dentin, composite, and porcelain. Applied Adhesion Science 2 (1):1-10. doi:10.1186/s40563-014-0025-x

34. Thalacker C, Loll H, Wiedig CA, Krueger DD (2012) Total-Etch Performance of One Bottle Self-Etch Adhesives. J Dent Res 91 (A):790

35. Suzuki T, Takamizawa T, Barkmeier WW, Tsujimoto A, Endo H, Erickson RL, Latta MA, Miyazaki M (2016) Influence of Etching Mode on Enamel Bond Durability of Universal Adhesive Systems. Oper Dent. doi:10.2341/15-347-L

36. Nguyen D, Chang K, Hedayatollahnajafi S, Staninec M, Chan K, Lee R, Fried D (2011) High-speed scanning ablation of dental hard tissues with a lambda = 9.3 mum CO2 laser: adhesion, mechanical strength, heat accumulation, and peripheral thermal damage. J Biomed Opt 16 (7):071410. doi:10.1117/1.3603996

37. Soderholm KJ, Soares F, Argumosa M, Loveland C, Bimstein E, Guelmann M (2008) Shear bond strength of one etch-and-rinse and five self-etching dental adhesives when

used by six operators. Acta Odontol Scand 66 (4):243-249. doi:10.1080/00016350802220088

38. Heintze SD, Rousson V (2012) Clinical effectiveness of direct class II restorations - a meta-analysis. J Adhes Dent 14 (5):407-431. doi:10.3290/j.jad.a28390

39. Sarrett DC (2007) Prediction of clinical outcomes of a restoration based on in vivo marginal quality evaluation. J Adhes Dent 9 Suppl 1:117-120

40. Andre CB, Gomes BP, Duque TM, Stipp RN, Chan DC, Ambrosano GM, Giannini M (2015) Dentine bond strength and antimicrobial activity evaluation of adhesive systems. J Dent 43 (4):466-475. doi:10.1016/j.jdent.2015.01.004

41. Pecora N, Yaman P, Dennison J, Herrero A (2002) Comparison of shear bond strength relative to two testing devices. J Prosthet Dent 88 (5):511-515. doi:10.1067/mpr.2002.129063

42. Teixeira CS, Chain MC (2010) Evaluation of shear bond strength between self-etching adhesive systems and dentin and analysis of the resin-dentin interface. Gen Dent 58 (2):e52-61

43. Munoz MA, Luque I, Hass V, Reis A, Loguercio AD, Bombarda NH (2013) Immediate bonding properties of universal adhesives to dentine. J Dent 41 (5):404-411. doi:10.1016/j.jdent.2013.03.001

44. Takamizawa T, Barkmeier WW, Tsujimoto A, Berry TP, Watanabe H, Erickson RL, Latta MA, Miyazaki M (2016) Influence of different etching modes on bond strength and fatigue strength to dentin using universal adhesive systems. Dent Mater 32 (2):e9-21. doi:10.1016/j.dental.2015.11.005

45. Ferracane JL, Hilton TJ (2016) Polymerization stress--is it clinically meaningful? Dent Mater 32 (1):1-10. doi:10.1016/j.dental.2015.06.020

46. Price RB, Derand T, Andreou P, Murphy D (2003) The effect of two configuration factors, time, and thermal cycling on resin to dentin bond strengths. Biomaterials 24 (6):1013-1021

47. Price RB, Hall GC (1999) In vitro comparison of 10-minute versus 24-hour shear bond strengths of six dentin bonding systems. Quintessence Int 30 (2):122-134

48. Munksgaard EC, Irie M, Asmussen E (1985) Dentin-polymer bond promoted by Gluma and various resins. J Dent Res 64 (12):1409-1411

Publishing Agreement

It is the policy of the University to encourage the distribution of all theses, dissertations, and manuscripts. Copies of all UCSF theses, dissertations, and manuscripts will be routed to the library via the Graduate Division. The library will make all theses, dissertations, and manuscripts accessible to the public and will preserve these to the best of their abilities, in perpetuity.

Please sign the following statement:

I hereby grant permission to the Graduate Division of the University of California, San Francisco to release copies of my thesis, dissertation, or manuscript to the Campus Library to provide access and preservation, in whole or in part, in perpetuity.

Author Signature

6/8/2017
Date