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Lack of Neutralization of 10-MDP Primers by Zirconia May Affect the Degree of Conversion of Dual-cure Resin Cement

DM De Paula • AD Loguercio • A Reis • S Sauro • AH Alves
PR Picanço • K Yoshihara • VP Feitosa

Clinical Relevance

Use of zirconia primers with a low pH and a high acidic monomer concentration should be employed in combination with dual-cure resin cements that are less sensitive to an acidic environment. Primers with lower 10-MDP concentrations attain better outcomes.

SUMMARY

Objective: To assess the effects of different concentrations of 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) included in experimental ceramic primers on the degree of conversion (DC) and microshear bond strength (µSBS) of a dual-cure resin cement, and on the acidity neutralization potential of zirconia (ZrO2) in comparison to hydroxyapatite (HAp).

Methods: Experimental ceramic primers were formulated using 5 wt%, 10 wt%, 20 wt%, or 40 wt% 10-MDP as an acidic functional monomer and camphorquinone (CQ)/amine or 1-phenyl-1,2-propanedione (PPD) as a photoinitiator system.

Diego M De Paula, DDS, MSc, Post-graduate program in dentistry, Department of Restorative Dentistry, Federal University of Ceará, Fortaleza, Brazil; Paulo Picanço School of Dentistry, Fortaleza, Brazil

Alessandro Loguercio, DDS, PhD, State University of Ponta Grossa, Ponta Grossa, Paraná, Brazil

Alessandra Reis, DDS, PhD, State University of Ponta Grossa, Ponta Grossa, Paraná, Brazil

Salvatore Sauro, DDS, Post-Graduate Program in Dentistry, Department of Restorative Dentistry, Federal University of Ceará, Fortaleza, Brazil; Dental Biomaterials – Departmento de Odontologia, Facultad de Ciencias de la Salud, CEU-Cardenal Herrera University, Valencia, Spain

Adyson H Alves, DDS, MSc student, Paulo Picanço School of Dentistry, Fortaleza, Brazil

Paulo R Picanço, DDS, MSc, PhD, Paulo Picanço School of Dentistry, Fortaleza, Brazil

Kumiko Yoshihara, Center for Innovative Clinical Medicine, Okayama University Hospital, Okayama, Japan

*Victor P Feitosa, DDS, MsC, PhD, professor, Post-graduate program in dentistry, Department of Restorative Dentistry, Federal University of Ceará, Fortaleza, Brazil; Paulo Picanço School of Dentistry, Fortaleza, Brazil

*Corresponding author: Department of Restorative Dentistry, Dental School – Federal University of Ceará, Rua Monsenhor Furtado S/N, Bairro Rodolfo Teofilo, 60430-325

Fortaleza, CE, Brazil; e-mail: victorpfeitosa@hotmail.com or victor.feitosa@facpp.edu.br

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Clearfil Ceramic Primer (Kuraray Dental, Tokyo, Japan) was used as the commercial control. Micro-Raman spectroscopy was used to assess the DC of uncured and light-cured resin cements applied onto primer-treated ZrO2 surfaces. The µSBS and pH of primers were assayed in a universal testing machine and by a digital pH meter (Tec-3MP; Tecnal, Piracicaba, Brazil), respectively. Statistical analysis was performed by one-way analysis of variance (ANOVA) and Tukey's test (p<0.05).

Results: DC was not affected until a concentration of 10% 10-MDP in CQ primer and 5% 10-MDP in PPD primer was reached, when compared with the positive control (*p*>0.05). Groups 10-MDP 5% in CQ and PPD primers showed the highest µSBS compared with the positive control (*p*>0.05); however, higher concentrations of 10-MDP induced significant DC and µSBS reduction (*p*<0.05). HAp neutralized 10-MDP primers, but ZrO2 provided higher acidity to the primers' pH.

Conclusion: 10-MDP monomer should be used in low concentrations in ZrO2 primers to avoid reduction of the polymerization and bond strength of resin cement.

INTRODUCTION

Seeking aesthetic dental treatments has increased the demand for metal-free prosthetic restorations. By replacing the metal framework for reinforced dental ceramics, several benefits are acquired beyond aesthetics, such as higher biocompatibility for nonprecious metal frameworks, lower thermal conductivity, higher hardness, and chemical stability.[1,2] Yttria-stabilized tetragonal ZrO_2 polycrystals (Y-TZP) ceramics may be applied as an alternative for the traditional metal framework.[3] Nevertheless, due to its high chemical stability and monolithic crystalline structure, conventional hydrofluoric acid conditioning is less effective on glass ceramics, thereby reducing the bonding ability when used along with dual-cure resin cements.[4]

Different chemical and mechanical surface pretreatments were, thus, recommended in order to improve the bonding of resin cements to ZrO_2 ceramics.[3,5] The use of chemical agents for resin cement luting Y-TZP structures has been shown to improve bonding to ZrO_2.[6] Therefore, techniques promoting less damage to Y-TZP ceramics,[7] along with producing functionalized surfaces, are desirable. Among these techniques, tribochemical silica coating and subsequent silanization have already demonstrated efficacy in enhancing the long-term durability of a resin–ZrO_2 bond[8]—even though such a procedure requires further laboratory steps and special equipment. Recently, there has been an increase in investigations and clinical applications of ZrO_2 primers and self-adhesive resin cements based on acidic functional monomers,[5] which improved the shear bond strength to Y-TZP ceramics.[6,9]

The most commonly used acidic functional monomer for ZrO_2 is 10-MDP,[9] and although most studies show that a higher bond strength results when a primer containing 10-MDP is used, this is not the consensus in the literature regarding reactions with a dual-cure resin cement.[9] This may be related to the fact that it is not exactly known what concentration of 10-MDP would provide best results.

Another problem related to the use of acidic functional monomers is that the presence of such monomers may interfere with the polymerization of dental adhesives and cements based on type II photoinitiator systems (such as camphoroquinone) with tertiary amine (CQ/amine), which might jeopardize the DC.[10] In the case of self-etch adhesives, dissolution of HAp from enamel/dentin and the reaction with the tertiary amine coinitiators in the primer may reduce this phenomenon due to the buffering of the acidic media[11] and binding of the functional monomer with calcium,[12] thereby avoiding the decrease on the DC during polymerization.[10] Such neutralization has been demonstrated with self-etch adhesives[10] as well as with self-adhesive resin cements.[13] Nevertheless, to the extent of our knowledge, no reports are available concerning the role of the reaction between the acidic functional monomer and Y-TZP ceramic on the neutralization trend of acidic pH from ceramic primers, which could potentially interfere with resin cement polymerization and bonding, depending also on the type of photoinitiator and presence of tertiary amine in ZrO_2 primer.

The aim of this study was to assess the effects of different concentrations of 10-MDP included in experimental ceramic primers on the DC and µSBS of a conventional dual-cure resin cement in comparison with a commercial ceramic primer. Additionally, the acidity neutralization potential of ZrO_2 and HAp were surveyed. The hypotheses tested are as follows: 1) the concentration of the acidic functional monomer does not interfere with the DC and adhesion of the resin composite cement applied to the Y-TZP-ceramic, 2) there is no effect of two photoinitiator systems in primers (with or without tertiary amine) on the DC and bond strength of resin cement to ZrO_2, and 3) ZrO_2 is not able to neutralize the pH of experimental ceramic primers.

METHODS AND MATERIALS

Reagents

10-MDP was donated by FGM Company (Joinville, Brazil) and used without further purification. CQ (photoinitiator) and ethyl 4-(dimethylamino) benzoate (EDAB, coinitiator) were donated by Esstech Inc (Essington, Pennsylvania, USA), while type 1 photoinitiator PPD (photoinitiator) was purchased from Sigma Aldrich Chemicals (St. Louis, Missouri, USA).

Experimental Primers

To formulate experimental ceramic primers, 10-MDP was employed as an acidic functional monomer and included in 5 wt%, 10 wt%, 20 wt%, or 40%, and diluted in 50 vol% ethanol/distilled water. In order to evaluate the influence of functional monomer acidity and photoinitiators, the primers were made light-curable by means of inclusion of CQ/EDAB or PPD. Clearfil Ceramic Primer (Kuraray Dental) was used for the commercial comparison primer (Table 1) and also it was added a negative control when no primer was applied.

Degree of Conversion

Y-TZP ceramic blocks (Zirconcad, Angelus, Londrina, Brazil) with dimensions of 13.2 x 13.2 x 3.2 mm were obtained and sintered according to the manufacturer's instructions. After that, all blocks were polished for 30 seconds with 600-, 800-, and 1200-grit silicon carbide papers under water irrigation, ultrasonicated for 10 minutes to obtain standardized flat surfaces, air-dried, and were then randomly assigned in one of the ten groups (n=3; three different ZrO_2 specimens tested in each group). Primer compositions are detailed in Table 1, and no application of ceramic primer was the negative control group. Primers were applied actively for 20 seconds using a microbrush and air-dried for 30 seconds with a strong blast of air. Thereafter, the dual-cure resin cement RelyX ARC (3M ESPE, St. Paul, Minnesota, USA) was used according to the manufacturer's instructions: a thin layer (1- ± 0.2-mm thick) was applied onto each ZrO_2 slab, covered with a Mylar strip, and then directly light-cured for 40 seconds using a Light Emitting Diode (LED) unit DB 685 (1100 mW/cm^2; Dabi Atlante, Ribeirão Preto, Brazil). Each resin cement specimen was mixed only after the complete Micro-Raman spectroscopy analysis of the previous specimen.

Micro-Raman spectroscopy analysis was used to assess the DC of the resin cement 10 minutes after it was light cured. The Micro-Raman spectrophotometer (Xplora, Horiba Jobin Yvon Inc, Paris, France) was, firstly, calibrated using a standard silicon sample supplied by the manufacturer. A helium-neon laser with 3.2 W of power and a 532 nm wavelength was used, with a 1.5-µm spatial resolution and a 2.5 cm^{-1} spectral resolution associated with a 10x magnification lens (Olympus, London, UK), to attain an approximately 60- x 70-µm field area with three accumulations of 10 seconds of acquisition time each. The DC was calculated based on a previous study[14] using the following formula:

$$DC = \left(1 - \frac{R_{cured}}{R_{uncured}}\right) \times 100,$$

Table 1. *Compositions of Zirconia Primers Tested*

Groups	Composition
CQ5	5% 10-MDP, 46.5% ethanol, 46.5% distilled water, 0.5% CQ, 1.5% EDAB
CQ10	10% 10-MDP, 44% ethanol, 44% distilled water, 0.5% CQ, 1.5% EDAB
CQ20	20% 10-MDP, 39% ethanol, 39% distilled water, 0.5% CQ, 1.5% EDAB
CQ40	40% 10-MDP, 29% ethanol, 29% distilled water, 0.5% CQ, 1.5% EDAB
PPD5	5% 10-MDP, 46.5% ethanol, 46.5% distilled water, 2% PPD
PPD10	10% 10-MDP, 44% ethanol, 44% distilled water, 2% PPD
PPD20	20% 10-MDP, 39% ethanol, 39% distilled water, 2% PPD
PPD40	40% 10-MDP, 29% ethanol, 29% distilled water, 2% PPD
Commercial comparison (Clearfil Ceramic Primer)	1–5% 10-MDP, 3-TMSPMA (silane), ethanol
Negative control	No primer

Abbreviations: 3-TMSPMA, 3-(Trimethoxysilyl)propyl methacrylate; 10-MDP, 10-methacryloyloxy-decyl-dihydrogen-phosphate, CQ, camphorquinone; EDAB, ethyl 4-(dimethylamino) benzoate; PPD, phenyl-propanedione.

where R is the ratio between the heights of the 1638 cm^{-1} and 1609 cm^{-1} peaks, after baseline correction, of uncured and light-cured material. Three readings were taken from the top surface of each specimen according to a previous study.[14] These readings were averaged to obtain one statistical unit (n=3). As three ZrO_2 specimens were assessed per group, nine spectra total were surveyed in each group.

Microshear Bond Strength

Y-TZP ceramic blocks (Zirconcad) with dimensions of 13.2 x 13.2 x 3.2 mm were obtained and sintered according to the manufacturer's instructions. They were embedded and fixed in PVC pipes by means of acrylic resin (JET; Artigos Odontologicos Classico Ltda, Campo Limpo Paulista, Brazil). The exposed flat ZrO_2 surfaces were polished as described above.

The µSBS specimens were bonded to the ZrO_2 surfaces using cylindrical translucent moulds (Tygon tubing, TYG-030; Saint-Gobain Performance Plastic, Clearwater, Florida, USA) as previously reported.[6] Six cylinders (0.75 mm diameter x 1 mm height) were bonded in each ZrO_2 block using the dual-cure resin cement RelyX ARC (3M ESPE) in a similar set-up of DC analysis (10 groups), resulting in 36 cement cylinders per group. The six results from cylinders tested from the same ZrO_2 block were averaged and used as a statistical unit (n=6, referring to the six ZrO_2 blocks per group). Previous to cement application, either experimental primers or the commercial primer (Table 1) were actively applied for 20 seconds followed by a strong 30 second blast of air to evaporate all the solvent and ensure the monomer was left on the surface. In the negative control group, no primer was used before resin cement bonding. Resin cement was applied in the cylinders and light-cured for 40 seconds according to the manufacturer's instructions with an LED unit (DB 685, output wavelength peak at 470 nm, with 1100 mW/cm^2 irradiance periodically checked by a radiometer). All cylinders were group-cured to avoid overlapping exposure to the curing light. Specimens were analyzed and those with defects were discarded and replaced. Before the bond strength survey, all specimens were stored immersed in distilled water at 37°C for 48 hours in the dark to ensure the chemical cure of the dual-cure cements.

Bonded specimens were mounted in a device for a µSBS test (Odeme Dental Research, Joaçaba, Brazil) adapted in a universal testing machine (EMIC DL 2000; São José dos Pinhais, Brazil). An orthodontic wire (0.4-mm diameter) was positioned surrounding and in contact with half of the cylinder, and it was connected to the load cell (500 N) of the machine to exert shear force in an upward direction. Each cylinder was tested individually with a 1 mm/minute crosshead speed up to the point of fracture. Maximum µSBS was recorded in N and transformed to MPa, with the analysis of each cylinder diameter to obtain the bonded area (mm^2).

After debonding, all ZrO_2 surfaces were examined with a stereomicroscope (SMZ800; Nikon, Tokyo, Japan) to determine the mode of failure, and which were classified in three types: A – adhesive fracture between ceramic and cement without signs of residual cement of ZrO_2 surface; C – cohesive failure of the cement, with the full area presenting cement remnants; and M – mixed fracture, with areas depicting adhesive debonding and some residual cement indicating partial cohesive failure.

Buffering of Primer Solutions

Initially, 1 mL of each primer solution was surveyed (n=3) for its pH by using a digital pH meter (Tec-3MP). After the initial acquisition, 10 aliquots of 0.1 g of HAp[15] (Sigma Aldrich) or ZrO_2 (Dinâmica Química Contemporânea, Diadema, São Paulo, Brazil) powders were added to each solution in order to track the variations in pH. At each aliquot, the primer was mixed for 60 seconds and the pH was re-assessed. Data was used to build a graph of the pH change for each powder. After the tenth aliquot, the final pH of each solution was used as the result for statistical analysis.

Statistical Analysis

The results of the DC and µSBS were statistically analyzed by Shapiro-Wilk normality test ($p>0.05$) and, after proving normal data, the data were analyzed by one-way ANOVA and Tukey's test ($p<0.05$), with 93.2% power. The initial and final pH of each primer were statistically analyzed separately by *t*-test (to compare HAp vs ZrO_2), with a 5% significance level.

RESULTS

The degree of conversion outcomes are depicted in Figure 1. The positive control Clearfil Ceramic Primer (mean 89.0% DC), negative control (mean 89.0% DC), CQ5 (mean 94.8% DC), CQ10 (mean 93.5% DC), CQ20 (mean 81.5% DC), and PPD5 (mean 92.1% DC) treatments induced statistically similar conversions and the highest conversions ($p>0.05$). The ZrO_2 treatment using PPD40 (44.6% mean DC) presented significantly lower DC values when compared with all groups ($p<0.05$). CQ40 and PPD20 presented intermediate results.

The results of µSBS (MPa) are shown in Figure 2. Groups with lower 10-MDP concentrations presented

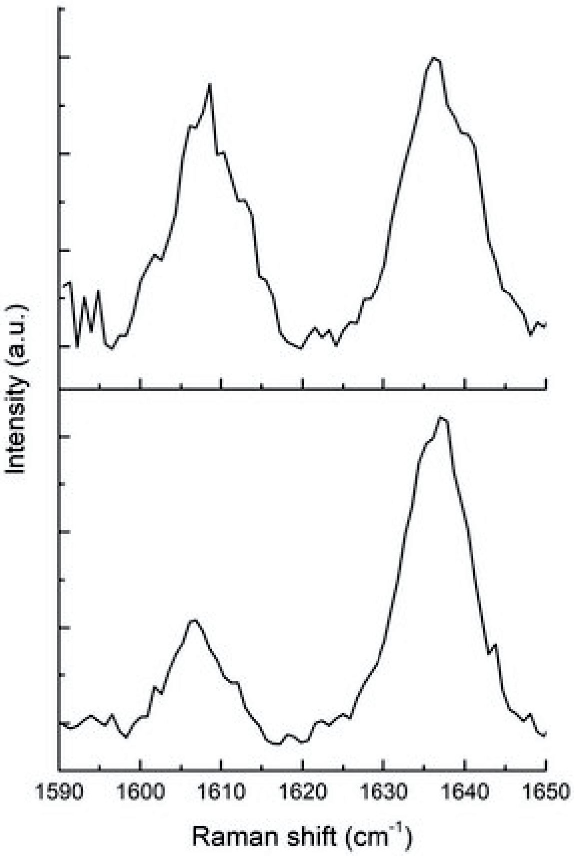

Figure 1. *Representative Raman spectra of uncured (bottom) and cured (top) resin cement onto zirconia specimen.*

similar and significantly higher µSBS, such as positive control Clearfil Ceramic Primer (14.0±1.2), CQ5 (13.4±2.1), and PPD5 (12.8±1.8) when compared with other groups (p<0.05). As the concentration of acidic functional monomer increased, µSBS dropped significantly, usually with no significant difference when the same concentration of photoinitiator was compared (p>0.05). With exception of PPD40 and CQ40, PPD40 (8.1 ± 0.7) achieved significantly lower µSBS values when compared with CQ40 (p<0.05). The lowest µSBS value was found for the negative control no-primer group (0.5 ± 0.2), which was significantly different in comparison to all the groups (p<0.05); also, in this group, premature failures were observed in most of the specimens.

The results of the pH values are shown in Figure 3. Overall, regardless of the photoinitiator that was employed, the pH of all primers increased with the addition of HAp, while the pH slightly reduced with the addition of ZrO_2 powder. The final pH was statistically different (p<0.05) between HAp and ZrO_2 powders for all the primers tested.

DISCUSSION

The efficiency and durability of adhesion between resin cement and ZrO_2 ceramics depends upon several factors, such as wettability, microretentions, and the chemical interaction of functional monomers. Indeed,

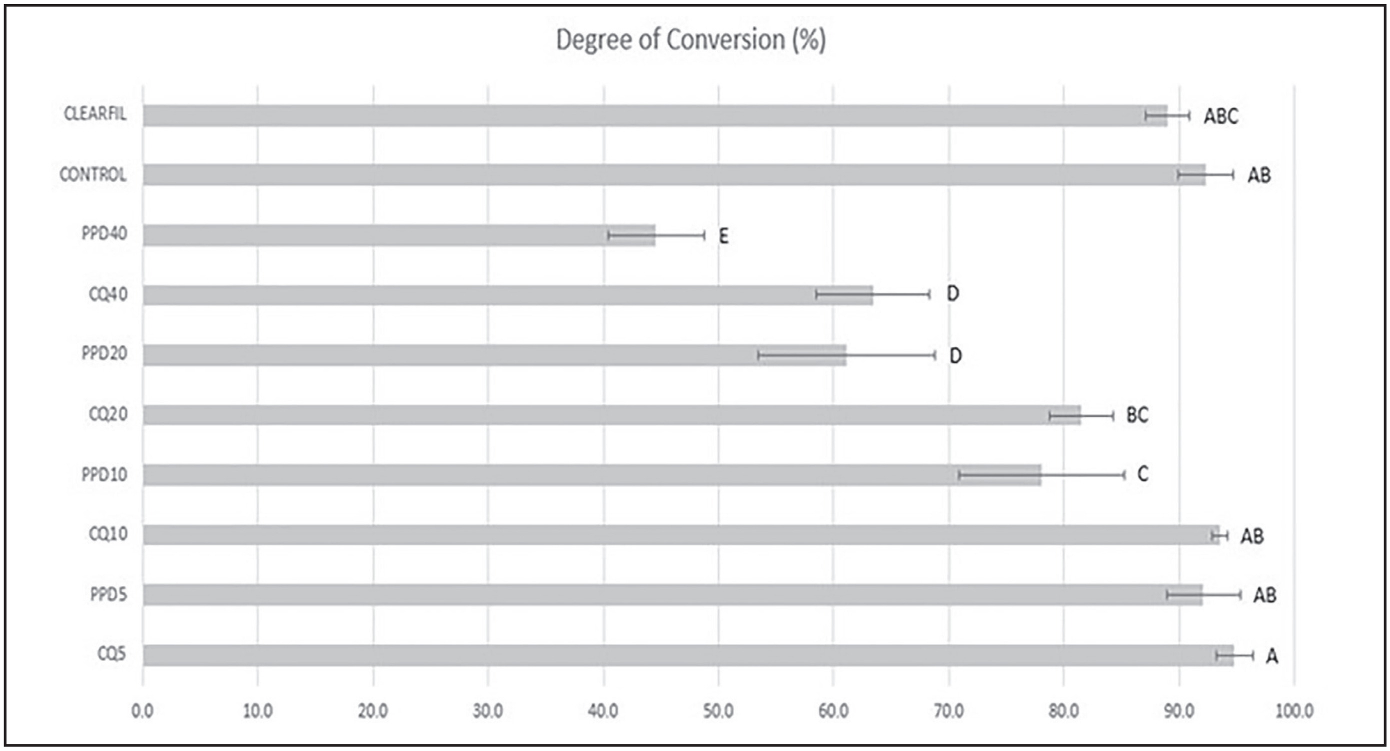

Figure 2. *Means and standard deviations of degree of conversion (%) results from resin cement applied onto treated zirconia specimens. Different letters indicate statistical difference (p<0.05).*

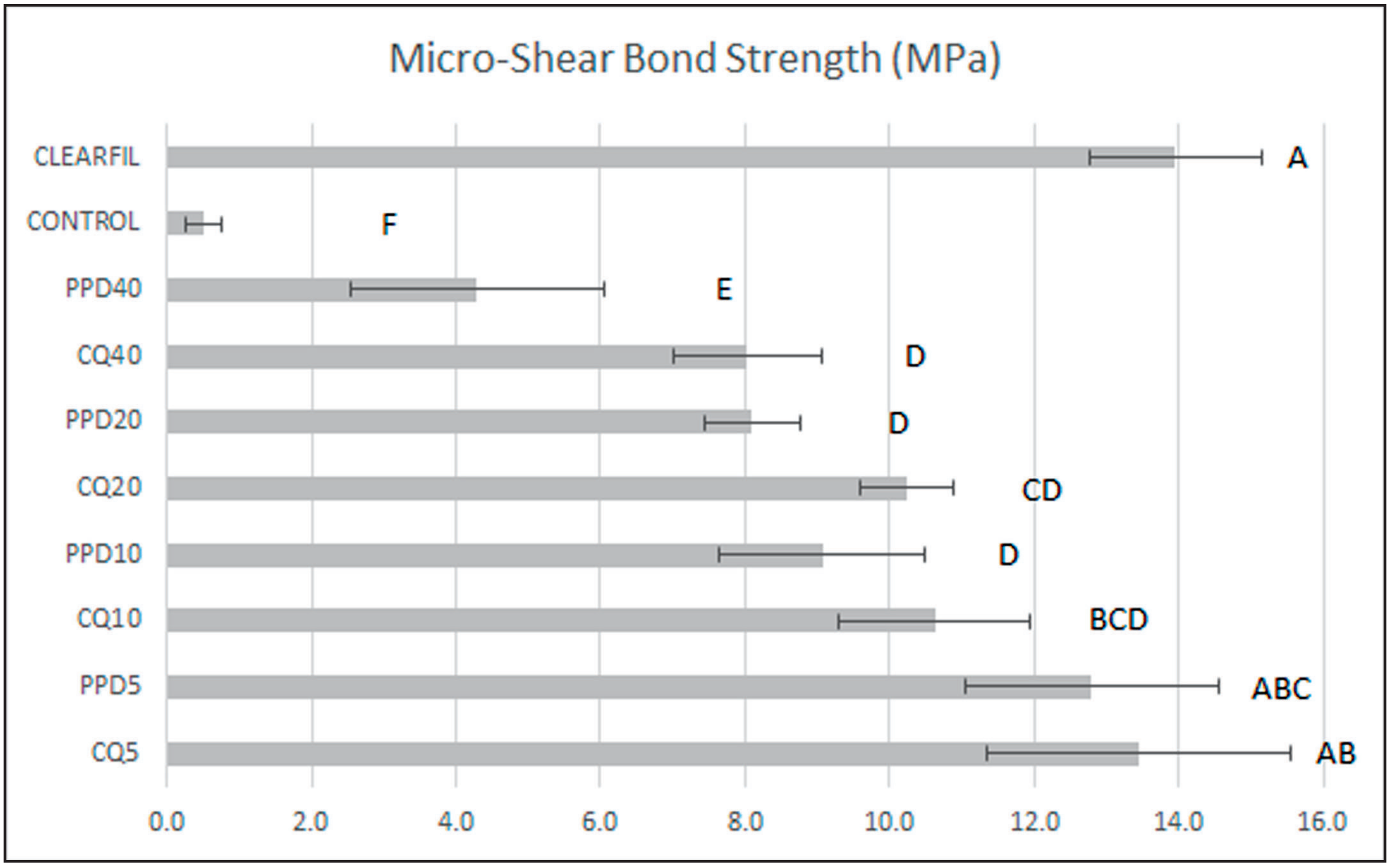

Figure 3. *Means and standard deviations of micro-shear bond strength (MPa) outcomes. Different letters indicate statistical difference ($p<0.05$).*

the interaction of an acidic monomer with a Y-TZP surface has proven to be a challenge;[16] besides, the optimal polymerization of resin cement is crucial to obtain high mechanical strength and stability of the ceramic-cement-dentin interface. In the present study, the DC of a commercial dual-cure resin cement applied onto a Y-TZP surface was investigated after the use of different ceramic primers containing a 10-MDP functional monomer and after they were combined with two photoinitiators. The first and second hypotheses tested were rejected because the concentration of the acidic monomer, as well as the two different photoinitiators tested, significantly altered the DC and μSBS of resin cement onto a Y-TZP ceramic, and the presence of high concentrations of acidic monomer together with PPD resulted in lower levels of these properties. However, the third hypothesis is accepted, as ZrO_2 powder was not able to neutralize the pH of the primers tested.

The conditioning of feldspathic, leucite-reinforced, and lithium dissilicate ceramics by hydrofluoric acid and subsequent silanization is a well-established method for luting glass ceramic prosthesis with a resin cement.[3] Silane increases the surface energy of these ceramics, thereby providing chemical bonding between the siloxane functionality of the molecule and the silica-rich inorganic phases.[6] As Y-TZP is a monolithic ceramic without the presence of glass or silica in composition, conditioning with hydrofluoric acid does not increase surface roughness, and silane does not ameliorate the bond strength.[7] A recent review from Özcan and others[5] concluded that among all these strategies, the optimal durability of resin cement–ZrO_2 bonds is attained by using a 10-MDP monomer containing primers and cements, even after thermocycling.

The DC of resin-based materials containing a CQ/amine photoinitiator system may be affected by the presence of acidic functional monomers.[17] Excited CQ after light exposure turns into a single state that reacts with hydrogen donators, such as tertiary amines, thereby transferring electrons and protons, generating free radicals, and starting polymerization.[18] However, tertiary amines in resin-based materials may also react as Lewis bases are being neutralized by acidic functional monomers, which can impair polymerization.[17] Hanabusa and others[10] demonstrated this reaction with 10-MDP and 4-META functional monomers, and depicted the negative effects on methacrylate-based polymerization initiated by the CQ/amine photoinitiator system. Nevertheless, in the presence of HAp (from enamel/dentin), its dissolution before light curing buffers acidic monomers and reduces the inhibitory influence on polymerization.[10]

Oguri and others[17] also tested the polymerization of CQ/amine and borate (type I photoinitiator) resins in the presence of an MAC-10 (11-methacryloxy-1,1-undecane dicarboxylic acid) acidic functional monomer. The DC in the CQ/amine system significantly dropped, while borate was not affected by the acidic monomer. In the present investigation, higher concentrations of an acidic functional monomer in experimental primers containing CQ/amine and PPD induced a lower DC to the resin cement; however, lower concentrations of 10-MDP had no influence. PPD's inclusion was proposed to investigate the influence of an amine-free photoinitiator system and its correlation with 10-MDP concentration. As for this photoinitiator, only ZrO_2 could neutralize acidic monomers. In the PPD groups, more pronounced negative effects were observed (Figures 1 and 2), as the lowest bond strength and conversion among primers was achieved with a PPD40 primer. This suggests that the presence of an amine coinitiator in 10-MDP–containing ceramic primers could result in the additional neutralization of the primers' acidity, resulting in a less negative influence on resin cement polymerization and bonding.

Another factor that significantly decreases the DC of dual-cure resin cements when they are used to lute ZrO_2 ceramics is the high opacity of ZrO_2. This reduces the light transmission and proper irradiance that reaches the underlying cement, thereby diminishing the polymerization, mechanical properties, and durability of resin cement.[19] In this study, light curing was performed directly over the resin cement without ZrO_2 between the cement and the light unit's tip, disregarding the interference of ceramic opacity. Therefore, the polymerization tested was predominantly light-initiated. The chemical curing of dual-cure resin cements could likely compensate for the negative effect of acidic functional monomers from ZrO_2 primers, but it was not investigated once the DC was attained 10 minutes after light curing. Future studies need to be done to test this hypothesis.

The reduction of polymerization conversion was concentration-dependent in 10-MDP–containing primers (Figure 1). Regarding Clearfil Ceramic Primer, the low concentration of 10-MDP (according to the manufacturer's MSDS) induces a higher pH and may leave free amine to react with CQ during light curing. Conversely, with experimental primers, the high concentrations of 10-MDP (40 wt%) decreased the pH (Figure 3) and possibly most functional monomers chemically bonded to ZrO_2, but a significant amount was free to react with amine, thereby reducing resin cement's degree of conversion. From a clinical perspective, the viability of using self-etch or universal adhesives with higher concentrations of 10-MDP[11] than ceramic primers should be reconsidered and checked for potential negative effects of dual-cure resin cement polymerization. Concerning 10-MDP–containing adhesives, the study of Llerena-Icochea and others[20] showed no differences among acidic monomer concentrations of 3–15 wt%. In fact, these results corroborate the present outcomes, once even the lowest concentrations of 10-MDP achieved adequate ZrO_2 bonding for the resin cement.

Indeed, some investigations demonstrated that a more alkaline pH favors the chemical interaction of 10-MDP with ZrO_2,[21] which contributes to the present findings and which suggest a reduction of 10-MDP concentration for optimal adhesion to ZrO_2. However, a further alternative could be the use of other acidic monomers in ceramic primers and universal adhesives. For instance, Chen and others[7] studied PENTA (dipentaerythritol penta-acrylate phosphate) as a replacement for 10-MDP in ceramic primers. They concluded that the bond strength of resin cement to Y-TZP may be improved by using this alternative monomer, and that the increase in monomer concentration only enhances bond affinity, but not necessarily the efficacy. Therefore, PENTA may be applied in a very low concentration, reducing its potential inhibitory effects on resin cement's polymerization, which was not truly investigated in that study.

The attempt to improve bond strength by increasing the concentration of the acidic monomer in ceramic primers seems to be inefficacious. A recent investigation[22] also showed, by nuclear magnetic resonance experiments, that high concentrations of 10-MDP in ZrO_2 primers increased intermolecular hydrogen bonding between monomers, thereby jeopardizing the chemical interaction formation of hydrogen and ionic bonds between 10-MDP and ZrO_2 ceramic.[21] As demonstrated herein, a high concentration of 10-MDP impairs the bond strength of resin cement to Y-TZP. The reduction in bond strength was positively correlated with an increase in 10-MDP concentration and the reduction of the ceramic primers' pH. This occurs due to the lack of neutralization of the primers' pH by the ZrO_2 surface. Rather, in the pH tracking experiment, ZrO_2 powder actually maintained or increased the acidity of primers (Figure 4). HAp, on the other hand,

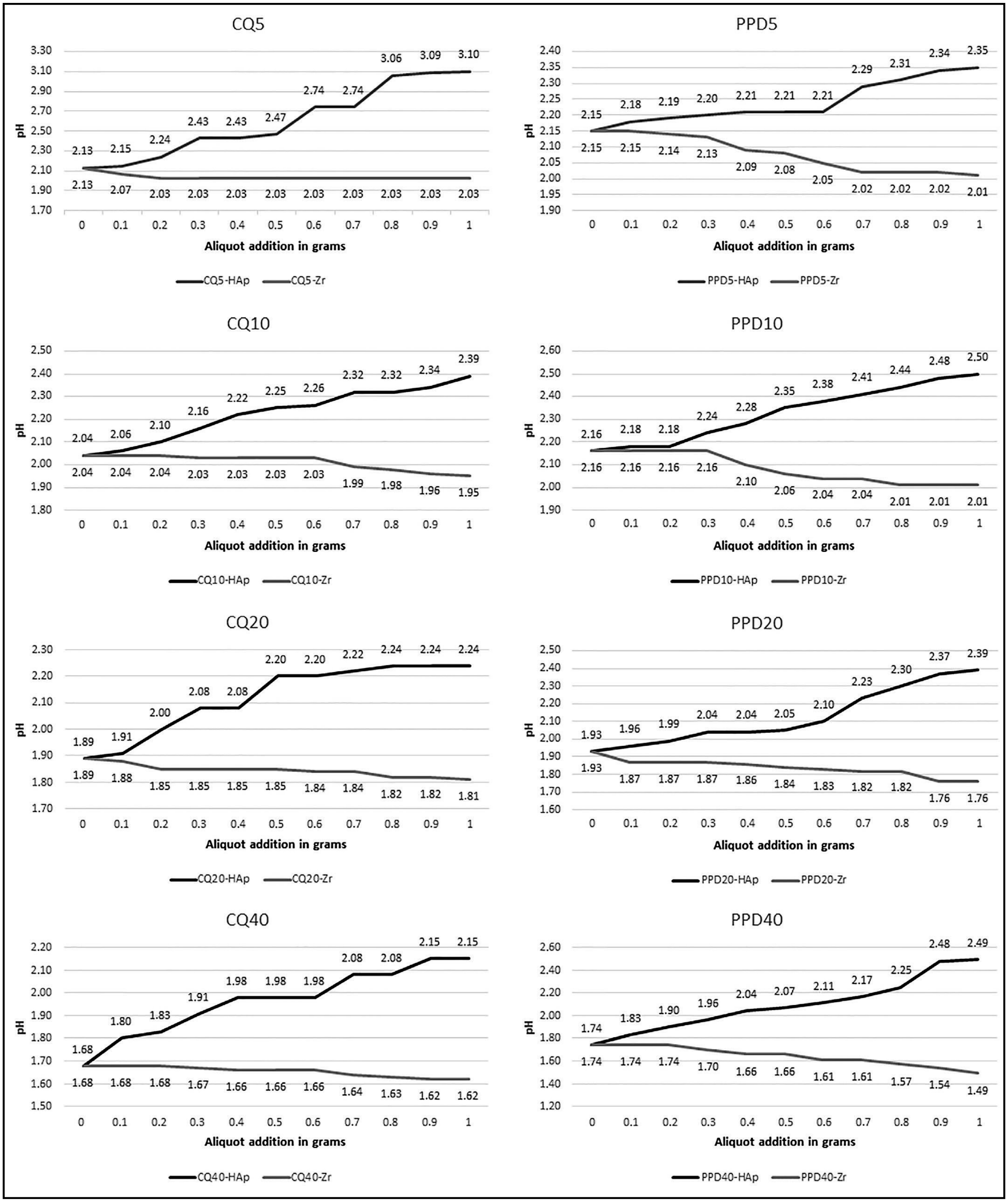

Figure 4. *Spreading of pH variation of 10-MDP–containing primers after the addition of 0.1 g aliquots of hydroxyapatite (Hap; black lines) or zirconia (gray lines). Experiments were performed in triplicate and the graphs were formed by the mean values. Final pH levels were significantly different between HAp and zirconia ($p<0.05$) for all primers.*

was able to effectively promote neutralization trend in primers. Indeed, the present outcomes suggest designing of ZrO_2 primers towards less concentrated solutions with acidic functional monomers possessing optimal chemical interaction with ZrO_2, to allow for a reduction of their concentration.

CONCLUSIONS

The ideal concentration of functional monomer 10-MDP to be used in ceramic primers should be up to 5 wt%, independently if combined with CQ/EDBA or PPD, to avoid the reduction of polymerization and bond strength of resin cement to ZrO_2. ZrO_2 ceramic does not possess the neutralization capacity for very acidic ceramic primers generated by functional monomers, especially in high concentrations.

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Conflict of Interest

The authors have no financial interest in any of the companies or products mentioned in this article.

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