

A Novel Approach for Improvement of the Interfacial Binding of Ceramics for Dental Materials: Chemical Treatment and Oxygen Plasma Etching

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Received 26 December 2006; accepted 6 May 2007

DOI 10.1002/app.28432

Published online 26 August 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Dental ceramic is one of the most widely used materials in the dental industry because of its extensive use in resin-bonded restorations and porcelain repair systems. In this study, two approaches were applied to dental ceramic surfaces for improvement in the wettability and surface energy of the effective resin–ceramic interfacial binding. One group of dental ceramics was treated by glow discharge with oxygen at a discharge power of 20 W and for an exposure time of 15 min. The other group was dipped onto hydrofluoric acid (HF) solution. Then, the samples were washed with distilled water and dried at the room temperature before the oxygen plasma treatment. The effectiveness of the two approaches was compared by means of changes in the surface wettability and polarity as measured by both the sessile drop and captive bubble techniques. Oxygen plasma treatment increased the surface wettability, but a greater increase was found with HF etching before the oxygen plasma treatment. This result was

demonstrated by the decrease in the static contact angle as measured by the sessile drop technique (53.6 ± 4.19 to 27.7 ± 3.30). In addition, with the combination of the pre-chemical treatment with HF and the oxygen plasma treatment, the polarity increased more dramatically (0.706 ± 0.013 to 0.845 ± 0.008). The surface chemical composition and physical morphology were investigated by X-ray photoelectron spectroscopy and scanning electron microscopy. Furthermore, the HF etching before oxygen plasma treatment was found to improve the shear bond strength, and it was significantly stronger than that of the groups treated with oxygen only for the resin composite materials ($p < 0.05$). This two-step treatment could be a new approach for the activation of dental ceramic discs. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2656–2664, 2008

Key words: cold plasma; dental polymers; strength; surfaces

INTRODUCTION

The establishment of a durable and reliable bond between a dental ceramic and a resin composite is important in dental practice because of its extensive use in resin-bonded restorations and porcelain repair systems. This bond is usually created via two mechanisms, micromechanical attachment by hydrofluoric acid (HF) etching and/or grit blasting and chemical bonding by a silane coupling agent.

The use of silane coupling agents in enhancing the bond of resin composites to dental ceramics is well accepted in the dental literature.^{1–3} Also, many

researchers have reported that the highest bond strengths were obtained with a combination of an HF-etched surface with a silane coupling agent.^{4–8} Silane treatment acts on the glass phase of dental ceramics and creates a new surface layer that is organophilic to the adhesive.⁹ However; in a study by Della Bona et al.,¹⁰ it was shown that silane treatment did not improve the wettability of the porcelain surface by the adhesive resin. This resulted from the lower surface energy of the silane-treated surface compared to the resin adhesive. The authors also indicated a decrease in the surface roughness due to the filling of the pores of the etched surface with a relatively thick layer of silane.¹¹

It has been hypothesized that the flow of a composite to a ceramic surface is proportional to the ceramic surface energy.¹² The etching of polymeric surfaces has been shown to improve wettability by increasing the surface energy.^{13–15} The aim of this study was to introduce novel methods for improving

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Contract grant sponsor: COST 527, Plasma Polymers and Related Materials Action.

the ceramic–resin bond strength of silica-based feldspathic ceramics, such that it would be possible to improve the modification chemistry with a silane coupling agent with the general formula R–Si–(ORO). The use of feldspathic porcelain for the fabrication of dental laminate veneer restorations provides extremely sophisticated effects of color, translucency, and aesthetics.^{16,17} The physical and mechanical properties of ceramic/resin composites depend primarily on the properties of the combined materials, the surface of the ceramics, the interface between the two components, and the mode of stress transfer at the interface, and increasing the surface energy is the main goal for improving ceramic–resin bonds as well. For this reason, oxygen plasma treatment was studied to increase the surface energies of dental ceramics as a first approach. Second, the pre-treatment of surfaces with HF plus oxygen plasma treatment was used before the silane treatment.

Contact angle methods used to determine the surface energy of solid phases are simple, useful, and very sensitive probes of interfacial phenomena. In the past several decades, numerous techniques have been used to measure the contact angle, which were inspired by the idea of an equation first derived by Thomas Young:¹⁸

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

It is well known that the Young equation [eq. (1)] is the thermodynamic equilibrium condition for an ideal solid–liquid–fluid capillary system. In this equation, γ_{lv} is the liquid–vapor surface tension, γ_{sv} is the solid–vapor surface tension, γ_{sl} is the solid–liquid surface tension, and θ is the Young contact angle.

According to Owens–Wendt theory, the total free surface energy (γ_{sv}) is the sum of its dispersive component (γ_{sv}^d) and polar component (γ_{sv}^p):

$$\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p \quad (2)$$

which can be estimated with two or more liquids with known polar and dispersive contributions for γ measurements.^{19,20}

Cold plasma treatments can advantageously replace thermal, radiative, or chemical processes for the surface modification of polymers, metals, and so on. In fact, these treatments can be easily controlled and are environmentally friendly. Moreover, plasma modifies the surface layer at a depth from 50 to 500 Å, depending on power and time, and leaves the bulk characteristics unaffected. Most applications of plasma technology to organic materials, such as film, paper, and textiles,²⁰ are carried out at low temperature and low pressure (0.01–1 mbar), although some processes under atmospheric pressure have been applied. In this general area, through the control of

the plasma variables, a great variety of surface properties can be improved, including wettability, dyeability, and printability.^{16,21} These results arise from four main effects due to glow discharge: etching, or ablation; an increase in microroughness, the generation of radicals; and plasma polymerization. Plasma treatments can also improve adhesion in adhesive polymer or metal polymer systems by increasing one or several of the following phenomena: the cleaning by ablation of low-molecular-weight species, dehydrogenation, chain scission combined with crosslinking, generation or incorporation of radicals and reactive species, structural modifications of the surface topography, and so on.^{22–24}

This study dealt with two approaches: oxygen cold plasma treatment and a combination of acid treatment and oxygen cold plasma treatment of dental ceramic discs. These two approaches were compared through surface wettability. The surface energy components and polarity were calculated with datasets obtained from static contact angle measurements. The surface chemistry was characterized by X-ray photoelectron spectroscopy (XPS). The morphology of the ceramic discs was studied by scanning electron microscopy (SEM). After the modification of dental ceramic disc with these two different approaches, the samples were treated with silane. Then, the shear bond strengths (MPa) between the modified dental ceramics and resin composites were tested.

EXPERIMENTAL

Materials

Feldspathic veneering porcelain included SiO₂, Al₂O₃, CaO, Na₂O, K₂O, B₂O₃, and ZnO and was supplied by Vita (Bad Sackingen, Germany) with the code VM7. Porcelain enchanter (4% w/w HF) was supplied by Bisco (Schaumburg, IL). The adhesive (bonding agent) contained water, ethanol, 2-hydroxyethyl methacrylate (HEMA), bisphenol A–diglycidylether dimethacrylate, dimethacrylates, photoinitiators, and a methacrylate functional copolymer of polyacrylic and polyitaconic acids that was obtained as a mixture from the manufacturer (3M ESPE, St. Paul, MN). RelyX veneer cement, a resin-based cement with the components bisphenol A–diglycidylether dimethacrylate, triethyleneglycoldimethacrylate, zirconia/silica, and fumed silica fillers (loading = 66 wt %), was supplied by 3M ESPE as well. *n*-Octane (purity = 99%, Aldrich Chemical, Inc., Gillingham, UK) was used for surface energy determination.

Oxygen plasma treatment

Ceramic discs 5 mm in diameter and 2 mm in height were prepared with a feldspathic porcelain (VM7,

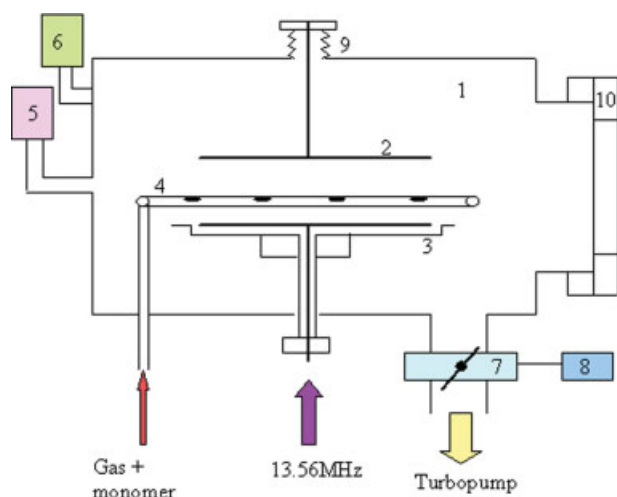


Figure 1 Diagram of the plasma reactor chamber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Vita) and were wet-grounded with 600-grid SiC abrasive. Specimens were divided into three groups ($n = 20$). In the control group, specimens were left untreated. In group 1 ($n = 20$) and group 2 ($n = 20$), the specimens were treated in a plasma system; a scheme of the reactor is reported in Figure 1.

Two sample treatments were used:

- Group 1: Oxygen plasma treatment.
- Group 2: Chemical treatment with 4% HF for 5 min, followed by oxygen plasma treatment.

During the preparation of the group 2 set, HF solution was spread onto the ceramic discs, and the discs were exposed for 3 min. Then, the samples were washed with distilled water and dried at the room temperature before oxygen plasma treatment.

The reactor consisted of a 21-L stainless steel vacuum chamber with ports for the pressure measurement, monomer, and gas inlets. The radio frequency (RF) (13.56 MHz) power generator output was connected to the powered electrode in the chamber via an automatic matching network unit. The RF power generator operated at a range of 0–600 W. Within the vacuum chamber were two horizontal steel parallel plate electrodes. The powered electrode was 160

mm in diameter; the grounded electrode was 200 mm in diameter. The distance between the electrodes could be varied by a bellows translational stage at the top of the grounded electrode; this distance was set to 75 mm. A gas shower ring set approximately 30 mm above the powered electrode allowed the uniform inlet of gases through a number of equally spaced holes approximately 1 mm in diameter. The control system for the reactor was based on MKS Instruments integrated control system 146C (Telford, UK). It provided pressure readings from the two pressure gauges and allowed the setting of the coreactant gas flow and regulation of the total working pressure via a throttle valve. The flow of gases was controlled by a mass flow controller and was set to 20 sccm (standard cm^3/min). The pumping system consisted of an EXT250 turbomolecular pump (MKS Instrument, Telford, UK) with a pumping speed of 240 L/s and an Edwards E2M18 rotary vane backing pump (MKS Instrument, Telford, UK). A base pressure of less than 5 mTorr was achieved before any treatment was conducted. A capacitive pressure gauge was used to monitor the pressure within the chamber during pumping and the plasma treatments. A cold cathode pressure gauge was used for low-pressure (<1 mTorr) measurements. These were also attached to the side ports on the chamber. The conditions of O_2 plasma treatment for both groups follows:

- Plasma power = 20 W.
- Plasma pressure = 50 mTorr.
- Gas = oxygen.
- Exposure time = 15 min.

Each group was further divided in to two subgroups ($n = 10$). One of these subgroups was used for shear bond strength measurement, whereas the other was used for contact angle measurements and surface analysis.

Contact angle measurement

A dedicated microscope (QX3 computer microscope, 60X, Intel, Santa Clara, CA) and software (Wettability Pro Classic, version 2.0.0, Prague, Czech

TABLE I
Contact Angles as Measured by the Sessile Drop Technique of the Untreated and Treated Ceramic Discs

Group	n	Mean	Standard deviation	Standard error	95% confidence interval for the mean	
					Lower bound	Upper bound
Control	10	53.600 ^a	4.195	1.326	50.598	56.601
Group 1	10	39.500 ^b	5.359	1.694	35.666	43.333
Group 2	10	27.700 ^c	3.301	1.044	25.338	30.061

Mean values with different superscripted letters differed significantly by Tukey's HSD test ($p < 0.05$). The control was untreated, group 1 was treated with oxygen plasma, and group 2 was treated with HF and oxygen plasma.

TABLE II
Surface Free Energy of Dispersive Component (γ_s^d) Values as Measured by the Captive Bubble Technique of the Untreated and Treated Ceramic Discs

Group	<i>n</i>	Mean	Standard deviation	Standard error	95% confidence interval for the mean	
					Lower bound	Upper bound
Control	10	16.634 ^a	0.379	0.119	16.363	16.905
Group 1	10	14.918 ^b	0.455	0.144	14.592	15.244
Group 2	10	8.407 ^c	0.195	0.061	8.267	8.547

Mean values with different superscripted letters differed significantly by Tukey's HSD test ($p < 0.05$). The control was untreated, group 1 was treated with oxygen plasma, and group 2 was treated with HF and oxygen plasma.

Republic) were used to measure the contact angles in a three-phase system consisting of water, a solid surface, and bubbles of air or liquid *n*-octane. The glass cell was filled with ultrapure water, and the samples were placed in it. A special L-shaped syringe needle containing *n*-octane (purity = 99%, Acros, Geel, Belgium) or gas (air) released bubbles of about 4 μ L beneath the sample. The supporting computer software used data from captured images to calculate the contact angles between *n*-octane and the solid surface and between air and the solid surface. The contact angle experiments were repeated 20 times for each sample surface. A schematic presentation of the experimental setup was given previously,¹⁹ and the Wendt–Owens method was applied for the determination of the polarity with two components. In addition to the captive bubble technique, the sessile drop technique was also used to show the changes in surface wettability. In this technique, the surface to be examined was placed onto a special holder, and water droplets were released on the surface at a 4- μ L volume, and the contact angles were measured and calculated as described previously. One-way analysis of variance was used to examine the influence of the different treatment methods on the wettability of the specimens tested. Tukey's HSD *post hoc* test was used to determine significant differences between the groups ($p < 0.05$).

XPS analysis

The chemical compositions of the untreated, oxygen-plasma-treated (group 1), and chemical-and plasma-

treated (group 2) dental ceramic surfaces were determined by XPS. The XPS measurements were made with a CLAM2 spectrometer (VG, East Grinstead, United Kingdom) in constant analyzer transmission mode with an Mg K α X-ray source. Survey scans were taken at a pass energy of 100 eV, and core level spectra were taken at 20 eV. Elemental compositions for these films were calculated with peak areas from the survey scans and experimentally derived sensitivity factors. The pressure in the analysis chamber was maintained at 5×10^{-8} Torr or lower during each measurement.

SEM analysis

SEM observation was also performed at Fraunhofer Institute of Germany with a KYKY-AMRAY 100B instrument (Amray Instrument, Bedford, UK). The surface morphologies of the samples were characterized at magnifications of 250 and 1000 \times .

Shear bond strength measurement

For shear bond strength testing, modified porcelain surfaces (group 1, group 2, and control group) were treated by silane and left to dry at room temperature. After the evaporation of the silane, one coat of an adhesive-resin-based luting agent was applied to the silane-treated surfaces and dried with an air syringe for 3 s. Immediately after the adhesive application, luting cement was injected into a silicone tube 3.5 mm in diameter and 4 mm in height, and the tube was positioned on the treated porcelain disc

TABLE III
Surface Free Energy of Polar Component (γ_s^p) Values as Measured by the Captive Bubble Technique of the Untreated and Treated Ceramic Discs

Group	<i>n</i>	Mean	Standard deviation	Standard error	95% confidence interval for the mean	
					Lower bound	Upper bound
Control	10	40.118 ^b	2.379	0.752	38.416	41.820
Group 1	10	47.863 ^a	1.974	0.624	46.451	49.275
Group 2	10	46.124 ^a	2.410	0.762	44.399	47.848

Mean values with different superscripted letters differed significantly by Tukey's HSD test ($p < 0.05$). The control was untreated, group 1 was treated with oxygen plasma, and group 2 was treated with HF and oxygen plasma.

TABLE IV
Surface Free Energy (γ_s) Values as Measured by the Captive Bubble Technique of the Untreated and Treated Ceramic Discs

Group	<i>n</i>	Mean	Standard deviation	Standard error	95% confidence interval for the mean	
					Lower bound	Upper bound
Control	10	56.753 ^b	2.387	0.754	55.045	58.460
Group 1	10	62.781 ^a	1.669	0.527	61.587	63.976
Group 2	10	54.531 ^b	2.344	0.741	52.854	56.208

Mean values with different superscripted letters differed significantly by Tukey's HSD test ($p < 0.05$). The control was untreated, group 1 was treated with oxygen plasma, and group 2 was treated with HF and oxygen plasma.

surfaces. The assembly was polymerized for 40 s with a halogen light 500 mW/mm² in intensity (Hi-Lux Ultra, Benlioglu, Ankara, Turkey), the silicone tube was removed, and the specimens were subjected to 1000 thermal cyclings between 5 and 55°C. The specimens were stored in distilled water for 20 days at room temperature before they were processed for shear bond strength testing. Shear bond strength values were determined with a universal testing machine (Lloyd-LRX, Lloyd Instruments, Fareham, United Kingdom) with a crosshead speed of 0.5 mm/min. The mean shear bond strength values (MPa) of each specimen group were determined and analyzed with an analysis of variance followed by a *post hoc* Tukey's HSD test ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Improvement in the surface wettability

Both the sessile drop and captive bubble techniques were used to characterize the surface wettability and energy values of group 1, group 2, and the control group. The results, as a mean of static contact angle values, are represented in Table I.

Increasing the surface hydrophilicity is the main goal in improving dental ceramic–resin bonds. The combination of acid pretreatment plus oxygen plasma treatment was used as a second approach and was compared with the oxygen plasma treatment. The static contact angle values indicated that this was a more effective idea for increasing the surface wettability. This result was correlated to the

decrease in static contact angle as measured by the sessile drop technique. The contact angles of the dental ceramic discs decreased from 53.6 ± 4.19 to 39.5 ± 5.35 with the oxygen plasma treatment. However, in group 2 (the combination of prechemical treatment with HF plus oxygen plasma treatment), the contact angle decreased more dramatically (from 53.6 ± 4.19 to 27.7 ± 3.30).

The contact angle results of air and *n*-octane from the captive bubble experiments were used to find the polar and dispersive components of the surface energy. The surface free-energy components are represented in Tables II–IV. Table V shows the polarity of the dental ceramic discs after treatment.

The polarity increased significantly from 0.706 ± 0.013 to 0.762 ± 0.012 in group 1 ($p < 0.05$). However, with the combination of prechemical treatment with HF plus oxygen plasma treatment (group 2), the polarity increased more dramatically from 0.706 ± 0.013 to 0.845 ± 0.008 ($p < 0.05$). This result was correlated with the decrease in the static contact angle as measured by the sessile drop technique. This showed that group 2 was more hydrophilic than group 1. An increase in the surface hydrophilicity and energy is the main goal in the improvement of dental ceramic–resin bonds. The combination of acid pretreatment plus oxygen plasma treatment was used as a second approach and compared with the oxygen plasma treatment alone. The values indicated that second approach was more effective in increasing the surface wettability and energy of the dental ceramic discs (Fig. 2).

TABLE V
Percentage Polarity Values as Measured by the Captive Bubble Technique of the Untreated and Treated Ceramic Discs

Group	<i>n</i>	Mean	Standard deviation	Standard error	95% confidence interval for the mean	
					Lower bound	Upper bound
Control	10	0.706 ^a	0.013	0.004	0.696	0.716
Group 1	10	0.762 ^b	0.012	0.003	0.753	0.770
Group 2	10	0.845 ^c	0.008	0.002	0.839	0.851

Mean values with different superscripted letters differed significantly by Tukey's HSD test ($p < 0.05$). The control was untreated, group 1 was treated with oxygen plasma, and group 2 was treated with HF and oxygen plasma.

TABLE VI
Summary of the Changes in the Elemental Composition of the Dental Ceramic Discs After Different Surface Treatments

Sample	C (%)	O (%)	Si (%)
Control	38.0	45.7	16.2
Group 1	9.2	66.6	24.0
Group 2	4.4	74.3	21.3

Effect of the surface treatments on the physical and chemical characteristics

The chemical composition of the untreated ceramic discs, group 1, and group 2 obtained from XPS wide scan spectra (Figs. 3–5) are presented next. The elemental compositions of the surfaces are listed in Table VI.

The surface chemical composition of the untreated ceramic dental discs included carbon, oxygen, and silicon elements; trace (<1%) amounts of aluminum, sodium, and phosphorous were also noted in some samples. The XPS results show that after the oxygen plasma treatment, the percentage of carbon decreased from 38 to 9.2% and also that the oxygen concentration increased from 45.7 to 66.6%. However, most significant changes were obtained with group 2, in which the dental ceramic discs were treated with 4% HF for 5 min and then plasma-treated with oxygen. In this approach, the elemental composition of C decreased from 38 to 4.4%, which is shown in Table VI. The oxygen concentration in the surface increased from 45.7 to 74.3%. The XPS results clearly show that in group 2, the oxygen

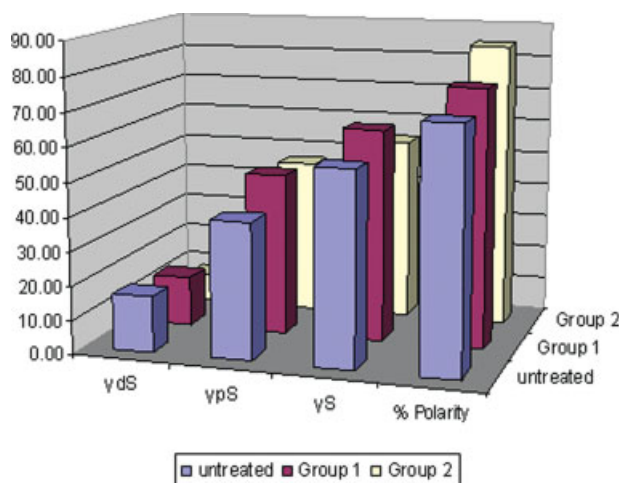


Figure 2 Effects of different surface treatments on the surface energy components of the dental ceramic discs. ydS, surface free energy of dispersive component; ypS, surface free energy of polar component; yS, surface free energy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

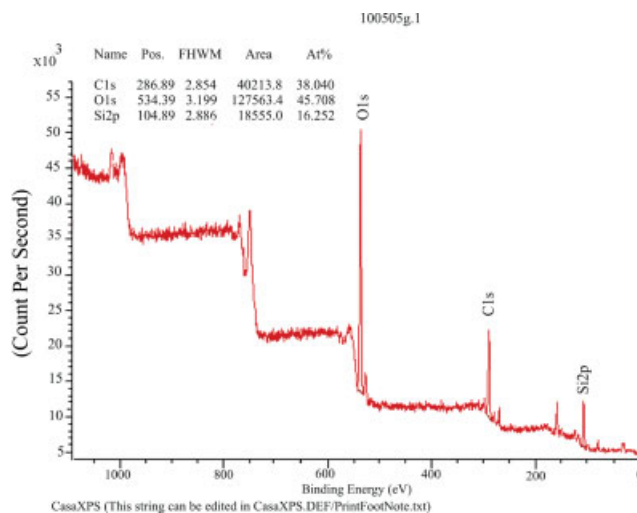


Figure 3 XPS spectrum of the untreated ceramic dental surfaces. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

plasma effectively penetrated the surface layer and removed the carbon contaminants that were not directly in the body of the ceramic composite. In addition, the increase in the Si content of the surface was considered good proof of effective cleaning within the oxygen treatment. The O/Si ratio was higher than expected (2:1 for SiO_2) for the treated surfaces, which potentially indicates a strongly hydrolyzed material with many silanol groups [e.g., $\text{SiO}(\text{OH})_2$ would give a ratio of 3 : 1].

SEM micrographs of the untreated and treated dental ceramic disc surfaces are shown in Figures 6–8. The untreated ceramic dental disc had spherical cracks and structures on their surfaces. After the ox-

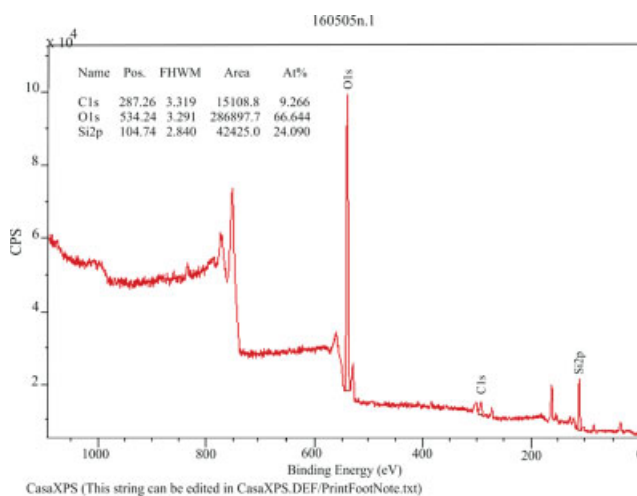


Figure 4 XPS spectrum of the ceramic dental surfaces (group 1 was treated with oxygen plasma; FWHM = full width at half-maximum). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

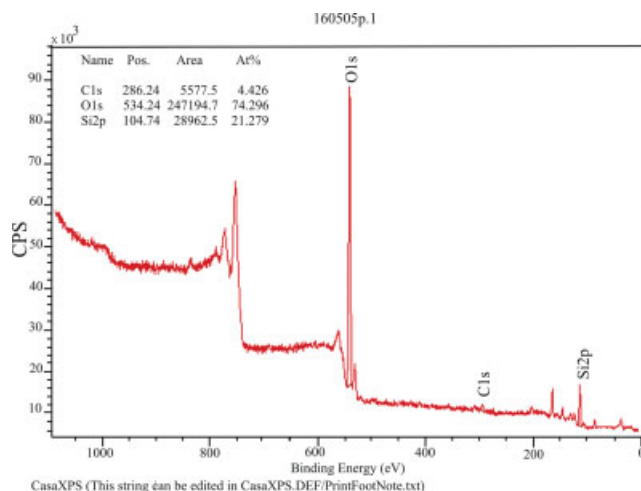


Figure 5 XPS spectrum of the ceramic dental surfaces (group 2 was pretreated with acid and then treated with oxygen; FWHM = full width at half-maximum). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

oxygen treatment (group 1), we observed that the ceramic discs had flatter surfaces. However, the SEM figures for group 2, with both acid and oxygen treatment, appeared to show that the surfaces were less rough than those of group 1.

SEM micrographs showed that the unmodified ceramic dentals disc had spherical cracks and structures on the surfaces. After the oxygen treatment, we observed that the ceramic discs had flatter surfaces. We believe this was due to etching with the oxygen treatment. However, the SEM figures for the samples treated with both acid and oxygen showed more flat surfaces than those in group 1. Acid treatment caused the polish of the surfaces of the group 1 samples. Furthermore, this could have been an effective factor in the increase in the efficiency of the oxygen treatment, which was proven by the XPS results and contact angle measurements.

Shear bond strength measurement

The shear bond strengths and standard deviations for each experimental group are listed in Table VII. For the control group without oxygen treatment, the shear bond strength was 51.8 ± 17.6 MPa. The group treated with oxygen plasma and the group treated with HF acid plus oxygen plasma showed shear bond strengths of 72.8 ± 16 and 78.4 ± 32.2 MPa, respectively.

The ceramic group receiving oxygen plasma treatment showed significantly improved shear bond strength compared with the untreated ceramics (cf. 51.8 ± 17.6 to 72.8 ± 16 MPa, respectively). However, there was a greater difference in the shear bonding strength in group 2, in which the ceramics were treated in HF solution and then etched with oxygen plasma. Static contact angle measurements showed that the surface energy and wettability increased with oxygen plasma treatment of the dental ceramic discs. However, a larger increase was found with chemical treatment with HF before oxygen plasma treatment. In addition, the polar energy of the dental ceramic discs increased more efficiently with the second approach. XPS results showed that acid treatment before the oxygen treatment increased the chemical percentage of oxygen onto the surface. The SEM results show that with the acid treatment in group 2, the surface was to some extent polished before the oxygen treatment. This could have been an effective factor in increasing the efficiency of the silane treatment and causing the improvement in interfacial bonding with the resin composites and porcelain samples.

CONCLUSIONS

Increasing the surface hydrophilicity and energy is the main goal in improving dental ceramic–resin

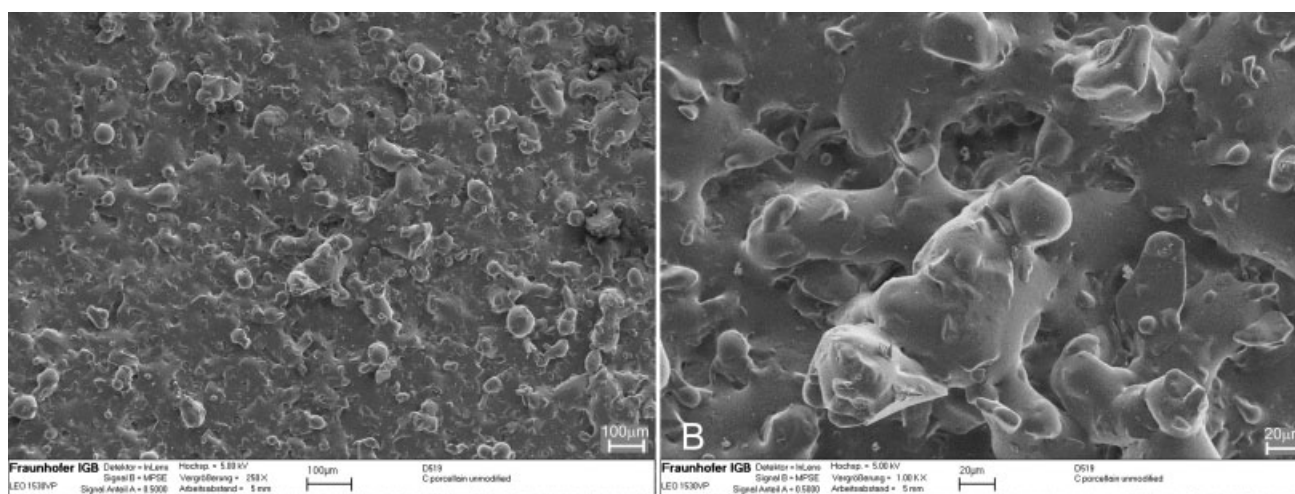


Figure 6 SEM micrographs of the surface of the unpolished ceramic at original magnifications of (a) 250 and (b) 1000 \times .

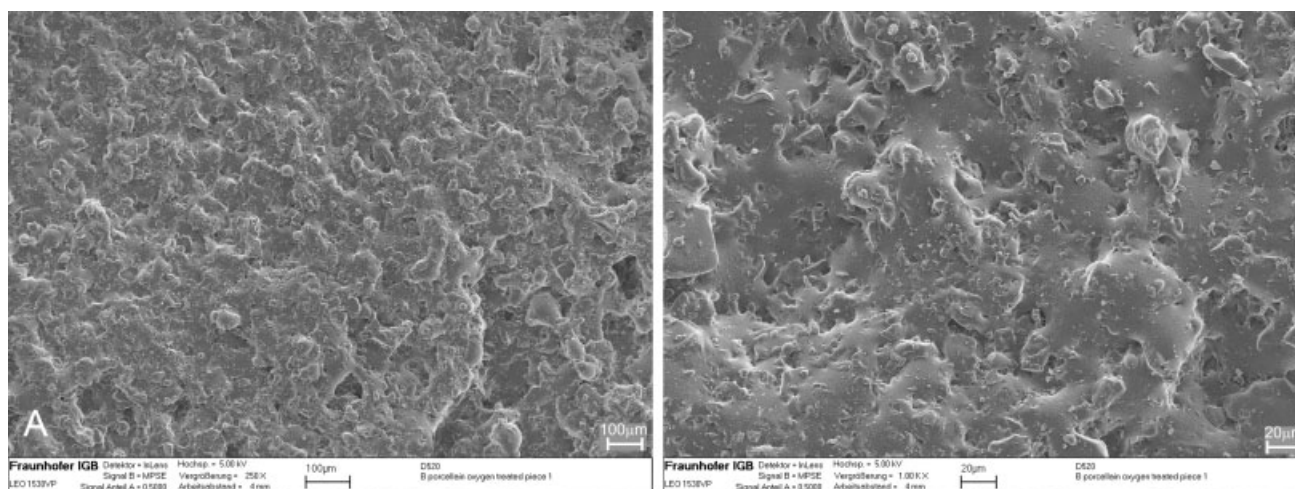


Figure 7 SEM micrographs of the oxygen-etched ceramic surface at original magnifications of (a) 250 and (b) 1000 \times .

bonds. In this study, a combination of acid pretreatment plus oxygen plasma treatment was used as a novel approach and compared with oxygen plasma treatment only. The values indicate that this novel approach was more effective in increasing the surface wettability and energy of the dental ceramic discs. The XPS results show that after the surface treatments of groups 1 and 2, the percentage of carbon decreased, and also, the oxygen concentration increased. However, the most significant changes were obtained in group 2, in which the dental ceramic discs were treated with 4% HF for 5 min and were then plasma-treated with oxygen. The XPS results clearly show that in group 2, the oxygen plasma effectively penetrated the surface layer and removed the carbon contaminants that were not directly in the body of the ceramic composite. SEM micrographs showed that the unmodified ceramic dental discs had spherical cracks and structures on

the surfaces. After the oxygen treatment, we observed that the ceramic discs had flatter surfaces. This was due to etching with the oxygen treatment. However, SEM figures for the samples that were treated with both acid and oxygen showed that the surfaces were flatter than those of the group 1. Acid treatment caused the polish of the surfaces of the group 1 samples. Furthermore, this could have been effective factor in increasing the efficiency of the oxygen treatment, which was proven by the XPS results and contact angle measurements. Shear bond strength results suggested that ceramic surface modification by HF acid plus oxygen plasma represented an optimal finding that may significantly improve the bond between the ceramic and resin composite material in dental applications. This approach not only provides the easy application and usability of a novel surface cold plasma modification technique; it also has the additional advantage of clinical use on

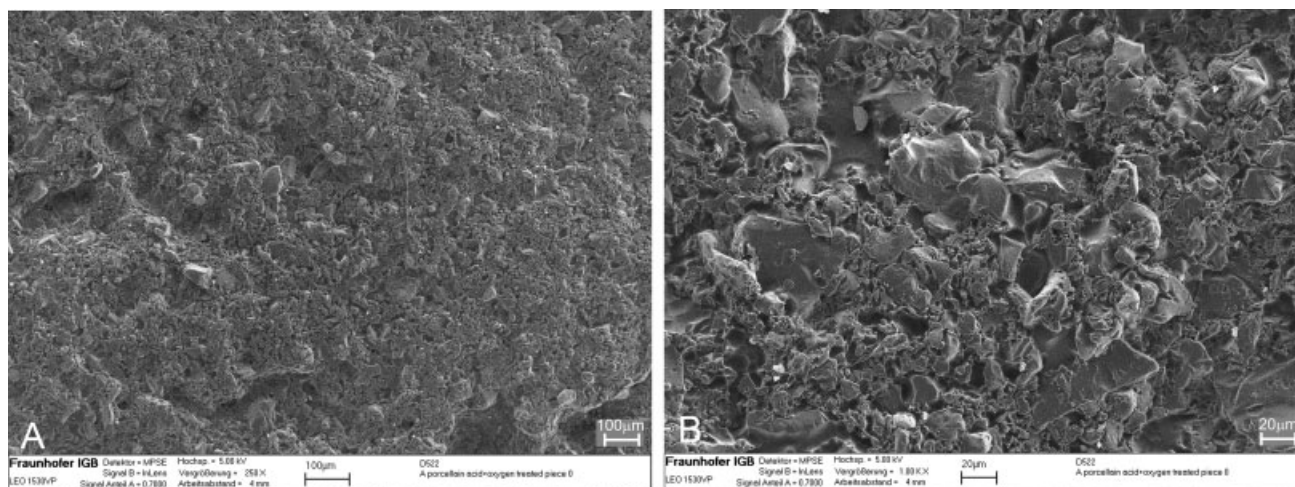


Figure 8 SEM micrographs of the acid-treated and then oxygen-etched ceramic surface at original magnifications of (a) 250 and (b) 1000 \times .

TABLE VII
Shear Bond Strength Values of the Untreated and Treated Ceramic Discs

Group	<i>n</i>	Treatment	Shear bond strength (MPa)
Control	10	Untreated	51.84 ^b (17.62)
Group 1	10	Oxygen plasma HF acid	72.83 ^a (16.02)
Group 2	10	and oxygen plasma	78.40 ^a (32.24)

Standard deviations are given in parentheses. Mean values with different superscripted letters differed significantly by Tukey's HSD test ($p < 0.05$).

ceramic alloys through an increase in the strength of adhesion to the composite material.

The authors thank Christian Oehr for giving us the opportunity to perform SEM analysis at the Fraunhofer Institute (Stuttgart, Germany).

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