Effect of different pH environments on the durability of bonds between zirconia and Ti-6Al-4V

Xin TAN, Shanshan GAO, Beilei LIU, Jie MIN, Qianqian ZHANG, Yuwei ZHAO and Haiyang YU

Department of Prosthodontics, State Key Laboratory of Oral Diseases & National Clinical Research Center for Oral Diseases, West China Hospital of Stomatology, Sichuan University, 14 Third Section, People’s South Road, Chengdu 610041, China

Corresponding author, Haiyang YU; E-mail: YHYmechanics@163.com

This study investigated the role played by different pH environments in the deterioration of bonds between Y-TZP and Ti-6Al-4V. One hundred and thirty-five specimens were randomly assigned to one of the following storage media at 37°C: (1) distilled water, pH 6.9, DW; (2) acidic solution, pH 1–2, CS; and (3) alkaline solution, pH 10–11, KS. Shear bond strength (SBS) tests were carried out at the 4-, 14-, and 30-day storage time intervals. The morphology characteristics and elements distribution of the fracture surfaces were analyzed. CS-30 showed the lowest mean SBS and the least amount of residual cement on the Ti-6Al-4V surface after the SBS tests. Bond strength tended to decrease with increasing storage time for the acidic group. Alkaline and neutral media showed little influence on the SBS of Y-TZP to Ti-6Al-4V in 30 days. Acidic environments should be properly avoided to obtain reliable long-term bonding strength between Ti-6Al-4V and Y-TZP.

Keywords: pH environments, Bonding durability, Zirconia, Ti-6Al-4V

INTRODUCTION

Zirconia and Ti-alloys are extensively used in dental implantology. Zirconia either makes up the crown or can be applied in the form of a coating onto the metallic core. Ti-alloys can be used to fabricate the abutment or constitute the metallic base under zirconia copings. A combination of the two kinds of material makes implant restoration exhibit good esthetics, superior biocompatibility, and enhanced mechanical properties.

Clinically, zirconia crown/coping is adhesively fixed to Ti-alloys abutment/base. The bond stability between them is a point of great importance. According to a previous study, suprastructures exposed to the loss of retention were at a higher risk of a technical or biological failure. However, the difficulty in zirconia bonding, limited bond area for Ti-alloy base and short (3–4 mm) abutment, and poor retention form of some angled abutments make implant restoration exhibit good esthetics, superior biocompatibility, and enhanced mechanical properties.

10-Methacryloyloxydecyl dihydrogen phosphate (MDP)-containing primers/cements have drawn substantial attention in recent years. As an adhesive monomer, 10-MDP consists of a long-chain methacrylate with a phosphoric acid group, which enables a stable chemical bond to ZrO₂ and many metals. The 10-MDP-substrate bonds can be formed at normal pressure and temperature and achieved via a brief contact period. Previous studies have demonstrated that 10-MDP-ZrO₂ bonds can withstand hydrothermal aging for 6 months. It seems that 10-MDP-containing cements are the best choice for bonding of implant restoration.

However, as water can diffuse through the resin matrix of any polymeric material and the bond interfaces, not only the resin cement but also the resin–substrate bonds undergo hydrolysis degradation, which is a biomolecular reaction involving water and the functional group possessing the labile bond. The rate of hydrolysis is influenced by many factors, including the type of chemical bond, pH, temperature, and water uptake. The pH particularly affects hydrolysis rates through catalysis and can dramatically influence the reaction between adhesive monomers and substrate. However, little information is available on whether pH fluctuations in the oral environment influence the stability of bonds between 10-MDP-containing cements and substrate, especially between 10-MDP and implant-related materials such as zirconia or Ti-alloys.

This study aimed to confirm whether pH levels in the mouth significantly affected the durability of bonds between Ti-6Al-4V and Y-TZP, and whether the process time affected the results. The null hypothesis tested was that no difference existed in the bond strength of Y-TZP bonded to Ti-6Al-4V stored in different-pH media over time.

MATERIALS AND METHODS

Detailed information of materials used in this study is listed in Table 1.

Specimen preparation
A total of 135 disks (3.0 mm in diameter and 3.0 mm in thickness) sectioned from machinable Y-TZP blocks (Zirconia-HT, Adite technology, QinHuangDao, China)
were sintered according to the manufacturer’s protocol, and 27 commercially available Ti-6Al-4V blocks (5×5×25 mm², Ti-JT, Adite technology) were machined. The bonding surface of Y-TZP disks and Ti-6Al-4V blocks were wet-polished with 600 and 800 grit silicon carbide paper (Struers, Copenhagen, Denmark) and then blasted with 50-μm alumina particles from a distance of 10 mm for 25 s at 0.2 MPa using a blasting device (DENTO-PREPTM, RONVIG Dental Mfg., Daugaard, Denmark). All the specimens were ultrasonically cleaned in ethanol for 5 min.

**Bonding specimen**
The cements (Multilink Speed, Ivoclar Vivadent, Schaan, Liechtenstein) were mixed according to the manufacturer’s protocol, and a thin layer was applied to the Y-TZP surface with a microbrush. The zirconia surface adhered to the Ti-6Al-4V surface, and the two joined specimens were axially loaded with a 1-N force for 1 min at room temperature. The excess cement was removed with a paintbrush, and the composite resins were photocured for 20 s using a light-emitting diode device (Demi⁺, Kerr, Orange, CA, USA) with an irradiance of 1,200 mW/cm².

**Different-pH environment treatment**
The hydrochloric acid and sodium hydroxide were purchased with high purity and then diluted to acidic/alkaline solution with distilled water. The specimens were randomly assigned to three groups (n=45) based on the exposure conditions: (1) distilled water (pH 6.8); (2) HCl solution (pH 1–2); and (3) NaOH solution (pH 10–11). Every group was further divided into three subgroups (n=15) according to the exposure time: (1) 4 days; (2) 14 days; and (3) 30 days. The pH of all the solutions was verified using a digital pH meter (Star A211, Thermo Scientific, Waltham, MA, USA) every day.

**Shear bond test and statistical analysis**
The shear bond test was performed using a Universal Testing machine (INSTRON-5565, INSTRON, Norwood, MA, USA) at 0.5 mm/s crosshead speed. The shear bond test values were recorded in MPa and submitted to analysis of variance and simple linear regression analysis (α=0.05).

**Fracture analysis and surface microscopic observation**
The failure characteristics of the bonded specimen were analyzed under an optical microscopy (BX51M,

---

**Table 1 Materials used in the present study**

| Material (Trade name) | Major composition | Manufacturer |
|-----------------------|-------------------|--------------|
| Y-TZP (Adite, Zirconia-HT) | ZrO₂ (94–95 wt%), Y₂O₃ (4.5–5.5 wt%), Al₂O₃ (<0.5 wt%) | Aidite technology, QinHuangDao, China |
| Ti-6Al-4V (Adite, Ti-JT) | Ti base, Al (5.5–6.75 wt%), V (3.5–4.5 wt%), Fe (<0.30 wt%), C (<0.008 wt%), N (<0.003 wt%) | Aidite technology |
| Resin cement (Multilink Speed) | Autopolymerizing matrix: dimethacrylate and acidic monomers; fillers (40 vol%): barium glass, ytterbium trifluoride, copolymer, and silicon dioxide; particle size: 0.1–7 μm | Ivoclar Vivadent, Schaan, Liechtenstein |
| Al₂O₃ (DENTO-PREPTM) | Al₂O₃ | RONVIG Dental Mfg., Daugaard, Denmark |
| NaOH (Sigma-Aldrich) | Purity (>97.0 wt%), Na₂CO₃ (<1.0 wt%), K (<0.02 wt%), Cl/Ca (<0.005 wt%), SO₄ (<0.003 wt%), Ag/Mg (<0.002 wt%), N/P/O4/Fe/Ni (<0.001 wt%), Hg (<0.1 ppm) | Sigma-Aldrich, St Louis, MO, USA |
| HCl (Sigma-Aldrich) | Purity (31.0–33.0 wt %), SO₄ (<0.5 wt%), Residue on Evaporation (<0.5 wt%), Fe (<5.0 ppm), As (<3.0 ppm), Cd/Pb (<1.0 ppm), Hg (<0.1 ppm) | Sigma-Aldrich |
OLYMPUS, Ishikawa, Japan), using the ImageJ software to determine the amount of resin remaining on the Y-TZP and Ti-6Al-4V sides after failure so as to clarify the fracture mechanism. Besides, representative specimens of each group were selected for qualitative scanning electron microscopy (SEM; Inspect F, FEI NanoPorts, Eindhoven, Netherlands) and 3D profilometer (Up Series, Rtec instruments, San Jose, CA, USA). Specimens were prepared according to the standard demand and analyzed at 80× and 5,000× magnification or 10× magnification (3D profilometer). Energy-dispersive spectroscopy (EDS; X-MAX 20, Oxford Instruments, UK) was used to characterize the relative elemental distribution on fracture interfaces and help identify failure modes.

**RESULTS**

Shear bond strength (SBS) evaluation

Table 2 shows the results of the statistical analysis of

![Fig. 2](image1.png) Amount of residual resin (%) on the Y-TZP side after failure in the SBS test.

No statistically significant differences between groups are linked by horizontal lines (p>0.05).

![Fig. 3](image2.png) Amount of residual resin (%) on the Ti-6Al-4V side after failure in the SBS test.

No statistically significant differences between groups are linked by horizontal lines (p>0.05).

| Treatment time (days) | pH environment |
|-----------------------|----------------|
|                       | pH (1–2)       | pH (6.9)       | pH (10–11)      |
| 4                     | 24.61±5.51 a A | 21.19±5.52 a A | 20.82±5.49 a A  |
| 14                    | 21.94±6.18 a A | 21.03±4.91 a A | 21.75±5.19 a A  |
| 30                    | 16.88±3.61 a B | 21.86±6.18 b A | 23.79±6.87 b A  |

Mean values with dissimilar small letters within each row and capital letters within each column are statistically significant different at p≤0.05.

Table 3 Results of simple linear regression analysis of SBS and processing methods

| Dependant variables | Independent variables | Unstandardized coefficients | t       | P     | r    | R²   |
|---------------------|-----------------------|-----------------------------|---------|-------|------|------|
| SBS (CS)            |                       | −0.284                      | −3.946  | 0.000*| 0.516| 0.266|
| SBS (DW)            | storagetime           | 0.027                       | 0.053   | 0.729 | 0.053| 0.003|
| SBS (KS)            |                       | 0.115                       | 1.422   | 0.162 | 0.212| 0.045|
| SBS (4-day)         | pH values             | −0.389                      | −1.762  | 0.085 | 0.260| 0.067|
| SBS (14-day)        |                       | −0.033                      | −0.150  | 0.881 | 0.023| 0.001|
| SBS (30-day)        |                       | 0.779                       | 3.410   | 0.001*| 0.461| 0.213|

*p<0.05; CS: acidic solution, pH1–2; DW: distilled water, pH6.9; KS: alkaline solution, pH10–11.
the SBS values. For 30-day groups, specimens at pH 1–2 showed the lowest bond strength (16.88±3.61 MPa), while those at pH 10–11 (23.79±6.87 MPa) and pH 6.9 (21.86±6.18 MPa) presented no significant differences in comparison with the respective baseline means. For storage periods of 4 and 14 days, negative significant differences were found among the three pH conditions. The linear regression analysis (Table 3) in the acidic medium revealed a negative linear relationship between SBS values and storage time \( (p<0.001) \), but no linear regression relationship was observed for the neutral and alkaline media. For the 30-day groups, a positive linear relationship was found between SBS and pH values \( (p=0.001) \); however, for the 4-day and 14-day groups, no significant linear regression relationship was observed between SBS and pH values (Table 3).

**Fracture analysis and surface microscopic observation**
Zirconia and Ti-6Al-4V presented different fracture interface characteristics after SBS tests.

The amount of residual cement on the zirconia surface in different pH environments showed a small change among different time groups (CS: 76.48–97.83%; DW: 74.85–96.48%; KS: 72.68–84.65%); all of them reached their peak on the 30th day (Fig. 2). For Ti-6Al-4V, all pH and storage time groups showed a similar area of the remaining cement except for the acidic media on the 30th day; the residual cement decreased by about 47% compared with the 4-day group (Fig. 3). SEM and 3D profilometer images also indicated the least amount of resin cement on the Ti-6Al-4V surface processed in acidic media for 30 days (Figs. 4 and 5). EDS identified the fracture mode as adhesive failure between cement and Ti-6Al-4V instead of cohesive failure of Ti-6Al-4V (Fig. 6).

---

**Fig. 4** Contrast of SEM images (80×) of debonded zirconia and Ti-6Al-4V surfaces from the three pH groups processed for 30 days. R, Resin cement; T, Ti-6Al-4V; Z, zirconia. Ti-6Al-4V processed with an acidic solution for 30 days showed the least area of residual cement on the fractured surface.

**Fig. 5** Comparisons of 3D topography of debonded zirconia and Ti-6Al-4V surfaces from the three pH groups processed for 30 days.
DISCUSSION

Resistance to the chemical degradation of dental materials is a principal requirement for intra-oral use and a relevant concern in choosing cement materials for restorations. It is crucial to the success of dental implant prostheses. Hence, the Y-TZP–Ti-6Al-4V bonding interface must resist degradation on exposure to harsh conditions arising from pH changes.

An acidic medium can be created in the oral environment as follows: (1) acidic food and beverages (i.e., citric, lactic, and acetic acids); (2) regurgitation of gastric acid; and (3) bacterial decomposition of debris. Alkaline media can be generated by intake of alkaline food or beverages (i.e., soda and soybean milk) and using oral care products such as mouth rinse, toothpaste, and so on. Although the extremely acidic and alkaline media used in the present study could not completely represent the actual pH of saliva, the conditions selected were based on the degradation process of resin cement or adhesive bond, and led to accelerated degradation effects similar to those observed in vivo.

The present study evaluated the effect of three pH environments on the stability of bonds between Y-TZP and Ti-6Al-4V using an 10-MDP-containing resin cement. In view of the low transmittance of zirconia and quick initial polymerization, a cement of dual-curing property was selected, which allowed the total conversion of unreacted constituents in cement. The most important adhesive monomer in the studied cement 10-MDP had three functional components: methacryloyl, dihydrogen phosphate, and decyl groups. The methacryloyl group is indispensable to copolymerize the 10-MDP monomers in the primer and the matrix monomers in the resin cement. The dihydrogen phosphate group chemically bonds to zirconia and metal oxides. The decyl group prevents the penetration of water into the adhesive interface, either reducing or retarding hydrolysis.

For the Y-TZP and Ti-6Al-4V bond complex, three aspects should be included when considering the influence of pH environments: (1) adhesive interface of Y-TZP–resin cement due to the formation of a coordinate bond (Zr-O-P bond) between 10-MDP and ZrO2. (2) Adhesive bonding between Ti-6Al-4V and resin cement, which is through a chemical interaction between 10-MDP monomer and oxide on the Ti-6Al-4V surface. To be more specific, it indicates phosphoric groups of 10-MDP and OH− groups of metal oxide chemically bonded by Bolger’s mechanism through the electrostatic interaction and depends on the isoelectric metallic oxide points and the constant acid dissociation of monomers. (3) The resin cement layer, whose mechanical performance is thought to have an impact on the final bond strength value. Water may cause the degradation of resin matrix and chemical bonds in the two adhesive interfaces, influencing the results of SBS and fracture modes.

Two main theories explained the mechanism of water sorption by a resin matrix. The free volumetric theory states that the molecules diffuse inside the material via micropores, structural defects, or along the filler–matrix interfaces without any actual binding to other polar molecules. The interaction theory states that water molecules form hydrogen bonds with special ionic groups of the polymer chain. Water can also breach the marginal seal by permeating from the surface of the resin–substrate interface, which is related to insufficient polymerization of the adhesive resin or the presence of low-molecular-weight oligomers, further causing degradation of 10-MDP-substrate bonds.
and microleakage\(^{11}\).

The SBS results suggested that none of the three pH media influenced the bond strength between Y-TZP and Ti-6Al-4V for a relatively short time (4 days). As the process time increased to 14 days, the acidic group showed a decreasing tendency. Finally, the lowest SBS occurred in the acidic group on the 30th day. The linear regression analysis indicated that SBS had a negative linear relationship with the storage time only for acidic groups. The analysis also showed a positive linear relationship of SBS with pH values only for the 30-day group, indicating that pH environments did influence the bond durability of Y-TZP to Ti-6Al-4V time-dependently. This was probably because the ions (i.e., OH\(^{-}\) and H\(^{+}\)) in different-pH solutions needed time to permeate into the inner part of the bond interfaces and act on them\(^{11,12}\) due to the limited area of contact (about 0.4 mm\(^2\)) and existence of hydrophobic constituents (i.e., decyl group) in cement\(^{10}\).

SBS had a negative linear relationship with the storage time for the acidic group. The fracture analysis showed that the adhesive bond between Ti-6Al-4V and cement became the weakest point of the bond complex in an acidic environment. As previously mentioned, the mechanism of 10-MDP bonding to Ti-6Al-4V was related to the dihydrogen phosphate group interacting with –OH of the metal oxide surface (Figs. 7 and 8). Therefore, it was carefully speculated that the acidic media decreased the bond stability of 10-MDP to Ti-6Al-4V via the infiltration of H\(^{+}\) ions of a strong acid (HCl) into the bond interface\(^{11,12}\). Then, the H\(^{+}\) ions protonated O\(^{2-}\) of the dihydrogen phosphate group to form stabler hydrogen bonds and thus weaken the hydrogen bonds between 10-MDP and metal oxide (Fig. 8), because the acidity of HCl was strong and it has better ability to offer H\(^{+}\) ions to form hydrogen bonds compared with –OH ions on the metal oxide surface\(^{31-33}\).

Although the fracture mode analysis indicated Ti-6Al-4V-cement interface as the weakest part, the negative effect of acidic media on the zirconia–cement interface or resin layer could not be denied because the SBS result for the 14-day group showed a decreasing tendency but the fracture mode was predominant cohesive failure of cement. In fact, Xie et al. demonstrated that acidic environments could accelerate the hydrolysis of Zr-O-P covalent bond\(^{9}\). Prakki et al. also proved that the negative effect of acidic media on the resin cement was slow acting\(^{34,35}\), which was in accordance with the finding of no significant difference between the 14-day and 4-day groups with a fracture of cement.

The neutral and alkaline groups showed similar SBS results at three time intervals and a significant negative change from the longitudinal view. For both groups, the amount of residual cement on zirconia (Fig. 2) and Ti-6Al-4V (Fig. 3) surface for three storage time groups was large and relatively stable, suggesting a good adhesive bonding of resin cement to substrates.

As for the distilled water group, the stability of SBS values could be explained in two possible ways: (1) the hydrolysis proceeded slowly, and therefore the storage time of 30 days was insufficient for the effects to be...
detected; (2) the rate of chemical reaction between the monomers and substrates for the two adhesive interfaces or the progression of polymerization in the resin cement was equal to the speed of hydrolysis.

Many previous studies explored the alkaline treatment and bonding. Xie et al. demonstrated that alkaline media promoted the coordination between 10-MDP and ZrO₂, thereby increasing the strength of the 10-MDP-zirconia bond. Besides, Kikuchi et al. showed that alkaline preconditioning might enhance the bond strength between 10-MDP and metal oxide by increasing the amount of –OH ions on the oxide surface. At the same time, Cilli et al. proved that highly alkaline media could cause accelerated degradation of dental composite resin. In the present study, the alkaline group did not present significantly higher bond strength compared with the neutral group, probably because SBS values comprehensively reflected the bond strength of the “sandwich-like” structure consisting of two adhesive interfaces and one resin cement layer. Further, different effects of the alkaline media on the three points might compromise each other and lead to the seemingly unchanged results.

Oral environment pH can be affected by multiple factors, such as intake of acidic/alkaline food and drinks, regurgitation of the gastric juice, maintenance of oral hygiene, and so on. Neither acidic nor alkaline materials in the oral environment can be totally removed until effective dental hygiene methods are taken because the residual acidic/alkaline materials adhere to tooth, restorations, plaque, or dental calculus and hence influence dental pH. Once the acidic/alkaline solution permeates into the cement layer between the crown and the abutment, it is difficult to remove using conventional oral hygiene methods. Therefore, the acid/alkaline exposure is far more frequent than expected. As SBS showed a positive linear relationship with pH values for the 30-day group and acidic environment could negatively influence the durability of bonds between Y-TZP and Ti-6Al-4V in the present study, clinicians should pay special attention to the patients with gastric acid reflux or acidic diet habits when their dental restorations include Y-TZP–Ti-6Al-4V bond interfaces. For the general patients, clinicians should also suggest them to reduce the intake of acidic food or drinks and, most importantly, maintain oral hygiene to extend the service life of related restorations.

This novel in vitro study explored the effects of different pH environments on the strength of bonds between Y-TZP and Ti-6Al-4V using a 10-MDP-containing resin cement. The evaluation indicated that SBS of Y-TZP to Ti-6Al-4V presented good stability in neutral and alkaline environments but could not endure the attack of acidic agents, especially the Ti-6Al-4V resin cement interface. The acid may interfere with the chemical reaction between metal oxide and 10-MDP and weaken the hydrogen bond formed between them. The presence of other aging factors, including dynamic fatigue loading and temperature changes in the oral cavity, may also contribute to the properties and corresponding degradation of the bonding interfaces. Therefore, further studies are required to elucidate the stability of bond interfaces in implant restoration.

**CONCLUSIONS**

The conclusions of the present study were as follows:

1. Acidic environments had time-dependent negative influence on the SBS between Ti-6Al-4V and Y-TZP using an 10-MDP-containing resin cement, which might be related to an increased adhesive failure between resin cement and Ti-6Al-4V.

2. Alkaline and neutral media showed little influence on the bond strength of Y-TZP to Ti-6Al-4V in 30 days.

**ACKNOWLEDGMENTS**

This study was supported by National Natural Science Foundation of China (No.81571006). Thanks are expressed to Aidite technology for assistance with Y-TZP and Ti-6Al-4V. We also thank MedSci for the English language review.

**REFERENCES**

1. Revathi A, Borras AD, Munoz AI, Richard C, Manivasagam G. Degradation mechanisms and future challenges of titanium and its alloys for dental implant applications in oral environment Materials. Mater Sci Eng C Mater Biol Appl 2017; 76: 1354-1368.

2. Cordeiro JM, Barão VA. Is there scientific evidence favoring the substitution of commercially pure titanium with titanium alloys for the manufacture of dental implants? Mater Sci Eng C Mater Biol Appl 2016; 71: 1201-1215.

3. Yan M, Kao CT, Ye JS, Huang TH, Ding SJ. Effect of preoxidation of titanium on the titanium–ceramic bonding. Surf Coat Technol 2007; 202: 288-293.

4. Brägger U, Karoussis I, Persson R, Pjetursson B, Salvi G, Lang N. Technical and biological complications and failures with single crowns and fixed partial dentures on implant of the ITI® Dental Implant System. Clin Oral Implants Res 2005; 16: 326-334.

5. Grasel R, Santos MJ, Rego HC, Rippe MP, Valandro LF. Effect of resin luting systems and alumina particle air abrasion on bond strength to zirconia. Oper Dent 2018; 43: 282-290.

6. Llerena-Icochea AE, Costa RM, Borges A, Bombonatti J, Furuse AY. Bonding polycrystalline zirconia with 10-MDP-containing adhesives. Oper Dent 2017; 42: 335-341.

7. Wandescher VF, Prochnow C, Rippe MP, Dorneles LS, Callegari GL, Baldissara P, et al. Retentive strength of Y-TZP crowns: Comparison of different silica coating methods on the intaglio surfaces. Oper Dent 2017; 42: E121-E33.

8. Fernandes CA, Ribeiro JC, Larson BS, Bonfante EA, Silva NR, Suzuki M, et al. Micromechanical bond strength of resin-based composites to Ti-6Al-4V. Dent Mater 2009; 25: 655-661.

9. Xie H, Tay FR, Zhang F, Lu Y, Shen S, Chen C. Coupling of 10-methacryloyloxydecyldimethoxyphosphoryl zirconia: Effect of pH reaction conditions on coordinate bonding. Dent Mater 2015; 31: 218-225.

10. Fonseca RC, de Almeida JG, Haneda IG, Adabo GL. Effect of metal primers on bond strength of resin cements to base metals. J Prostheth Dent 2009; 101: 262-268.

11. Chen C, Chen Y, Lu Z, Qian M, Xie H, Tay FR. The effects of...
water on degradation of the zirconia-resin bond. J Dent 2017; 64: 23-29.
12) da Silva EM, Goncalves L, Guimaraes JG, Poskus LT, Fellows CE. The diffusion kinetics of a nanofilled and a midfilled resin composite immersed in distilled water, artificial saliva, and lactic acid. Clin Oral Investig 2011; 15: 393-401.
13) Marghalani HY. Sorption and solubility characteristics of self-adhesive resin cements. Dent Mater 2012; 28: 187-198.
14) Sano H, Yoshikawa T, Pereira PN, Kanemura N, Morigami M, Tagami J, et al. Long-term durability of dentin bonds made with a self-etching primer, in vivo. J Dent Res 1999; 78: 906-911.
15) Cilli R, Pereira JC, Prakki A. Properties of dental resins submitted to pH catalysed hydrolysis. J Dent 2012; 40: 1144-1150.
16) Gopferich A. Mechanisms of polymer degradation and erosion. Biomaterials 1996; 17: 103-114.
17) Ping Y, Zhou X, Arola DD, Jie M, Peng Z, Gao S. Effect of acidic agents on the wear behavior of a polymer infiltrated ceramic network (PICN) material. J Mech Behav Biomed Mater 2017; 74: 154-163.
18) Sulaiman TA, Abdulmajeed AA, Shahramian K, Hupa L, Donovan TE, Vallittu P, et al. Impact of gastric acidic challenge on surface topography and optical properties of monolithic zirconia. Dent Mater 2015; 31: 1445-1452.
19) de Gee AJ, Wendt SL, Werner A, Davidson CL. Influence of enzymes and plaque acids on in vitro wear of dental composites. Biomaterials 1996; 1517: 1327.
20) Schneider R, de Goes MF, Henriques GE, Chan DC. Tensile bond strength of dual curing resin-based cements to commercially pure titanium. Dent Mater 2007; 23: 81-87.
21) Yanagida H, Matsumura H, Taira Y, Atsuta M, Shimoe S. Adhesive bonding of composite material to cast titanium with varying surface preparations. J Oral Rehabil 2002; 29: 121-126.
22) Yanagida H, Matsumura H, Atsuta M. Bonding of prosthetic composite material to Ti-6Al-7Nb alloy with eight metal conditioners and a surface modification technique. Am J Dent 2001; 14: 291.
23) Taira Y, Matsumura H, Yoshida K, Tanaka T, Atsuta M. Influence of surface oxidation of titanium on adhesion. J Dent 1998; 26: 69-73.
24) Ohno H, Endo K, Yamane Y, Kawashima I. Adhesion of adhesive resin to dental precious metal alloys. Part II. The relationship between surface structure of Au-In alloys and adhesive ability with 4-META resin. Dent Mater J 1998; 17: 285-293.
25) Mertens T, Gammel FJ, Kolb M, Rohr O, Kotte L, Tschöcke S, et al. Investigation of surface pre-treatments for the structural bonding of titanium. Int J Adhes Adhes 2012; 34: 46-54.
26) Hibino Y, Kuramochi K, Hoshino T, Moriyama A, Watanabe Y, Nakajima H. Relationship between the strength of glass ionomers and their adhesive strength to metals. Dent Mater 2002; 18: 552-557.
27) Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater 2006; 22: 211-222.
28) Oyague RC, Monticelli F, Toledano M, Osorio E, Ferrari M, Osorio R. Effect of water aging on microtensile bond strength of dual-cured resin cements to pre-treated sintered zirconium-oxide ceramics. Dent Mater 2009; 25: 392-399.
29) Ortengren U, Andersson F, Elgh U, Tersellius B, Karlsson S. Influence of pH and storage time on the sorption and solubility behaviour of three composite resin materials. J Dent 2001; 29: 35-41.
30) Yiu CK, King NM, Pashley DH, Suh BI, Carvalho RM, Carrilho MR, et al. Effect of resin hydrophilicity and water storage on resin strength. Biomaterials 2004; 25: 5789-5796.
31) Kuo SW, Huang CF, Chang FC. Study of hydrogen-bonding strength in poly(ε-caprolactone) blends by DSC and FTIR. J Polym Sci B Polym Phys 2003; 139: 1348-1359.
32) Kuo SW, Chan SC, Hewder Wu A, Chang FC. An unusual, completely miscible, ternary hydrogen-bonded polymer blend of phenoxy, phenolic, and PCL. Macromolecules 2005; 38: 4729-4736.
33) Kuo SW. Hydrogen-bonding in polymer blends. J Polym Res 2008; 15: 459-486.
34) Prakki A, Cilli R, Mondelli RF, Kalachandra S, Pereira JC. Influence of pH environment on polymer based dental material properties. J Dent 2005; 33: 91-98.
35) Munchow EA, Ferreira AC, Machado RM, Rodrigoes-Junior SA, Zanchi CH. Effect of acidic solutions on the surface degradation of a micro-hybrid composite resin. Braz Dent J 2014; 25: 321-326.
36) Kituchi T, Yoshida N, Shimakura M, Ohtani M, Nemoto T, Yokobori M. The clinical application of resin facing titanium crown by non-retention method. The influence of heating time on the bond strength. Nihon Hotetsu Shika Gakkai Zasshi 2002; 64: 46-54.
37) Ban S. Effect of alkaline treatment of pure titanium and its alloys on the bonding strength of dental veneering resins. J Biomed Mater Res A 2003; 66: 138-145.
38) Tsuchimoto Y, Yoshida Y, Takeuchi M, Mine A, Yatani H, Tagawa Y, et al. Effect of surface pre-treatment on durability of resin-based cements bonded to titanium. Dent Mater 2006; 22: 545-552.
39) Yap AU, Tan SH, Wee SS, Lee CW, Lim EL, Zeng KY. Chemical degradation of composite restoratives. J Oral Rehabil 2001; 28: 1015-1021.