Original Article

Influence of Hydrophilic Pre-treatment on Resin Bonding to Zirconia Ceramics

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Abstract

Atmospheric plasma or ultraviolet (UV) treatment alters the surface characteristics of tetragonal zirconia polycrystal (TZP), increasing its hydrophilicity by reducing the contact angle against water to zero. This suggests that such treatment would increase the wettability of bonding resin. The purpose of this study was to determine how increasing the hydrophilicity of TZP through plasma irradiation, UV treatment, or application of ceramic primer affected initial bonding with resin composites. Here, the effect of each pre-treatment on the hydrophilicity of TZP surfaces was determined by evaluating change in shear bond strength. Plasma irradiation, UV, or ceramic primer pre-treatment showed no significant effect on bonding strength between TZP surfaces and resin composites. In addition, alumina blasting yielded no significant increase in bond strength. Plasma irradiation, UV treatment, or ceramic primer pre-treatment did not lead to significant increase in bond strength between TZP and resin composites.

Key words: Hydrophilic treatment — Surface modification — Surface wettability — Tetragonal zirconia polycrystal (TZP) — Adhesive resin

Introduction

There has been a recent trend in clinical dentistry toward the use of tetragonal zirconia polycrystal (TZP) ceramics as they offer esthetic and mechanical advantages as a core (coping) material^{23,25)}. However, bond strength and durability between resin composites and TZP is inferior to that obtainable with other

types of ceramic or that between metal and adhesive resin^{13,19,29)}. Therefore, when fracture occurs in the TZP coping of a ceramic-faced crown, restoration is more difficult than with other types of all-ceramic restoration or where porcelain has been fused to a metal crown. Many studies have investigated how bond strength between TZP and resin materials might be improved, but the optimum method

Table 1 Materials used

Product	Code	Manufacturer	Components
Clearfil Protect Bond	CPB	Kuraray Noritake Dental, Tokyo, Japan	Bis-GMA, HEMA, MDP, hydrophilic dimethacrylate, dl-camphorquinone, photoinitiators, accelerators, silanized colloidal silica, NaF
Clearfil S ³ Bond Plus	SBP	Kuraray Noritake Dental, Tokyo, Japan	Bis-GMA, HEMA, MDP, hydrophilic aliphatic dimethacrylate, hydrophobic aliphatic methacrylate, colloidal silica, CQ, ethanol, accelerators, NaF, water
Clearfil Ceramic Primer	Primer	Kuraray Noritake Dental, Tokyo, Japan	3-trimethoxysilylpropyl methacrylate, ethanol, MDP
Clearfil Majesty	CM	Kuraray Noritake Dental, Tokyo, Japan	Bis-GMA, silanated barium glass filler, pre-polymerized organic filler, hydrophobic aromatic dimethacrylate, hydrophobic aliphatic dimethacrylate, CQ, accelerators, initiators, pigments

Bis-GMA: bisphenol A glycidyl dimethacrylate, CQ: dl-camphorquinone, HEMA: 2-hydroxyethyl methacrylate, MDP: 10-methacryloxydecyl dihydrogen phosphate, NaF: sodium fluoride

remains to be established^{1,3,8,13,20,26}.

In recent years, there has been increased interest in the use of TZP in dental implants^{4,5,22}. To enhance osseointegration in such TZP implants, it is essential to achieve adhesion between the implant body and human plasma⁹. Therefore, it is crucial that the surface of the implant be hydrophilic.

Plasma irradiation or ultraviolet (UV) treatment of TZP is used to increase its hydrophilicity²⁸. These treatments alter the initial interaction between the implant and the body by changing the wettability of the TZP surface^{31,34,35}. Changes in hydrophilicity may also affect bonding between TZP and resin composites through a similar process.

The objective of this study was to investigate how enhancement of hydrophilicity through plasma irradiation, UV treatment, or application of ceramic primer affected the initial bonding properties of TZP with resin composites. In addition, the effects of alumina sandblasting pre-treatment were also evaluated based on its necessity. The null hypothesis was as follows:

1. Plasma irradiation, UV treatment, or application of ceramic primer to a TZP surface would not contribute to increased bonding to resin composites.

2. Differences in the composition of bonding resins would have no effect on their bonding with TZP.

Materials and Methods

1. Materials used

Table 1 shows the materials used in this study. Two types of regular bonding resin, Clearfil Protect Bond (CPB) and Clearfil S³ Bond Plus (SBP), and a direct bonding type resin composite, Clearfil Majesty (CM), were used.

2. Preparation of specimens

Cylindrical Y-TZP discs 13 mm in diameter (TZ-3YB-E, Tosoh, Tokyo, Japan) were fabricated using a cutting machine into thicknesses of 2 mm and embedded in resin (Scandiplex, Fritsch Japan, Yokohama, Japan). The adherent surfaces were sequentially polished with #240–1200 water-resistant SiC paper (Polished). Surfaces blasted with 50- μ m alumina for 20 sec from a distance of 1 cm were also prepared (Blasted). After ultrasonic cleaning for 30 min, the samples were directly subjected to plasma irradiation (Plasma) for 10 sec (NJZ-2820, Nagano Japan Radio Co.,

Table 2 Shear bond strength (MPa) after surface pre-treatment (Polished)

	Clearfil Protect Bond (CPB)	Clearfil S ³ Bond Plus (SBP)
Plasma	7.96 ± 2.76 ^b	11.58 ± 2.69 ^a
UV	8.29 ± 2.28 ^b	10.54 ± 2.80 ^{ab}
Primer	9.04 ± 2.16 ^{ab}	9.96 ± 1.46 ^{ab}
Untreated	8.49 ± 1.71 ^b	10.15 ± 2.38 ^{ab}

Same letters indicate no significant difference (Tukey's HSD Test, $p > 0.05$). (Mean ± SD)

Table 3 Shear bond strength (MPa) after surface pre-treatment (Blasted)

	Clearfil Protect Bond (CPB)	Clearfil S ³ Bond Plus (SBP)
Plasma	8.41 ± 1.85	9.88 ± 2.96
UV	11.28 ± 3.25	11.09 ± 4.40
Primer	9.30 ± 1.40	10.04 ± 2.22
Untreated	8.94 ± 2.97	10.20 ± 2.32

No significant differences were observed among all groups (One-way ANOVA, $p > 0.05$). (Mean ± SD)

Ltd., spot diameter of 4 mm, 150 W, gas flow volume 6 liter/min), UV treatment for 60 min (BioForce Nanosciences, Stockholm, Sweden, 19 mW/cm²), or ceramic primer (Primer) for 10 sec (Kuraray Noritake Dental, Primer, Tokyo, Japan). Untreated specimens were also prepared as a control (Untreated). Double-sided tape was used to attach acrylic rings 6 mm in width and 2 mm in length to the treated TZP surfaces. Bonding resin was applied to the inner walls of the ring before irradiation with G light prima (Normal mode; GC, Tokyo, Japan) for 10 sec. The rings were then filled with resin composite and irradiated again for 40 sec. Specimens were stored in water at 37°C.

3. Shear bond testing and statistical analysis

After 7 days, shear bond strength was measured using a universal testing machine (AG-I 20kN, Shimadzu, Kyoto, Japan) with a cross-head speed of 1 mm/min. Ten samples were fabricated for each condition. An ANOVA and Tukey's HSD test were used for the statistical analysis ($p < 0.05$).

4. Wettability of bonding material on TZP surface

One droplet of bonding material (CPB,

SBP) was applied to each treated TZP surface by using the sessile drop method. Contact angle was determined using a contact angle meter (Phoenix α, Meiwafofosis, Tokyo, Japan).

Results

Table 2 shows the shear bond strengths of TZP and resin composite without alumina blast pre-treatment. In both the CPB and SBP groups, no significant difference was observed among the 4 treatment types (Plasma, UV, Primer, and Untreated). In the Plasma group, SBP showed significantly greater bond strength than CPB ($p = 0.018$). Table 3 shows the shear bond strengths of TZP and resin composite with alumina blast pre-treatment. An ANOVA revealed no significant differences ($p > 0.05$).

In terms of the wettability of the bonding material on the TZP surfaces, minimal differences were seen in contact angle (11–20°) among the groups (Plasma, UV, Primer, and Untreated). Alumina blast pre-treatment did not influence these results (Fig. 2 and Table 4). No significant differences were observed in contact angle among the 8 groups ($p > 0.05$).

Table 4 Contact angle (degree) against bonding agent on TZP surface

Surface treatment	Clearfil Protect Bond (CPB)	Clearfil S ³ Bond Plus (SBP)
Polished + Plasma	15°	12°
Polished + UV	18°	13°
Polished + Primer	19°	15°
Polished + Untreated	20°	17°
Blasted + Plasma	14°	11°
Blasted + UV	15°	13°
Blasted + Primer	16°	13°
Blasted + Untreated	18°	14°

Fig. 1 Cross-sectional views of water droplet on TZP with 3 different surface treatments
 CA: Contact angle against distilled water on zirconia surface after each surface treatment.
 Atmospheric Pressure Plasma Device (NJZ-2820, Nagano Japan Radio Co., Ltd.)
 Plasma spot width: diameter, 4 mm, Output: 150 W, Irradiation time: 10 sec, Gas used: CDA
 (Clean dry air), Gas flow volume: 6 liter/min
 Ultraviolet Device (BioForce Nanosciences, Stockholm, Sweden)
 Irradiation time: 60 min, Output: 19 mW/cm², Wavelength: 185–254 nm

Discussion

Atmospheric plasma irradiation produces plasma (ionization state) at low temperatures. Functional groups are introduced to the irradiated surface and surface properties such as surface energy and electrical charges can be controlled^{32,33,35}. Superhydrophilicity as a result of UV irradiation of TiO₂ surfaces was discovered in 1997³⁰, and was also developed in ZrO₂ in the same manner²⁴. The results of one earlier study indicated that UV-induced superhydrophilicity enhanced initial adhesion of osteoclasts to TZP surfaces³¹.

Our previous study demonstrated that the contact angle between distilled water and a mirror-polished TZP surface was 78.7 ± 8.3°. However, when atmospheric-pressure plasma or UV treatment was used, the contact angle became 0° (Fig. 1). These treatments clearly

increase the wettability of water on TZP surfaces. These changes in wettability may influence bonding between TZP and resin. In that study, we were investigating the effects of atmospheric-pressure plasma or UV radiation on bonding between TZP and bonding resin.

In the present study, hydrophilic treatment of the TZP surface did not lead to an improvement in bonding. The wettability of bonding agents was investigated and analyzed through contact angle. The results indicate that the contact angles were all within the range of 11–20° and that difference in surface treatment did not influence this angle (Fig. 2). These agents have similar contact angles though bonding agents contain a hydrophilic group. This is most likely the reason that hydrophilic treatment did not increase bond strength.

The application of a silane coupling agent is

Fig. 2 Cross-sectional views of bonding-agent droplet on TZP with 4 different surface treatments

known to be effective when bonding resin composite on conventional feldspathic porcelain²⁷. This treatment is ineffective for TZP, however⁶). To increase the adhesive strength of TZP and resin composites, primers containing phosphate ester, carboxylic acid, or phosphoric acid type monomers are used in a clinical setting due to their effectiveness^{12,21,26}. Clearfil Ceramic Primer contains a mixture of 3-methacryloxypropyl trimethoxy silane and phosphate monomer MDP. Although a slight increase in the wettability of the adhered surface may be expected, siloxane bonds may not be detected because no silica is present on the TZP surface. The effectiveness of MDP in Clearfil Ceramic Primer has been reported when bonding zirconia to adhesive resin cement¹². However, it is apparent that its use leads to many failures at the adhesive interface^{10,11}. In the present study, treatment with Clearfil Ceramic Primer was also expected to increase bond strength. The results, however, indicated that this effect was insignificant. Magne *et al.* reported that when the adhesive resin cement Panavia F 2.0 (Kuraray Noritake Dental) was applied to TZP, an increase was detected in bond strength, but that this increase was statistically insignificant²⁶. They assumed that the use of an MDP-containing primer might not be essential when using a MDP-containing luting agent. In a similar manner, pre-treatment using Clearfil Ceramic Primer may not be essential before application of either CPB or SBP, as these also con-

tain MDP.

Bonding between TZP and resin composites is enhanced through mechanical pre-treatment or alumina blasting⁷. This process not only cleans the TZP surface, but also roughens and increases the surface area available for adhesion. The combination of alumina blasting and MDP primer treatment has been reported to be very effective in increasing bonding, though the increase was statistically insignificant¹⁸. Being an extremely hard material, it is difficult to trim TZP samples after bonding. Therefore many studies apply the macro shear bond test¹⁰. The macro shear bond test was used for this study as well (area of adhesive surface, $3 \times 3 \times 3.14 = 28.26 \text{ mm}^2$). However, the mean bond strength and standard deviation were both small values here. This suggests that it is difficult to identify significance through this method. When atmospheric pressure plasma was applied without alumina blasting, SBP showed significantly higher adhesive strength than CPB. Overall, SBP displayed greater adhesive strength, although the difference was not statistically significant. Consequently, the second null hypothesis can be rejected. A 2-step self-etch adhesive⁷, CPB consists of the hydrophobic monomers Bis-GMA and TEGDMA, the hydrophilic monomers HEMA and MDP, and light-cured catalysts^{15,17}. However, it does not contain water or organic catalysts. On the other hand, as an all-in-one adhesive, SBP needs to possess a self-etching function, and

therefore contains water and ethanol. Due to this difference in composition, all-in-one adhesives have lower viscosity than 2-step-etch adhesives^{14,16}. Consequently, they blend on the TZP surface better than 2-step-etch adhesives², which may increase bond strength. No significant differences were observed among the 8 groups using SBP in the present study. This suggests that the level of adhesion seen with SBP here was due to its inherent hydrophilicity rather than the effects of atmospheric pressure plasma or UV treatment. Thus the first null hypothesis can also be rejected.

The application of TZP frames to all-ceramic-restorations will most likely continue to increase in a clinical setting. It is important to find ways to improve repair methods when chipping occurs at the TZP/ceramic interface. Therefore it is essential to find methods to improve bonding between TZP and resin composites.

Conclusion

Atmospheric-plasma, UV, or ceramic primer treatment of TZP surfaces yielded no increase in bond strength between those surfaces and the resin composite (Clearfil Majesty). The same absence of an increase in bond strength was also noted with alumina sandblast treatment. Further study is needed to establish how bond strength might be improved in resin composite and TZP restorations.

Conflict of Interest

The authors declare no conflict of interest.

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