J Mater Sci (2011) 46:2755–2763
DOI 10.1007/s10853-010-5149-1

The effect of plasma polymer coating using atmospheric-pressure glow discharge on the shear bond strength of composite resin to ceramic

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Received: 28 September 2010 / Accepted: 30 November 2010 / Published online: 29 December 2010

Abstract If plasma technology can come out of the vacuum chamber and plasma can be extruded through a small pencil-type torch, it can be applied widely to dental practices. For this study, we designed a small pencil-type non-thermal atmospheric-pressure glow discharge plasma torch. The purpose of this study was to determine the effect of plasma polymer coating on the adhesion of composite resin to feldspathic porcelain. The effect of plasma polymer coating was evaluated using shear bond strength (SBS) test. Contact angle measurements and fracture mode analysis were also performed. Among the groups treated with plasma polymer coating, the SBS of the adhesive (Adper Scotchbond Multi-Purpose, 3M ESPE) to the ceramic surface pre-treated sequentially with water plasma and triethyleneglycol dimethacrylate (TEGDMA) plasma in helium gas was significantly higher than that of the adhesive to the untreated surface ($p < 0.05$). In this group, the predominant fracture mode was mixed fracture, where small cohesively fractured fragments of ceramic were dispersed on the adhesively fractured flat adhesive surface. However, the SBS values of all the plasma polymer-coated groups were lower than those obtained through a routine porcelain bonding procedure with HF acid and silane coupling agent ($p < 0.05$). The non-thermal atmospheric-pressure plasma polymer coating technique was found to have a potential promoting adhesion to dental materials.

Introduction

Plasma is recognized as a fourth state of matter together with gases, liquids, and solids [1]. More or less ionized gas in plasma consists of electrons, ions, and neutral components in fundamental and excited states [2, 3]. Plasmas are electrically neutral, but they contain free charge carriers and are electrically conductive and chemically active. They are classified as either cold or thermal, depending on their activation method and working power [2]. Due to the wide range of temperatures they emit, plasma technology has been used for various applications such as surface treatments and coatings, waste destruction, gas treatments, chemical synthesis, machining, and high-precision mass spectrometric analysis by plasma-source [2, 4–7]. Thermal plasmas, especially arc plasma, have been extensively industrialized [2]. In the dental field, non-thermal plasmas have been studied for the purposes of modifying titanium implant surfaces [8, 9], improving mechanical properties of fiber-reinforced acrylic resin materials [10], and increasing bond strength between fiber posts and core resin [11] and between composite luting agents and ceramics [12]. These non-thermal plasmas use radio frequency (RF) sources with a high power supply in a vacuum chamber.

Dental bonding deals with bondings to various substrates, ranging from well-achieved bondings to enamel and ceramics to relatively weak ones to dentin, polymers, and metals. Ceramic bonding is quite reliable when the surface of the feldspathic porcelain is treated with both hydrofluoric acid (HF) etching and silane coupling agent

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coating [13], but dentin bonding has complicated problems due to its low bond strength and long-term hydrolytic bond degradation [14]. The excellent adhesion imparted by the deposition mechanism of a plasma polymer to a substrate can be utilized to improve the adhesion characteristics of other materials [15]. Plasma polymers have been suggested to be adhesion promoters for any kind of substrate materials and to provide water resistivity of adhesion [15]. Therefore, non-thermal atmospheric-pressure glow discharge (AGD) plasmas may be used to improve the adhesion effectiveness and durability between various restoratives and tooth substrates. However, only a few studies have attempted to use the non-thermal AGD plasma for dental applications such as cavity preparation and bleaching [3, 16]. In our laboratory, a small pencil-type plasma torch that can be used to apply plasma or plasma polymers directly to teeth or restoratives in a patient's mouth and to modify the surfaces of restoratives or implants at chair-side was designed.

In this study, among various dental adherents, feldspathic porcelain was chosen to evaluate the effectiveness of plasma polymer coating on adhesion, due to its consistent surface structure, composition, and reliable reports on its bond strength [13, 17]. We evaluated the hypothesis that the plasma polymer coating procedure would promote adhesion by plasma polymer deposition and increase the bond strength of composite resin to ceramic. For the purpose, the effect of plasma adhesion on the bond strength of composite resin to ceramic was evaluated. The plasma-coated ceramic surfaces were characterized using contact angle measurements, and the fractured surfaces were evaluated using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

Materials and methods

The AGD plasma reactor shown in Fig. 1a is composed of three parts: a mass flow system, a plasma torch, and a reactor for plasma polymer deposition. The pencil-type plasma torch is composed of an outer ceramic tube (4 mm in inner diameter) wrapped with a ground electrode and an

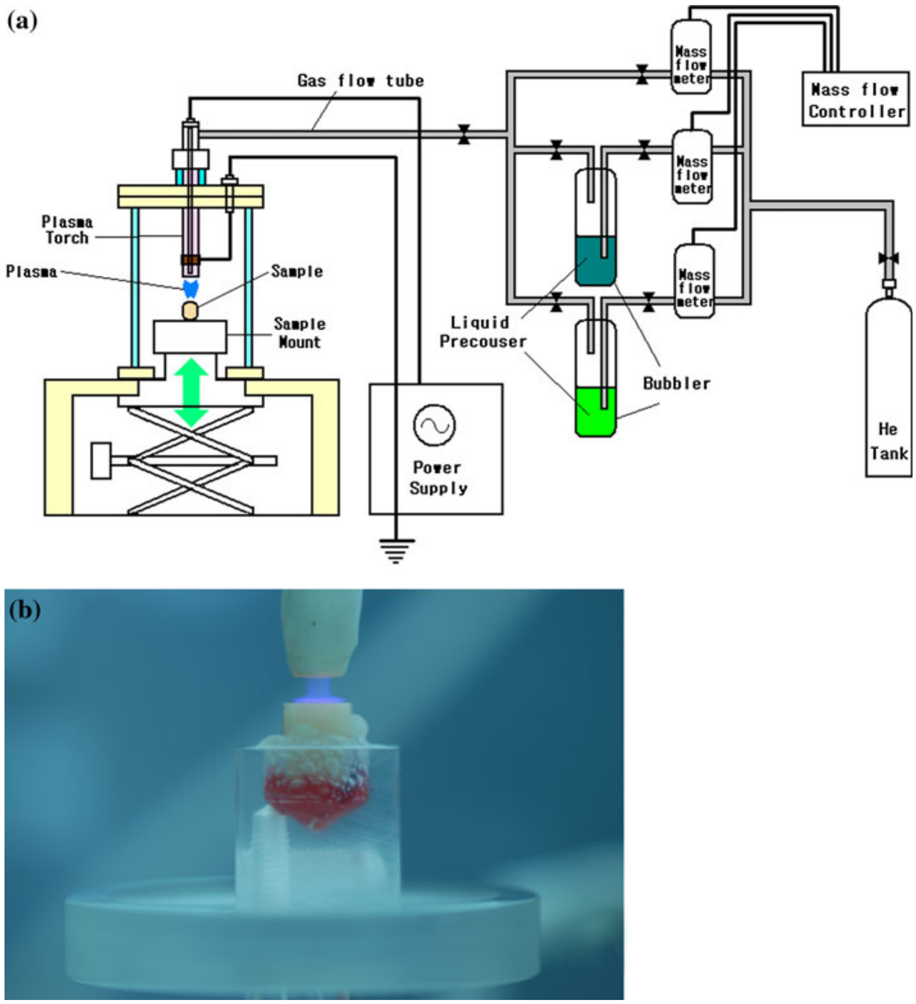


Fig. 1 **a** Schematic illustration of the non-thermal atmospheric glow discharge (AGD) plasma equipment used in this study. **b** Plasma flame was applied to the sample on a stand through a pencil-type plasma torch which was located 0.5 cm above the sample surface

inner ceramic needle tube (2 mm in diameter) containing a hot metal rod electrode that passes through the center of the outer tube. Helium (He) was delivered into the tube at a flow rate of 2 L/min as a carrier gas, carrying vaporized distilled water (DW) for cleaning and hexamethyldisiloxane (HMDSO) or triethyleneglycol dimethacrylate (TEGDMA) for plasma polymerization, after passing through a glass bubbler. Between the metal rod electrode and the ground electrode connected around the tip of the ceramic tube, a radio frequency (RF) voltage of 2 kV was applied at 15 kHz. For standardization, the flow rate of the vaporized water and monomers was controlled at a rate of 50 standard cubic centimeters (sccms) using a mass flow controller (FC7700C, Aera Japan, Hachioji, Japan). The distance between the surface of the porcelain sample and the tip of the plasma torch could be adjusted according to the deposition rate of the plasma polymer and the cleaning effects.

Fifty pressed CAD/CAM ceramic blocks (8 × 10 × 15 mm) of feldspathic porcelain (VITABlOCS Mark II for CEREC/inLab, 2M2C I10, Lot No. 14800; Vita Zahfabrik, Bad Säckingen, Germany) were embedded in acrylic molds with self-curing acrylic resin. In order to create uniform surface roughness and parallel surface geometry for shear loading, the top surfaces of the ceramic blocks were polished with 500 grit silicon carbide abrasive paper (Buehler Ltd, Lake Bluff, IL, USA) under running water using an automatic polishing machine (Rotopol-V; Struers Ltd, Glasgow G60 5EU, UK). The samples were stored in a chamber of 100% relative humidity at room temperature from the beginning of the experiment until the shear bond strength (SBS) test [7, 12].

Prepared ceramic blocks were randomly divided into five groups (Table 1). In group 1, the control group, the Adper Scotchbond Multi-Purpose (SBMP, Lot No. 9RL; 3M ESPE, St. Paul, MN, USA) adhesive was applied to the polished surfaces of ceramic blocks with no treatment. The adhesive was light-cured for 20 s using a halogen light source (VIP, light intensity 600 mW/cm^2; Bisco Inc, Schaumburg, IL, USA). In the experimental groups, the ceramic specimen was placed on a stand in an atmospheric-pressure acrylic chamber which had a passive outlet for He gas. The stand was used to position the polished top surface of the specimen 0.5 cm below the tip of the plasma torch (Fig. 1b). In group 2, the polished ceramic surface was exposed to non-thermal AGD plasma carrying vaporized TEGDMA in helium gas. The SBMP adhesive was immediately applied to the plasma polymer-coated surface and light-cured for 20 s. In group 3, an additional step of plasma surface treatment with vaporized DW in helium gas was applied to clean the adherent surface. After the cleaning step, the plasma polymer coating step with vaporized TEGDMA in helium gas with consecutive adhesive application and light-curing were completed, as in group 2. In group 4, HMDSO was additionally used as a precursor monomer since the plasma polymer from HMDSO had siloxane and silane groups for bonding with ceramic. The procedures were performed sequentially in the order of plasma cleaning with water, plasma polymer coating with HMDSO, plasma polymer coating with TEGDMA, adhesive application, and adhesive light-curing for 20 s. In group 5, the polished surfaces of the ceramic blocks were treated according to a routine clinical protocol for bonding feldspathic porcelain, consisting of surface etching with 4% buffered hydrofluoric acid gel (HF, Porcelain Etchant, Lot No. 0800003209; Bisco Inc) for 4 min, washing, drying with compressed air from a three-way syringe, coating the surface with a silane coupling agent (Monobond-S, Lot No. M08100; Ivoclar Vivadent AG, Liechtenstein), drying, adhesive application, and light-curing for 20 s.

A metal iris, a stainless steel coin (8 mm in diameter and 1.5 mm in height) with a concentric hole (3 mm in diameter) in the center, was used as a mold for packing

Table 1 Experimental groups and procedures used in this study

Groups	Surface treatment procedures	Remarks
Group 1	g	Untreated, negative control group
Group 2	c, g	Plasma polymer coating with TEGDMA
Group 3	a, c, g	Plasma surface cleaning and plasma polymer coating with TEGDMA
Group 4	a, b, c, g	Plasma surface cleaning and plasma polymer coating with HMDSO and TEGDMA, consecutively
Group 5	d, e, f, g	Hydrofluoric acid etching and silane application, routine bonding procedure for feldspathic porcelain

a, plasma surface treatment with vaporized DW in helium gas; b, plasma polymer coating with vaporized HMDSO in helium gas; c, plasma polymer coating with vaporized TEGDMA in helium gas; d, etching with 4% buffered hydrofluoric acid gel for 4 min; e, washing and drying with compressed air from a three-way syringe; f, silane coupling agent coating and drying with compressed air from a three-way syringe; g, sequential bonding procedures after surface treatment of the polished surfaces of ceramic blocks, including the immediate coating of the Adper Scotchbond Multi-Purpose (3M ESPE) adhesive, light-curing for 20 s, composite packing into the inner hole of the iris on the specimen surface, and light-curing for 40 s

TEGDMA triethyleneglycol dimethacrylate; *HMDSO* hexamethyldisiloxane

Table 2 Measurements of water contact angles from various ceramic surfaces prepared according to the plasma surface treatment protocols used in this study

Groups	Surface treatments	Contact angle (°)
Polished ceramic surface	a	12.1 ± 1.7
Polishing/water cleaning	a, b	Less than 5
Polishing/water cleaning/TEGDMA plasma coating	a, b, c	Less than 5
Polishing/TEGDMA plasma coating	a, c	Less than 5
Polishing/water cleaning/HMDSO plasma coating	a, b, d	85.3 ± 8.5
Polishing/water cleaning/HMDSO plasma coating/TEGDMA plasma coating	a, b, d, c	30.8 ± 2.6
Polishing/water cleaning/TEGDMA plasma coating/adhesive light-curing (OIL)	a, b, c, e	45.2 ± 3.5

Surface treatments of each group were performed in a sequential manner designated with the following abbreviations: a, polishing with #500 SiC paper; b, plasma surface cleaning with vaporized water in helium gas; c, plasma polymer coating with vaporized TEGDMA in helium gas; d, plasma polymer coating with vaporized HMDSO in helium gas; e, adhesive coating and light-curing for 20 s

OIL, oxygen-inhibited layer, the contact angle of the oxygen-inhibited layer remaining on the cured adhesive was measured to approximate the contact angle measurement of the uncured adhesive itself

TEGDMA triethyleneglycol dimethacrylate; *HMDSO* hexamethyldisiloxane

composite [18]. The iris was coated with Teflon to prevent it from adhering to the cured adhesive of the ceramic surface. The iris was pressed against the treated ceramic surface, and a composite resin (Filtek Z-250, A3 shade, Lot No. N111413; 3M ESPE) was filled into the hole. It was then light-cured for 40 s. All the specimens were stored in a humid chamber at room temperature (22 °C) for 24 h before testing.

Shear bond strength was measured at a crosshead speed of 1.0 mm/min using a universal testing machine (UTM, LF Plus; Lloyd Instruments LTD, Fareham Hampshire, UK). After debonding, fracture analysis was performed using a stereomicroscope (SZ40, Olympus Corp, Tokyo, Japan), and photographs of both sides of the fracture surfaces were taken. The failure modes were classified as adhesive fracture (A), fracture between the polished ceramic surface and the cured adhesive layer; mixed fracture (M), fracture meandering from the adhesive interface to the ceramic surface, where as a result, small fragments of ceramic were observed on the adhesively fractured flat adhesive surface; or cohesive fracture of ceramic (C), an oblique fracture of the ceramic adherend. The microscopic images at various magnifications and constituting elements of the fractured surfaces in the selected debonded specimens from each group were evaluated using a field-emission scanning electron microscope (FE-SEM, S-4700, HITACHI high technologies Co, Tokyo, Japan) operating at 15 kV and an embedded energy dispersive spectrometer (EDS, EX-220, Horiba, Kyoto, Japan).

In order to verify the effects of plasma cleaning with DW and plasma polymer coating with HMDSO or TEGDMA, a contact angle meter (Phoenix 150; Surface Electro Optics, Seoul, Korea) was used to measure the water contact angles on a series of ceramic surfaces, such as those polished with #500 SiC paper, those plasma-treated with water after polishing, those plasma polymer coated with TEGDMA on the polished and water plasma-treated surface, those plasma polymer coated with TEGDMA on the polished surface, those plasma polymer coated with HMDSO on the polished and water plasma-treated surface, those plasma polymer coated with TEGDMA on the polished, water plasma-treated, and HMDSO plasma-coated surface, and those surfaces on which the adhesive was applied and cured after plasma treatment (Table 2). By gently dropping a deionized water droplet onto the treated surface using a micro-syringe, the static contact angle was automatically obtained from the photo image collected by the embedded software.

The data obtained from the SBS test were analyzed statistically using a Kruskal–Wallis non-parametric test, and post hoc multiple comparison tests were also conducted with a Dunnett test at a 5% level of significance. Failure mode data were analyzed using a Chi-square test.

Results

Table 3 shows the SBSs of composite resin to variously treated surfaces of feldspathic porcelain blocks. Compared to the SBS of the adhesive of SBMP to untreated ceramic surfaces (group 1), the SBS value of the adhesive to the ceramic surface exposed to non-thermal AGD plasma carrying vaporized TEGDMA (group 2) increased slightly, but the difference was not statistically significant. However, when the plasma polymer coating with vaporized TEGDMA was performed after pre-treatment of the adherent surface with plasma carrying vaporized DW (group 3), the SBS of the adhesive was significantly higher than both those to the untreated surface (group 1) and to the surface coated only with TEGDMA (group 2, $p < 0.05$).

Table 3 Shear bond strength (SBS) of the composite resin to various plasma-treated surfaces of feldspathic porcelain and the distribution of fracture modes observed from the fractures due to shear load

Groups (abbreviation)	SBS[†]	Fracture modes		
		Adhesive	Mixed	Ceramic cohesive
Group 1 (PUT)	$11.5 \pm 2.3^{a\S}$	9	1	0
Group 2 (T)	14.8 ± 3.7^{a}	7	3	0
Group 3 (WT)	20.0 ± 3.9^{b}	3	7	0
Group 4 (WHT)	14.7 ± 4.0^{ab}	10	0	0
Group 5 (FS)	31.0 ± 6.0^{c}	0	0	10

Fracture modes: adhesive fracture, fracture between the polished ceramic surface and the cured adhesive layer; mixed fracture, fracture meandering from the adhesive interface to the ceramic surface, where, as a result, a small fragment of ceramic was observed on the adhesive surface covering the fractured bottom surface of the composite resin in the iris; cohesive fracture of ceramic, oblique fracture of the ceramic adherend

PUT untreated except polishing; *T*, TEGDMA plasma coating after polishing; *WT*, after polishing, sequential DW plasma treatment, and TEGDMA plasma coating; *WHT*, after polishing, sequential DW plasma treatment, and plasma polymer coating with HMDSO and TEGDMA; *FS*, hydrofluoric acid etching and silane coupling agent coating

[†] Values are means ± standard deviations in MPa, and sample numbers are 10

[§] The same superscript represents no statistically significant difference ($p > 0.05$)

The SBS value was still lower than the bond strength to the ceramic surface etched with HF acid and consecutively coated with silane coupling agent (group 5, $p < 0.05$), a routine bonding procedure for feldspathic porcelain in dental clinics. Sequential plasma polymer coatings with HMDSO and TEGDMA after plasma cleaning with water (group 4) also failed to obtain significantly different SBS values from those of the untreated control group (group 1).

In group 1, the fractures caused by shear loading mostly occurred at the interface between the polished ceramic surface and the cured adhesive layer (adhesive fractures, Fig. 2a and Table 3). With plasma polymer coating (group 2), small cohesively fractured fragments of ceramic were observed on the adhesively fractured flat adhesive surface after shear fracture (mixed fractures, Fig. 2b). When plasma surface cleaning with vaporized DW was performed additionally before plasma polymer coating with TEGDMA (group 3), the incidence of mixed fractures increased significantly (Chi-square test, $p < 0.05$). The small fragments observed on the adhesive surface at the bottom of the iris were found to be ceramic after line scanning with EDS (Fig. 3). In group 4, all of the fractures that occurred were adhesive. In group 5, all specimens

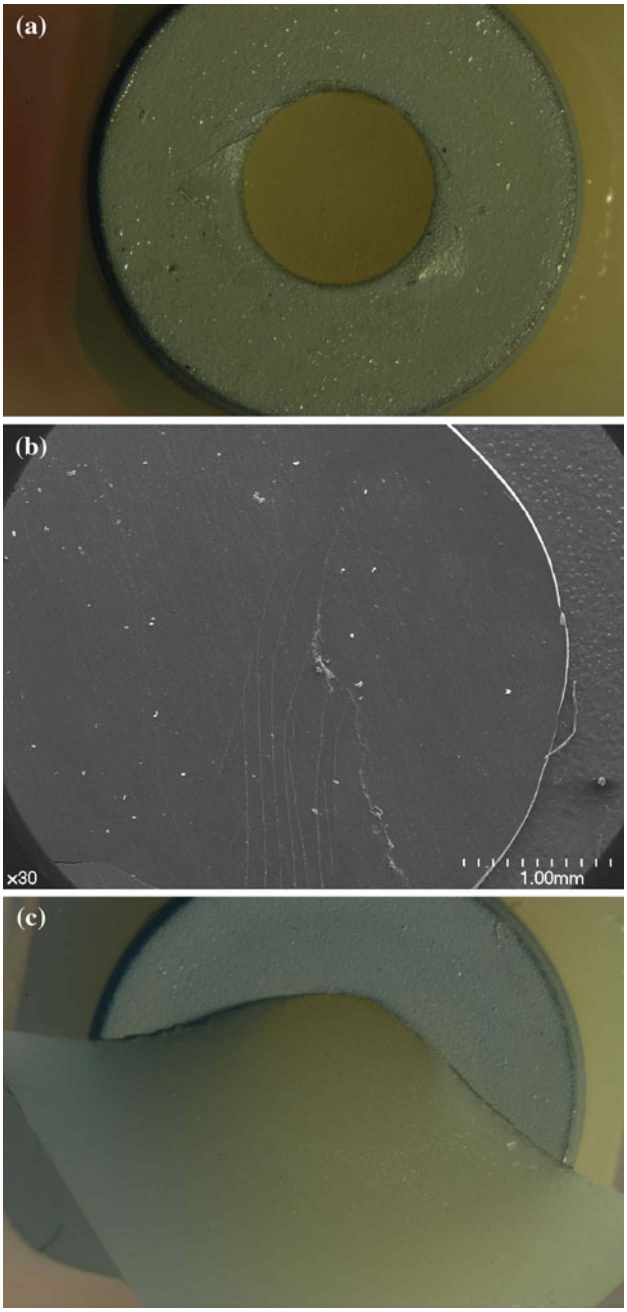


Fig. 2 The fractured surfaces obtained after the shear bond strength test. **a** In group 1, the fractured surfaces due to shear loading appeared flat and shiny, like the original polished surfaces of the ceramic blocks. The fracture occurred at the interface between the polished ceramic surface and the cured adhesive layer (Adhesive fracture). **b** In group 2 with the plasma polymer coating, small fragments of ceramic were occasionally observed on the adhesive surface covering the fractured bottom surface of the composite resin in the iris (Mixed fracture). When the plasma surface treatment with DW was additionally performed before plasma polymer coating with TEGDMA (group 3), the incidence of mixed fracture increased. **c** In group 4, cohesive fracture of ceramic was observed at the opposite side of the loading plunger in all specimens

showed cohesive fractures of the ceramic at the opposite side of the loading plunger (Fig. 2c). From the EDS line scanning of fragments on the adhesively fractured flat adhesive surface at the bottom of an iris from group 3 (Fig. 3), the composing elements of ceramic such as Si and Al were detected (asterisk), although they were not detected on the flat smooth surface.

The contact angle measurement of the ceramic specimens was 12.1° ± 1.7° when the surface was tested in an initial polished state. When the polished surface was altered through water plasma cleaning or TEGDMA plasma coating, the contact angle decreased to less than 5°. However, when the plasma polymer coating was performed with hydrophobic HMDSO, the contact angle increased to 85.3° ± 8.5°, even though it was applied on the hydrophilic surface obtained via water plasma cleaning. Once the surface was coated with HMDSO and when hydrophilic TEGDMA was applied to the hydrophobic surface obtained through HMDSO treatment, the contact angle decreased (30.8° ± 2.6°) but could not be lowered to the value of the TEGDMA-coated surface. Compared to the contact angle of the water droplet on the uncured oxygen-inhibited layer of the adhesive (45.2° ± 3.5°), the polished surface or the various plasma-treated surfaces used in this study were more hydrophilic, except for the HMDSO plasma-treated surface.

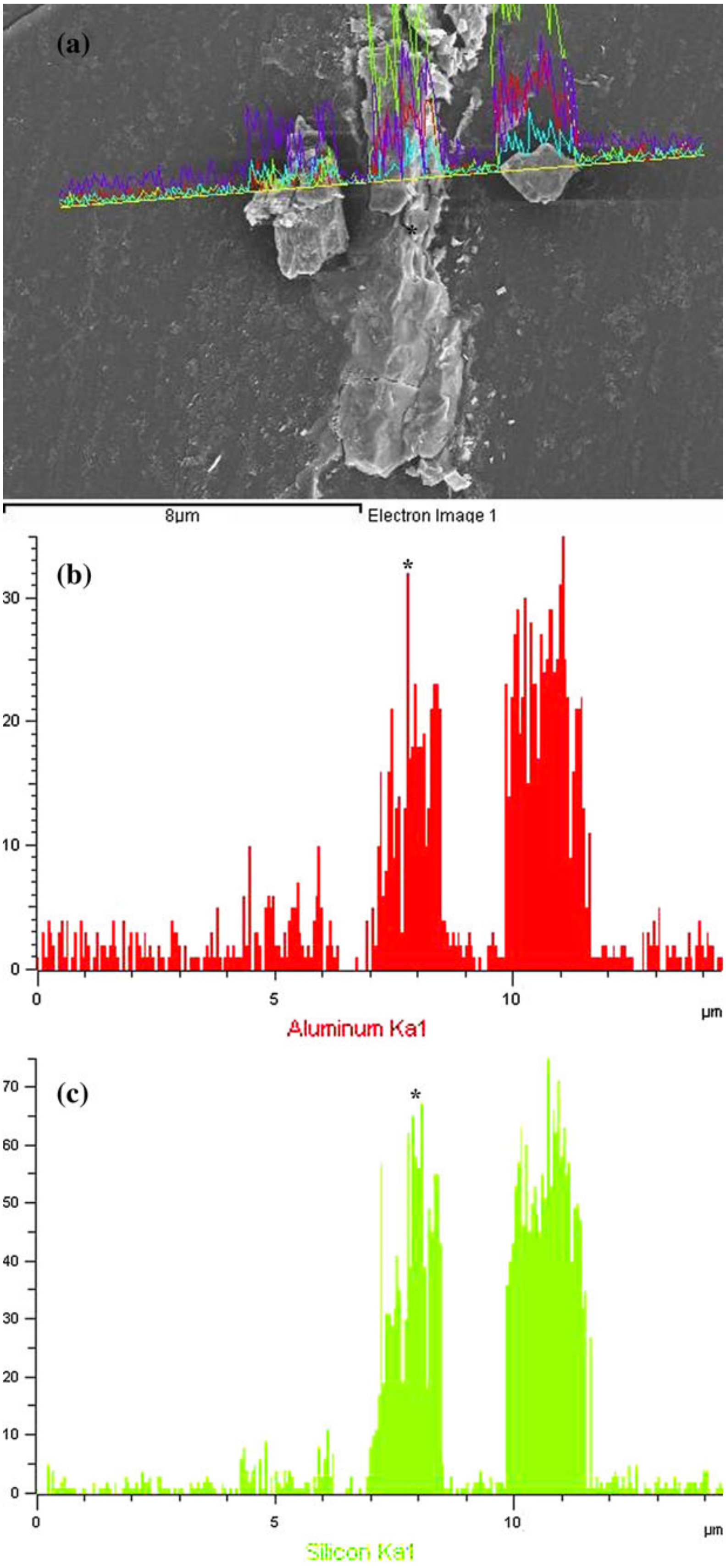
Discussion

In order to apply plasma technology to various fields of clinical dental practice, the equipment needs to come out of the vacuum chamber and to have a small handpiece shape. Outside the vacuum chamber, when the pressure or feeding power density is low, the plasma temperature (or gas temperature) is fixed by a heavy particle temperature due to the low density of excited atoms and the huge mass difference between electrons and heavy particles [2]. Even though they are excited or ionized, the inelastic collisions between electrons and heavy particles do not raise the temperature of the heavy particles [2]. To expose the materials to plasma without a vacuum system, the RF frequency of the steady-state uniform glow discharge at atmospheric-pressure must be in the appropriate range. If the RF frequency is too low, the discharge will not be initiated, and if it is too high, the plasma will form a filamentary discharge between the electrode plates or will be transformed to an arc discharge [19]. The resulting low temperature and chemically active species can be applied to tooth substrates and dental materials in the oral cavity for various purposes. Although many kinds of atmospheric plasma jets that function in open air have been introduced, there have been few reports on the application of atmospheric plasma technology in dental practice [3, 16]. In this study, we applied new innovative non-thermal AGD equipment to ceramic bonding.

In the clinic, feldspathic porcelain restorations are bonded according to a routine protocol using hydrofluoric acid etching and silane coupling agent coating such as ceramic primer [13]. In this study, the plasma polymer coating was evaluated as a chemical mediator for ceramic bonding and as an effective substitute for HF etching and silane coupling agent coating. In the SBS test, although the bond strength obtained after plasma polymer coating with only TEGDMA (group 2) failed to show a statistical difference from the bond strength obtained from the polished surface (group 1, negative control group), the bond strength obtained after sequential plasma surface cleaning with DW and plasma polymer coating with TEGDMA (group 3) was significantly greater than that of the negative control group (group 1). The results showed that the non-thermal AGD plasma polymer coating technique could contribute to the enhancement of ceramic bonding with conventional dental adhesives. Additional surface treatment with water plasma seemed to have the effect of surface activation due to the ionized –OH radicals or at least the effect of cleaning, which was similar to the effect of the oxygen plasma used to increase the hydrophilicity under vacuum conditions [2, 12, 15, 20]. It was assumed that the –OH radicals created a very hydrophilic surface. The values of groups 2, 3, and 4 were comparable to the results obtained by Derand et al. (15.2 ± 2.6 MPa in SBS) in a reactor using plasma deposition consisting of the activation of substrate surfaces with oxygen, RF plasma deposition with HMDSO, and additional activation of the polymer with oxygen [12]. Polar liquids, such as ethanol or methanol, can also be good candidates for surface modification to graft hydroxyl group (–OH) [21]. Further study using ethanol or methanol plasma is needed to modify the hydrophilicity of the substrate surface.

This study also evaluated the effect of HMDSO deposition on ceramics because, in many studies on plasma adhesion performed in a vacuum chamber, HMDSO was used as a precursor monomer to coat a thin film onto substrates [12, 22]. Plasma polymer coating with HMDSO has been proven to be an effective primer coating for adhesion promotion because –Si–O– bonds are known to form covalent bonds with metal and ceramic, and oxygen has been widely used as a carrier gas in plasma surface treatment [12, 20, 22]. Radicals like Si–O, Si–C, Si–O–Si, or Si–CH(x) (x can be 2, 3, or 4), dissociated from HMDSO molecules by high energy electrons, can react with surface metal, metal oxide, or metal hydrate to form metallic-silane, metallic-siloxane, organo-metallic-silane, or organo-metallic-siloxane. M–Si or M–O–Si is known to create very stable chemical bonds [8, 23]. However, an additional

Fig. 3 **a** SEM image of the fractured surface at the bottom of the composite resin in the iris after the shear bond strength test. Small fragments (*asterisk*) observed on the flat fractured surface were confirmed as ceramic according to EDS line scanning; **b** and **c**, from EDS line scanning, elements of ceramic, such as Si and Al, were detected in the fragments, but not on the flat smooth surface, demonstrating that there was an island of ceramic on the flat cured bonding layer which masked the underlying composite resin



HMDSO plasma polymer coating (group 4) applied before TEGDMA plasma coating failed to show a significant difference in SBS from that of the negative control (group 1). Although radicals like Si–O, Si–C, Si–O–Si, or Si–CH(x) (x can be 2, 3, or 4) that dissociated from the HMDSO molecule were expected to promote the adhesion between the ceramic primed by the monomer and the overlying adhesive, all of the specimens in group 4 showed adhesive fractures (Table 3). It seemed that hydrophilic adhesive failed to adequately wet the hydrophobic surface of the plasma polymer of HMDSO.

Group 5, which consisted of specimens bonded with HF etching and silane coupling agent coating, showed significantly higher bond strength than the other groups, and all specimens exhibited cohesive fractures in the ceramic (Fig. 2c). Among the groups in which specimens were treated with plasma polymer coating, only group 3 showed a significantly higher bond strength (Kruskal–Wallis test, $p < 0.05$) and significantly more mixed fractures (Chi-square test, $p < 0.05$, Table 3 and Figs. 2b and 3) than did the negative control group. At the fractured bottom surface of the composite resin in the iris, the specimens showing mixed fractures had small fragments of ceramic on the flat adhesive layer that resulted from the adhesive fracture between the polished surface of the ceramic and the adhesive layer (Fig. 3). These fragments demonstrated that there was an island of cohesively fractured ceramic fragments on the flat cured adhesive layer and that the element Si, included in the composite resin as filler, was masked by the adhesive layer. Although it was not clear whether the plasma-coated polymer was on the polished ceramic surface or on the composite resin side due to its extremely thin thickness, the adhesive layer must have been attached to the composite resin side. The small fragments observed especially at the point at which the plasma flame was directly applied were confirmed as ceramic according to an EDS scan. Even though the effective area of the flame was small, the fragment of ceramic cohesive fracture showed that the non-thermal AGD plasma polymer coating technique could contribute to enhance the ceramic bonding of conventional dental adhesives.

The water contact angle of the HMDSO plasma polymer coating (85.3° ± 8.5°) was higher than that of the TEGDMA plasma polymer coating (less than 5^{o}). During the pilot study, it was also found that, because the adhesive (SBMP adhesive) aggregated on the HMDSO plasma-coated surface, the surface could not be coated and failed to obtain good bond strength due to the poor wetting. In the other conditions of contact angle measurement, the values of the substrate surfaces were lower than those of the adhesive (45.2° ± 3.5°, Table 2). Although the exact level of fracture could not be differentiated, the relatively low bond strength and high number of adhesive fractures in group 4 were assumed to be attributed to the large difference in the hydrophobicity between HMDSO and TEGDMA. Therefore, the hydrophilicity of the plasma polymer-coated substrate surface was necessary to facilitate the wetting of the adhesive. In this study, we chose TEGDMA as the precursor monomer, a constituent of dental adhesives which is more hydrophilic than other adhesive ingredients such as Bis-GMA and which can be vaporized due to its high volatility. In this study, helium gas was used as the carrier gas because of its inertness and ability to stabilize a glow discharge outside of a vacuum chamber [2]. Although plasma treatments of oxygen, air, nitrogen, and argon gases increased wettability [24], oxygen is an electron-negative gas that requires a much higher breakdown voltage to generate plasma. Argon also requires high breakdown voltage. As a result, the plasma temperature was elevated to the level at which the plasma could not be applied to vital teeth. Moreover, because oxygen can also be involved in co-polymerization with monomer gas, it was difficult to prepare a stable AGD and to create a plasma polymer with proper characteristics.

Conclusions

In this study, the effect of plasma polymer coating on bond strength was not sufficient to replace the contemporary protocol involving HF etching and silane coupling agent coating. However, we found that the non-thermal AGD plasma polymer coating technique could contribute to enhance the ceramic bonding of conventional dental adhesives. The non-thermal atmospheric-pressure plasma polymer coating technique was found to have a potential promoting adhesion to dental materials.

Acknowledgements This study was supported by the Korea Research Foundation (KRF) grant funded by the Korean government (MEST, No. 2009-0070771).

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